

# **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 2010**

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Sezione della Protezione dell'Aria, dell'Acqua e del Suolo  
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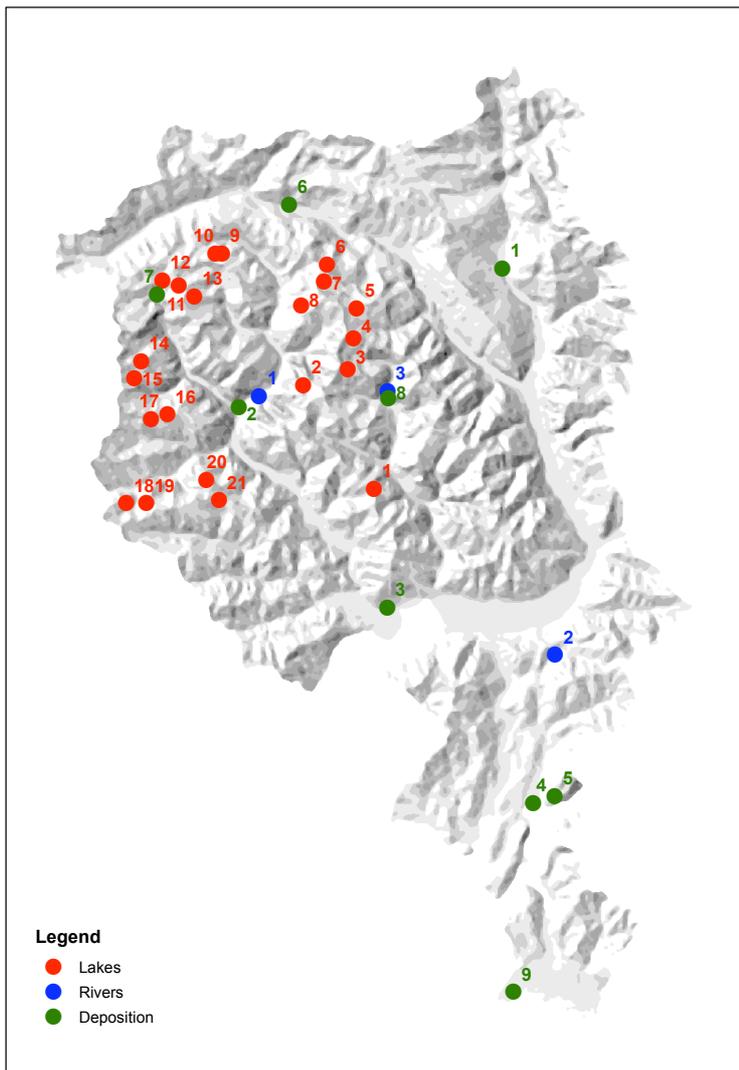
# Introduction

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 (LRTAP) in 1985, when it was recognised 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 harmonisation of monitoring methods. The Programme is planned and coordinated by a Task Force under the leadership of Norway. Up to now chemical and site data from more than 200 catchments in 16 countries in Europe and North America are available in the database of the Programme Centre. Switzerland joined the Programme in 2000 by order of the Swiss Federal Office for the Environment.

# 1 Study site

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 Canton 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, 20 lakes (21 from 2006) and 3 rivers have been monitored. In addition, wet deposition has been monitored at 9 sampling stations distributed over all Canton 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 2580 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), implying larger catchment areas and therefore less sensitivity toward acidification than lakes. The geographic distribution of lakes, rivers and wet deposition sampling sites are shown in Fig. 1.1, while their main geographic and morphometric parameters are resumed in Tab. 1.1, 1.2 and 1.3.

Figure 1.1 Sampling sites



**Table 1.1 Lake parameters**

Lake number	Lake name	Longitude CH m	Latitude CH m	Longitude	Latitude	Altitude m a.s.l.	Catchment area ha	Lake area ha	Max depth m
1	Lago del Starlaresc da Sgiöf	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 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
12	Lago Bianco	683030	145330	8°31'10"	46°27'15"	2077		ca. 4.0	
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'Orsalia	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 Sfilie	681525	124213	8°29'46"	46°15'52"	1909	63	2.8	12
20	Lago di Sascöla	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

**Table 1.2 River parameters**

River number	River name	Sampling site	Longitude CH m	Latitude CH m	Longitude	Latitude	Altitude m a.s.l.	Catchment area km <sup>2</sup>
1	Maggia	Brontallo	692125	134375	8°38'8"	46°21'16"	610	ca. 189
2	Vedeggio	Isonne	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 1.3 Parameters of wet deposition monitoring sites**

Sampling site number	Sampling site	Longitude CH m	Latitude CH m	Longitude	Latitude	Altitude 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

## 2 Water chemistry analysis

### 2.1 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) the buffer capacity of the north-western part of Canton 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. Freshwaters are considered acidic when alkalinity < 0  $\mu\text{eq l}^{-1}$ , sensitive to acidification when  $0 < \text{alkalinity} < 50 \mu\text{eq l}^{-1}$  and with low alkalinity but not sensitive to acidification when  $50 < \text{alkalinity} < 200 \mu\text{eq l}^{-1}$  (Mosello et al., 1993). With decreasing acid neutralizing capacity, pH also decreases. It is reported that at pH < 6 the release of metals from soils or sediments becomes more and more important. The release of aluminium at low pH is particularly important because of its toxic effects on organisms.

### 2.2 Sampling methods

In order to monitor and assess acidification of freshwaters in acid sensitive areas of Canton Ticino, the amount of wet deposition and water chemistry of 20 Alpine lakes (21 from 2006) and 3 rivers (Maggia, Vedeggio, Verzasca) has been monitored.

From 2000 to 2005 lake surface water was sampled twice a year (1 at beginning of summer, 1 in autumn). After 2006 lakes were monitored three times a year (1 at beginning of summer, 2 in autumn) and the alkaline Lago Bianco was added to the monitored lakes in order to compare biology of Alpine lakes with acid sensitive and alkaline characteristics. Before 2000 lake surface water was sampled irregularly. Lake surface water was collected directly from the helicopter. River water has been sampled monthly since 2000. Weekly sampling of rainwater with wet-only samplers started in 1988.

### 2.3 Analytical methods

Measured parameters, conservation methods, analytical methods and quantification limits are resumed in Tab 2.1. The quality of the data was assured by participating regularly at national and international intercalibration tests. In addition, data were accepted only 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 Forest (UNECE, 2009). Furthermore, the data were checked for outliers. If available, as for metals, dissolved concentrations were compared with total concentrations.

**Table 2.1 Measured parameters, conservation methods, analytical methods, accuracy and quantification limits**

*CA, PC, GF, PP stay for cellulose acetate, polycarbonate, glass fibre and polypropylene, respectively. 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)	0.5 $\mu\text{S cm}^{-1}$
alkalinity	No	No	potentiometric Gran titration	0.001 meq l <sup>-1</sup>
				Quantification limit
Ca <sup>2+</sup>	CA filter	PP bottle, 4°C	ion cromatography	0.010 mg l <sup>-1</sup>
Mg <sup>2+</sup>	CA filter	PP bottle, 4°C	ion cromatography	0.005 mg l <sup>-1</sup>
Na <sup>+</sup>	CA filter	PP bottle, 4°C	ion cromatography	0.005 mg l <sup>-1</sup>
K <sup>+</sup>	CA filter	PP bottle, 4°C	ion cromatography	0.010 mg l <sup>-1</sup>
NH <sub>4</sub> <sup>+</sup>	CA filter	PP bottle, 4°C	spectrophotometry	3 $\mu\text{g N l}^{-1}$
SO <sub>4</sub> <sup>2+</sup>	CA filter	PP bottle, 4°C	ion cromatography	0.005 mg l <sup>-1</sup>
NO <sub>3</sub> <sup>-</sup>	CA filter	PP bottle, 4°C	ion cromatography	0.010 mg N l <sup>-1</sup>
NO <sub>2</sub> <sup>-</sup>	CA filter	PP bottle, 4°C	spectrophotometry	1 $\mu\text{g N l}^{-1}$
Cl <sup>-</sup>	CA filter	PP bottle, 4°C	ion cromatography	0.010 mg l <sup>-1</sup>
soluble reactive P	CA filter	PP bottle, 4°C	spectrophotometry	4 $\mu\text{g P l}^{-1}$
soluble reactive Si	CA filter	PP bottle, 4°C	ICP-OES with ultrasonic nebulizer	0.003 mg Si l <sup>-1</sup>
total P	No	glass bottle, immediate mineralisation	persulphate digestion, spectrophotometry	4 $\mu\text{g P l}^{-1}$
DOC	PC filter	brown glass bottle, + H <sub>3</sub> PO <sub>4</sub>	UV-persulfate	0.05 mg C l <sup>-1</sup>
soluble Al	PC filter	acid washed PP bottle, +HNO <sub>3</sub> , 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 $\mu\text{g l}^{-1}$
total Al	No	acid washed PP bottle, +HNO <sub>3</sub> , 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 $\mu\text{g l}^{-1}$
soluble Cu	PC filter	acid washed PP bottle, +HNO <sub>3</sub> , 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 $\mu\text{g l}^{-1}$
total Cu	No	acid washed PP bottle, +HNO <sub>3</sub> , 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 $\mu\text{g l}^{-1}$
soluble Zn	PC filter	acid washed PP bottle, +HNO <sub>3</sub> , 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 $\mu\text{g l}^{-1}$
total Zn	No	acid washed PP bottle, +HNO <sub>3</sub> , 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 $\mu\text{g l}^{-1}$
soluble Pb	PC filter	acid washed PP bottle, +HNO <sub>3</sub> , 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 $\mu\text{g l}^{-1}$
total Pb	No	acid washed PP bottle, +HNO <sub>3</sub> , 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 $\mu\text{g l}^{-1}$
soluble Cd	PC filter	acid washed PP bottle, +HNO <sub>3</sub> , 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 $\mu\text{g l}^{-1}$
total Cd	No	acid washed PP bottle, +HNO <sub>3</sub> , 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 $\mu\text{g l}^{-1}$

## 2.4 Statistical methods used for trend analysis

For the period 2000-2009 we utilized the Mann-Kendall test to detect temporal trends in rainwater quality, wet deposition and lake- and river water chemistry (Dietz and Kileen, 1981). For concentrations in precipitation, a seasonal partial Mann-Kendall (Libiseller and Grimvall, 2002) was performed on monthly mean deposition and the amount of monthly precipitation. The latter was added as covariate in order to include meteorological influences in the study. For depositions the influence of precipitation was not considered because its real impact on surface waters is the ultimate goal. A simple seasonal Mann-Kendall test was therefore performed. For values of concentrations, depositions and precipitations the test statistics were summed over before conditioning. For lake chemistry a seasonal Mann-Kendall test was performed. Two seasons were chosen: season 1 (June-July) and season 2 (September-November). Similarly to precipitation, for river chemistry a seasonal partial Mann-Kendall test (Libiseller and Grimvall, 2002) was performed. As covariate was included the average daily discharge of the sampling day. The two sided test for the null hypothesis that no trend is present was rejected for p-values below 0.05.

Estimates for temporal variations of rainwater concentrations, wet depositions, river and lake water chemistry were quantified with the seasonal Kendall slope estimator (Gilbert, 1987).

## 2.5 Results and discussion

### 2.5.1 Wet deposition

#### Seasonal variation

Monthly and yearly mean concentrations in precipitation were calculated by weighting weekly concentrations with the sampled precipitation volume, while monthly and yearly wet deposition were calculated by multiplying monthly and yearly concentrations with the precipitation volume measured by MeteoSwiss. In particular, for our sampling sites, data from the following pluviometric stations of MeteoSwiss have been chosen: Acquarossa -> Comprovasco, Bignasco -> Cevio, Locarno Monti -> Locarno Monti, Lugano -> Lugano, Monte Brè -> Lugano, Piotta -> Piotta, Robiei -> Robiei, Sonogno -> Sonogno, Stabio -> Stabio.

The amount of monthly precipitation at each sampling site during 2010 and their average values during the period 2000-2010 are reported in Fig. 2.1. Similarly, seasonal variations of monthly mean rainwater concentrations of the main chemical parameters during 2010 and their mean values during the period 2000-2010 are shown in Fig. 2.2. Average monthly precipitation is low from December to April and high from May to November. Highest precipitation volumes normally occur in May, August and November. Compared to average values precipitation of 2010 was particularly high in May.

Monthly average sulphate concentrations are high during summer months and low during winter months at sampling stations with low concentrations (Bignasco, Piotta, Robiei, Sonogno). At sites with higher concentrations, the period with high sulphate concentrations starts already in late winter. This seasonality is in contrast with concentrations of SO<sub>2</sub> in the air (high in winter and low in summer). Therefore SO<sub>2</sub> cannot be the main factor influencing seasonality of sulphate concentrations in rainwater. Interestingly, dividing sulphate concentrations with concentrations of SO<sub>2</sub> for all sampling sites maximum summer values and minimum winter values can be observed (data not shown), suggesting that the oxidation rate of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> is higher in summer than in winter (Hedin et al. 1990). The observed seasonality of sulphate concentration in rainwater is therefore the result of the combination with the seasonality of SO<sub>2</sub> concentration in the air and the oxidation rate from SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup>. Compared to the mean values concentrations of sulphate during 2010 were in general lower. However, exceptional high values occurred in May at Lugano and Monte Brè. These peaks were accompanied by high concentrations of base cations. Most probably these concentrations peaks were the consequence of the volcanic eruption at Eyafjellajokull (Iceland) in April 2010. A sulphate concentration peak, combined with base cations and bicarbonate peaks, that however we are not able to explain, occurred also in January at Sonogno. However, comparing the concentrations of the single events responsible for these peaks it appears that sulphate concentrations at Lugano (1157 meq m<sup>-3</sup>) and Monte Brè (965 meq m<sup>-3</sup>) are much higher than at Sonogno (106 meq m<sup>-3</sup>).

Monthly mean concentrations of nitrate are highest in February-March and lowest in December-January. Differently, concentrations of NO<sub>2</sub> in the air are highest in November-February in and lowest in May-August. Dividing concentrations of nitrate with those of NO<sub>2</sub> maximum values occur during summer and minimum values during winter (data not shown), suggesting that, as already observed for sulphate, oxidation rate of NO<sub>x</sub> to NO<sub>3</sub><sup>-</sup> is higher in summer than in winter (Hedin et al. 1990). The concentration peak of nitrate in February-March is therefore most probably the result of the remaining high concentrations of NO<sub>2</sub> and the already increasing oxidation rates of NO<sub>x</sub> to NO<sub>3</sub><sup>-</sup> in spring. The seasonality of nitrate during 2010 is similar to that of the mean values during 2000-2010 but values are lower.

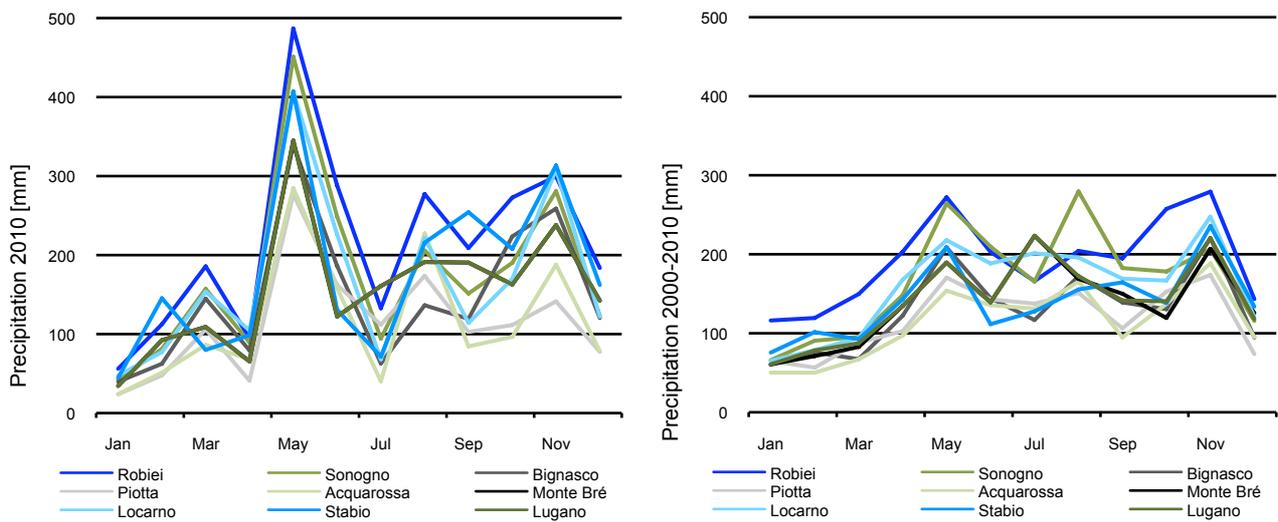
The seasonality of monthly mean ammonium concentrations is very similar to that of sulphate. Hedin et al. 1990 explained this similarity with a chemical coupling between ammonia and sulphate, with acidic sulphate aerosol acting as a vehicle for long-range transport of ammonia. Seasonal variations in 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<sub>2</sub>. The seasonality of ammonium during 2010 is similar to the average values during the period 2000-2010 but the concentrations are lower.

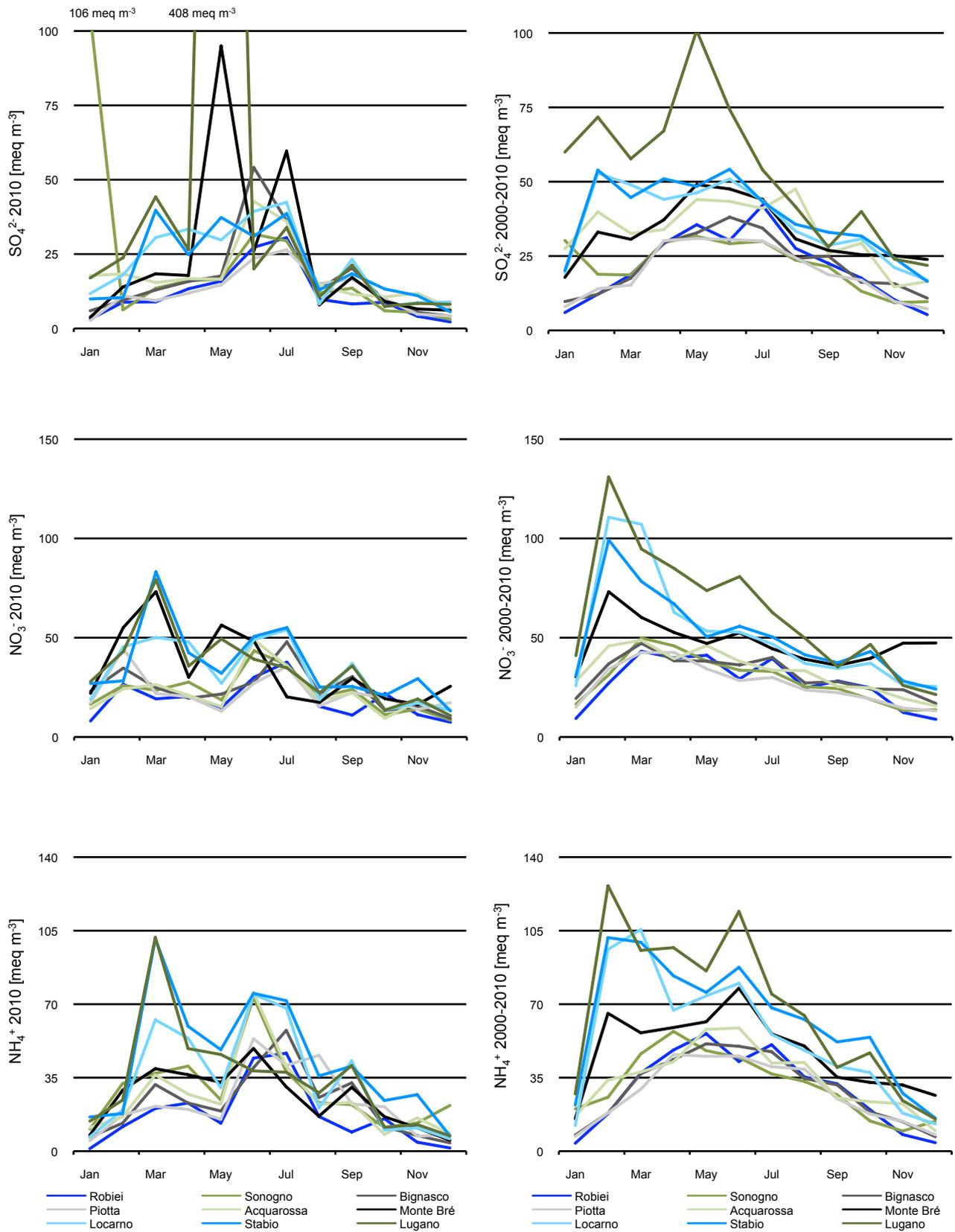
The seasonality of the monthly mean concentrations of base cations and bicarbonate are very similar indicating the two are connected to each other. During the last 11 years highest concentrations of base cations and bicarbonate occurred in April-June and October-November overlapping with periods rich in precipitation. It is possible that increased precipitation increase the possibility of the occurrence of alkaline rain events. Opposite to base cations and bicarbonate behaves acidity, whose monthly mean concentrations are highest during winter and lowest during spring and autumn, indicating that the concentrations of base cations and bicarbonate are the main responsible in determining the seasonality of acidity. Similar to the period 2000-2010, during 2010 highest concentrations of base cations, bicarbonate and lowest acidity occurred in April-June, when precipitation was also highest. As a consequence of decreased acidity during summer, pH values are also highest during summer.

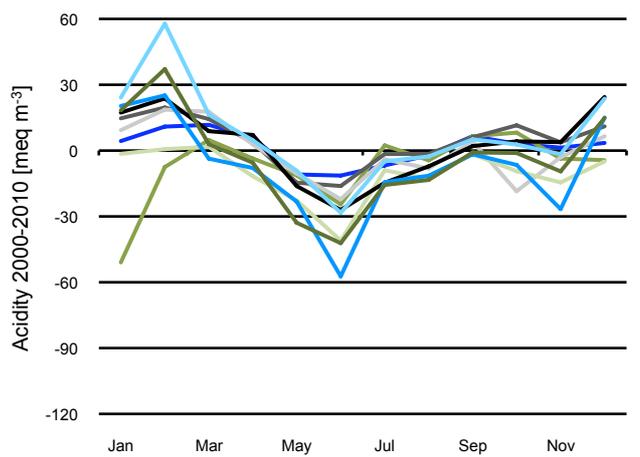
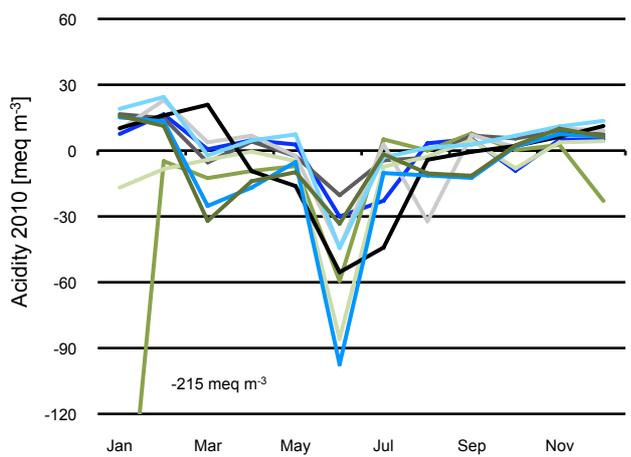
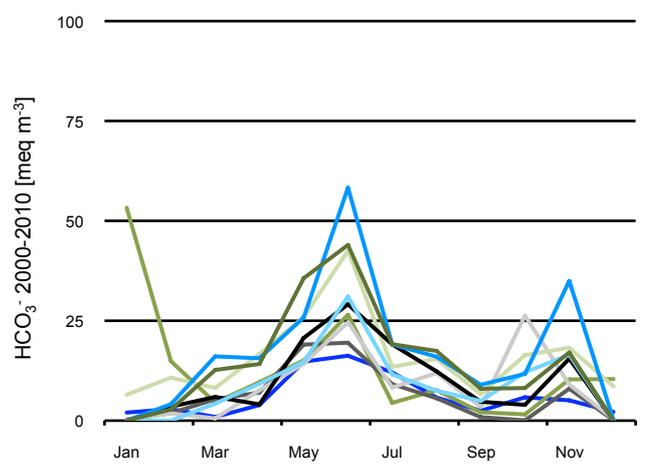
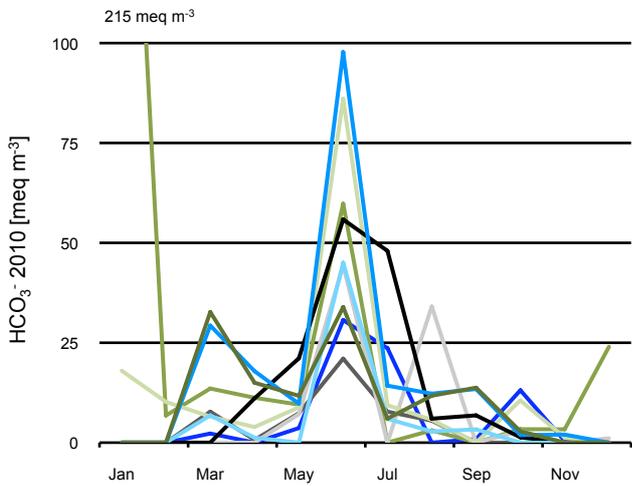
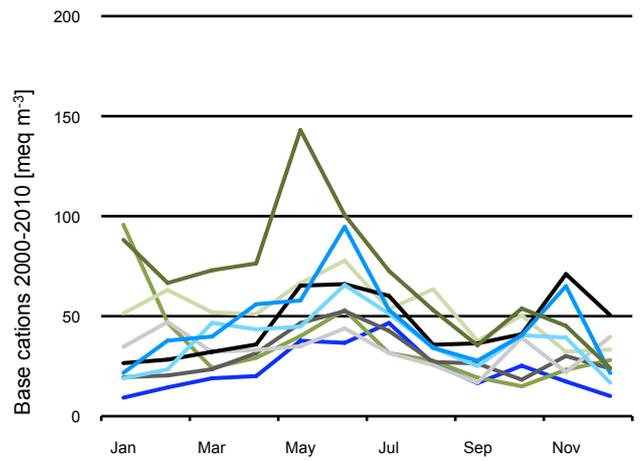
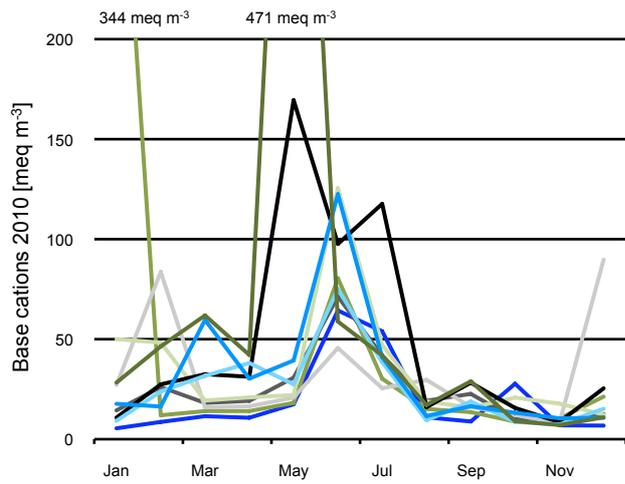
**Figure 2.1 Monthly precipitation**

*Data from MeteoSwiss*



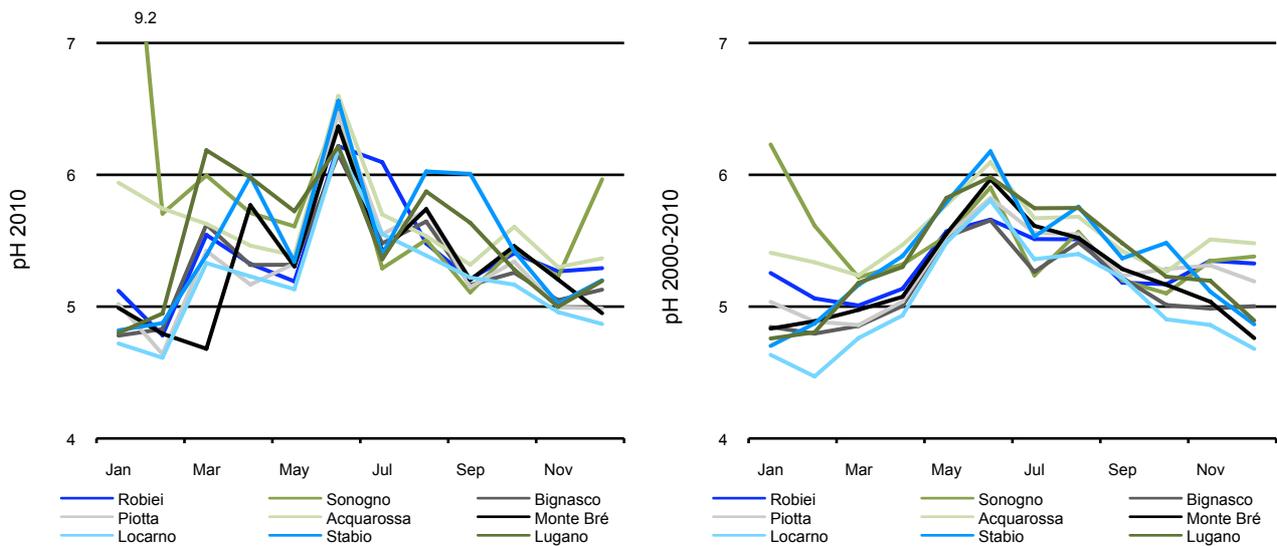
**Figure 2.2 Seasonal variations of monthly average rain water concentrations**  
*Base cations correspond to the sum of calcium, magnesium, sodium and potassium.*





— Robiei      — Sonogno      — Bignasco  
 — Piotta      — Acquarossa      — Monte Bré  
 — Locarno      — Stabio      — Lugano

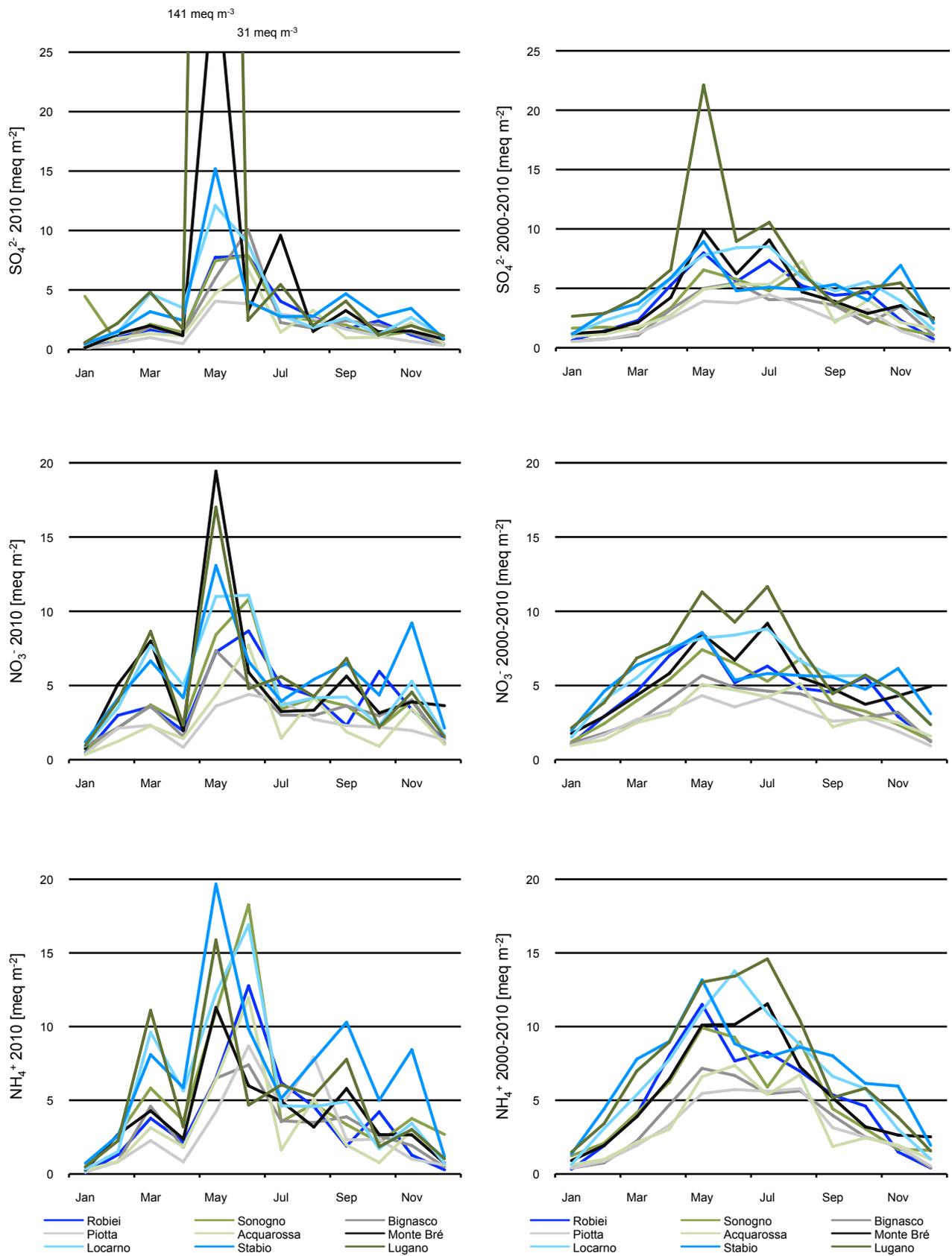
— Robiei      — Sonogno      — Bignasco  
 — Piotta      — Acquarossa      — Monte Bré  
 — Locarno      — Stabio      — Lugano

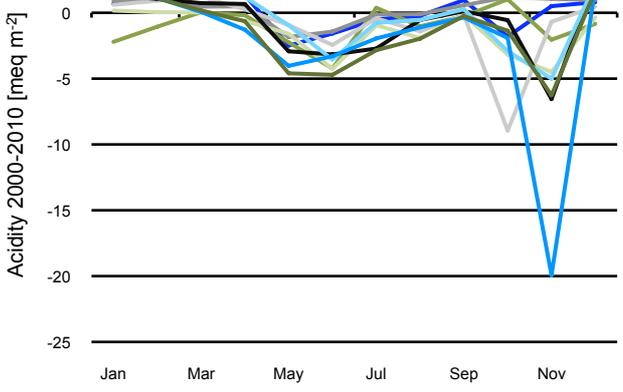
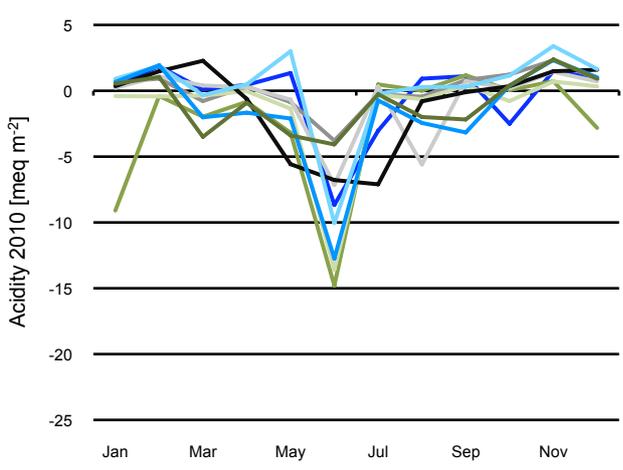
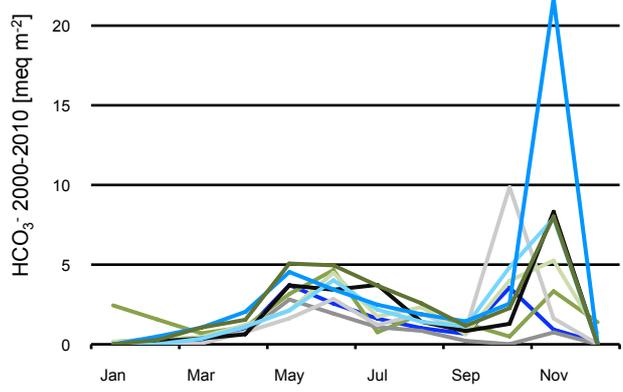
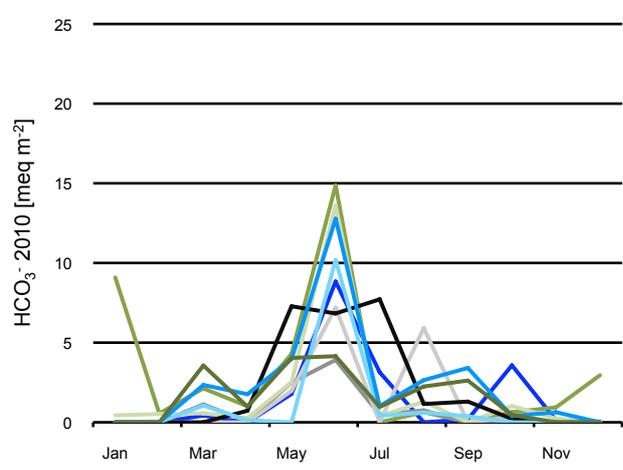
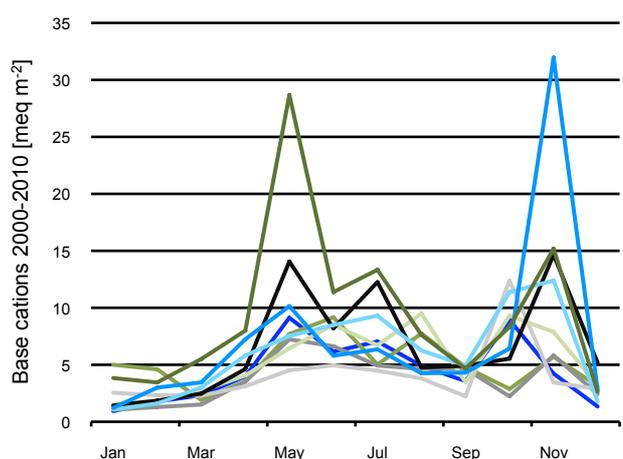
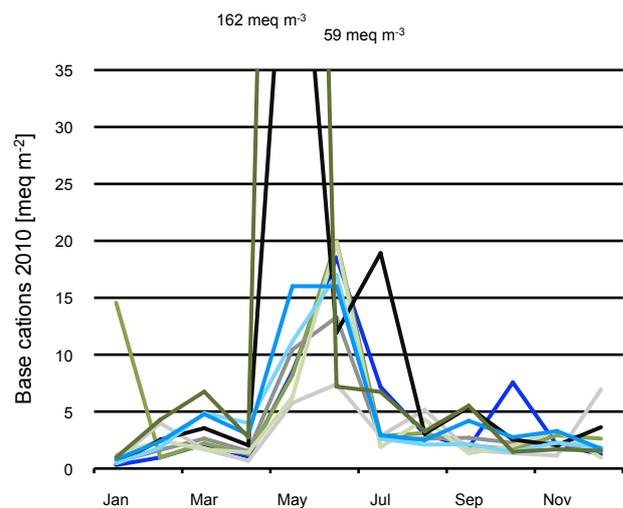


Depositions behaved similar to concentrations, with the difference that rain water volume gained further importance (Fig. 2.3). For sulphate, nitrate and ammonium, highest deposition during the period 2000-2010 occurred in summer and lowest in winter. During 2010 monthly mean deposition was in general similar to the mean values of the last 11 years. For Lugano and Monte Brè, as already observed for concentrations, deposition of sulphate and base cations in May was very much influenced by the volcanic eruption at Eyafjellajókull (Iceland). Comparing average monthly deposition of 2000-2010 of base cations, bicarbonate and acidity with concentrations it results that the autumn peak is more pronounced than the spring-summer peak. Differently, the seasonality of monthly mean deposition of base cations, bicarbonate and acidity of 2010 are similar to their concentrations with maximum values during spring-summer for base cations and bicarbonate and lowest during spring-summer for acidity.

**Figure 2.3 Seasonal variations of monthly wet deposition**

Base cations correspond to the sum of calcium, magnesium, sodium and potassium.





- Robiei
- Sonogno
- Bignasco
- Piotta
- Acquarossa
- Monte Bré
- Locarno
- Stabio
- Lugano

- Robiei
- Sonogno
- Bignasco
- Piotta
- Acquarossa
- Monte Bré
- Locarno
- Stabio
- Lugano

## Spatial variation

Annual average rainwater concentrations of the main chemical parameters and their yearly deposition rates during are shown in Tab. 2.2.

**Table 2.2 Yearly mean rain water concentrations and deposition rates during 2010**

Sampling site	Precipitation (mm)	Analysed precipitation (mm)	Conductivity 25°C ( $\mu\text{S cm}^{-1}$ )	pH	Ca <sup>2+</sup>		Mg <sup>2+</sup>		Na <sup>+</sup>		K <sup>+</sup>		NH <sub>4</sub> <sup>+</sup>		HCO <sub>3</sub> <sup>-</sup>		SO <sub>4</sub> <sup>2-</sup>		NO <sub>3</sub> <sup>-</sup>		Cl <sup>-</sup>		Acidity = H <sup>+</sup> - HCO <sub>3</sub> <sup>-</sup>			
					Concentration (meq m <sup>-3</sup> )	Deposition (meq m <sup>-2</sup> )	Concentration (meq m <sup>-3</sup> )	Deposition (meq m <sup>-2</sup> )	Concentration (meq m <sup>-3</sup> )	Deposition (meq m <sup>-2</sup> )	Concentration (meq m <sup>-3</sup> )	Deposition (meq m <sup>-2</sup> )	Concentration (meq m <sup>-3</sup> )	Deposition (meq m <sup>-2</sup> )	Concentration (meq m <sup>-3</sup> )	Deposition (meq m <sup>-2</sup> )	Concentration (meq m <sup>-3</sup> )	Deposition (meq m <sup>-2</sup> )	Concentration (meq m <sup>-3</sup> )	Deposition (meq m <sup>-2</sup> )	Concentration (meq m <sup>-3</sup> )	Deposition (meq m <sup>-2</sup> )	Concentration (meq m <sup>-3</sup> )	Deposition (meq m <sup>-2</sup> )	Concentration (meq m <sup>-3</sup> )	Deposition (meq m <sup>-2</sup> )
					Acquarossa	1388	1232	9	5.5	23	31	7	10	3	4	1	2	28	38	15	21	19	26	22	31	3
Bignasco	1774	1437	8	5.2	12	21	2	4	5	8	2	4	20	35	3	6	15	26	21	38	4	7	3	5		
Locarno Monti	2020	1727	11	5.1	17	34	3	6	5	10	1	2	32	65	6	13	21	43	30	60	5	10	1	2		
Lugano	1854	1504	20	5.4	39	73	8	15	30	56		63	33	62	10	19	92	171	34	62	9	16	-6	-10		
Monte Brè	1854	1456	14	5.3	40	74	9	17	9	16	6	11	26	49	15	28	33	62	33	61	8	16	-10	-18		
Piotta	1377	1139	9	5.3	13	17	3	4	9	12	3	4	26	36	12	17	14	19	20	28	9	12	-7	-9		
Robiei	2599	1945	7	5.3	11	28	6	16	2	5	1	3	17	43	6	17	12	31	18	47	2	5	-1	-4		
Sonogno	2116	1894	9	5.5	19	40	6	12	5	10	2	5	30	64	19	41	17	35	22	47	4	9	-16	-34		
Stabio	2132	1968	11	5.3	16	34	3	6	7	14	2	5	40	85	13	28	21	45	32	68	6	12	-8	-17		

Comparing average values of yearly mean rainwater concentrations and depositions from the period 2000-2010 of the different sampling sites the following observations on spatial distribution can be done.

In general, ion concentrations of anthropogenic origin (sulphate, nitrate, ammonia) increase from sites with low latitudes to high latitude and from high altitude to low altitude. Highest concentrations occur at Lugano and Stabio and 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. Concentrations of base cations, bicarbonate and acidity correlate better with the amount of precipitation. In fact, lower yearly precipitation results in smaller dilution of single alkaline rain events on an annual base, leading to higher mean concentrations of base cations and bicarbonate and lower concentrations of acidity. Highest concentrations of base cations, bicarbonate and lowest concentrations of acidity are measured at Acquarossa and Lugano and lowest concentrations of base cations, bicarbonate and highest concentrations of acidity at Bignasco and Robiei.

Wet deposition of chemical parameters depends by both concentration and the amount of precipitation. Highest precipitation usually occurs in the north-western part of Canton Ticino. The reason for this distribution is 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. Highest deposition rates of ammonia, nitrate and sulphate occur at Locarno, Lugano, Stabio while lowest can be observed at Acquarossa, Bignasco, Piotta. For base cations and bicarbonate, deposition rates are highest at Lugano and Stabio and lowest at Bignasco and Robiei. The opposite occurs for acidity (highest rates at Bignasco and Robiei and lowest at Lugano, Stabio). A detailed analysis on spatial distribution of rain water quality and deposition rates is described in (Steingruber and Colombo, 2010).

## Temporal variations

The amount of yearly precipitation at each sampling site is reported in Fig. 2.4, while variation of yearly average rainwater concentrations and deposition rates of the main chemical parameters during time are shown in Fig. 2.5. Compared to the time series, 2010 was an average wet year. In general, the measured concentrations and depositions were similar to values of 2009. An exception are yearly average concentrations and depositions of sulphate and base cations at Lugano and Monte Brè, influenced by the volcanic eruption at Eyafjallajokull (Iceland) in April 2010.

For some parameters temporal trends in concentrations are immediately visible (see decrease in concentrations of sulphate, in acidity and increase in pH). Other parameters seem to be very much influenced by precipitation (i.e. high concentrations of nitrate and ammonia during very dry years). For a trend analysis, that has the purpose to evaluate the influence of air pollutants on rainwater quality, it is useful to consider precipitation as a covariate (or explanatory variable) performing a seasonal partial Mann-Kendall test (see ch. 2.4). Results of the test and estimates for the temporal variation of the concentrations using the seasonal Kendall slope estimator for the two periods 1990-2000 and 2000-2010 are presented in Tab. 2.3

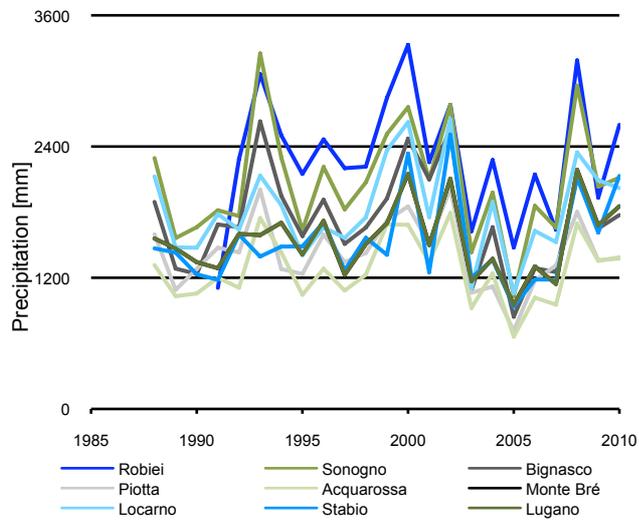
During the period 1990-2000 sulphate concentrations decreased significantly only at Piotta and almost at Locarno, but from 2000 it decreased significantly at all sampling sites. Nitrate concentrations started to decrease significantly only after 2000 at 4 sites (Acquarossa, Binasco, Locarno, Piotta). Similarly, first signs of a significant reduction of ammonium concentrations appear only after 2000 (Locarno, Robiei, Stabio). It derives, that with respect to sulphate, nitrogen compounds in rainwater started to decrease later, which is not surprising considering that concentrations of SO<sub>2</sub> started to decrease earlier and more effectively than NO<sub>x</sub> and NH<sub>3</sub> (Künzler, 2005). From the graphs in Fig. 2.5 the reduction in concentrations of nitrate and ammonium after 2000 is not evident because the trend is hid by the influence of the amount of yearly precipitation. In fact, during particularly dry years like 2003 and 2005 concentrations peaked because of a concentration effect. Interesting but more difficult to explain is the significant decrease in chloride concentrations at Acquarossa, Locarno from 1990-2000 and at Acquarossa, Locarno and Sonogno but at a considerable lower rate. Literatures from sea-close countries describe the years from 1988 to 1992 as a period with particularly intensive storms, with numerous sea-salt episodes leading to increased deposition of chloride (Evans and Montheith, 2001). Although Switzerland is situated far from the sea it is possible that chloride concentrations in this region's precipitation were also somehow influenced by this phenomenon. Another reason could as well consist in the increasing control of hydrochloric acid emissions from waste incineration plants, coal-fired power plants and from the chemical industry. Base cations also decrease significantly at 4 sites after 2000 (Acquarossa, Locarno, Sonogno, Stabio). Acidity, that can be calculated as the difference between acid anions and base cations and ammonia, decreased significantly from 1990-2000 at Acquarossa, Locarno and Piotta, after 2000 acidity decreased significantly further at Monte Brè, Locarno and Stabio. At most other sites the decrease in acid anions was probably compensated by a simultaneous decrease in ammonia and base cations. The reduction rates were higher during the first decade. In general, acidity decreased from values around 30-40 meq/m<sup>3</sup> to values around 0 meq/m<sup>3</sup> on average. However, it can happen that single particularly intense rain events with alkaline characteristics can heavily influence yearly mean acidity shifting it toward negative values. Such negative peaks can be observed at sampling stations Acquarossa, Locarno Monti and Piotta in 2000 (alkaline event in october) and at Monte Bré, Locarno Monti, Lugano and Stabio in 2002 (alkaline event in November) and are accompanied by peaks in concentrations of base cations and bicarbonate. We remember that both events lead to floods in the region. When and why such events appear is still not clear. Rogora et al. (2004) observed an increased frequency of alkaline rain events especially during the last decade, many of them caused by deposition of Saharan dust. It is possible that rain rich years increase the chance of the occurrence of alkaline rain events. In addition the reduction of sulphate concentrations during the last 2 decades probably decreased the capacity of rainwater to neutralize alkaline rain events making them more observable in rainwater chemistry. If climate change may also influence the occurrence of alkaline rain events by increased long distance transport of dust is not known. In summary,

decreasing sulphur emissions and during the last years also decreasing nitrate and ammonia emissions and increasing number of alkaline rain events generated a decrease of acidity and an increase of pH of rainwater (Fig. 2.6).

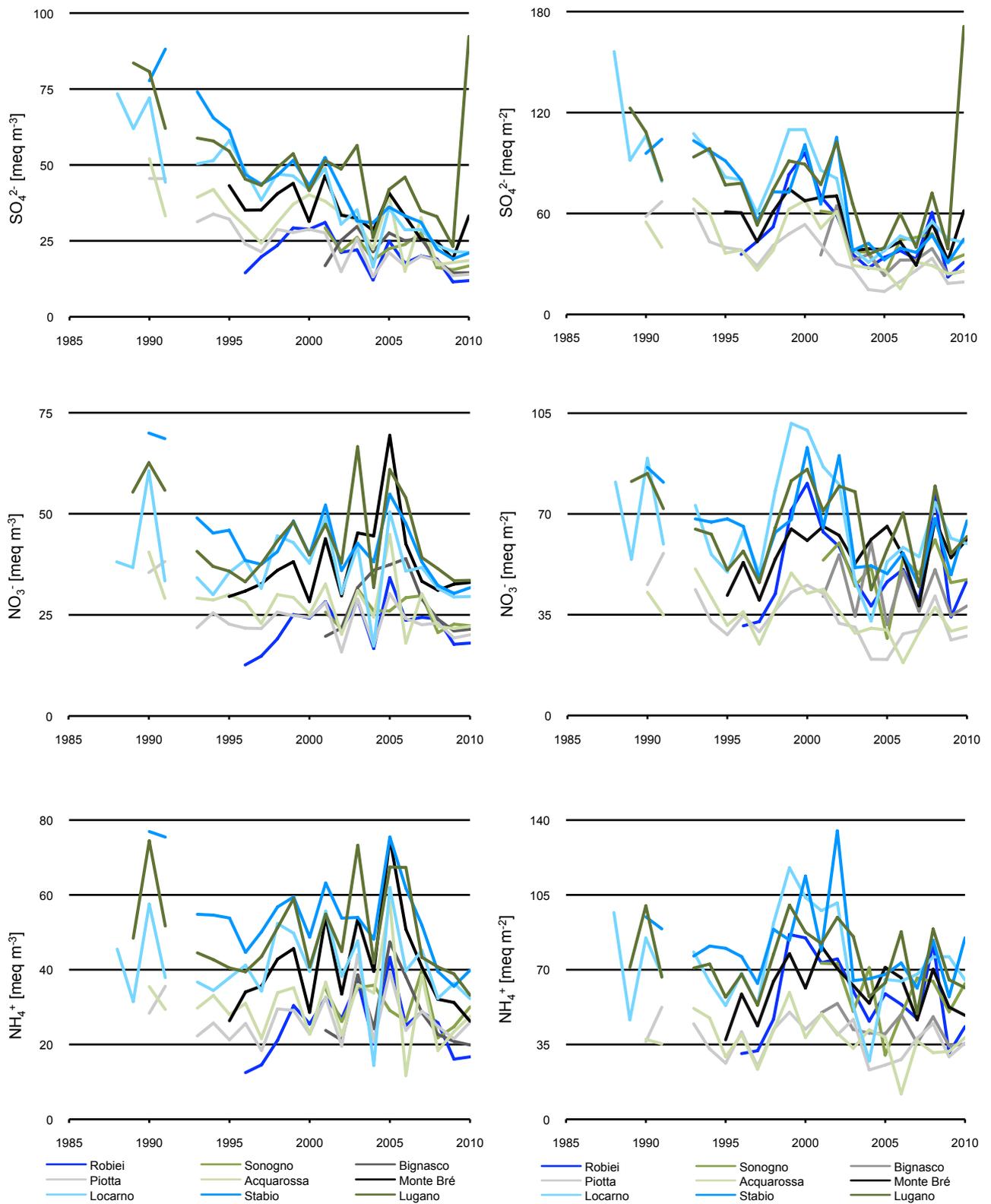
In order to evaluate the influence of wet deposition on surface water quality a trend analysis of monthly mean deposition for the two periods 1990-2000 and 2000-2010 with the seasonal Mann-Kendall test was performed. Results from the trend analysis and estimates for the temporal variations in deposition using the Sen's slope are presented in Tab. 2.4.

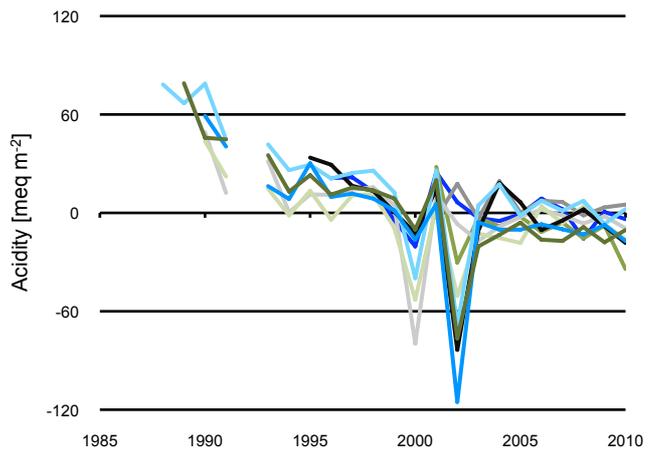
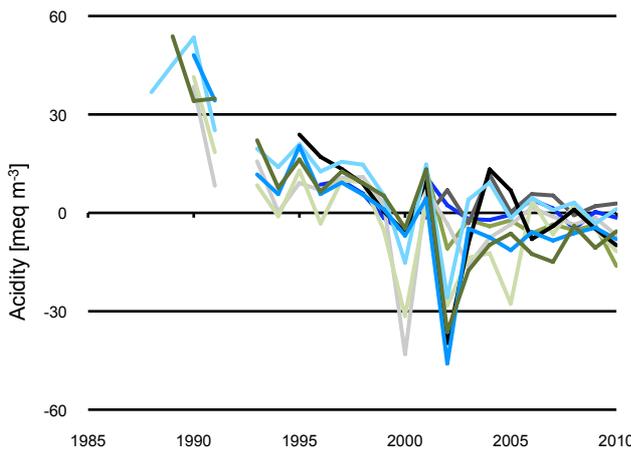
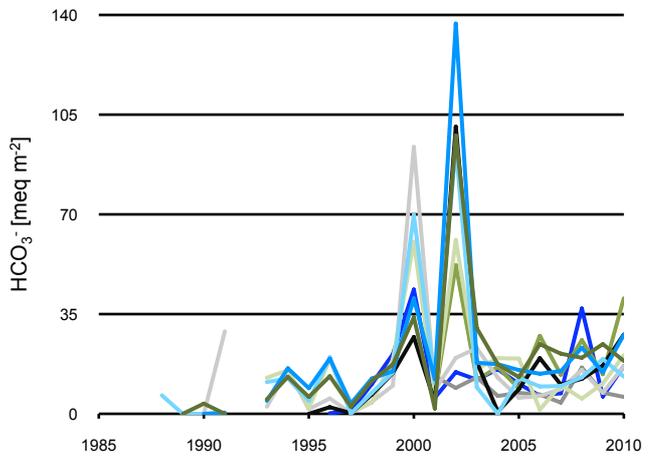
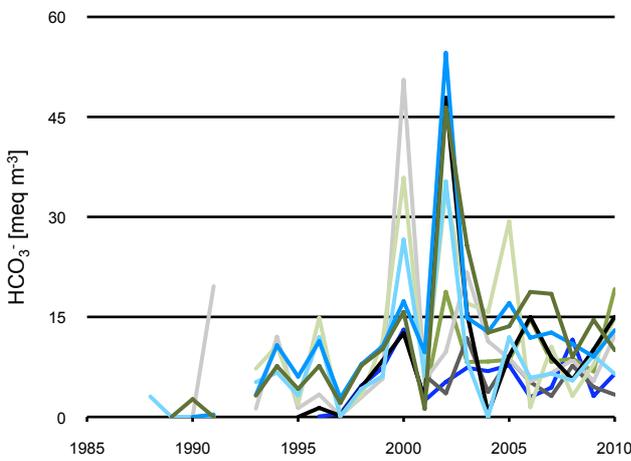
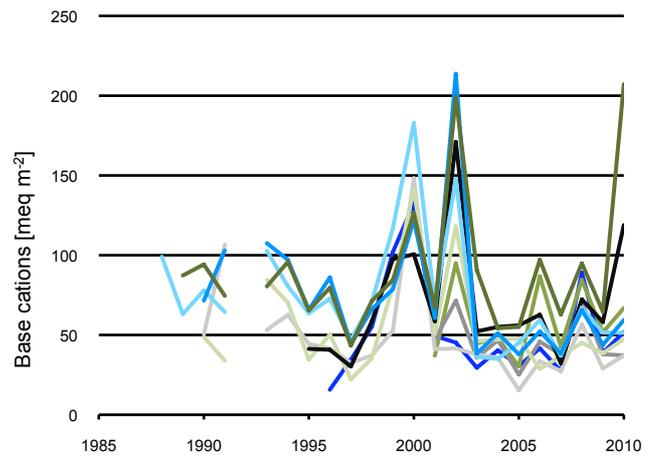
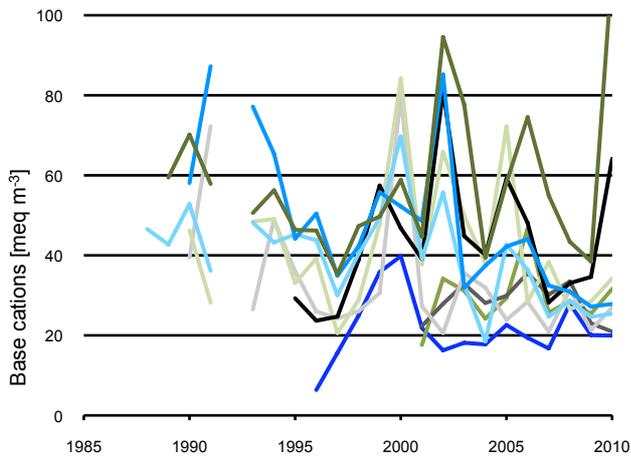
Temporal variations in deposition of sulphate, nitrate, ammonia, base cations, bicarbonate and acidity were similar to those observed for concentrations with the difference that the firsts are more influenced by the amount of precipitation. In fact, the rain rich years 1998-2002 are characterized by increased deposition rates. Because of this rain rich period falling at the beginning of the second trend analysis, from 2000 to 2010 trends in depositions of anthropogenic pollutants (sulphate, nitrate, ammonium) are more pronounced than those observed for concentrations and become significantly negative at most sites. This observation is important to consider when interpreting results from trend analysis in surface waters during the same time period.

**Figure 2.4 Yearly precipitations**  
*Data from MeteoSwiss*



**Figure 2.5** Temporal variations of annual mean rain water concentrations and deposition rates  
*Base cations correspond to the sum of calcium, magnesium, sodium and potassium.*





- |           |              |             |
|-----------|--------------|-------------|
| — Robiei  | — Sonogno    | — Bignasco  |
| — Piotta  | — Acquarossa | — Monte Bré |
| — Locarno | — Stabio     | — Lugano    |

Figure 2.6 Temporal variations of annual mean pH of rain water

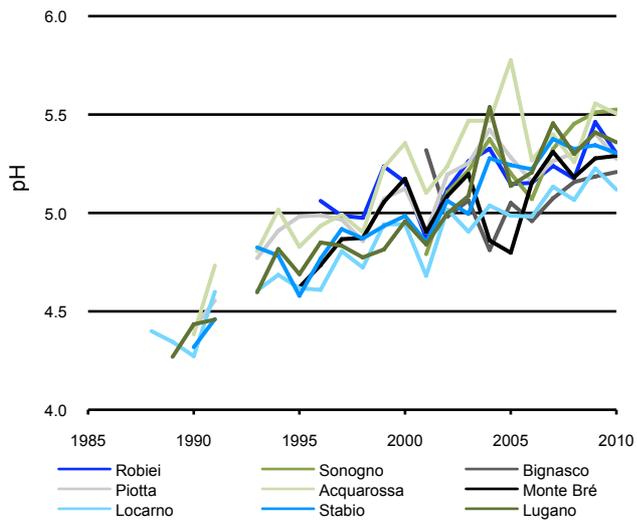


Table 2.3 Results from trend analyses (significant trends in red) performed on mean monthly concentration weighted with the precipitation volume during the period 1990-2000 and 2000-2010. *p* corresponds to the probability level obtained with the partial seasonal Mann-Kendall test and the rate ( $\text{meq m}^{-2} \text{yr}^{-1}$ ) to the seasonal Kendall slope estimator.

Period		1990-2000					2000-2010								
Station		Acquarossa	Locarno	Lugano	Piotta	Stabio	Acquarossa	Bignasco	Monte Brè	Locarno	Lugano	Piotta	Robiei	Sonogno	Stabio
SO <sub>4</sub> <sup>2-</sup>	p	0.248	0.054	0.478	0.046	0.221	0.004	0.026	0.003	0.004	0.011	0.007	0.003	0.010	0.004
	rate	-1.32	-3.70	-2.72	-1.47	-3.84	-2.25	-0.21	-1.33	-2.59	-3.24	-0.89	-1.44	-1.14	-2.42
NO <sub>3</sub> <sup>-</sup>	p	0.175	0.303	0.642	0.219	0.433	0.042	0.038	0.165	0.021	0.123	0.029	0.075	0.104	0.098
	rate	-1.46	-1.30	-1.63	-0.66	-3.06	-0.63	-1.05	-0.56	-2.00	-1.57	-0.48	-0.66	-0.61	-1.28
Cl <sup>-</sup>	p	0.029	0.043	0.485	0.183	0.334	0.008	0.520	0.298	0.009	0.105	0.175	0.725	0.046	0.508
	rate	-0.92	-1.15	-0.70	-0.48	-1.01	-0.21	0.14	0.00	-0.27	-0.41	-0.18	-0.03	-0.10	-0.12
HCO <sub>3</sub> <sup>-</sup>	p	0.006	0.215	0.925	0.077	0.288	0.153	0.815	0.028	0.455	0.412	0.095	0.417	0.414	0.061
	rate	0.00	0.00	0.00	0.00	0.00	-0.36	0.02	0.10	0.00	0.12	0.00	0.00	0.00	0.12
NH <sub>4</sub> <sup>+</sup>	p	0.137	0.584	0.669	0.884	0.791	0.113	0.149	0.103	0.012	0.086	0.076	0.004	0.083	0.049
	rate	-1.73	-0.72	-0.01	0.28	-1.44	-1.05	-1.05	-0.60	-1.46	-1.89	-0.68	-0.87	-0.99	-0.94
Base cations	p	0.734	0.201	0.291	0.304	0.372	0.016	0.277	0.360	0.018	0.071	0.086	0.095	0.021	0.008
	rate	-0.09	-1.57	-1.10	-1.43	-2.90	-2.33	-0.16	-0.01	-1.93	-1.93	-0.75	-0.50	-0.76	-0.92
H <sup>+</sup>	p	0.002	0.033	0.423	0.019	0.604	0.256	0.344	0.016	0.013	0.030	0.032	0.092	0.075	0.004
	rate	-2.04	-3.54	-2.96	-1.36	-2.13	-0.10	-0.15	-0.23	-0.75	-0.28	-0.23	-0.34	-0.35	-0.77
Acidity	p	0.002	0.044	0.337	0.031	0.407	0.724	0.600	0.008	0.034	0.070	0.435	0.373	0.250	0.003
	rate	-4.43	-5.48	-3.69	-2.04	-3.29	0.23	-0.56	-1.18	-0.93	-1.51	-0.12	-0.50	-0.87	-1.57

Table 2.4 Results from trend analyses (significant trends in red) performed on mean monthly deposition weighted with the precipitation volume during the period 1990-2000 and 2000-2010. *p* corresponds to the probability level obtained with the partial seasonal Mann-Kendall test and the rate ( $\text{meq m}^{-2} \text{yr}^{-1}$ ) to the seasonal Kendall slope estimator.

Period		1990-2000					2000-2010								
Station		Acquarossa	Locarno	Lugano	Piotta	Stabio	Acquarossa	Bignasco	Monte Brè	Locarno	Lugano	Piotta	Robiei	Sonogno	Stabio
SO <sub>4</sub> <sup>2-</sup>	p	0.039	0.080	0.061	0.033	0.080	0.022	0.017	0.008	0.019	0.066	0.025	0.019	0.011	0.004
	rate	-0.63	-1.91	-0.14	-0.88	-1.91	-2.38	-1.21	-1.75	-4.37	-5.26	-0.78	-2.99	-0.89	-2.42
NO <sub>3</sub> <sup>-</sup>	p	0.060	0.109	0.081	0.045	0.109	0.022	0.037	0.008	0.021	0.090	0.050	0.093	0.015	0.098
	rate	-0.47	0.67	1.68	-0.04	0.67	-1.26	-1.33	0.01	-1.25	-2.57	-0.44	-1.42	-0.02	-1.28
Cl <sup>-</sup>	p	0.161	0.961	0.787	0.046	0.961	0.068	0.139	0.273	0.036	0.852	0.032	0.033	0.500	0.508
	rate	-0.92	-1.03	-0.32	-0.48	-1.03	-0.12	0.14	0.00	-0.12	-0.54	-0.03	0.06	0.13	-0.12
HCO <sub>3</sub> <sup>-</sup>	p	0.533	0.046	0.122	0.415	0.046	0.137	0.022	0.011	0.013	0.046	0.132	0.028	0.200	0.061
	rate	0.16	0.00	0.00	0.00	0.00	-0.22	0.02	0.21	0.00	0.41	0.00	0.00	0.11	0.12
NH <sub>4</sub> <sup>+</sup>	p	0.047	0.023	0.034	0.015	0.023	0.022	0.009	0.007	0.012	0.028	0.016	0.029	0.012	0.049
	rate	-0.08	0.85	2.43	-0.04	0.85	-1.09	-1.05	-0.84	-1.93	-3.98	-0.37	-3.41	-0.02	-0.94
Base cations	p	0.122	0.109	0.118	0.117	0.109	0.031	0.015	0.026	0.015	0.078	0.221	0.029	0.067	0.008
	rate	0.97	-0.45	1.65	-0.75	-0.45	-2.16	-0.16	-0.20	-2.67	-2.14	-0.15	0.29	0.08	-0.92
H <sup>+</sup>	p	0.174	0.267	0.889	0.203	0.267	0.700	0.045	0.153	0.027	0.030	0.330	0.270	0.287	0.004
	rate	-1.80	-5.76	-2.29	-0.90	-5.76	-0.13	-0.15	-0.47	-1.21	-0.88	-0.45	-0.86	-0.66	-0.77
Acidity	p	0.886	0.053	0.414	0.585	0.053	0.123	0.022	0.032	0.015	0.069	0.140	0.044	0.510	0.003
	rate	-4.10	-5.53	-2.66	-2.23	-5.53	0.12	-0.56	-1.67	-1.68	-1.97	0.20	-0.99	-1.61	-1.57

## 2.5.2 Alpine rivers

### Spatial variations

During 2010 river water was sampled at the following days: 11.1, 8.2, 8.3, 12.4, 3.5, 7.6, 5.7, 3.8, 6.9, 4.10, 8.11, 13.12. Annual mean concentrations of the chemical parameters measured in river Maggia, Vedeggio and Verzasca during 2010 are shown in Tab. 2.5. Conductivity, concentrations of calcium, sodium, potassium, sulphate, chloride, alkalinity and pH were highest in river Maggia, followed by Vedeggio and Verzasca. As discussed in Steingruber and Colombo (2006), differences in catchments 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 rate related to increased buffering capacity in the watershed of river Maggia. 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 rather new 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) and therefore much more weathered and fractured, increasing the surface that can interact with water from precipitations. Interestingly, highest and lowest nitrate concentrations were measured in rivers Vedeggio and Maggia, respectively. The low nitrate concentrations in river Maggia may be a consequence of its large watershed, being able to retain more nitrogen.

During 2010 average alkalinity was 257  $\mu\text{eq l}^{-1}$  in river Maggia, 155  $\mu\text{eq l}^{-1}$  in river Vedeggio and 78  $\mu\text{eq l}^{-1}$  in river Verzasca. Based on these data river Verzasca and river Vedeggio have low alkalinities (50-200  $\mu\text{eq l}^{-1}$ ), but no river is sensitive to acidification. The same is suggested by their minimum alkalinities that were always  $> 0 \mu\text{eq l}^{-1}$ . Average pH was 7.4 in river Maggia, 7.1 in river Vedeggio and 6.8 in river Verzasca. Their minimum pH's were not much lower (Maggia: 6.9, Vedeggio: 6.9, Verzasca: 6.6). As a consequence of the relatively high pH's, dissolved aluminium concentrations were on average low. However, higher aluminium concentrations up to 579  $\mu\text{eq l}^{-1}$  in river Maggia, 46  $\mu\text{eq l}^{-1}$  in river Vedeggio and 49  $\mu\text{eq l}^{-1}$  in river Verzasca occurred during high flow events in April-June.

**Table 2.5 Average concentrations in river water during 2010.**

*Average values with some or all single values below the quantification limit were preceded with <.*

River name	Year	pH	Conductivity 25°C ( $\mu\text{S cm}^{-1}$ )	Alkalinity ( $\mu\text{eq l}^{-1}$ )	Ca <sup>2+</sup> (mg l <sup>-1</sup> )	Mg <sup>2+</sup> (mg l <sup>-1</sup> )	Na <sup>+</sup> (mg l <sup>-1</sup> )	K <sup>+</sup> (mg l <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (mg N l <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg l <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg N l <sup>-1</sup> )	Cl <sup>-</sup> (mg l <sup>-1</sup> )	DOC (mg C l <sup>-1</sup> )	SiO <sub>2</sub> (mg l <sup>-1</sup> )	Al <sub>dissolved</sub> ( $\mu\text{g l}^{-1}$ )	Al <sub>tot</sub> ( $\mu\text{g l}^{-1}$ )	Cu <sub>dissolved</sub> ( $\mu\text{g l}^{-1}$ )	Cu <sub>tot</sub> ( $\mu\text{g l}^{-1}$ )	Zn <sub>dissolved</sub> ( $\mu\text{g l}^{-1}$ )	Zn <sub>tot</sub> ( $\mu\text{g l}^{-1}$ )
Maggia	2010	7.4	58.8	257	7.98	0.65	1.66	1.42	0.013	9.17	0.58	1.28	0.52	4.75	11.1	13.1	<0.3	<0.4	<0.8	1.0
Vedeggio	2010	7.1	44.2	155	4.89	0.95	1.68	0.55	0.009	6.07	1.02	1.09	0.58	6.45	10.0	14.8	<0.3	<0.4	1.0	1.1
Verzasca	2010	6.8	23.6	78	3.55	0.27	0.84	0.62	0.005	4.40	0.74	0.19	0.17	3.89	18.0	25.2	<0.5	<0.6	2.9	3.3

### Seasonal variations

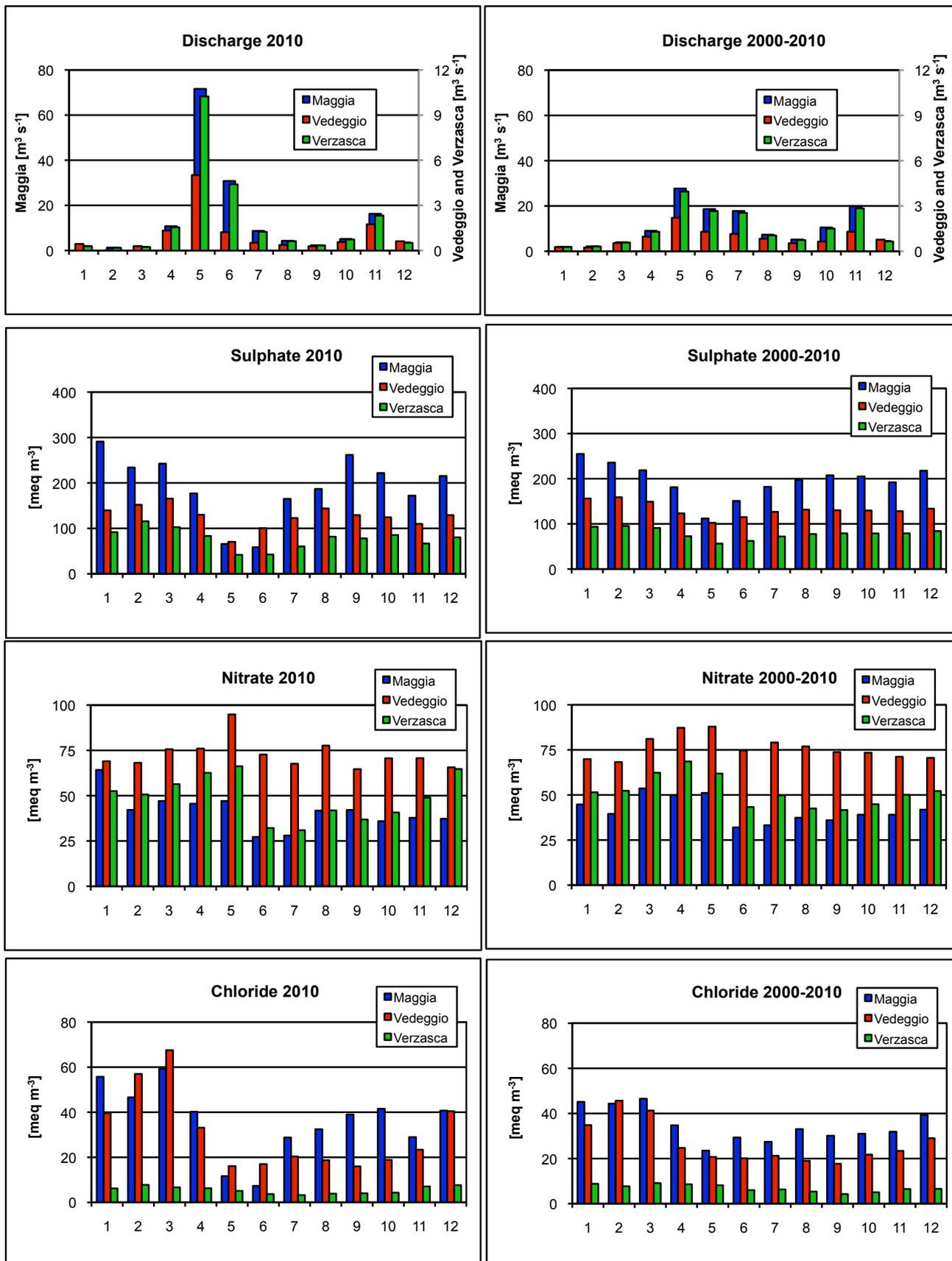
Fig. 2.7 shows the variations of the discharge and the main chemical parameters during sampling days in 2010 and their mean during the period 2000-2010. Discharge curves follow well the seasonality of precipitation (Fig. 2.1), with low values during winter and higher values during the rest of the year. During 2010 discharge

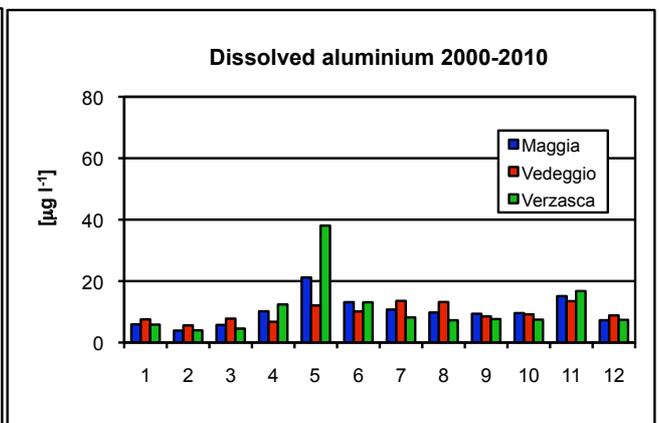
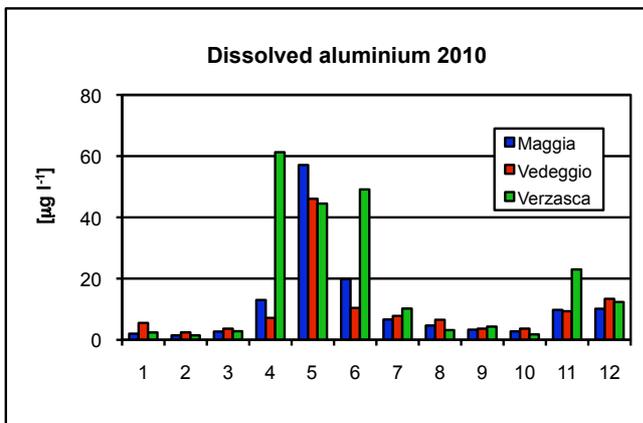
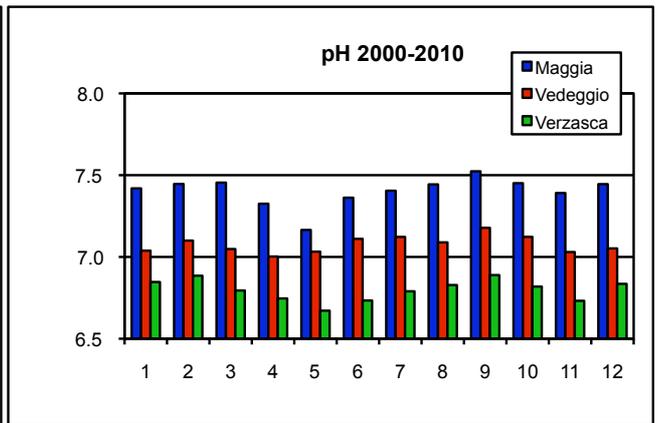
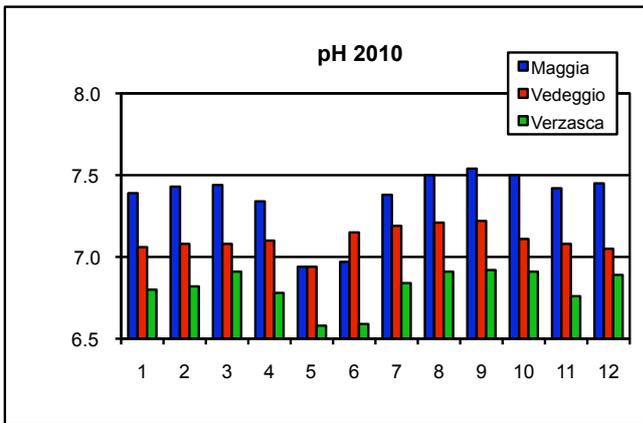
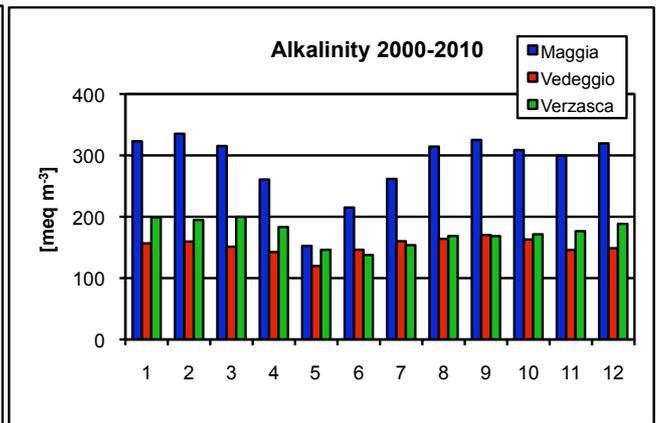
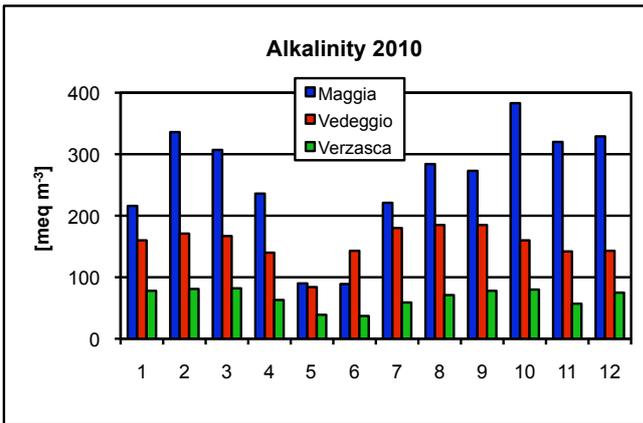
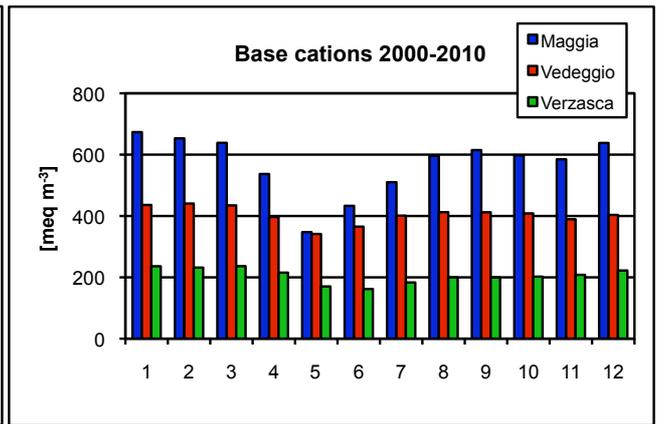
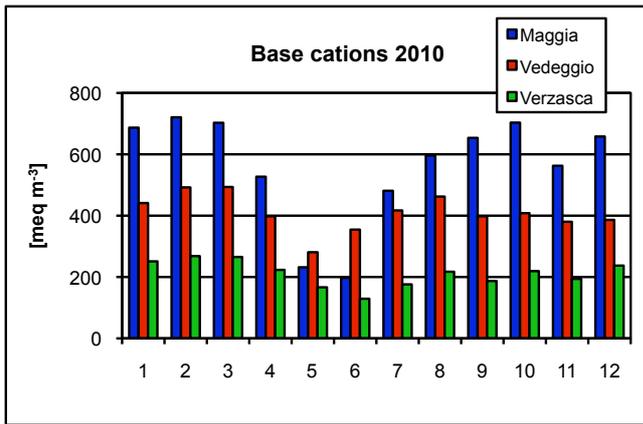
peaks occurred in May and November. Compared to average values discharges during 2010 were particularly high in May. Because water quality of surface waters and rain differ greatly, Steingruber and Colombo (2006) suggested the following mechanisms occurring during rain events and/or snow melt: a dilution of sulphate, base cations and a combination of dilution and consumption of alkalinity. Because of rain acidity river pH clearly decreases during rain events. Differently, aluminium concentrations seem to reach its highest concentrations during high flow events (May-June and November-December, suggesting leakage from soils, probably enhanced by lower pH values during these occasions. Also nitrate concentrations seem to behave opposite to sulphate, chloride, base cations, alkalinity and pH and its variations are more difficult to understand. Highest concentrations normally occur from January to May. More than one factor probably determines its variation of concentrations e.g. higher values during the first months of the year because of higher concentrations in rainwater during that period (Fig. 2.8), increase during intense precipitation or snow melt because of leakage from soils, decrease during photosynthetic activity because of assimilation.

Figure 2.7 Daily mean discharge and concentrations of the main chemical parameters in river water during sampling days in 2010 and their average monthly values during the period 2000-2010.

Base cations correspond to the sum of calcium, magnesium, sodium and potassium.

Discharge of river Vedeggio at Isona was measured by IST (2001-2011). Discharge of river Verzasca at Sonogno and Maggia at Bignasco (without influence of hydropower production) were estimated by discharge values of Verzasca at Lavertezzo published by BWG (2001-2004) and BAFU (2005-2011).





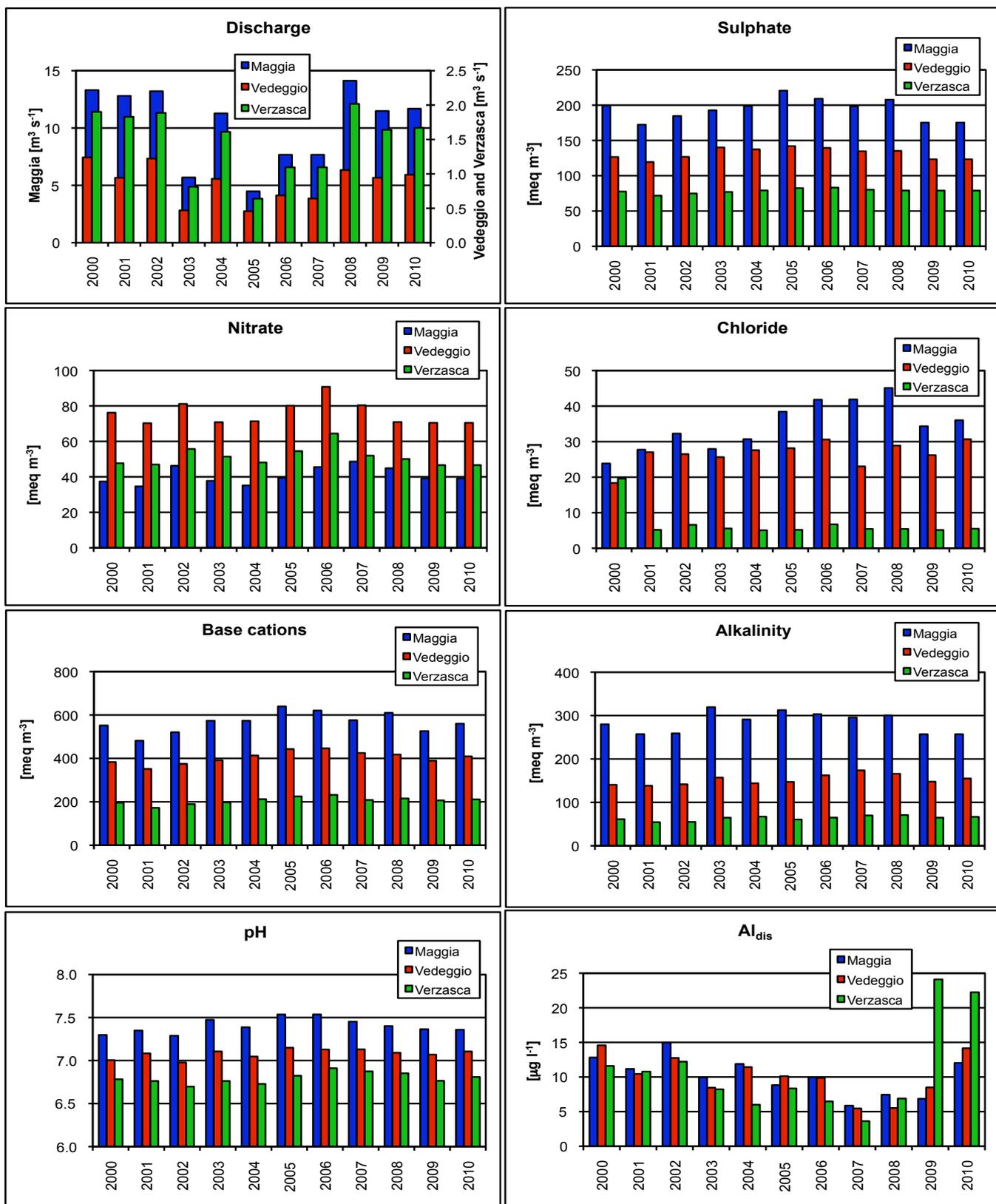
## Temporal variations

In order to detect time trends, annual mean concentrations of sulphate, nitrate, base cations, alkalinity, pH and dissolved aluminium from 2000 to 2010 are presented graphically in Fig. 2.8. Since, as described for seasonal variations in river chemistry, concentrations are very much related to the river discharge, a yearly trend in river chemistry is difficult to detect at a glance. We performed a partial seasonal Mann-Kendall test for the period 2000-2010 with concentrations as response variables and discharge as explanatory variable. Results of the trend analysis are shown in Tab. 2.6. Differently than what observed for precipitation, sulphate and nitrate concentrations in river water did not decrease significantly during the last 11 years. Nevertheless, alkalinity decreased significantly in river Verzasca and river Vedeggio, probably as a consequence of an increase of base cations. The reason for the increase in base cations is not clear yet. Increased weathering rates due to climate warming is a possibility. The increase in base cations is also almost significant in river Maggia. However, probably because of an almost significant increase in concentrations of nitrate, temporal variations of alkalinity are not significant. It is interesting to observe that concentrations of nitrate increase only in river Maggia, where concentrations are, as discussed before, lowest probably a consequence of its larger watershed, being able to retain more nitrogen (longer average residence time). It is possible that soils in the watershed of river Maggia, having absorbed more nitrogen in the past start now to be saturated, decreasing gradually the percentage of nitrogen that can be retained.

**Figure 2.8 Annual mean discharge and annual mean concentrations of the main chemical parameters in river water from 2000 to 2010**

Base cations correspond to the sum of calcium, magnesium, sodium and potassium.

Discharge of river Vedeggio at Isonne was measured by IST (2001-2011). Discharge of river Verzasca at Sonogno and Maggia at Bignasco (without influence of hydropower production) were estimated by discharge values of Verzasca at Lavertezzo published by BWG (2001-2004) and BAFU (2005-2011).



**Table 2.6 Results from trend analyses (significant trends in red) during the period 2000-2010.**

*p* corresponds to the probability level obtained with the partial seasonal Mann-Kendall test and the rate ( $\text{meq m}^{-3} \text{ yr}^{-1}$  for anions and cations,  $\text{mg l}^{-1} \text{ yr}^{-1}$  for  $\text{SiO}_2$ ) with the seasonal Kendall slope estimator.

River	SO <sub>4</sub> <sup>2-</sup>		NO <sub>3</sub> <sup>-</sup>		Cl <sup>-</sup>		Base cations		H <sup>+</sup>		Alcalinity	
	p	rate	p	rate	p	rate	p	rate	p	rate	p	rate
Maggia	0.431	1.19	0.076	0.58	0.004	1.75	0.067	6.29	0.385	0.00	0.906	-0.88
Vedeggio	0.527	0.17	0.774	-0.06	0.283	0.13	0.087	5.33	0.251	0.00	0.051	2.21
Verzasca	0.092	0.50	0.781	-0.17	0.221	0.00	0.008	3.48	0.286	0.00	0.018	1.08

### 2.5.3 Alpine lakes

During 2010 sampling of alpine lakes occurred at the following days: 5.7, 13.9, 12.10. Yearly mean concentrations of the main chemical parameters measured in lake surface water during 2010 are presented in Tab. 2.7. Means were calculated by averaging first the two autumn values and then the autumn with the summer value.

With exception of Lago Bianco, the chemical water composition is typical for carbonate poor mountain regions: low conductivity, alkalinity and pH and small nutrient and DOC concentrations. Average conductivity at 25°C varied between 7.4 and 17.0  $\mu\text{S cm}^{-1}$ , alkalinity between -4.8 and 74.0  $\text{meq m}^{-3}$ , pH between 5.3 and 6.9, sulphate between 16.0 and 83.4  $\text{meq m}^{-3}$ , nitrate between 12.1 and 28.0  $\text{meq m}^{-3}$ , dissolved organic carbon between 0.1 and 0.6  $\text{mg C l}^{-1}$ , reactive dissolved silica between 0.9 and 3.3  $\text{mg SiO}_2 \text{l}^{-1}$  and total dissolved aluminium between 1.1 and 65.1  $\mu\text{g l}^{-1}$ .

**Table 2.7 Average lake surface water concentrations during 2010**

*Average values with some values below the quantification limit were preceded with <*

Lake name	Conductivity 25°C ( $\mu\text{S cm}^{-1}$ )	pH	Alkalinity (meq $\text{m}^{-3}$ )	Ca <sup>2+</sup> (meq $\text{m}^{-3}$ )	Mg <sup>2+</sup> (meq $\text{m}^{-3}$ )	Na <sup>+</sup> (meq $\text{m}^{-3}$ )	K <sup>+</sup> (meq $\text{m}^{-3}$ )	NH <sub>4</sub> <sup>+</sup> (meq $\text{m}^{-3}$ )	SO <sub>4</sub> <sup>2-</sup> (meq $\text{m}^{-3}$ )	NO <sub>3</sub> <sup>-</sup> (meq $\text{m}^{-3}$ )	Cl <sup>-</sup> (meq $\text{m}^{-3}$ )	DOC (mg C $\text{l}^{-1}$ )	SiO <sub>2</sub> (mg $\text{l}^{-1}$ )	Al <sub>dissolved</sub> ( $\mu\text{g l}^{-1}$ )	Al <sub>tot</sub> ( $\mu\text{g l}^{-1}$ )	C <sub>dissolved</sub> ( $\mu\text{g l}^{-1}$ )	C <sub>tot</sub> ( $\mu\text{g l}^{-1}$ )	Zn <sub>dissolved</sub> ( $\mu\text{g l}^{-1}$ )	Zn <sub>total</sub> ( $\mu\text{g l}^{-1}$ )
Lago del Starlaresc da Sgiöf	8.9	5.4	-2.8	31.0	7.9	11.3	4.2	2.0	25.5	26.0	4.2	0.6	1.6	65.1	76.1	0.3	0.4	4.3	4.6
Lago di Tomè	8.7	5.6	2.5	41.3	5.3	10.9	3.4	0.7	24.6	28.0	2.6	0.2	1.9	25.4	28.0	0.3	0.3	3.6	3.9
Lago dei Porchieisc	17.0	6.7	51.5	114.6	10.2	15.8	9.8	0.7	61.4	21.0	2.5	0.2	3.1	2.0	3.0	<0.2	<0.3	1.7	1.8
Lago Barone	8.2	6.0	11.3	45.2	5.0	8.5	3.6	2.8	27.6	17.8	2.6	0.3	1.3	4.7	7.0	0.3	0.4	2.4	2.8
Laghetto Gardiscio	7.8	5.3	-4.8	23.2	6.3	6.0	5.1	1.5	28.4	13.8	2.1	0.1	0.9	52.0	56.8	0.3	0.4	4.1	4.6
Lago Leit	15.8	6.4	25.3	81.2	23.3	14.9	10.5	0.9	83.4	13.6	2.5	0.3	2.1	2.8	5.7	<0.3	0.4	4.8	4.9
Lago di Morghirolo	12.0	6.5	34.0	69.7	14.6	13.5	10.7	0.7	43.4	14.0	3.1	0.3	2.0	1.7	3.1	<0.3	<0.4	2.4	2.6
Lago di Mognòla	15.4	6.8	46.5	88.2	19.0	20.5	11.3	0.3	57.9	18.6	2.8	0.3	2.9	3.7	5.9	0.3	0.3	1.5	1.7
Laghetto Inferiore	9.6	6.5	31.0	57.0	7.8	11.6	8.3	0.6	25.3	18.1	2.4	0.3	1.6	4.8	7.3	0.3	0.3	1.8	1.9
Laghetto Superiore	9.0	6.5	32.0	51.0	7.1	10.3	7.0	0.8	22.2	15.8	2.8	0.4	1.4	4.4	5.7	<0.3	<0.3	1.7	1.8
Lago Nero	13.5	6.7	50.8	91.9	11.7	13.0	9.1	1.1	45.2	12.2	2.6	0.3	1.5	1.6	2.6	<0.3	0.5	2.6	3.0
Lago Bianco	68.8	7.5	362.8	556.2	63.4	13.0	17.3	0.3	245.1	10.5	2.6	0.3	2.0	8.2	8.4	<0.3	<0.3	1.1	1.3
Lago della Froda	12.2	6.6	46.8	90.5	7.5	10.1	5.4	0.5	37.9	12.8	1.9	0.3	1.6	2.0	3.2	<0.2	<0.3	2.2	2.5
Lago d'Antabia	11.5	6.8	55.8	81.4	5.5	15.5	5.7	0.5	18.8	19.6	2.3	0.2	2.4	2.1	2.8	<0.2	<0.3	0.8	1.1
Lago della Crosa	7.4	6.4	20.3	43.7	4.5	9.4	4.3	0.5	16.0	17.6	2.6	0.2	1.6	1.1	1.3	<2	<0.2	1.3	2.0
Lago d'Orsalia	8.5	6.4	27.0	55.4	5.8	10.4	3.6	0.8	16.1	22.3	2.5	0.2	1.6	4.1	6.8	<0.2	<0.3	1.5	1.7
Schwarzsee	10.1	6.5	35.0	68.9	7.5	11.4	5.4	0.4	23.7	20.2	2.8	0.3	2.0	4.5	5.1	<0.3	0.3	2.7	3.3
Laghi dei Pozzöi	8.1	6.4	29.0	47.6	8.2	12.9	3.6	0.5	21.6	12.1	3.1	0.5	2.2	10.8	18.4	<0.3	<0.4	1.6	1.8
Lago di Sfilie	9.3	6.5	30.5	54.0	9.1	14.0	4.4	0.7	25.7	16.6	3.0	0.6	2.2	11.6	17.4	<0.3	<0.3	3.5	3.8
Lago di Sascòla	9.6	6.0	9.3	46.1	10.3	12.2	6.9	0.9	28.3	25.5	3.7	0.6	1.9	22.2	36.4	0.4	0.5	3.8	4.1
Lago d'Alzasca	16.0	6.9	74.0	103.3	17.8	19.9	11.5	0.8	39.3	17.6	3.4	0.4	3.3	2.2	12.3	<0.3	<0.4	1.3	1.6

In order to better compare chemistry of lakes with low alkalinities, values of the main parameters measured during 2010 and their mean values from 2000 to 2010 are shown graphically in Fig. 2.9.

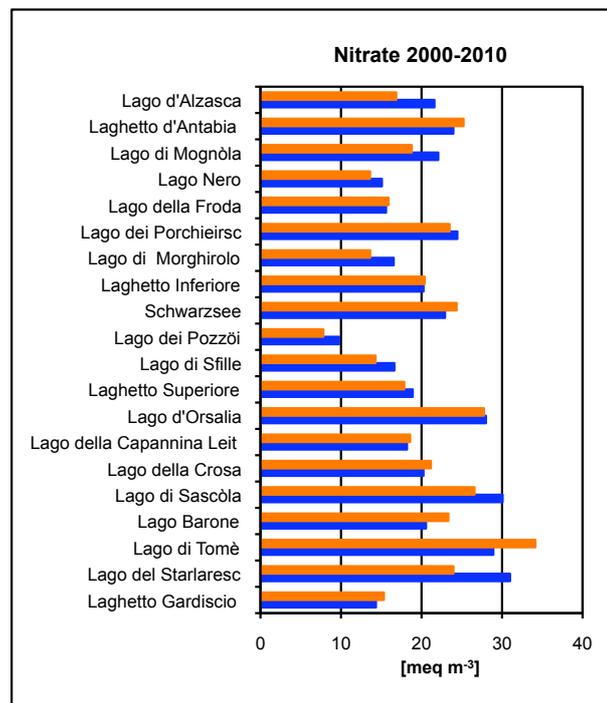
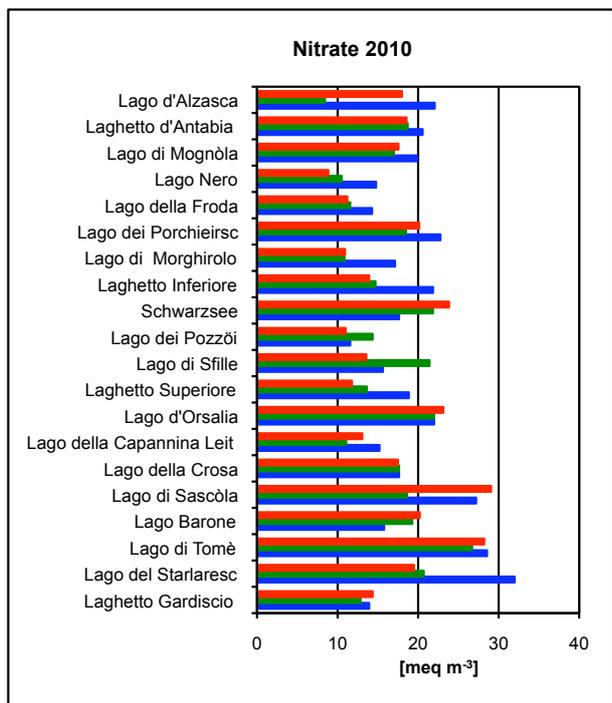
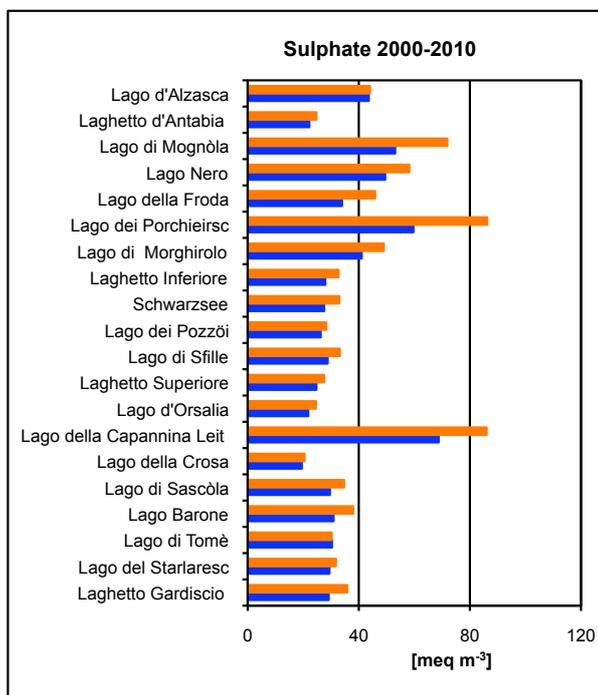
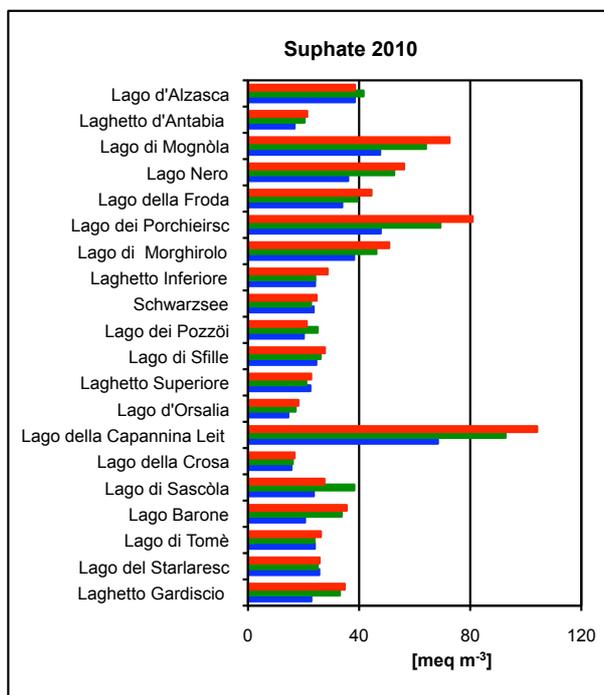
In general values from 2010 are not much different from their means during the last 11 years. During 2010 alkalinities below 0 meq m<sup>-3</sup> were detected in 3 lakes (Laghetto Gardiscio and Lago del Starlaresc da Sgiof during 3 sample events and Lago di Tomè once). Only one lake had alkalinities always above 50 meq m<sup>-3</sup> (Lago d'Alzasca) and was therefore not sensitive to acidifications. All other 19 lakes were at least temporary sensitive to acidification (0 < alkalinity < 50 meq m<sup>-3</sup>). It also immediately appears that alkalinity correlates well with pH and concentrations of aluminium. Lakes with lowest alkalinities had also lowest pH and highest concentrations of aluminium. Particularly high concentrations of aluminium were measured in lakes with pH's <= 6 like Lago del Starlaresc da Sgiof, Lago, Laghetto Gardiscio, Lago di Tomè and Lago di Sascòla where concentrations of aluminium ranged between 4 and 75 µg l<sup>-1</sup>. In general concentrations of base cations also correlate well with alkalinity, which is not surprising since in nature carbonate is often associated with calcium or magnesium. Differently, because of their mainly atmospheric origin, sulphate and nitrate concentrations do not correlate with alkalinity. Highest concentrations of sulphate occur in lakes with catchments rich in geogenic sulphate (Lago della Capannina Leit, Lago dei Porchieirsc, Lago di Mognòla, Lago Nero, Lago di Morghirolo, Lago della Froda). Because deposition of sulphate does not differ greatly between lakes, concentrations of sulphate in the other lakes are similar to each other. For nitrate, differences in concentrations among lakes are more difficult to understand. Similarly to sulphate, deposition of nitrate is probably similar for all lakes, so that differences in concentrations may result as a consequence of the presence of geogenic nitrate and the retention capacity of the catchment.

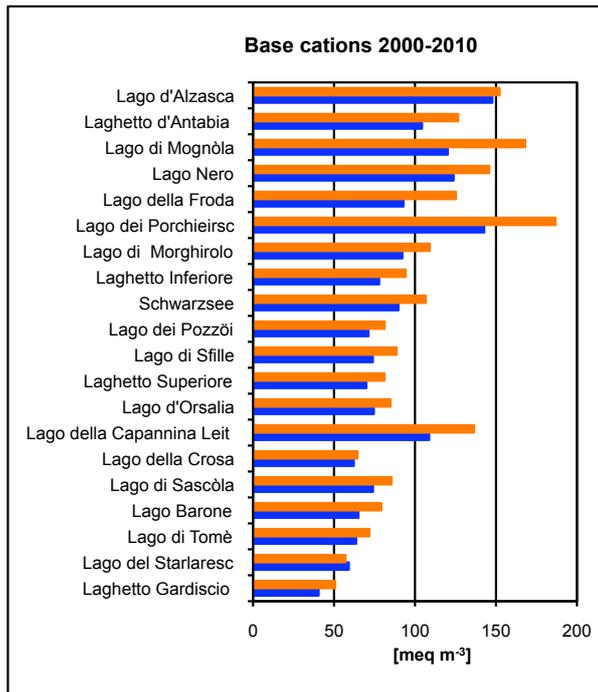
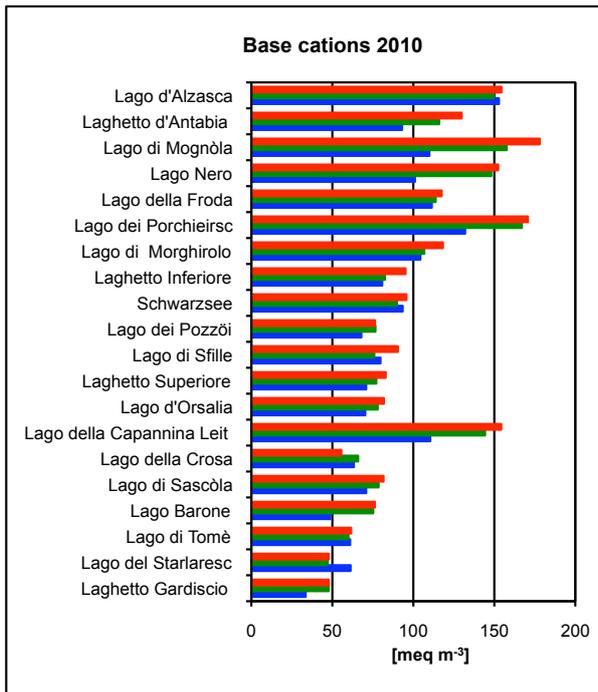
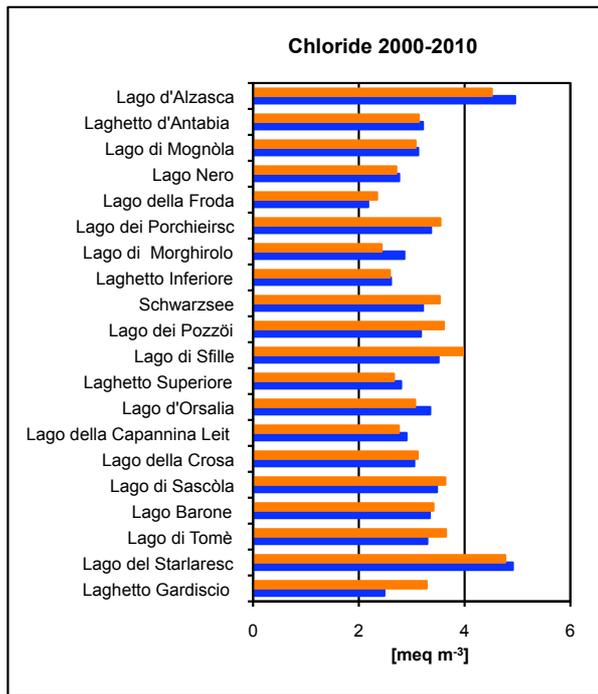
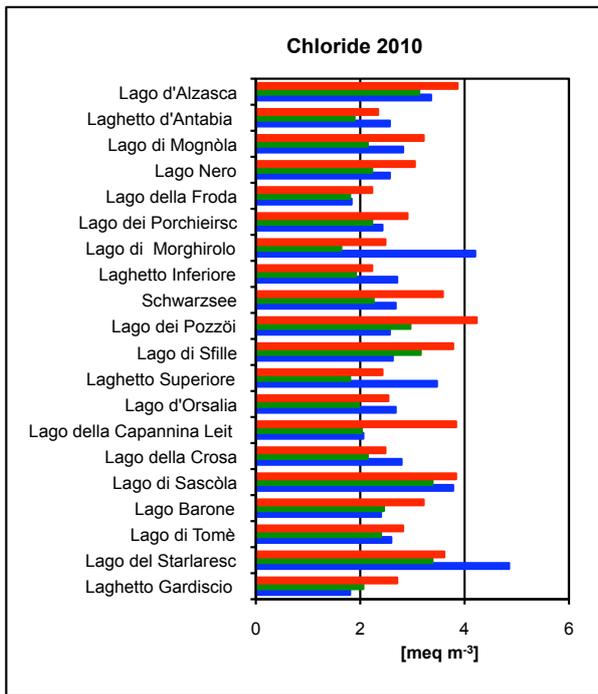
Fig. 2.9 also shows some seasonal differences. These are mostly in agreement with seasonal variations observed for rivers. In most lakes alkalinity and pH and concentrations of sulphate and base cations are lower in July than in September and October. As discussed for rivers, the elevated discharge in spring causes a dilution of sulphate, base cations and a combination of dilution and consumption of alkalinity. Concentrations of nitrate seem to differ more between the months June/July, September/October in lakes compared to rivers. Concentrations in lakes are often higher at the beginning of the summer compared to fall. More than one factor may be responsible for it: e.g. leakage from soils during elevated discharge periods, nitrate peaks during snow melt, period of poor photosynthetic activity.

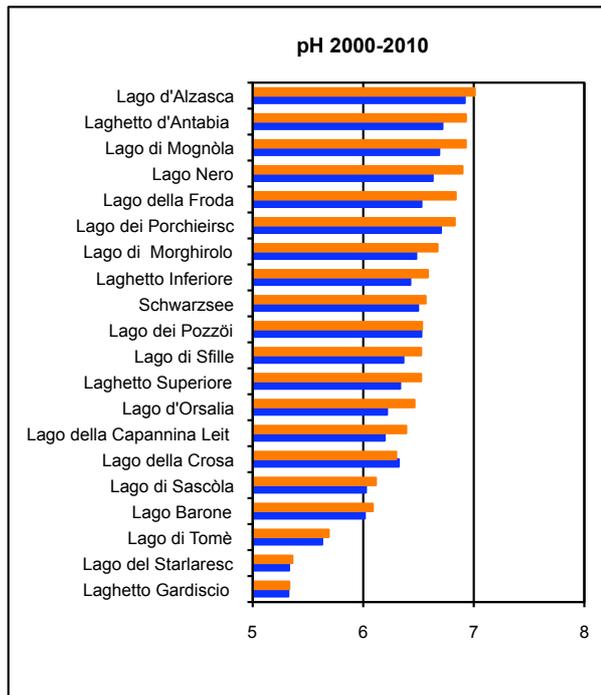
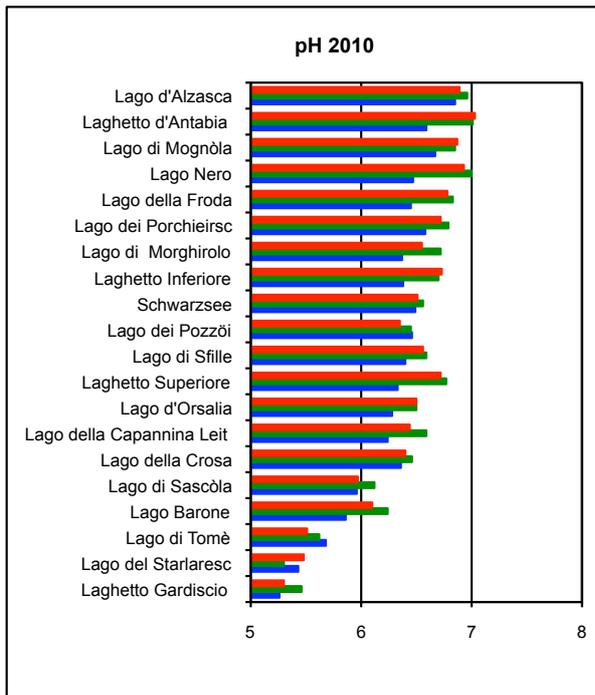
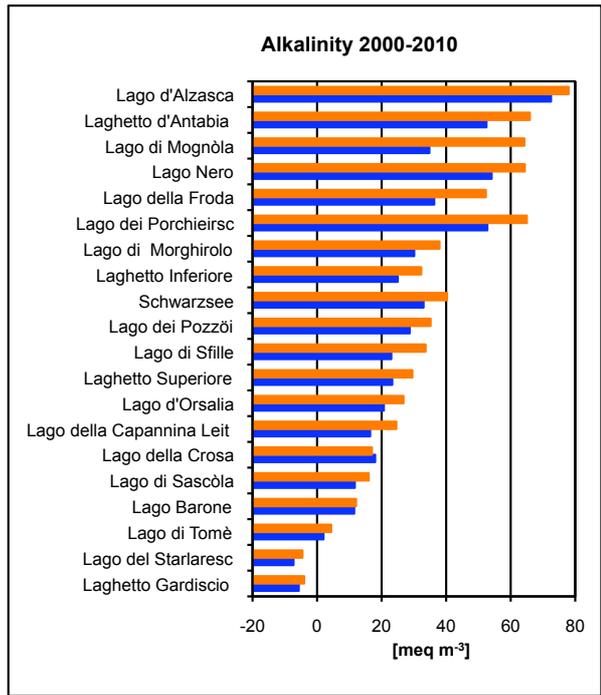
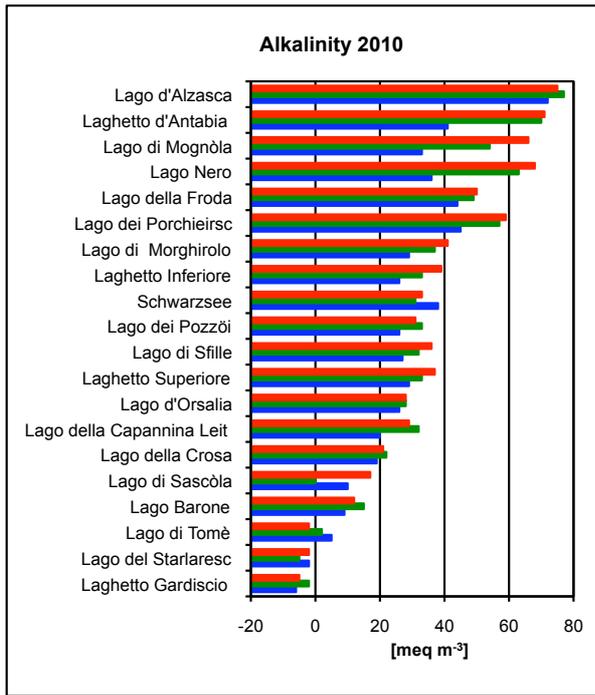
**Figure 2.9 Annual average concentrations of the main chemical parameters in 20 Alpine lakes during 2010 and their average values from 2000 to 2010.**

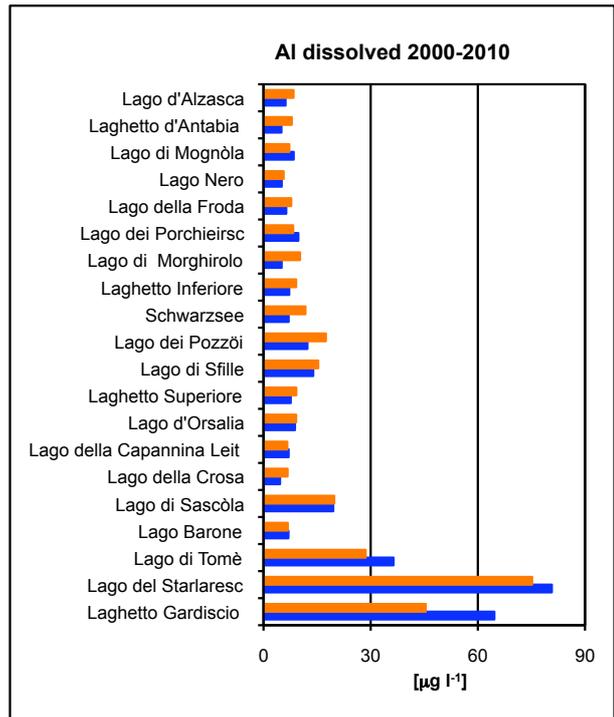
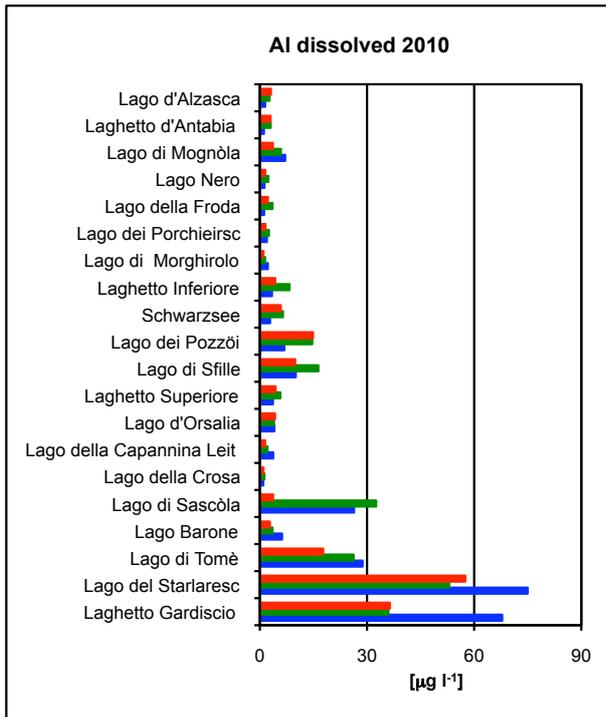
*Blue: summer, green: autumn 1, red: autumn 2; orange: mean autumn*

*Base cations correspond to the sum of calcium, magnesium, sodium and potassium.*







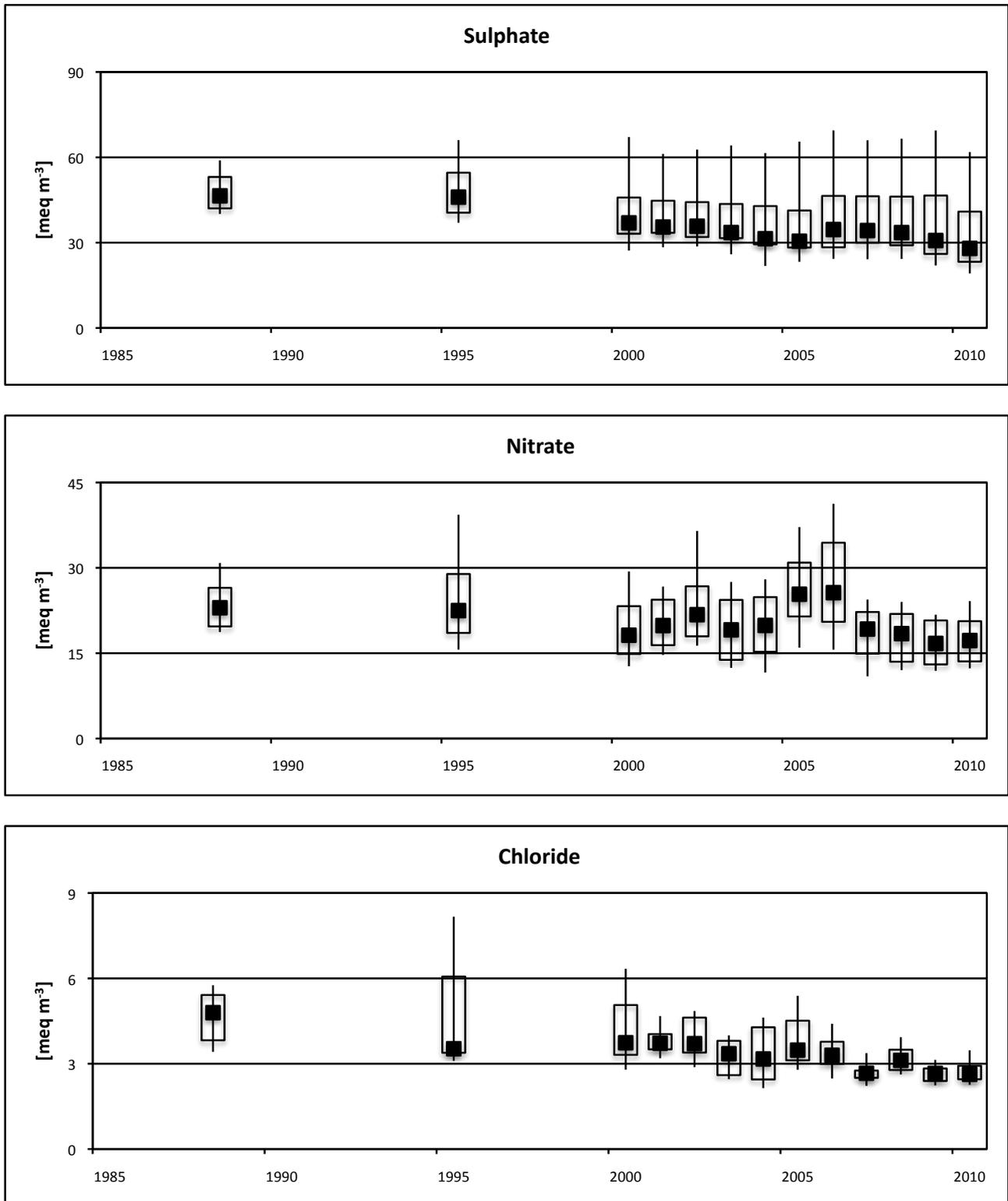


In order to show temporal variations of lake quality, annual median values of pH, alkalinity and concentrations of base cations, sulphate and nitrate of all lakes with their 10th, 25th, 75th and 90th percentile values are represented in Fig. 2.10. Only years, where all 20 alpine lakes have been monitored were chosen. As already discussed in Steingruber and Colombo (2006), after 1980's sulphate concentrations decreased, mainly because of the reduction of the sulphur content in heating oils and the partial substitution of sulphur rich carbon with other fossil fuels. As a consequence lake alkalinity and pH increased. For base cations and nitrate concentrations no trend seem to exist. Aluminium concentrations of the 3 most acidic lakes are presented in Fig. 2.11. A decrease in concentrations can be observed.

Results of a detailed trend analysis of the main parameters during the last 11 years are presented in Tab.2.8. Accordingly to what observed for rainwater concentrations, in 9 lakes a significant decrease in sulphate concentrations can be observed. However, only in 3 lakes (Lago di Sfille, Laghetto Superiore and Lago del Starlaresc da Sgiof) this decrease caused recently a significant increase in lake alkalinity. Trends in concentrations of nitrate are still not significant. However, in 10 lakes concentrations of chloride decreased significantly, reflect the trend in chloride deposition at some sampling stations. This phenomena may be the result of reduced sea-salt episodes and/or the increasing control of hydrochloric acid emissions from waste incineration plants, coal-fired power plants and from the chemical industry.

Figure 2.10 Temporal variations of annual median values and their 10<sup>th</sup>, 25<sup>th</sup>, 75<sup>th</sup>, 90<sup>th</sup> percentiles of parameters measured in 20 Alpine lakes from 1988 to 2010

Base cations correspond to the sum of calcium, magnesium, sodium and potassium.



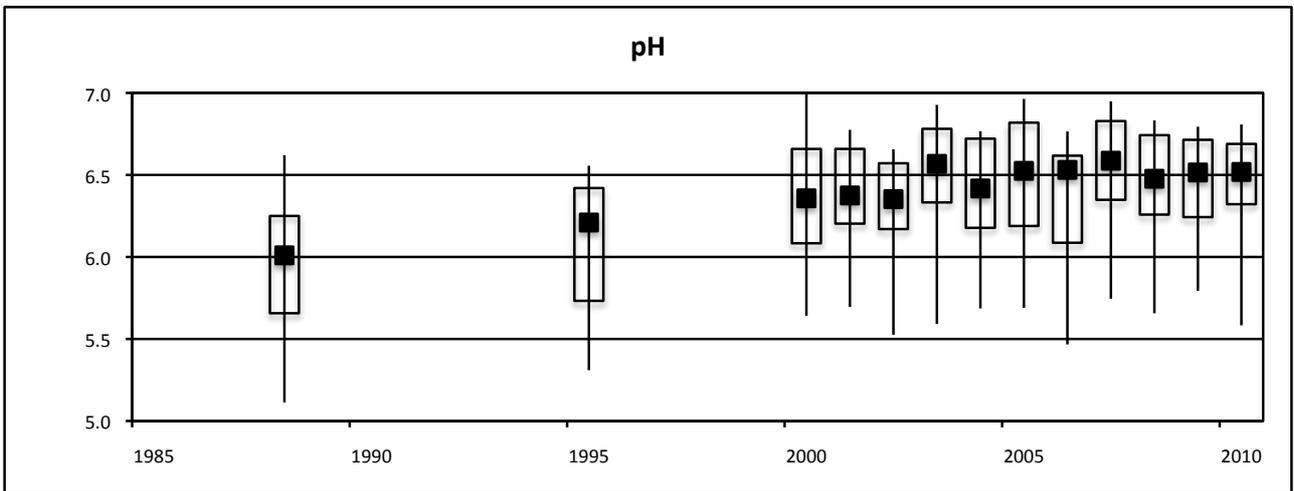
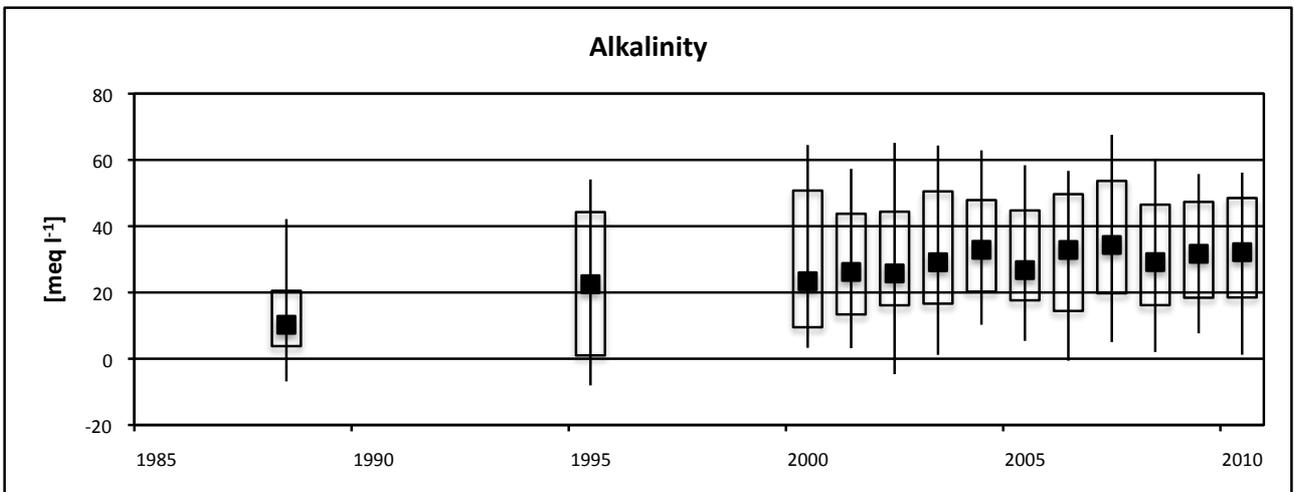
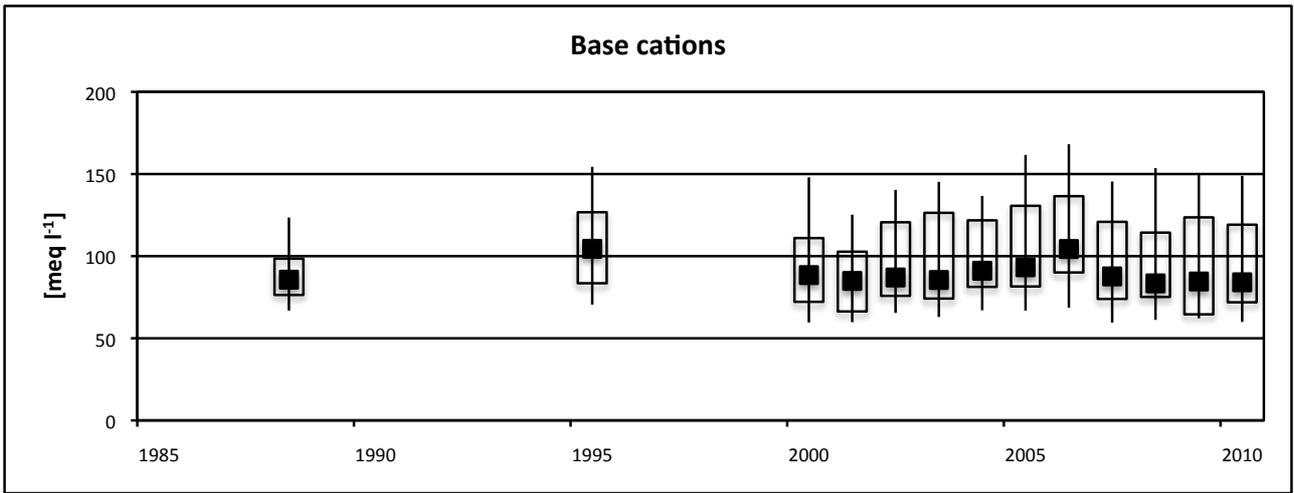
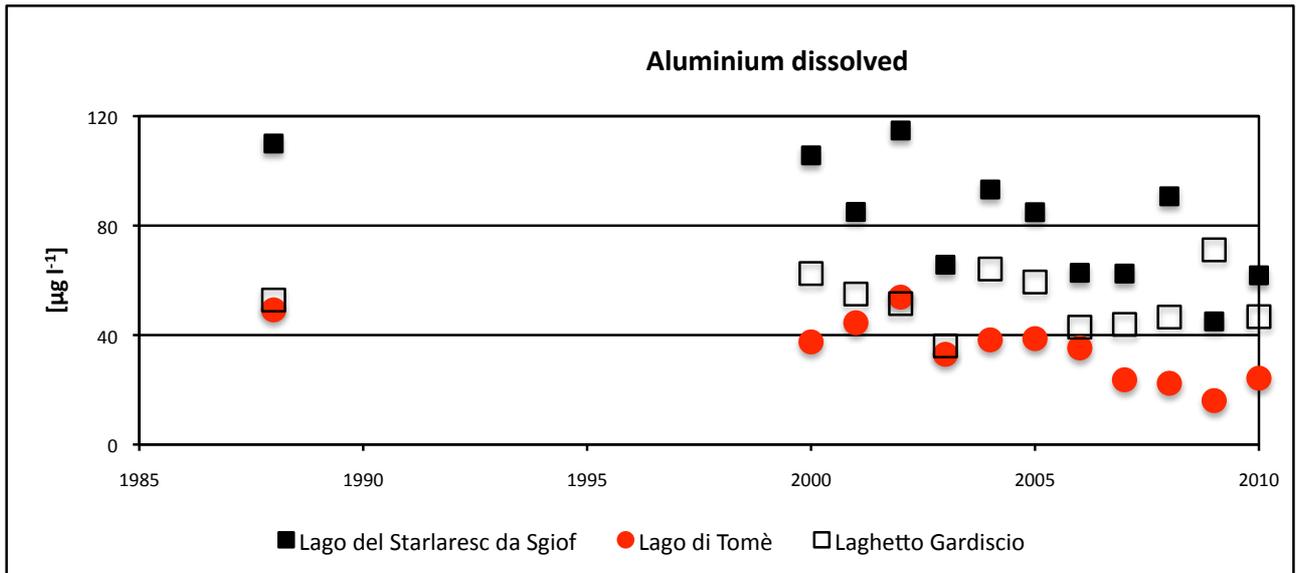


Figure 2.11 Temporal variations of dissolved aluminium in the 3 most acidic lakes from 1988 to 2010



**Table 2.8 Results from trend analyses (significant trends in red) during the period 2000-2010.**

*p* corresponds to the probability level obtained with the seasonal Mann-Kendall test and the rate ( $\text{meq m}^{-3} \text{yr}^{-1}$  for anions and cations,  $\text{mg l}^{-1} \text{yr}^{-1}$  for  $\text{SiO}_2$ ) with the seasonal Kendall slope estimator.

Lake	SO <sub>4</sub> <sup>2-</sup>		NO <sub>3</sub> <sup>-</sup>		Cl <sup>-</sup>		Base cations		H <sup>+</sup>		Alcalinity		Al <sub>dis</sub>	
	p	rate	p	rate	p	rate	p	rate	p	rate	p	rate	p	rate
Lago del Starlaresc da Sgiöf	0.001	-0.95	0.096	-0.74	0.024	-0.23	0.024	-1.14	0.024	-0.45	0.044	1.14	0.078	-3.93
Lago di Tomè	0.004	-1.21	0.053	-0.71	0.056	-0.12	0.168	-0.96	0.546	-0.07	0.290	0.49	0.012	-3.06
Lago dei Porchieisc	0.625	-0.68	0.560	-0.44	0.079	-0.17	0.959	0.47	0.401	0.00	0.683	-0.14	0.541	-0.17
Lago Barone	0.212	-0.74	0.060	-0.52	0.026	-0.10	0.822	-0.72	0.514	0.03	0.951	-0.06		
Laghetto Gardiscio	0.142	-0.57	0.370	-0.18	0.048	-0.13	0.627	-0.23	0.528	0.04	0.953	0.00		
Lago Leit	0.110	0.82	0.140	-0.26	0.005	-0.12	0.043	2.49	0.921	0.00	0.234	0.36		
Lago di Morghirolo	0.064	0.16	0.460	-0.14	0.114	-0.11	0.087	1.60	0.789	0.00	0.093	0.54		
Lago di Mognòla	0.300	0.14	0.716	-0.25	0.202	-0.08	0.606	0.34	0.839	0.00	0.344	-0.30		
Laghetto Inferiore	0.013	-0.69	0.217	-0.24	0.066	-0.11	0.543	0.13	0.416	0.00	0.173	0.33		
Laghetto Superiore	0.005	-0.77	0.074	-0.37	0.042	-0.08	0.765	0.33	0.270	-0.01	0.036	0.56		
Lago Nero	0.656	-0.61	0.895	0.05	0.621	0.00	0.133	-0.70	0.513	0.01	0.951	-1.25		
Lago della Froda	0.833	0.05	0.259	-0.40	0.066	-0.06	0.075	1.78	0.573	0.00	0.572	0.55		
Lago d'Antabia	0.002	-0.87	0.072	-0.45	0.012	-0.12	0.567	-1.28	0.582	0.01	0.320	-1.63		
Lago della Crosa	0.005	-0.71	0.735	0.06	0.049	-0.07	0.933	-0.08	0.215	-0.01	0.081	0.37		
Lago d'Orsalia	0.004	-0.92	0.126	-0.60	0.033	-0.11	0.599	-0.65	0.136	-0.01	0.084	0.61		
Schwarzsee	0.123	-0.70	0.105	-0.70	0.011	-0.15	0.351	-0.51	0.788	0.00	0.729	-0.13		
Laghi dei Pozzöi	0.019	-0.88	0.794	-0.03	0.053	-0.13	0.778	-0.40	0.817	0.00	0.611	-0.20		
Lago di Sfilie	0.010	-0.67	0.182	-0.47	0.005	-0.17	0.943	0.15	0.239	-0.01	0.021	1.06		
Lago di Sascòla	0.188	-0.45	0.153	-0.43	0.127	-0.14	0.296	-0.97	0.818	0.00	0.668	0.25		
Lago d'Alzasca	0.236	-0.17	0.735	-0.15	0.168	-0.09	0.174	1.61	0.549	0.00	0.243	1.10		

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