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)

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Content

Abstract

Compared to previous years, 2011 was rather dry. In general, concentrations of the main chemical parameters in precipitation and wet depositions were comparable to values of the last years. For some parameters temporal trends in concentrations are immediately visible. From 1990 as a consequence of reduced SO_2 emissions, yearly deposition of sulphate decreased below 50 meq m^{-2} at all stations. Because of the reduction of the emissions of NO_x and NH_3, deposition of nitrate and ammonium also slightly decreased during the last decade especially at the more polluted sites (Locarno Monti, Lugano, Stabio). It followed a reduction of deposition of acidity from 60 meq m^{-2} to 0 meq m^{-2}, on average. For rivers both seasonal and yearly mean concentrations were similar to values of the last 10 years and no significant trend could be observed. Differently, in lakes in agreement with wet deposition, concentrations of sulphate and nitrate also decreased, leading to an increase of alkalinity and pH. It followed also a significant decrease of concentrations of aluminium in the most acid lakes Lago Tomé and Lago del Starlaresc da Sgiof (pH < 6) to values around 20 mg l^{-1} in the first and close to 40 mg l^{-1} in the second. Nevertheless, a recovery of macroinvertebrate in these lakes cannot yet be observed and moderately sensitive species, as they occur in the other less acid monitored lakes with pH >= 6.5 (Lago Bianco, Laghetto Inferiore, Lago Superiore) are still rare or absent. For what concerns concentrations of DDT's, PCB's and mercury in fish angled in Laghetto Superiore during 2010, values are in the same range as those measured in previous years. Concentrations of DDT's and mercury did not vary significantly. Differently, concentrations of PCB's seemed to decrease after 2003.

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 20 countries in Europe and North America are available in the database of the Programme Centre. Switzerland joined the Programme in 2000 on behalf of the Swiss Federal Office for the Environment with the support of Canton Ticino.

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

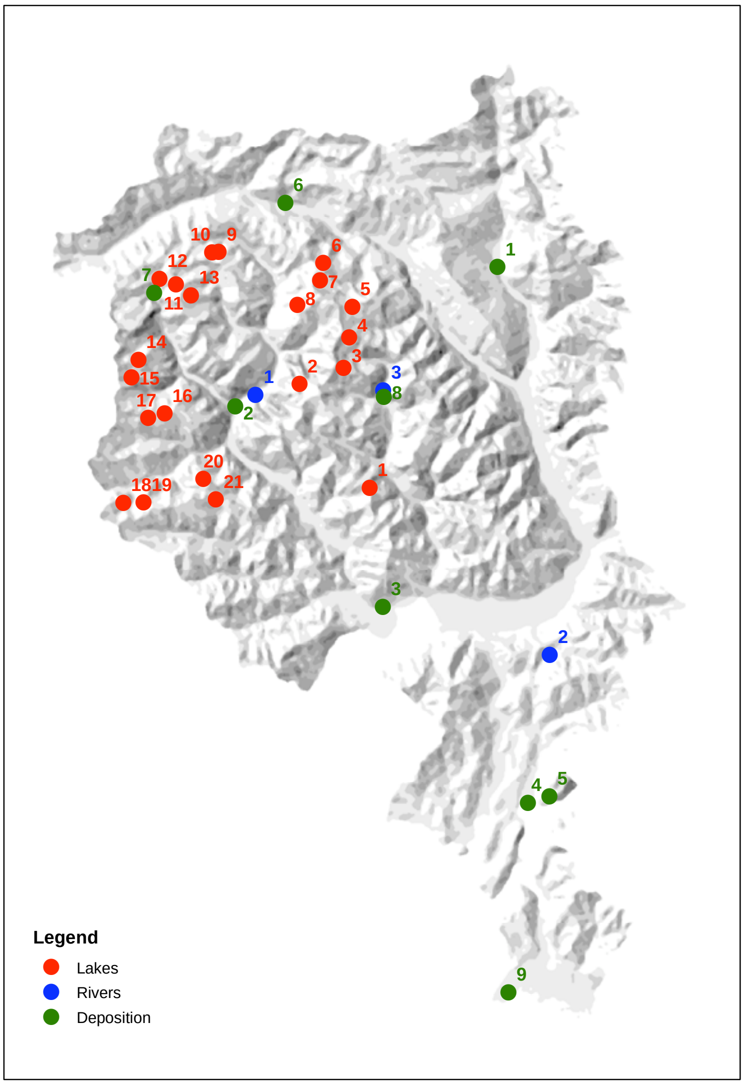


Table 1.1 Lake parameters

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 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 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'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

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^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 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 meq m^{-3}, sensitive to acidification when 0 < alkalinity < 50 meq m^{-3} and with low alkalinity but not sensitive to acidification when 50 < alkalinity < 200 meq m^{-3} (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 water chemistry of 20 Alpine lakes (21 from 2006) and 3 rivers (Maggia, Vedeggio, Verzasca) and wet deposition 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 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 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 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	0.010 mg l^{-1}
Mg^{2+}	CA filter	PP bottle, 4°C	ion cromatography	0.005 mg l^{-1}
Na^{+}	CA filter	PP bottle, 4°C	ion cromatography	0.005 mg l^{-1}
K^{+}	CA filter	PP bottle, 4°C	ion cromatography	0.010 mg l^{-1}
NH_4^{+}	CA filter	PP bottle, 4°C	spectrophotometry	3 µg N l^{-1}
SO_4^{2+}	CA filter	PP bottle, 4°C	ion cromatography	0.005 mg l^{-1}
NO_3^{-}	CA filter	PP bottle, 4°C	ion cromatography	0.010 mg N l^{-1}
NO_2^{-}	CA filter	PP bottle, 4°C	spectrophotometry	1 µg N l^{-1}
Cl^{-}	CA filter	PP bottle, 4°C	ion cromatography	0.010 mg l^{-1}
soluble reactive P	CA filter	PP bottle, 4°C	spectrophotometry	4 µg P l^{-1}
soluble reactive Si	CA filter	PP bottle, 4°C	ICP-OES with ultrasonic nebulizer	0.003 mg Si l^{-1}
total P	No	glass bottle, immediate mineralisation	persulphate digestion, spectrophotometry	4 µg P l^{-1}
DOC	PC filter	brown glass bottle, + H_3PO_4	UV-persulfate	0.05 mg C l^{-1}
soluble Al	PC filter	acid washed PP bottle, +HNO_3, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 µg l^{-1}
total Al	No	acid washed PP bottle, +HNO_3, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 µg l^{-1}
soluble Cu	PC filter	acid washed PP bottle, +HNO_3, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 µg l^{-1}
total Cu	No	acid washed PP bottle, +HNO_3, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 µg l^{-1}
soluble Zn	PC filter	acid washed PP bottle, +HNO_3, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 µg l^{-1}
total Zn	No	acid washed PP bottle, +HNO_3, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 µg l^{-1}
soluble Pb	PC filter	acid washed PP bottle, +HNO_3, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 µg l^{-1}
total Pb	No	acid washed PP bottle, +HNO_3, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 µg l^{-1}
soluble Cd	PC filter	acid washed PP bottle, +HNO_3, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 µg l^{-1}
total Cd	No	acid washed PP bottle, +HNO_3, 4°C	Adsorptive Stripping Voltammetry (AdSV)	0.2 µg l^{-1}

2.4 Results and discussion

2.4.1 Wet deposition

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 2011

Sampling site	Precipitation (mm)	Analysed precipitation (mm)	Conductivity 25°C (µS cm^{-1})	pH	Ca^{2+}		Mg^{2+}		Na^{+}		K^{+}		NH_4^{+}		HCO_3^{-}		SO_4^{2-}		NO_3^{-}		Cl^{-}		Acidity = $H^{+}– HCO_3^{-}$	
					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	1048	926	9	5.6	19	19	5	5	5	5	2	2	29	24	13	14	19	19	23	24	5	5	-11	-11
Bignasco	1477	1262	9	5.4	15	23	3	4	4	6	1	2	26	39	5	8	17	25	25	37	4	6	-1	-1
Locarno Monti	1578	1436	13	5.3	21	33	4	7	6	10	2	3	39	61	8	13	26	41	34	54	5	8	-3	-5
Lugano	1179	906	12	5.4	19	23	4	4	5	6	4	5	42	49	13	16	23	28	34	40	5	5	-10	-12
Monte Brè	1179	618	10	5.2	17	20	4	5	6	7	2	3	24	27	11	12	16	19	24	29	6	7	-4	-4
Piotta	1269	1153	8	5.5	14	17	3	3	9	11	2	3	23	29	9	11	15	20	18	23	8	10	-5	-7
Robiei	2071	1653	7	5.5	21	43	2	4	2	5	1	2	21	44	13	28	13	28	19	39	2	4	-10	-21
Sonogno	1829	1487	9	5.5	13	40	3	12	5	10	2	5	29	64	11	41	16	35	22	47	4	9	-8	-34
Stabio	1239	1136	13	5.4	20	24	4	5	7	8	2	2	49	60	16	20	24	30	36	45	6	8	-12	-15

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. On average 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. On average 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 in general at Locarno Monti, Lugano, Stabio while lowest can be observed at Acquarossa, Bignasco, Piotta. For base cations and bicarbonate, deposition rates are usually 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).

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 mean 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 2011 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 2011 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 2011 was lower in most months. Only in June and July precipitation was significantly higher than average. The wettest months in 2011 were July, June followed by November.

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_2 in the air (high in winter and low in summer). Therefore SO_2 cannot be the main factor influencing seasonality of sulphate concentrations in rainwater. Interestingly, dividing sulphate concentrations with concentrations of SO_2 for all sampling sites maximum summer values and minimum winter values can be observed (data not shown), suggesting that the oxidation rate of SO_2 to SO_4^{2-} 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_2 concentration in the air and the oxidation rate from SO_2 to SO_4^{2-}. Compared to the mean values concentrations of sulphate during 2011 were in general lower, especially at the beginning of the year at sites where concentrations are usually higher. Sulphate peaks occurred at Piotta and Monte Brè in May, at Acquarossa in October and at Stabio (and Locarno Monti) in December. The peaks in October and December coincided with very low precipitation volumes, explaining the higher concentrations due to a concentration effect of solutes. In fact, other solutes concentrations (nitrate, cloride, base cations, ammonia) were also slightly elevated. Differently, the peaks in May at Piotta and Monte Brè coincided also with peaks in concentrations of bicarbonate and low acidity suggesting the occurrence of a small alkaline rain event.

Monthly mean concentrations of nitrate are highest in February-March and lowest in December-January. Differently, concentrations of NO_2 in the air are highest in November-February in and lowest in May-August. Dividing concentrations of nitrate with those of NO_2 maximum values occur during summer and minimum values during winter (data not shown), suggesting that, as already observed for sulphate, oxidation rate of NO_x to NO_3^- 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_2 and the already increasing oxidation rates of NO_x to NO_3^- in spring. From April to December the seasonality of nitrate during 2011 is similar to that of the mean values during 2000-2010 but values are lower. Significantly lower than average were, especially at the more polluted sites (Lugano, Stabio, Locarno Monti), the concentrations in February and March. Exceptions are the peaks at Acquarossa in October and at Stabio (and Locarmo Monti) in December already explained in the former paragraph.

Monthly mean chloride concentrations are in general very low. Higher values can be measured during winter months when chloride is spread on the roads to inhibit ice formation. This happens regularly at Piotta. Other peaks mainly occur in winter in concomitance with very low monthly precipitation volumes (see Stabio and Monte Brè in December 2011).

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_2. Similar to what already observed for sulphate and nitrate, the seasonality of ammonium during 2011 was similar to the average values during the period 2000-2010 but the concentrations are in general lower especially at the beginning of the year at the usually more polluted sites.

The seasonality of the monthly mean concentrations of base cations and bicarbonate are very similar indicating the two are in general connected to each other. During 2000-2010 concentrations of base cations and bicarbonate are on average highest in April-June and October-November overlapping with periods rich in precipitation. It is possible that more numerous rain events 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. As a consequence of decreased acidity during summer, pH values are also highest during summer. During 2011 particular high concentrations of base cations, bicarbonate and low acidity occurred in May at Piotta and Monte Brè and at Robiei in September-October.

Figure 2.1 Monthly precipitation
Data from MeteoSwiss

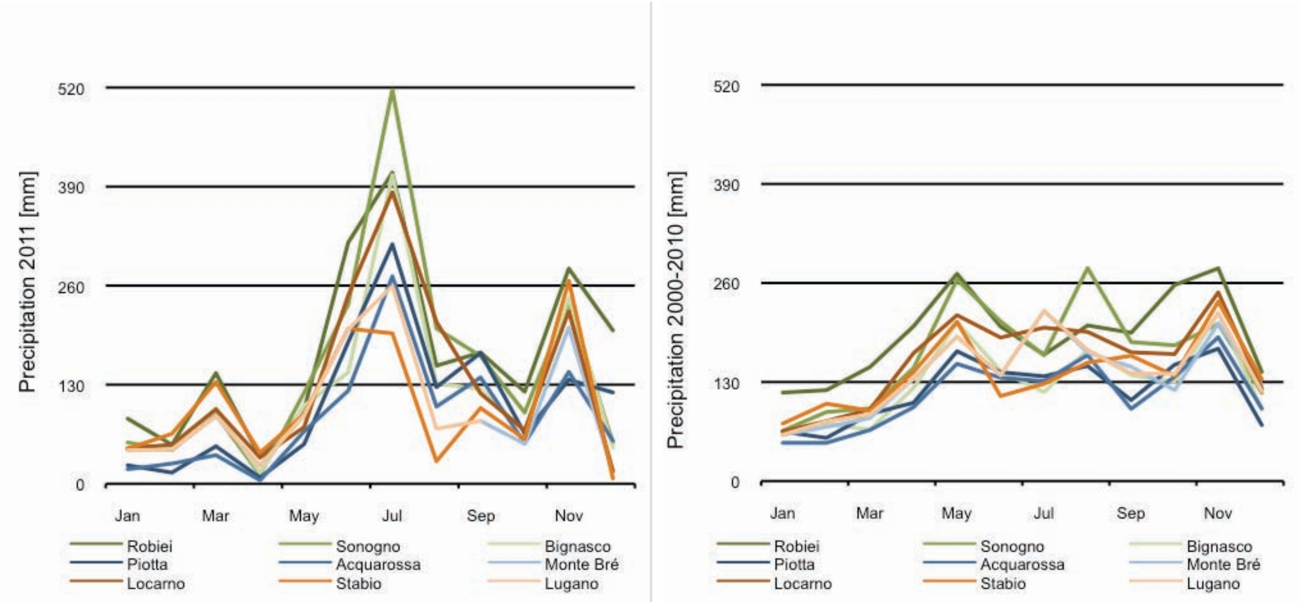
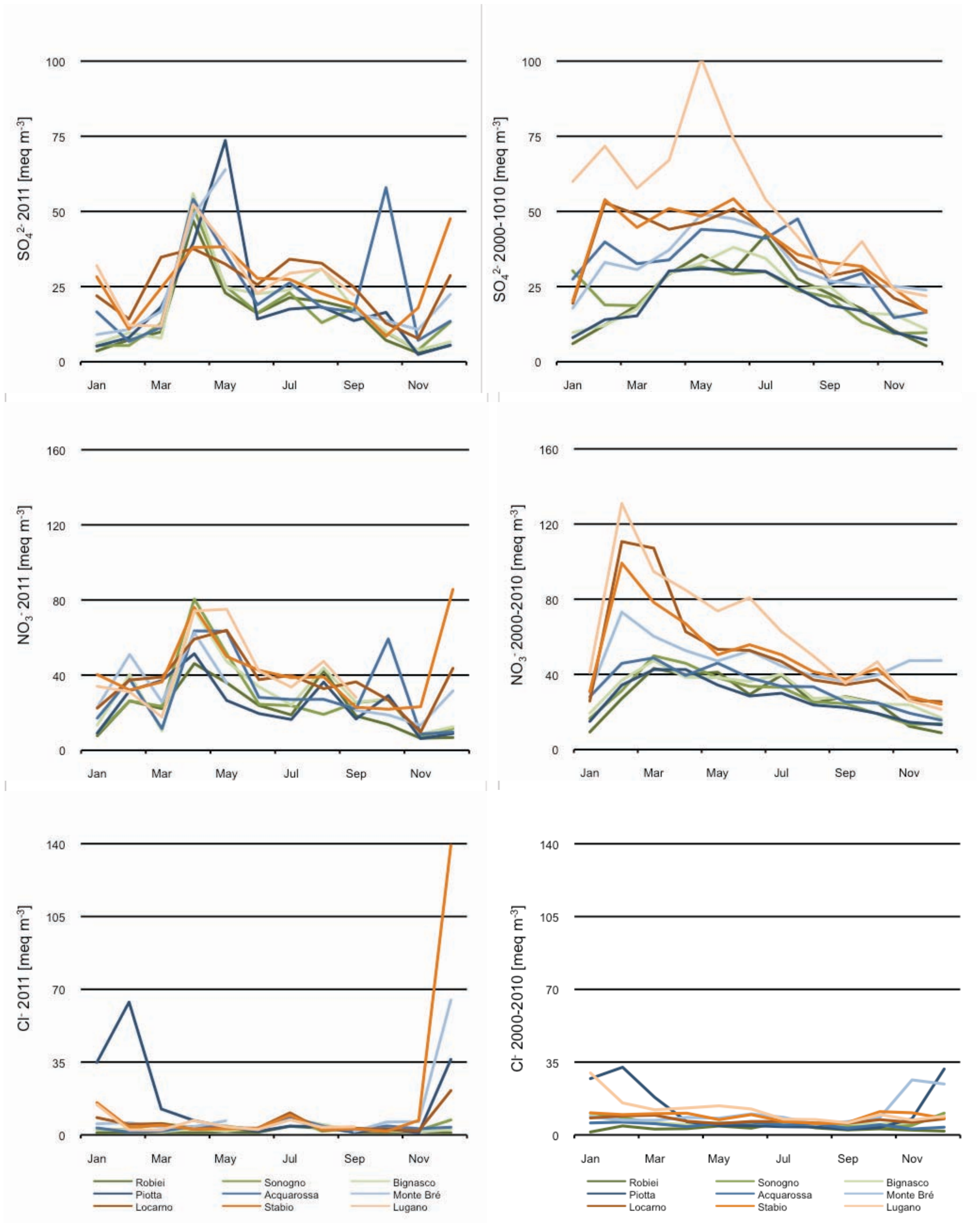
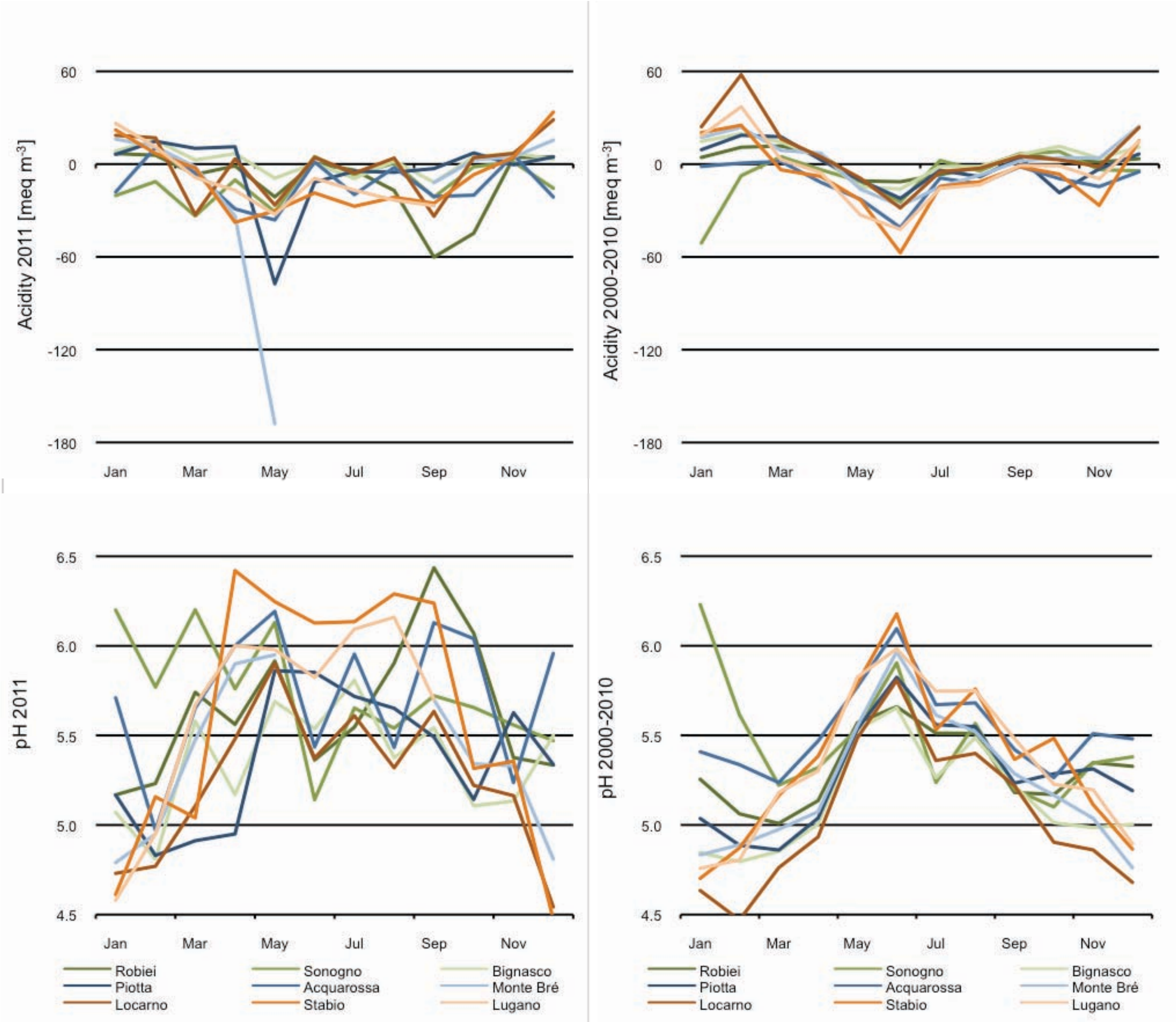


Figure 2.2 Seasonal variations of monthly average rain water concentrations

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



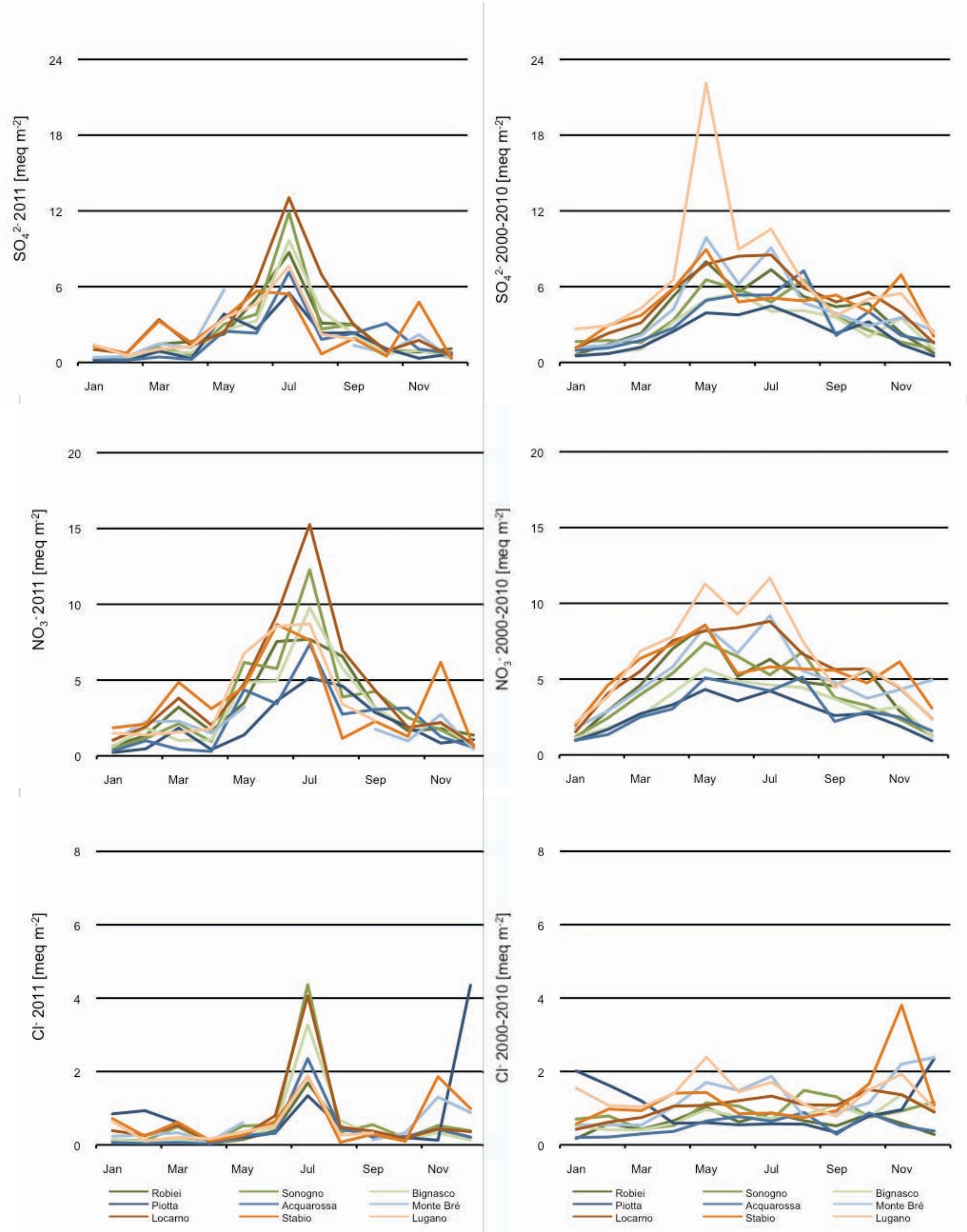
NH$_4^+$ 2011 [meq m^{-3}]
NH$_4^+$ 2000- 2010 [meq m^{-3}]
Base cations 2011 [meq m^{-3}]
Base cations 2000-2010 [meq m^{-3}]
HCO$_3^-$ 2011 [meq m^{-3}]
HCO$_3^-$ 2000-2010 [meq m^{-3}]
169 meq m^{-3}
Jan Mar May Jul Sep Nov
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Monte Bré
Locarno
Stabio
Lugano

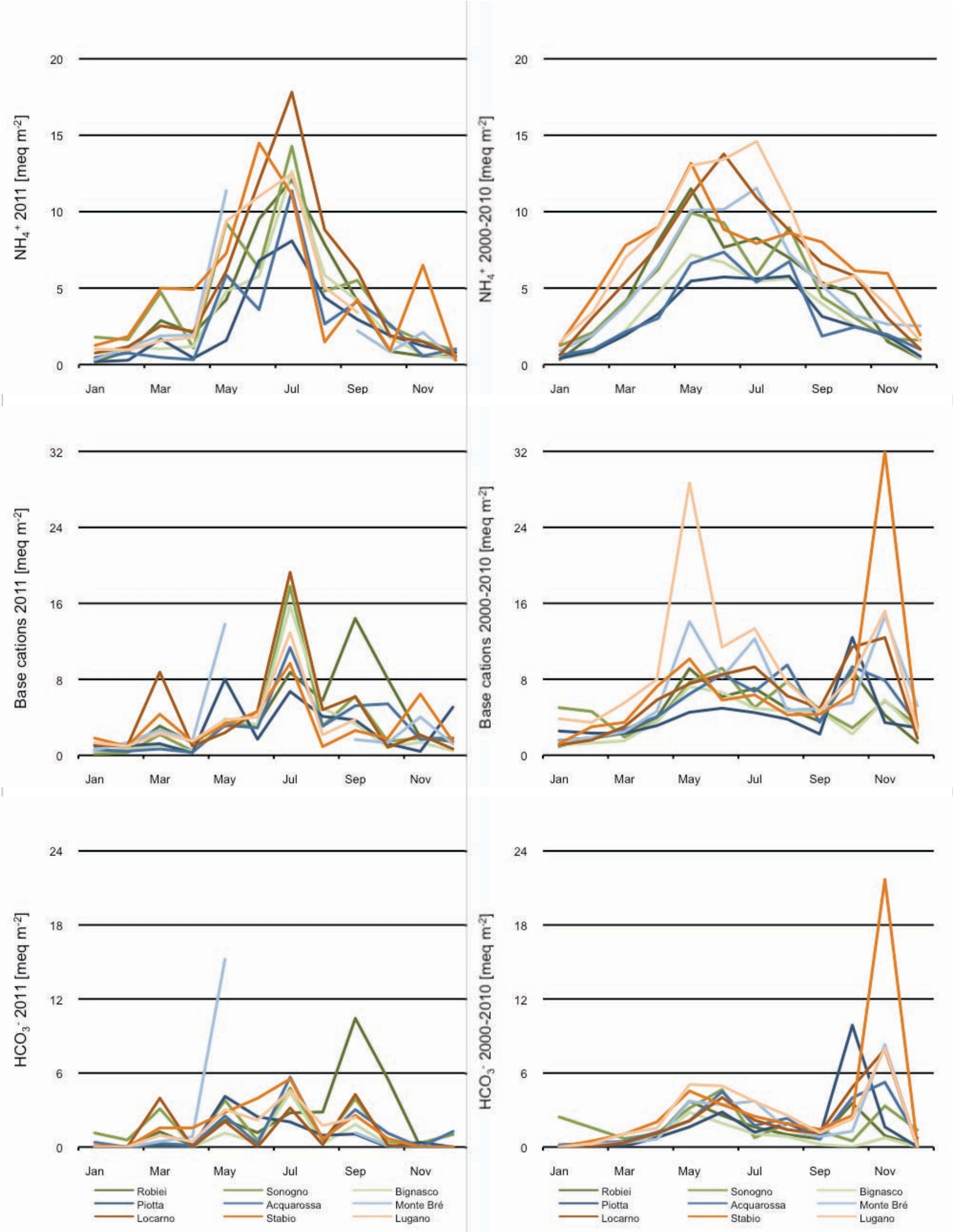


Depositions behaved similar to concentrations, with the difference that rain water volume gained further importance (Fig. 2.3). For sulphate, nitrate and ammonium, highest deposition during the period 2000-2010 occurred in summer and lowest in winter. During 2011 monthly mean deposition was in general similar to the mean values from 2000 to 2010, with higher values in July due to the higher precipitation volumes.

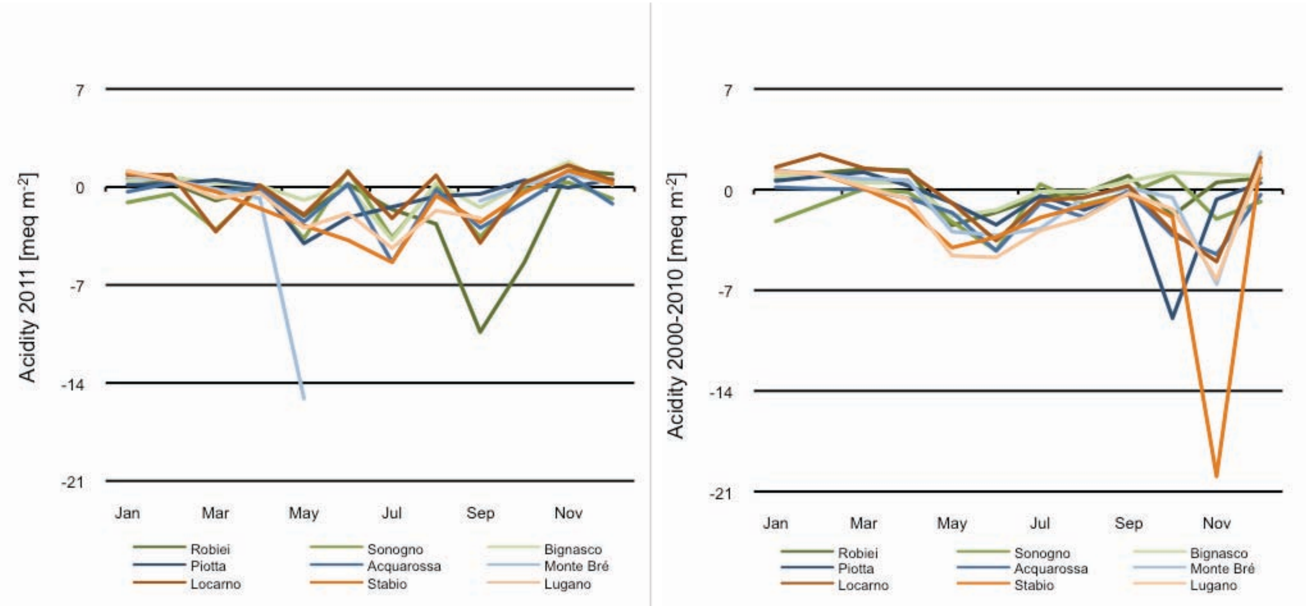
Figure 2.3 Seasonal variations of monthly wet deposition

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





NH4+ 2011 [meq m-2]
NH4+ 2000-2010 [meq m-2]
Base cations 2011 [meq m-2]
Base cations 2000-2010 [meq m-2]
HCO3- 2011 [meq m-2]
HCO3- 2000-2010 [meq m-2]
Jan
Mar
May
Jul
Sep
Nov
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Monte Bré
Locarno
Stabio
Lugano



<u>Spatial variation</u>

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 2011

Sampling site	Precipitation (mm)	Analysed precipitation (mm)	Conductivity 25°C (µS cm^{-1})	pH	Ca^{2+}		Mg^{2+}		Na^+		K^+		NH_4^+		HCO_3^-		SO_4^{2-}		NO_3^-		Cl^-		Acidity = $H^+ - HCO_3^-$	
					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	1048	926	9	5.6	19	19	5	5	5	5	2	2	29	24	13	14	19	19	23	24	5	5	-11	-11
Bignasco	1477	1262	9	5.4	15	23	3	4	4	6	1	2	26	39	5	8	17	25	25	37	4	6	-1	-1
Locarno Monti	1578	1436	13	5.3	21	33	4	7	6	10	2	3	39	61	8	13	26	41	34	54	5	8	-3	-5
Lugano	1179	906	12	5.4	19	23	4	4	5	6	4	5	42	49	13	16	23	28	34	40	5	5	-10	-12
Monte Brè	1179	618	10	5.2	17	20	4	5	6	7	2	3	24	27	11	12	16	19	24	29	6	7	-4	-4
Piotta	1269	1153	8	5.5	14	17	3	3	9	11	2	3	23	29	9	11	15	20	18	23	8	10	-5	-7
Robiei	2071	1653	7	5.5	21	43	2	4	2	5	1	2	21	44	13	28	13	28	19	39	2	4	-10	-21
Sonogno	1829	1487	9	5.5	13	40	3	12	5	10	2	5	29	64	11	41	16	35	22	47	4	9	-8	-34
Stabio	1239	1136	13	5.4	20	24	4	5	7	8	2	2	49	60	16	20	24	30	36	45	6	8	-12	-15

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. On average 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 stronger 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. On average 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 on 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 the transport of air masses rich in humidity 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 in general at Locarno Monti, Lugano, Stabio while lowest can be observed at Acquarossa, Bignasco, Piotta. For base cations and bicarbonate, deposition rates are usually 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 since 1988 are shown in Fig. 2.5. Compared to the time series, 2011 was a rather dry year. In general, the measured concentrations and depositions were similar to values of the last years.

For some parameters temporal trends in concentrations are immediately visible. Sulphate concentrations and depositions decreased after 1990 at all sampling stations as a consequence of reduced SO_2 emissions. The sulphate peak at Lugano in 2012 was the consequence of the volcanic eruption at Eyafjellajokull (Iceland) in April 2010 (Steingruber and Colombo, 2011; UACER, 2011). The decrease in emissions of NO_x and NH_3 caused until to now only a slight decrease in concentrations, while their depositions are still much influenced by the precipitation volume, so that high deposition values still occur during wet years. Base cations also seem to slightly decrease, however their annual mean concentrations and depositions can vary greatly from year to year reaching high values during years with single events rich in base cations. Concentrations and depositions of acidity, that can be calculated as the difference between acid anions and base cations and ammonia, decreased significantly at most sites. In general, concentrations and depositions of acidity decreased from values around 30-40 meq/m^3 and 60 meq/m^2, respectively to values around 0 meq/m^3 and 0 meq/m^2 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. A more detailed trend analysis is described in Steingruber and Colombo (2010) and Steingruber and Colombo (2011).

Figure 2.4 Yearly precipitations

Data from MeteoSwiss

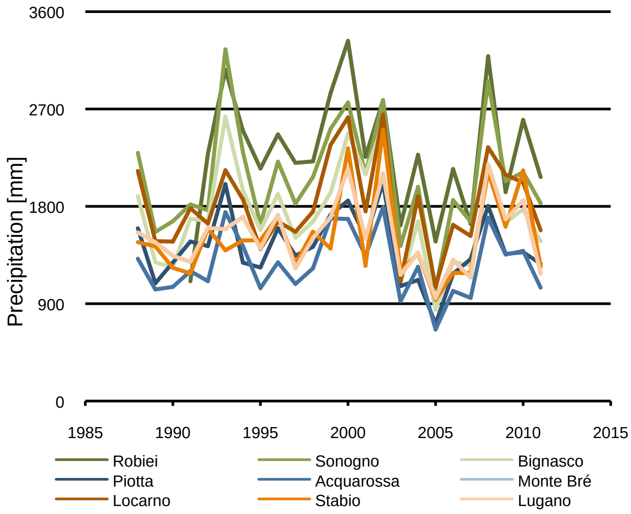
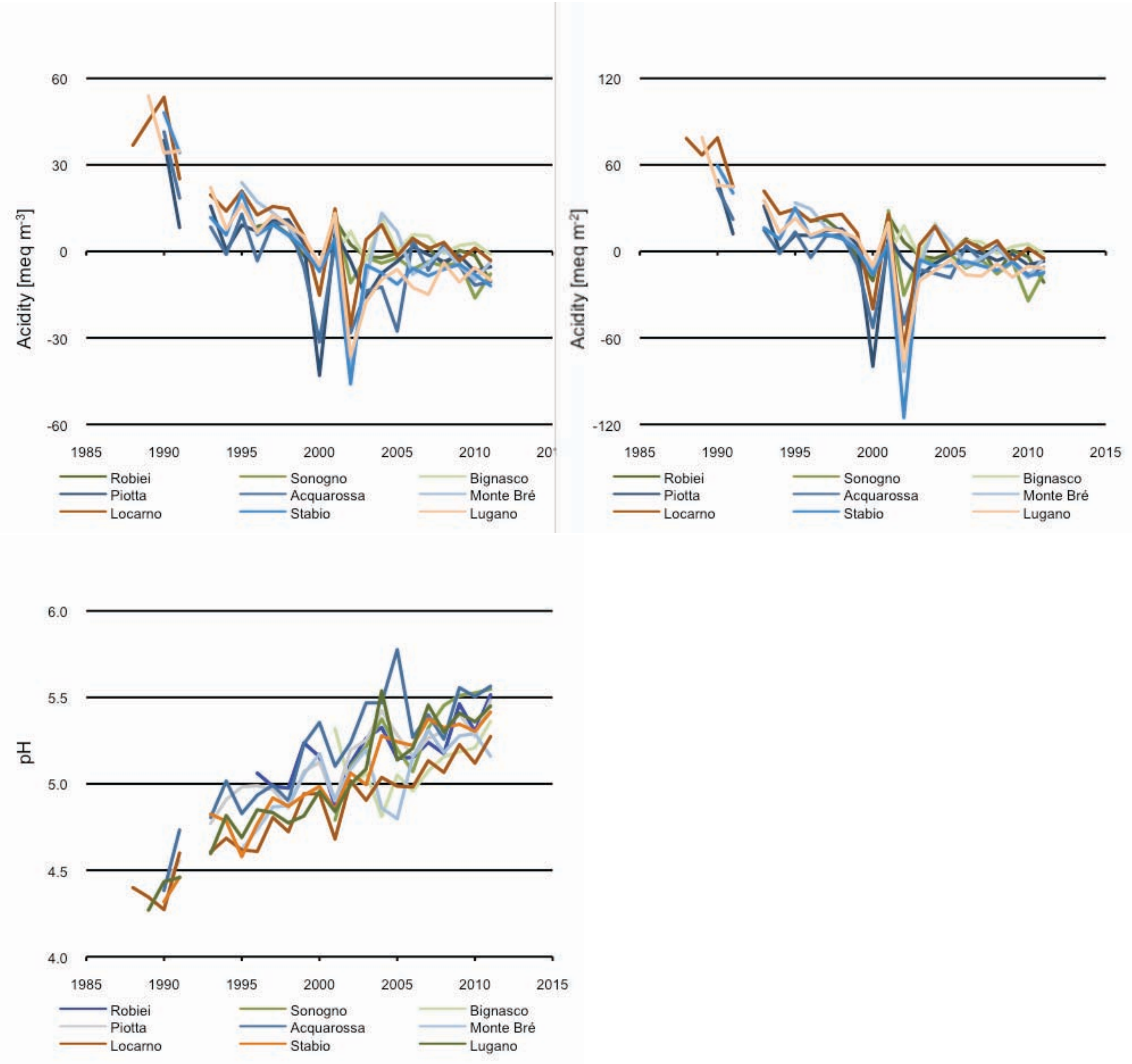


Figure 2.5 Temporal variations of annual mean rain water concentrations, deposition rates and pH
Base cations correspond to the sum of calcium, magnesium, sodium and potassium.


NH4+ [meq m-3]
NH4+ [meq m-2]
Base cations [meq m-3]
Base cations [meq m-2]
HCO3- [meq m-3]
HCO3- [meq m-2]
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Monte Brè
Locarno
Stabio
Lugano


Acidity [meq m⁻³]
60
30
0
-30
-60
1985
1990
1995
2000
2005
2010
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Monte Bré
Locarno
Stabio
Lugano
Acidity [meq m⁻²]
120
60
0
-60
-120
1985
1990
1995
2000
2005
2010
2015
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
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Monte Bré
Locarno
Stabio
Lugano

2.4.2 Alpine rivers

Spatial variations

During 2011 river water was sampled at the following days: 17.1, 21.2, 21.3, 18.4, 16.5, 14.6, 11.7, 8.8, 5.9, 3.10, 14.11, 12.12. Annual mean concentrations of the chemical parameters measured in river Maggia, Vedeggio and Verzasca during 2011 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 2011 average alkalinity was 291 meq m^{-3} in river Maggia, 163 meq m^{-3} in river Vedeggio and 75 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 6.8 in river Verzasca. Their minimum pH's were not much lower (Maggia: 7.3, Vedeggio: 6.8, Verzasca: 6.7). As a consequence of the relatively high pH's, dissolved aluminium concentrations were on average low and mainly < 10 meq m^{-3}. However, higher aluminium concentrations up to 42 meq m^{-3} in river Maggia, 28 meq m^{-3} in river Vedeggio and 73 meq m^{-3} in river Verzasca occurred during high flow event in August.

Table 2.5 Average concentrations in river water during 2011.
Average values with some or all single values below the quantification limit were preceded with <.

River name	pH	Conductivity 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})	NH4+ (meq m-3)	SO_4^{2-} (meq m^{-3})	NO_3^- (meq m^{-3})	Cl^- (meq m^{-3})	DOC (mg C l^{-1})	SiO_2 (mg l^{-1})	$Al_{dissolved}$ (µg l^{-1})	Al_{tot} (µg l^{-1})	$Cu_{dissolved}$ (µg l^{-1})	Cu_{tot} (µg l^{-1})	$Zn_{dissolved}$ (µg l^{-1})	Zn_{total} (µg l^{-1})
Maggia	7.4	60.6	291	408	54	71	37	1	179	36	34	0.75	4.98	9.2	10.4	<0.2	<0.2	<0.8	1.1
Vedeggio	7.1	41.8	163	235	73	66	12	0	114	63	24	0.80	7.14	9.7	10.8	<0.3	<0.3	0.8	1.0
Verzasca	6.8	22.7	75	139	18	29	15	0	69	42	6	0.61	4.00	13.1	14.9	<0.3	<0.4	1.6	1.7

Seasonal variations

Fig. 2.6 shows the seasonal variations of the daily mean discharges during the sampling days and of the monthly mean discharge in 2011 and their average monthly values during the period 2000-2010. Average monthly 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. For the period 2000-2010 the average daily mean discharges during sampling days correspond well with the average monthly mean discharge for the rivers Vedeggio and Verzasca. For river Maggia average monthly mean discharge is significantly higher in September and October, probably due to preferential water release of the hydropower producer during these months lasting only a few days, therefore occurring less frequently during sampling days. With respect to average values of the period 2000-2010 monthly mean discharge of 2011 was lower in May because of the dry winter with little snow and higher in July because of the high precipitation volume in this month. For river Maggia in September and October the discharge was lower than usual, indicating that the usual water releases by the hydropower producers did not occur during this year. The daily mean discharges during 2011 indicates that sampling occurred during high flow events in August and September.

Seasonal variations of the concentrations of the main chemical parameters of 2011 are mostly very similar to their average values during 2000-2010: for sulphate, chloride, base cations lower values in spring-summer when monthly mean river discharge is higher and higher values during the rest of the years when monthly mean discharge is lower. For nitrate highest values occur during spring. 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, chloride and a combination of dilution and consumption of alkalinity. Because of rain acidity river pH clearly decreases during rain events. 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. 2.2), increase during intense precipitation or snow melt because of leakage from soils, decrease during photosynthetic activity because of uptake by vegetation and algae during the vegetation period. Concentrations of aluminium seem to reach its highest concentrations during high flow events. In fact their average concentrations during 2000-2010 are highest during May and November when average daily discharge was also higher, suggesting leakage from soils, probably enhanced by lower pH values during these occasions. During 2011 highest values were measured during the high flow events in August and September.

Figure 2.6 Daily mean discharge during sampling days and monthly mean discharge in 2011 and their average monthly values during the period 2000-2010.

Discharge of river Vedeggio at Isone was measured by IST (2001-2012). Discharge of river Verzasca at Sonogno and Maggia at Cavergno were estimated by discharge values of Verzasca at Lavertezzo and Maggia at Bignasco published by BWG (2001-2004) and BAFU (2005-2012).

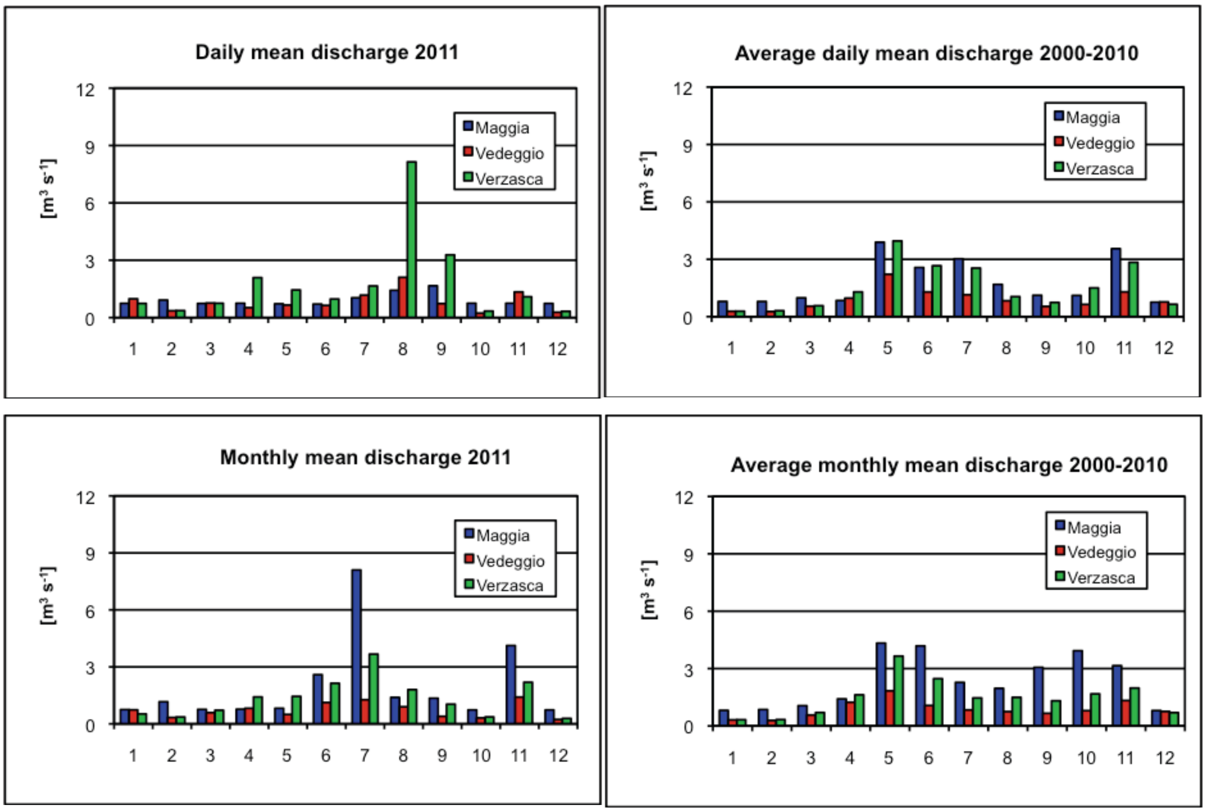
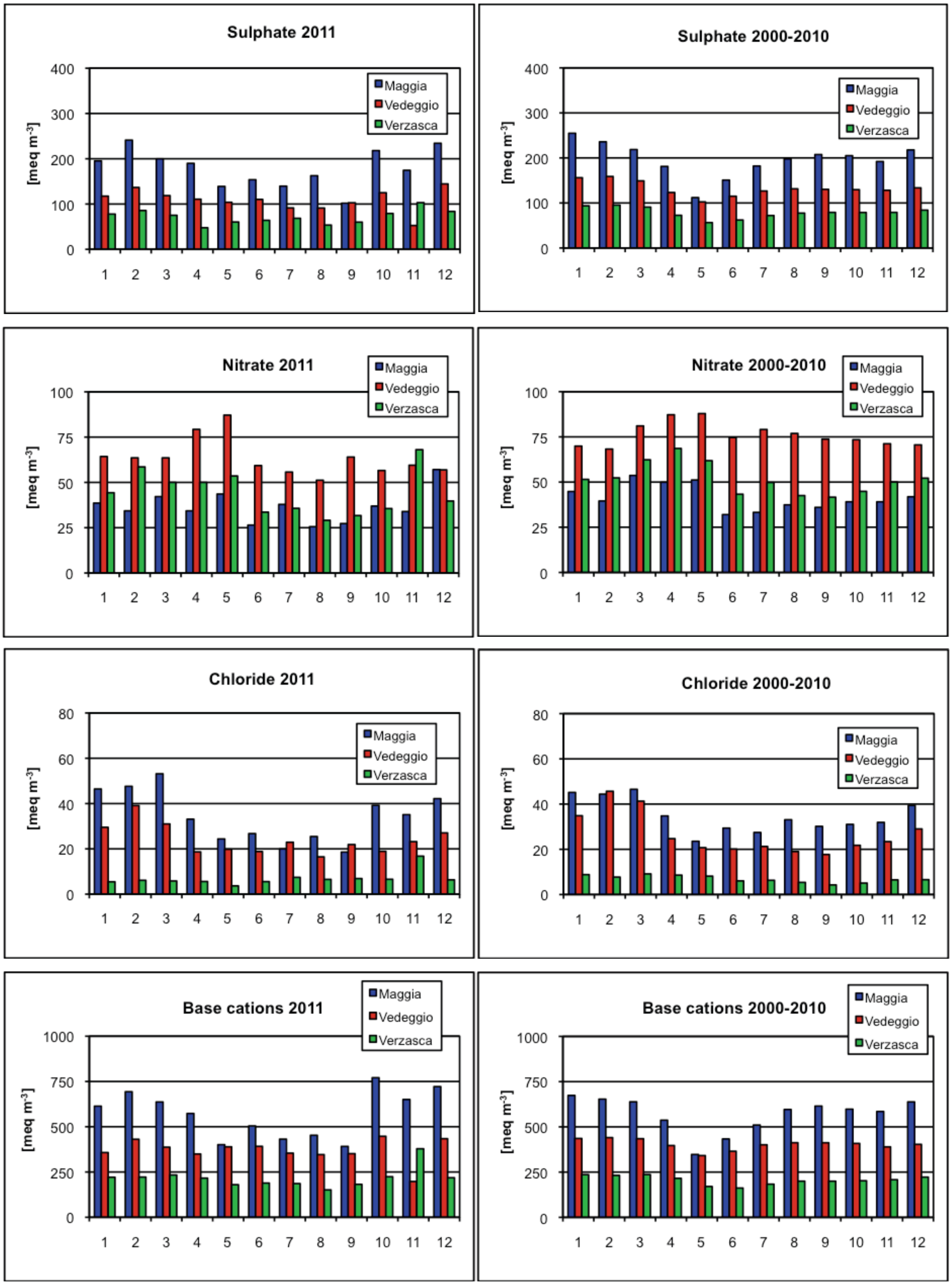
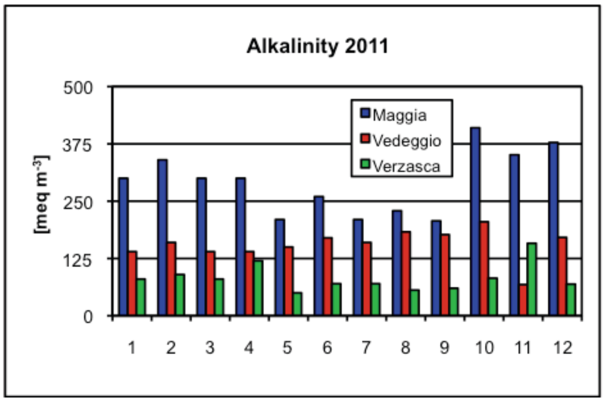
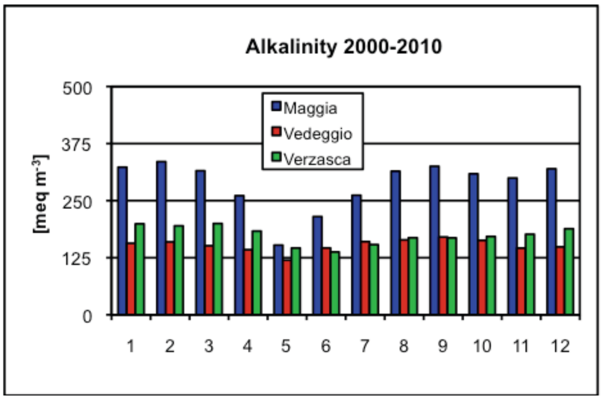


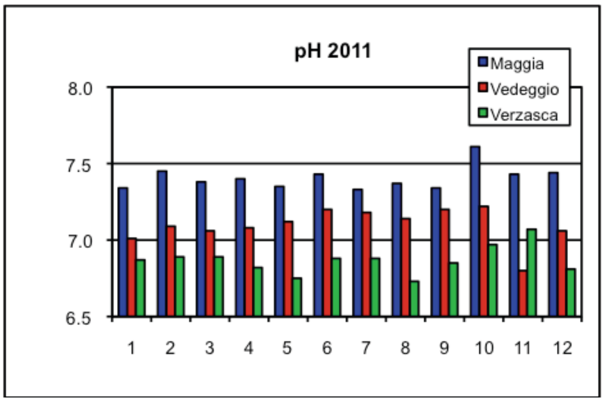
Figure 2.7 Concentrations of the main chemical parameters in river water during sampling days in 2011 and their average values from 2000 to 2010.

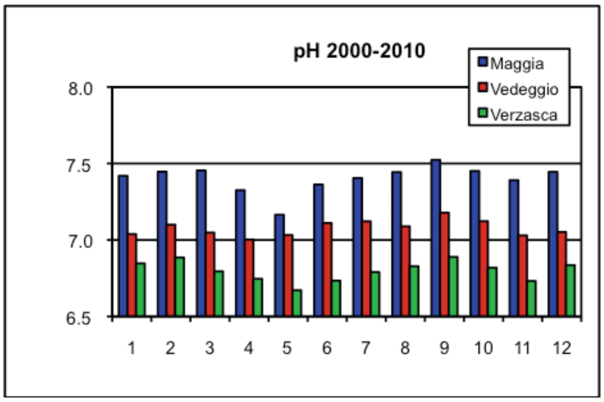
Base cations correspond to the sum of calcium, magnesium, sodium and potassium.

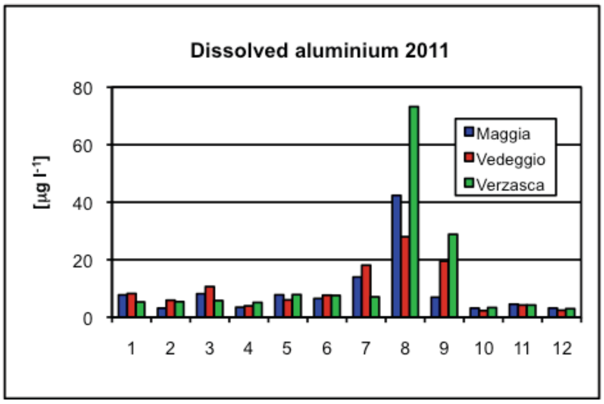


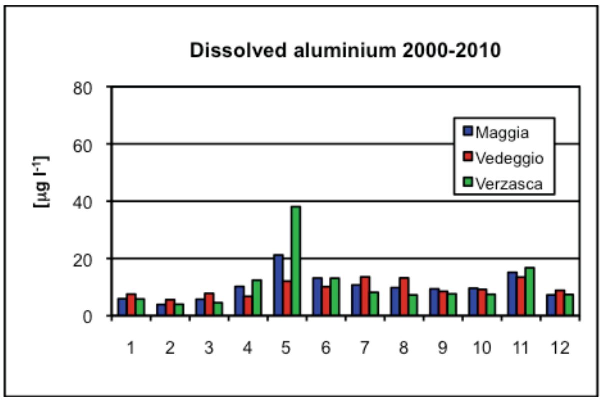

Alkalinity 2011
[meq m^{-3}]
500
375
250
125
0
1 2 3 4 5 6 7 8 9 10 11 12
Maggia
Vedeggio
Verzasca

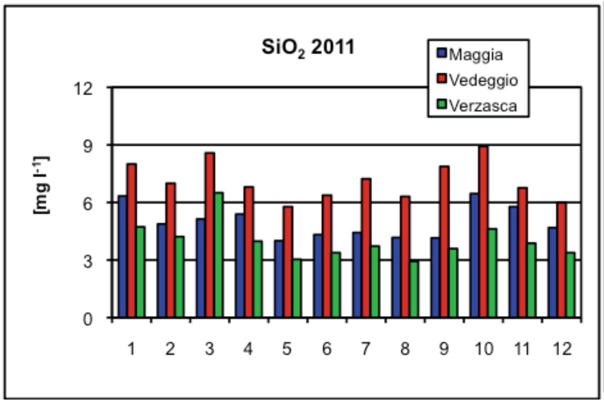

Alkalinity 2000-2010
[meq m^{-3}]
500
375
250
125
0
1 2 3 4 5 6 7 8 9 10 11 12
Maggia
Vedeggio
Verzasca

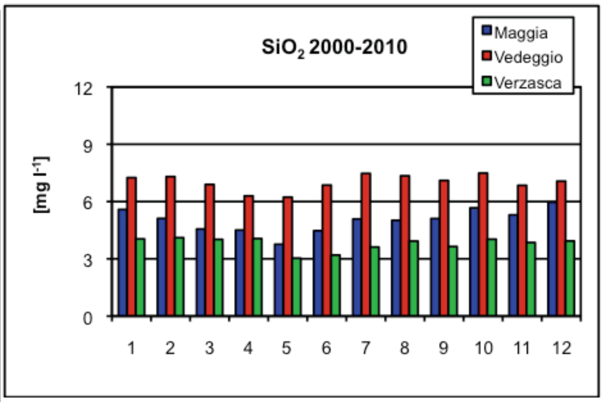

pH 2011
8.0
7.5
7.0
6.5
1 2 3 4 5 6 7 8 9 10 11 12
Maggia
Vedeggio
Verzasca


pH 2000-2010
8.0
7.5
7.0
6.5
1 2 3 4 5 6 7 8 9 10 11 12
Maggia
Vedeggio
Verzasca


Dissolved aluminium 2011
[µg l^{-1}]
80
60
40
20
0
1 2 3 4 5 6 7 8 9 10 11 12
Maggia
Vedeggio
Verzasca


Dissolved aluminium 2000-2010
[µg l^{-1}]
80
60
40
20
0
1 2 3 4 5 6 7 8 9 10 11 12
Maggia
Vedeggio
Verzasca


SiO_2 2011
[mg l^{-1}]
12
9
6
3
0
1 2 3 4 5 6 7 8 9 10 11 12
Maggia
Vedeggio
Verzasca


SiO_2 2000-2010
[mg l^{-1}]
12
9
6
3
0
1 2 3 4 5 6 7 8 9 10 11 12
Maggia
Vedeggio
Verzasca

Temporal variations

In order to detect time trends, annual mean concentrations of sulphate, nitrate, chloride, base cations, alkalinity, pH and dissolved aluminium and the annual mean discharges from 2000 to 2011 are presented graphically in Fig. 2.8 and 2.9, respectively. 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. A more detailed time trend analysis of the period 2000-2010 is described in Steingruber and Colombo (2011).

Figure 2.8 Annual mean discharge in river water from 2000 to 2011

Discharge of river Vedeggio at Isone was measured by IST (2001-2012). Discharge of river Verzasca at Sonogno and Maggia at Cavergno were estimated by discharge values of Verzasca at Lavertezzo and Maggia at Bignasco published by BWG (2001-2004) and BAFU (2005-2012).

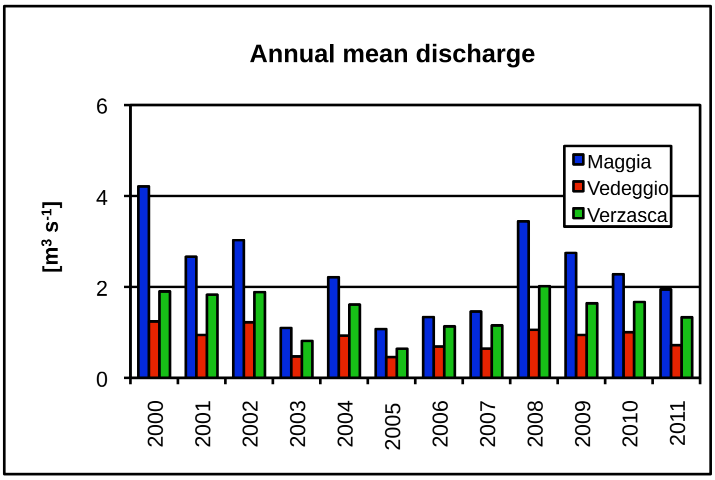
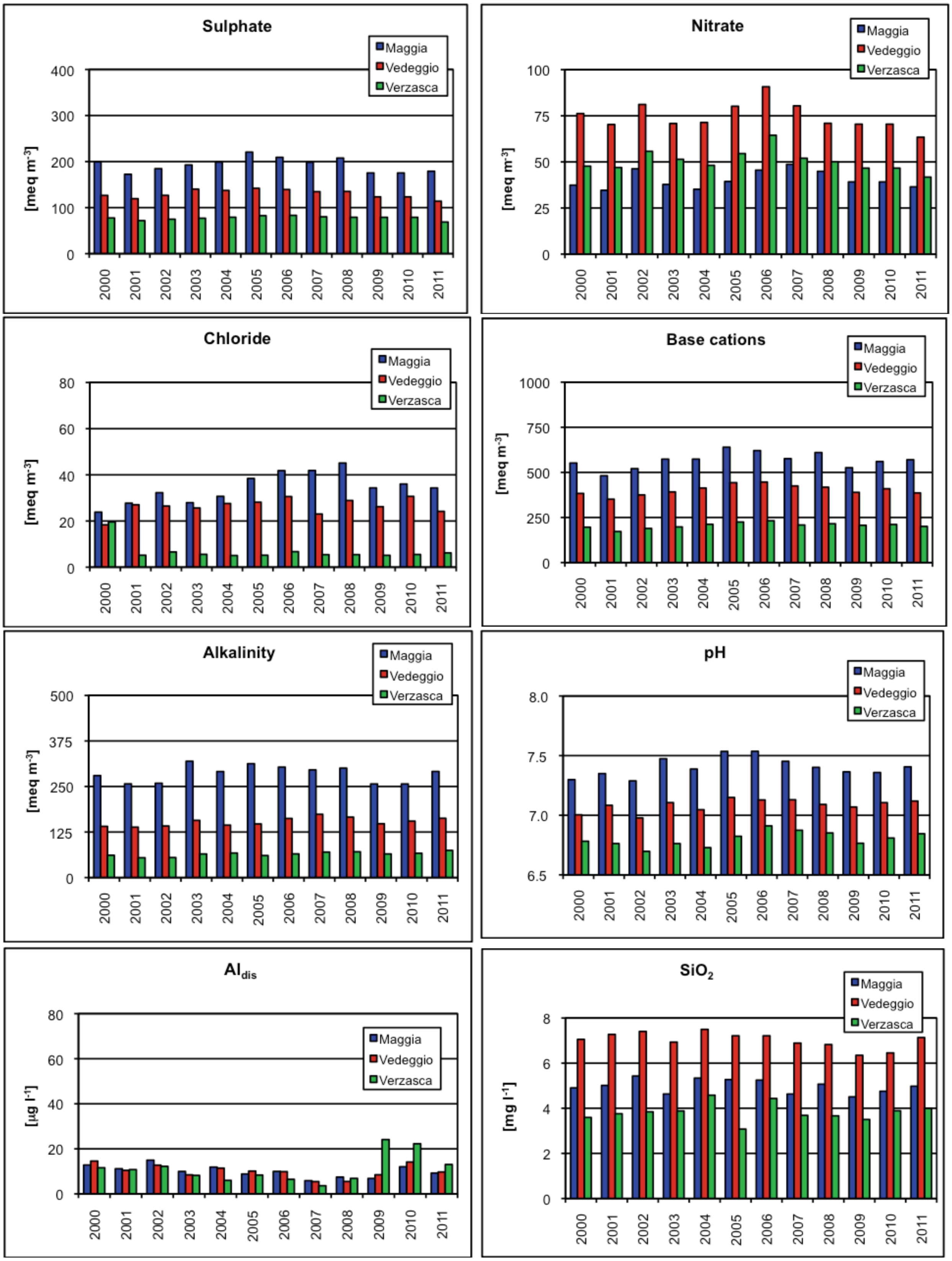


Figure 2.9 Annual mean concentrations of the main chemical parameters in river water from 2000 to 2011

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

Discharge of river Vedeggio at Isone was measured by IST (2001-2012). Discharge of river Verzasca at Sonogno and Maggia at Cavergno were estimated by discharge values of Verzasca at Lavertezzo and Maggia at Bignasco published by BWG (2001-2004) and BAFU (2005-2012).



2.4.3 Alpine lakes

Spatial variations

During 2011 sampling of alpine lakes occurred at the following days: 4.7, 12.9, 11.10. Yearly mean concentrations of the main chemical parameters measured in lake surface water during 2011 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 19.7 $\mu S\ cm^{-1}$, alkalinity between -3.0 and 78.0 meq m^{-3}, pH between 5.5 and 7.1, sulphate between 16.0 and 76.0 meq m^{-3}, nitrate between 6.0 and 25.0 meq m^{-3}, dissolved organic carbon between 0.4 and 1.0 mg C l^{-1}, reactive dissolved silica between 1.2 and 3.6 mg $SiO_2\ l^{-1}$ and dissolved aluminium between 1.4 and 56.2 $\mu g\ l^{-1}$.

Table 2.7 Average lake surface water concentrations during 2011

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

Lake name	Conductivity 25°C (µS cm^{-1})	pH	Alkalinity (meq m^{-3})	Ca^{2+} (meq m^{-3})	Mg^{2+} (meq m^{-3})	Na^{+} (meq m^{-3})	K^{+} (meq m^{-3})	NH_4^{+} (meq m^{-3})	SO_4^{2-} (meq m^{-3})	NO_3^{-} (meq m^{-3})	Cl^{-} (meq m^{-3})	DOC (mg C l^{-1})	SiO_2 (mg l^{-1})	$Al_{dissolved}$ (µg l^{-1})	Al_{tot} (µg l^{-1})	$Cu_{dissolved}$ (µg l^{-1})	Cu_{tot} (µg l^{-1})	$Zn_{dissolved}$ (µg l^{-1})	Zn_{total} (µg l^{-1})
Lago del Starlaresc da Sgiof	8.1	5.9	10	29	10	11	4	2	25	17	3	1.01	1.8	49.9	58.5	<0.2	<0.2	2.7	3.2
Lago di Tomè	8.5	5.9	7	42	6	13	3	1	27	25	3	0.54	2.4	22.4	25.5	<0.2	<0.2	2.0	2.4
Lago dei Porchieirsc	19.7	6.9	66	136	13	19	11	0	76	20	2	0.48	3.6	3.0	3.6	<0.2	<0.2	1.5	1.9
Lago Barone	9.2	6.3	17	56	6	11	4	1	36	18	2	0.48	1.8	2.2	3.7	<0.2	<0.2	1.1	1.4
Laghetto Gardiscio	8.2	5.5	-3	28	9	8	7	2	36	14	3	0.36	1.2	56.2	65.9	<0.2	<0.2	3.7	4.2
Lago Leit	18.4	6.5	29	93	30	17	12	1	106	12	2	0.55	2.4	3.0	4.6	<0.2	<0.2	1.0	1.1
Lago di Morghirolo	12.4	6.7	39	69	16	14	11	0	50	13	2	0.55	2.2	1.4	2.6	<0.2	<0.2	2.4	2.5
Lago di Mognòla	16.5	6.9	56	94	22	23	12	0	64	15	2	0.53	3.6	5.5	6.9	<0.2	<0.2	0.6	0.6
Laghetto Inferiore	9.1	6.8	33	55	8	12	8	0	26	14	2	0.78	1.6	14.0	20.0	<0.2	<0.2	0.5	0.7
Laghetto Superiore	8.7	6.7	32	52	8	11	7	0	22	14	3	0.83	1.5	10.1	16.1	<0.2	<0.2	1.2	1.2
Lago Nero	16.4	7.1	70	112	15	16	12	0	59	10	2	0.62	1.2	3.6	4.0	<0.2	<0.2	0.7	0.8
Lago Bianco	95.3	7.7	530	803	90	18	23	0	324	9	3	0.53	2.3	9.4	10.4	<0.2	<0.2	0.2	0.4
Lago della Froda	12.5	6.9	47	0	8	11	6	0	39	12	2	0.62	1.7	7.2	8.3	<0.2	<0.2	0.6	0.8
Lago d'Antabia	11.9	6.9	57	83	6	18	6	1	20	20	3	0.51	2.5	4.0	4.9	<0.2	<0.2	0.4	0.5
Lago della Crosa	7.4	6.4	21	43	5	8	4	1	16	19	3	0.53	1.7	1.6	2.4	<0.2	<0.2	0.9	1.1
Lago d'Orsalìa	9.3	6.5	30	62	7	13	4	1	19	24	3	0.53	1.8	3.6	7.1	<0.2	<0.2	0.4	0.5
Schwarzsee	9.4	6.6	35	61	7	11	5	0	22	17	3	0.59	2.0	8.8	14.7	<0.2	<0.2	1.1	1.2
Laghi dei Pozzöi	8.4	6.6	39	48	9	15	4	1	23	6	3	1.01	2.4	11.5	23.8	<0.2	<0.2	1.1	1.3
Lago di Sfille	8.4	6.5	25	44	9	14	3	1	24	12	3	0.95	2.2	17.6	27.2	<0.2	<0.2	1.1	1.2
Lago di Sascòla	9.6	6.2	15	42	13	13	8	1	29	24	2	0.89	2.1	17.6	30.5	<0.2	<0.2	1.4	1.5
Lago d'Alzasca	15.6	7.0	78	101	18	20	11	1	37	16	4	0.87	3.0	7.1	7.4	<0.2	<0.2	<0.5	0.7

In order to better compare chemistry of lakes with low alkalinities, values of the main parameters measured during 2011 and their mean values from 2000 to 2010 are shown graphically in Fig. 2.10.

In general values from 2011 are not much different from their of the period 2000-2010. During 2011 alkalinities below 0 meq m^{-3} were only detected in Laghetto Gardiscio, while alkalinities constantly above 50 meq m^{-3} were measured in Lago d'Alzasca, Lago di Mognòla and Lago Nero. All other 17 lakes were at least temporary sensitive to acidification (0 < alkalinity < 50 meq m^{-3}). 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 mainly measured in lakes with pH's <= 6 like Lago del Starlaresc da Sgiof, Lago, Laghetto Gardiscio, Lago di Tomè where concentrations ranged from 12 to 63 µg l^{-1}. 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.

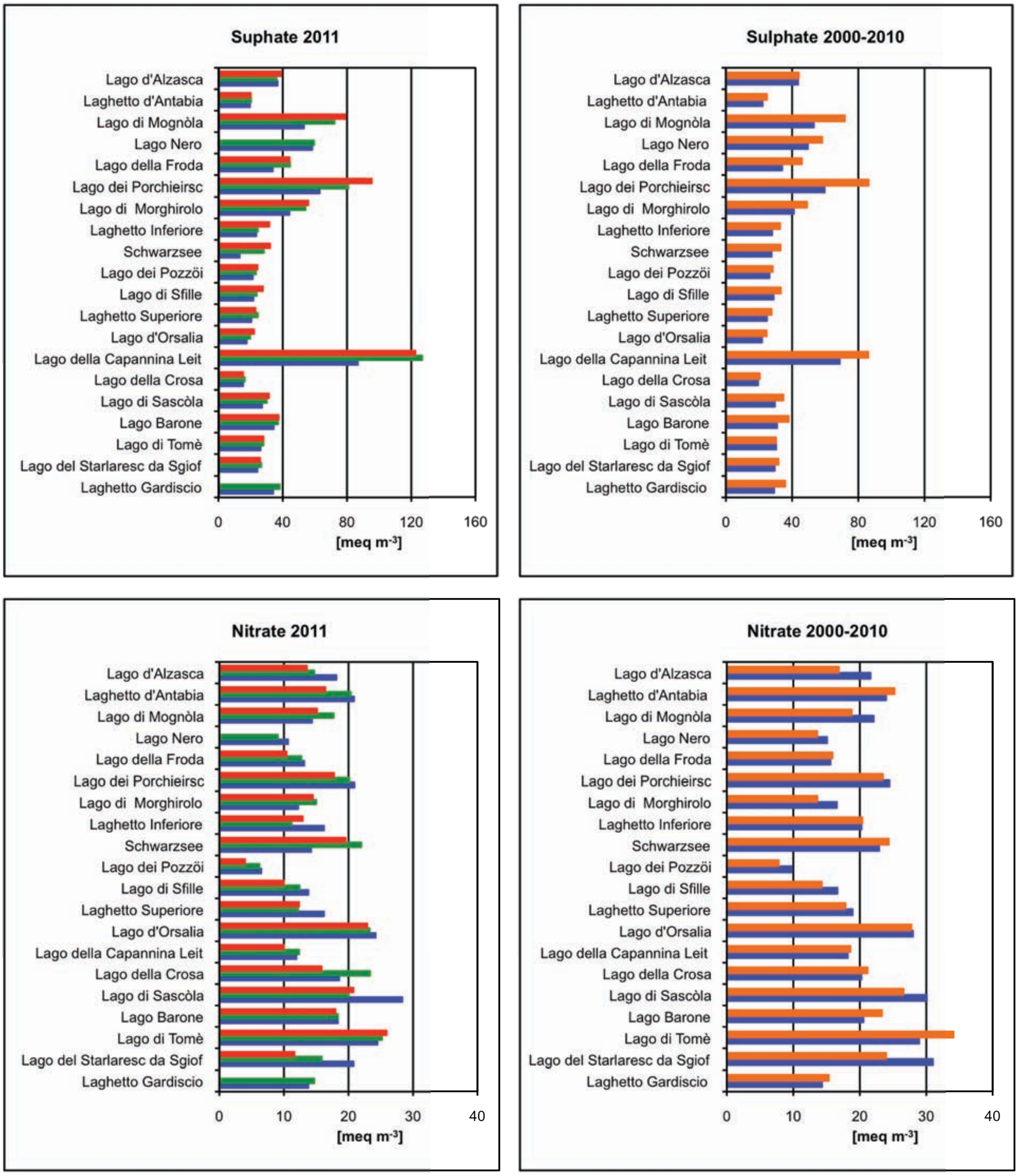
<u>Seasonal variations</u>

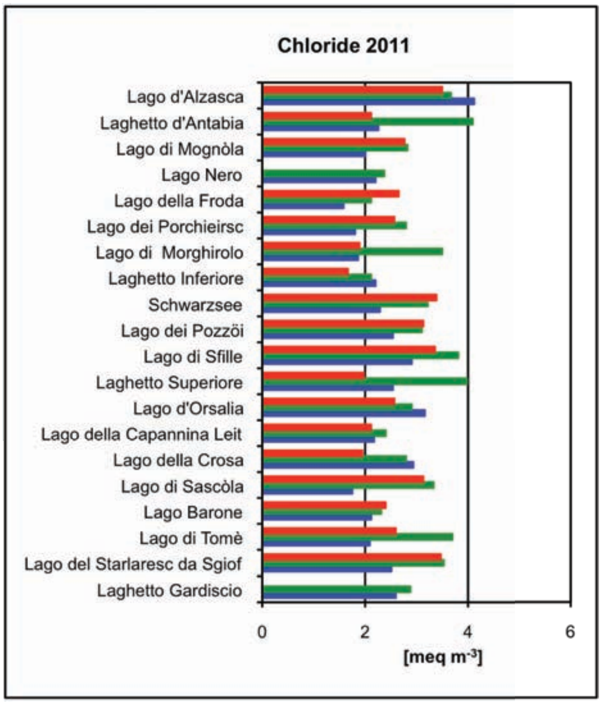
Fig. 2.10 also shows some seasonal differences. These are mostly in agreement with seasonal variations observed for rivers. In most lakes alkalinity and pH and concentrations of sulphate and base cations are lower in July than in September and October. As discussed for rivers, the elevated discharge 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.

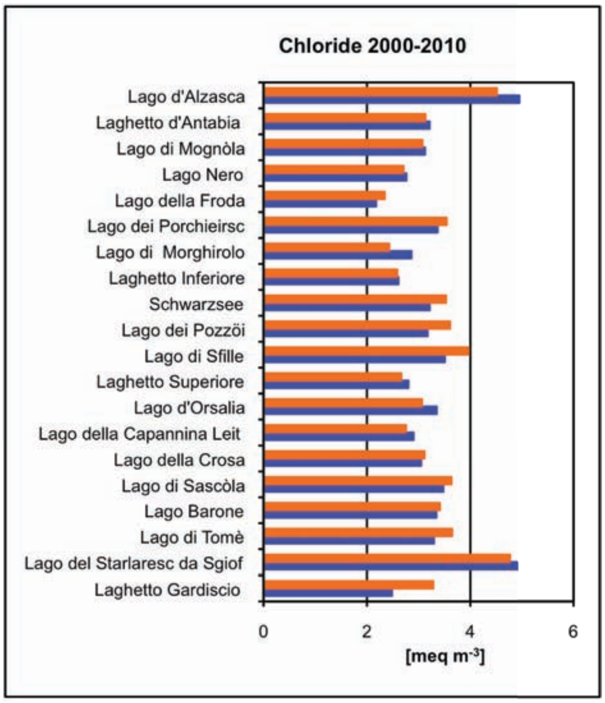
Figure 2.10 Annual average concentrations of the main chemical parameters in 20 Alpine lakes during 2011 and their average values from 2000 to 2010.

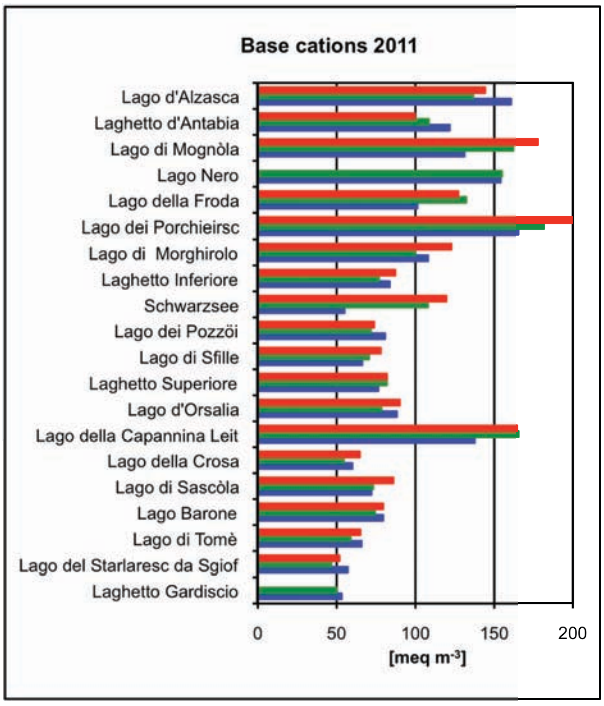
Blue: summer, green: autumn 1, red: autumn 2; orange: mean autumn

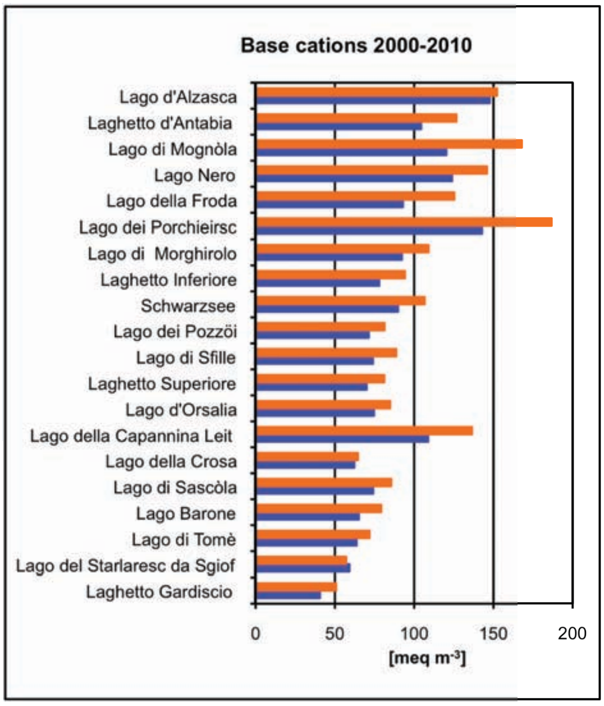
Base cations correspond to the sum of calcium, magnesium, sodium and potassium.

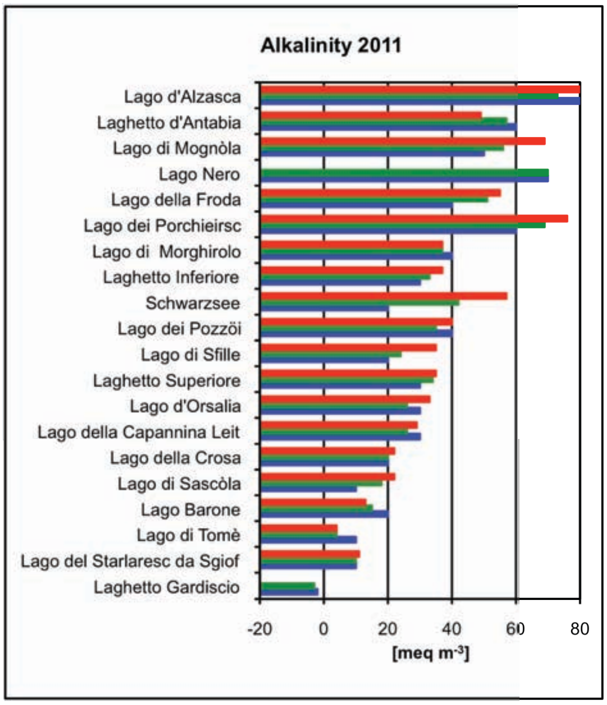


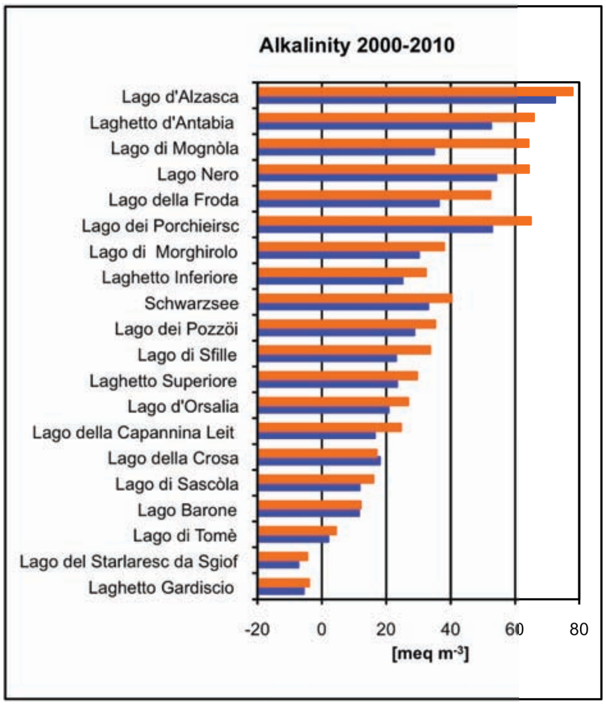

Chloride 2011
Lago d'Alzasca
Laghetto d'Antabia
Lago di Mognòla
Lago Nero
Lago della Froda
Lago dei Porchieirsc
Lago di Morghirolo
Laghetto Inferiore
Schwarzsee
Lago dei Pozzöi
Lago di Sfille
Laghetto Superiore
Lago d'Orsalia
Lago della Capannina Leit
Lago della Crosa
Lago di Sascòla
Lago Barone
Lago di Tomè
Lago del Starlaresc da Sgiof
Laghetto Gardiscio
0
2
4
6
[meq m-3]

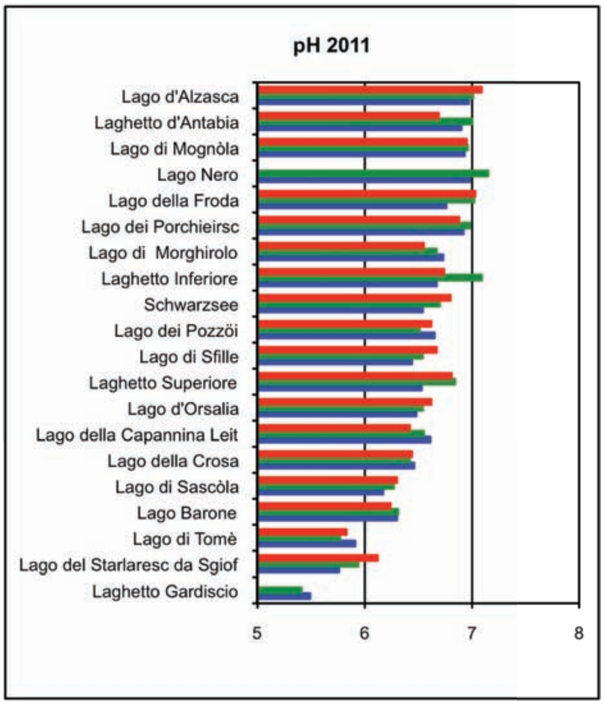

Chloride 2000-2010
Lago d'Alzasca
Laghetto d'Antabia
Lago di Mognòla
Lago Nero
Lago della Froda
Lago dei Porchieirsc
Lago di Morghirolo
Laghetto Inferiore
Schwarzsee
Lago dei Pozzöi
Lago di Sfille
Laghetto Superiore
Lago d'Orsalia
Lago della Capannina Leit
Lago della Crosa
Lago di Sascòla
Lago Barone
Lago di Tomè
Lago del Starlaresc da Sgiof
Laghetto Gardiscio
0
2
4
6
[meq m-3]

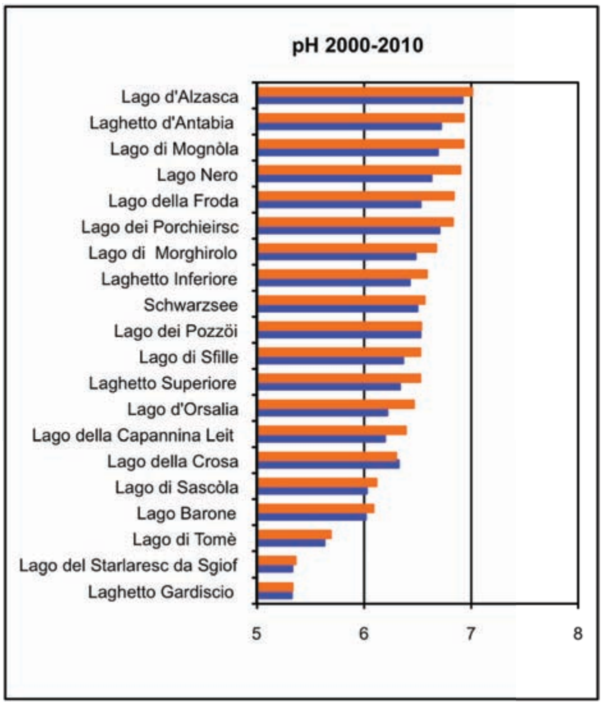

Base cations 2011
Lago d'Alzasca
Laghetto d'Antabia
Lago di Mognòla
Lago Nero
Lago della Froda
Lago dei Porchieirsc
Lago di Morghirolo
Laghetto Inferiore
Schwarzsee
Lago dei Pozzöi
Lago di Sfille
Laghetto Superiore
Lago d'Orsalia
Lago della Capannina Leit
Lago della Crosa
Lago di Sascòla
Lago Barone
Lago di Tomè
Lago del Starlaresc da Sgiof
Laghetto Gardiscio
0
50
100
150
200
[meq m-3]

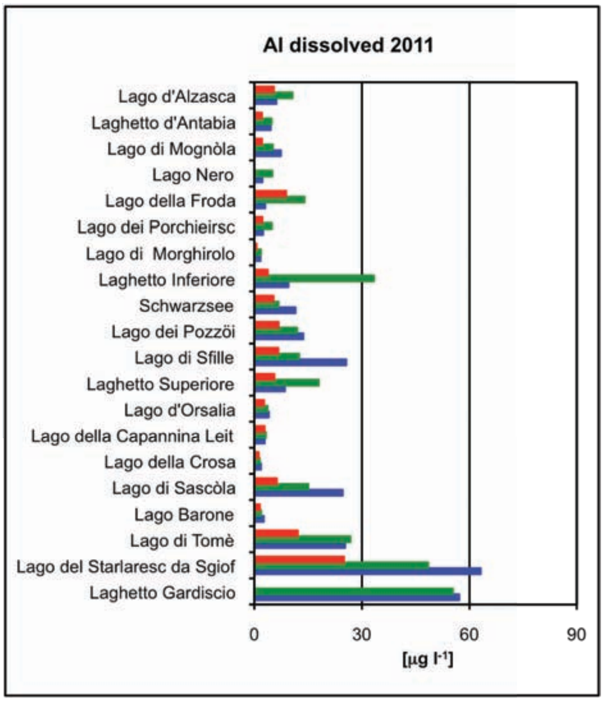

Base cations 2000-2010
Lago d'Alzasca
Laghetto d'Antabia
Lago di Mognòla
Lago Nero
Lago della Froda
Lago dei Porchieirsc
Lago di Morghirolo
Laghetto Inferiore
Schwarzsee
Lago dei Pozzöi
Lago di Sfille
Laghetto Superiore
Lago d'Orsalia
Lago della Capannina Leit
Lago della Crosa
Lago di Sascòla
Lago Barone
Lago di Tomè
Lago del Starlaresc da Sgiof
Laghetto Gardiscio
0
50
100
150
200
[meq m-3]

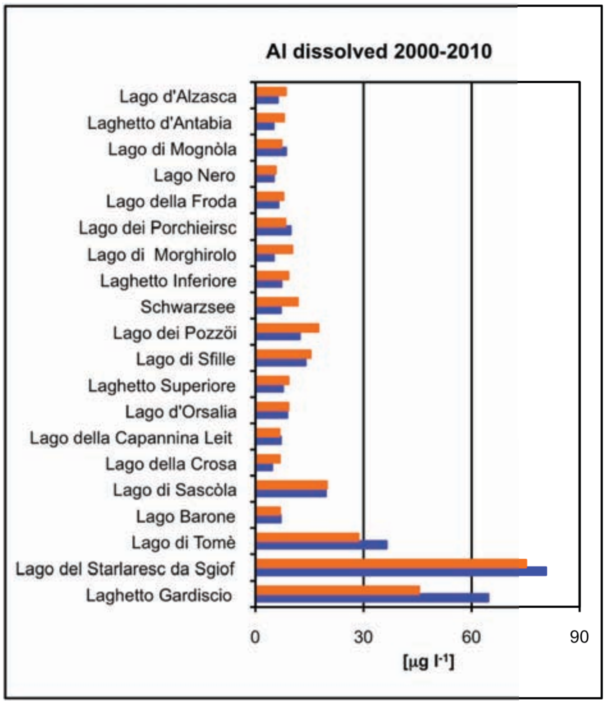

Alkalinity 2011
Lago d'Alzasca
Laghetto d'Antabia
Lago di Mognòla
Lago Nero
Lago della Froda
Lago dei Porchieirsc
Lago di Morghirolo
Laghetto Inferiore
Schwarzsee
Lago dei Pozzöi
Lago di Sfille
Laghetto Superiore
Lago d'Orsalia
Lago della Capannina Leit
Lago della Crosa
Lago di Sascòla
Lago Barone
Lago di Tomè
Lago del Starlaresc da Sgiof
Laghetto Gardiscio
-20 0 20 40 60 80
[meq m-3]


Alkalinity 2000-2010
Lago d'Alzasca
Laghetto d'Antabia
Lago di Mognòla
Lago Nero
Lago della Froda
Lago dei Porchieirsc
Lago di Morghirolo
Laghetto Inferiore
Schwarzsee
Lago dei Pozzöi
Lago di Sfille
Laghetto Superiore
Lago d'Orsalia
Lago della Capannina Leit
Lago della Crosa
Lago di Sascòla
Lago Barone
Lago di Tomè
Lago del Starlaresc da Sgiof
Laghetto Gardiscio
-20 0 20 40 60 80
[meq m-3]


pH 2011
Lago d'Alzasca
Laghetto d'Antabia
Lago di Mognòla
Lago Nero
Lago della Froda
Lago dei Porchieirsc
Lago di Morghirolo
Laghetto Inferiore
Schwarzsee
Lago dei Pozzöi
Lago di Sfille
Laghetto Superiore
Lago d'Orsalia
Lago della Capannina Leit
Lago della Crosa
Lago di Sascòla
Lago Barone
Lago di Tomè
Lago del Starlaresc da Sgiof
Laghetto Gardiscio
5 6 7 8


pH 2000-2010
Lago d'Alzasca
Laghetto d'Antabia
Lago di Mognòla
Lago Nero
Lago della Froda
Lago dei Porchieirsc
Lago di Morghirolo
Laghetto Inferiore
Schwarzsee
Lago dei Pozzöi
Lago di Sfille
Laghetto Superiore
Lago d'Orsalia
Lago della Capannina Leit
Lago della Crosa
Lago di Sascòla
Lago Barone
Lago di Tomè
Lago del Starlaresc da Sgiof
Laghetto Gardiscio
5 6 7 8


Al dissolved 2011
Lago d'Alzasca
Laghetto d'Antabia
Lago di Mognòla
Lago Nero
Lago della Froda
Lago dei Porchieirsc
Lago di Morghirolo
Laghetto Inferiore
Schwarzsee
Lago dei Pozzöi
Lago di Sfille
Laghetto Superiore
Lago d'Orsalia
Lago della Capannina Leit
Lago della Crosa
Lago di Sascòla
Lago Barone
Lago di Tomè
Lago del Starlaresc da Sgiof
Laghetto Gardiscio
0
30
60
90
[µg l-1]

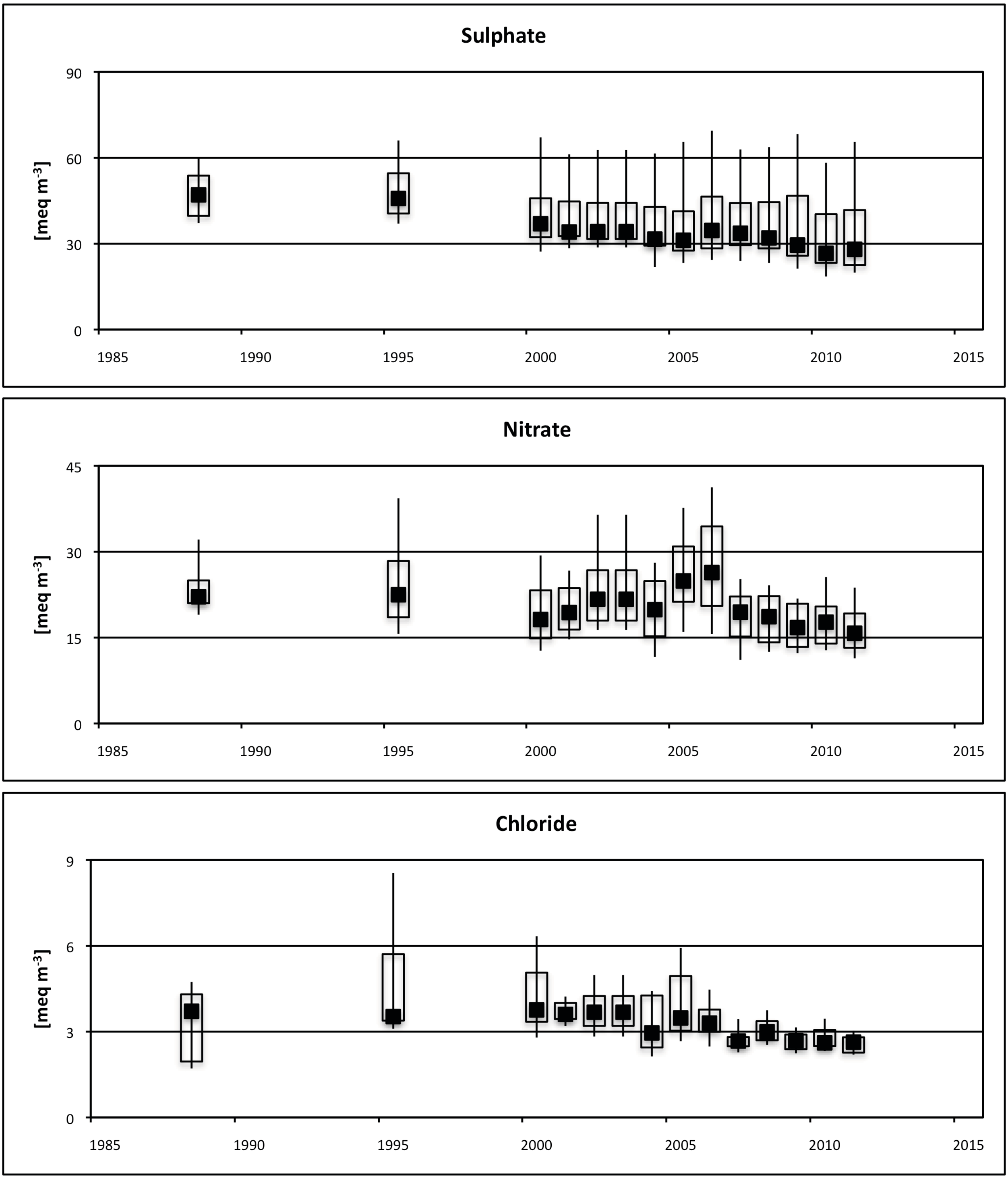

Al dissolved 2000-2010
Lago d'Alzasca
Laghetto d'Antabia
Lago di Mognòla
Lago Nero
Lago della Froda
Lago dei Porchieirsc
Lago di Morghirolo
Laghetto Inferiore
Schwarzsee
Lago dei Pozzöi
Lago di Sfille
Laghetto Superiore
Lago d'Orsalia
Lago della Capannina Leit
Lago della Crosa
Lago di Sascòla
Lago Barone
Lago di Tomè
Lago del Starlaresc da Sgiof
Laghetto Gardiscio
0
30
60
90
[µg l-1]

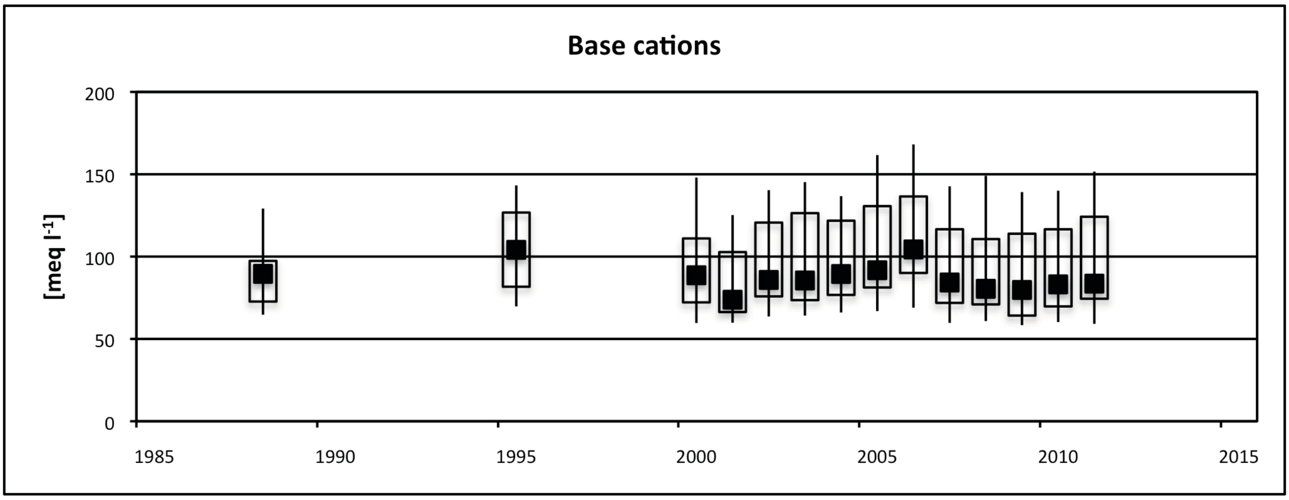
Temporal variations

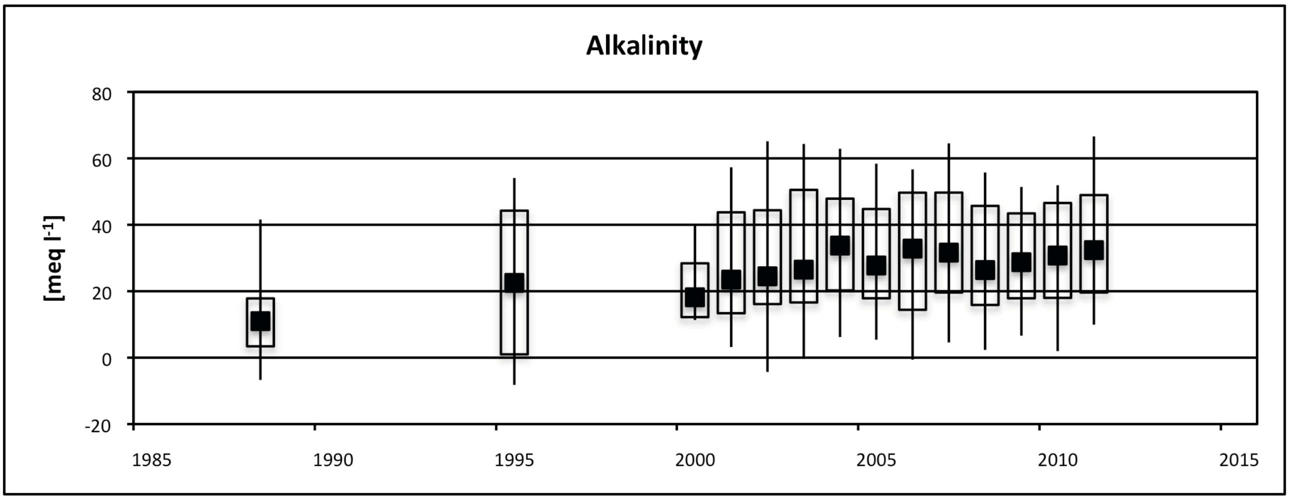
In order to show temporal variations of lake quality, annual median values of pH, alkalinity and concentrations of base cations, sulphate and nitrate of all lakes with their 10th, 25th, 75th and 90th percentile values are represented in Fig. 2.11. Only years, where all 20 alpine lakes have been monitored 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 combustibles with other fossil fuels. As a consequence lake alkalinity and pH increased. Concentrations of nitrate also seem to have slightly decreased as a consequence of reduced emissions of NO_X. Aluminium concentrations of the 3 most acidic lakes are presented in Fig. 2.12. A decrease in concentrations can be observed for Lago del Starlaresc da Sgiof and Lago di Tomè. A more detailed trend analysis for the period 2000-2010 has been perfomed in Steingruber and Colombo (2011).

Figure 2.11 Temporal variations of annual median values and their 10^{th}, 25^{th}, 75^{th}, 90^{th} percentiles of parameters measured in 20 Alpine lakes from 1988 to 2011

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




Base cations
[meq l-1]
200
150
100
50
0
1985
1990
1995
2000
2005
2010
2015


Alkalinity
[meq l-1]
80
60
40
20
0
-20
1985
1990
1995
2000
2005
2010
2015

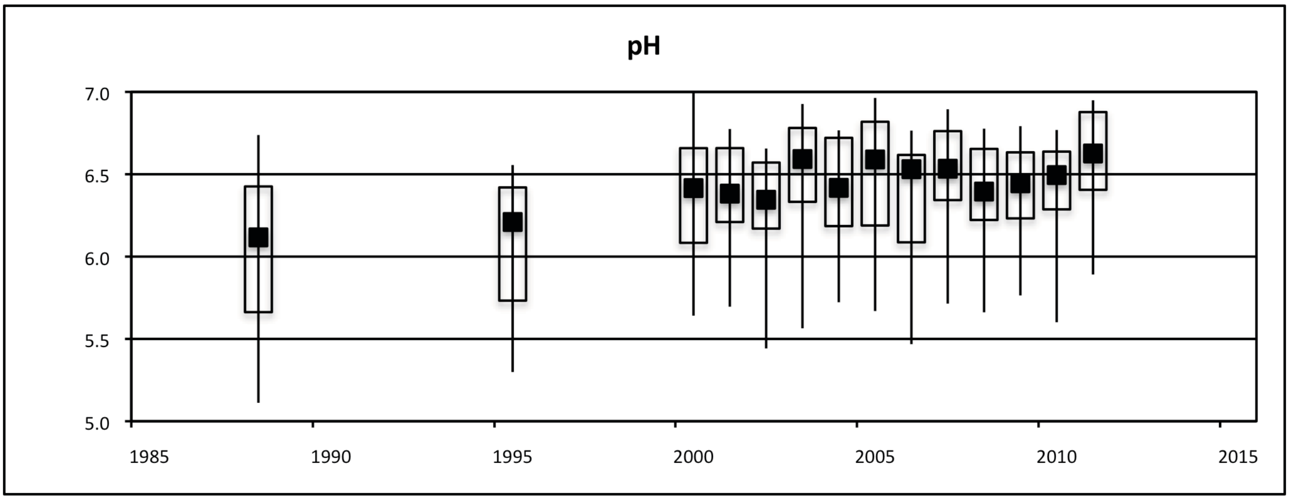
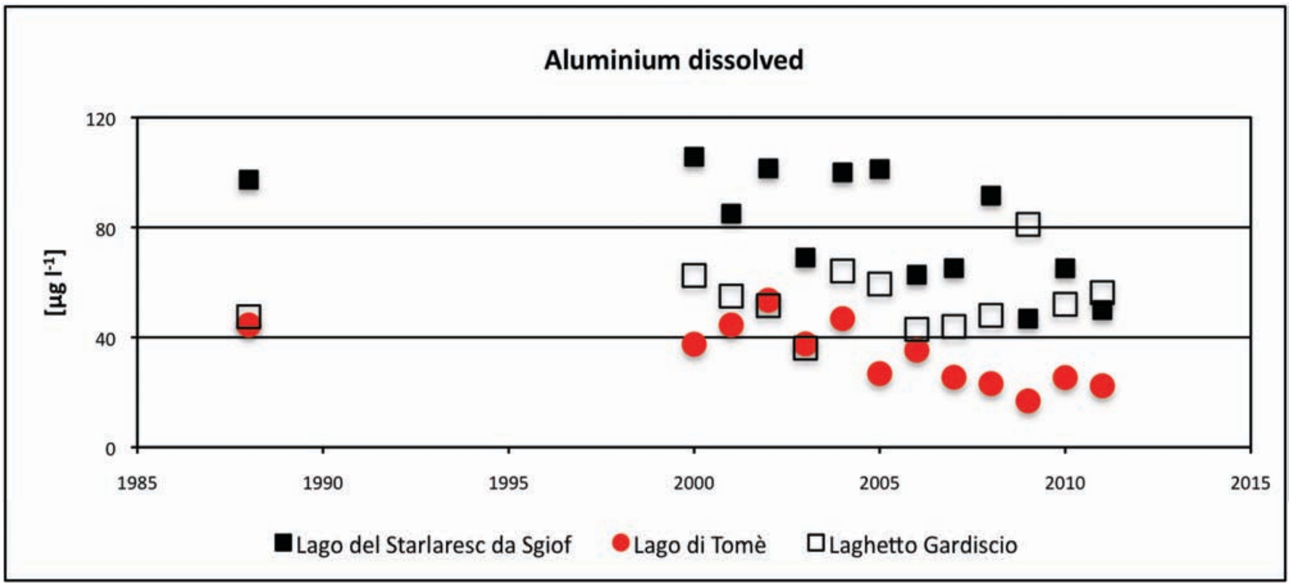

pH
7.0
6.5
6.0
5.5
5.0
1985
1990
1995
2000
2005
2010
2015

Figure 2.12 Temporal variations of dissolved aluminium in the 3 most acidic lakes from 1988 to 2010



3 Macroinvertebrates as bioindicators

3.1 Introduction

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. To study biological recovery at sites with acidification problems macroinvertebrates were included as bioindicators in the monitoring programme. Since 2000 macroinvertebrates are monitored regularly in 4 lakes (Laghetto Inferiore, Laghetto Superiore, Lago di Tomè, Lago del Starlaresc da Sgiof) and 3 rivers (Maggia, Vedeggio, Verzasca). In order to better interpret results from Alpine lakes, from 2006 the alkaline lake Lago Bianco was also added to the monitoring list. Samples taken by the Institute of Ecosystem Studies in Pallanza in 1991 at Laghetto Superiore and Laghetto Inferiore were analysed during 2008.

3.2 Methods

Macroinvertebrate samples were collected by "kicksampling" according to the ICP Waters Manual (ICP Waters Programme Centre, 2010). Sampling in river Maggia, Vedeggio and Verzasca occurred 4-8 times a year, while in lakes (Laghetto Inferiore, Laghetto Superiore, Lago di Tomè, Lago del Starlaresc da Sgiof, Lago Bianco) samples were collected from the littoral and the emissary 2-3 times a year. Macroinvertebrates were conserved in 70% ethanol.

Until 2007 chironomidae were only determined at the family level, from 2008, thanks to the collaboration with the Institute of Ecosystem Studies in Pallanza, we started to determine *Chironomidae* and *Oligochaeta* of old lake samples down to genus and eventually species level, so that now we have a detailed analysis of *Chironomidae* and *Oligochaeta* of the years 1991, 2003 and 2007. The analysis of this data is going to be published separately. In order, to determine the „biological health" of surface waters with respect to acidification different approaches were used. The taxa richness is often regarded as indicator for the "health" of a biological community. For all samples the total E.B.I. taxa number according to Ghetti (1986) and the number of families of the orders *Ephemeroptera, Plecoptera, Trichoptera* (number EPT families) were calculated. Both the taxa richness and the number of EPT families are indicators for the "health" of a biological community. In particular, the EPT index is often used as water quality indicator because macroinvertebrates belonging to the orders of *Ephemeroptera, Plecoptera* and *Trichoptera* are highly sensitive to pollution. In addition, for river samples the German classification system of Braukmann and Biss (2004) was used. Since to the species *Crenobia alpina.* and *Pisidium sp.* no indicator values were assigned by Braukmann and Biss (2004), according to their occurrence at pH >5.0, >4.7, respectively (Fjellheim and Raddum 1990), we attributed them indicator an value of 3 and 4. This categorisation system permits to evaluate and assess the acidity of rivers on the basis of macroinvertebrate populations. For high altitude alpine lakes, because of their natural poorness in taxa, it still does not exist a viable macroinvertebrate classification method that is able to describe water acidity. However, it is possible to study the presence of acid sensitive species in the samples.

3.3 Results and discussion

3.3.1 Lakes

Because of the high altitudes and therefore extreme physical-chemical conditions the population of macroinvertebrates in Alpine lakes is expected to be generally poor (Fjellheim et al., 2000; Hieber, 2002; Marchetto et al., 2004). It is also known that outlets from Alpine lakes represent unique aquatic environments and are inhabited by both lake and stream organisms (Hieber, 2002). We therefore expect a different macroinvertebrate composition in samples from the emissary and the littoral (Tab. 3.1). In fact, the species diversity no. total taxa, no. taxa E.B.I) were usually higher in the emissary than in the littoral. Similarly, behaved the number of EPT families. In the littoral of all lakes *Diptera* (mainly *Chironomidae*) was mostly the dominant order, often followed by *Oligochaeta*. In the emissaries other orders like *Plecoptera* were also quantitatively important.

Variations in macroinvertebrate population among lakes are probably influenced mainly by differences in water acidity, morphology and temperature. Highest pH's occur in Lago Bianco, followed by Laghetto Superiore and Inferiore, Lago di Tomè and Lago del Starlaresc da Sgiof. During 2011 average pH's were 7.7, 6.8, 6.7, 5.9, 5.9, respectively. While for the lakes with higher pH (Bianco, Inferiore and Superiore) the species diversity (see no. total taxa, no. taxa E.B.I, no. EPT families) in the emissaries were similar, while in the littoral of Lago Bianco values were significantly lower, probably because of the particular substrate of this lake (very fine). The number of total taxa, taxa E.B.I. and EPT families in the more acidic lake Tomeo were also similar to lakes Inferiore, Superiore, Bianco (only emissary), but significantly lower in Lago del Starlaresc da Sgiof.

In all lakes *Diptera* was mainly represented by *Chironomidae* and the widespread diffusion of *Oligochaeta* and the acid tolerant *Chironomidae* is typical for Alpine lakes and lake outlets (Fjellheim et al., 2000; Hieber, 2002; Marchetto et al., 2004). The order *Ephemeroptera*, to which belong many of the most acid sensitive species was present only in the emissaries of lakes Bianco, Inferiore and Superiore. Because of its wetland characteristics, Lago del Starlaresc da Sgiof is the only lake that is inhabited by *Odonata* (=*Others*). *Heteroptera* were also only found in Lago del Starlaresc da Sgiof and *Megaloptera* appeared in Lago di Tomè and Lago del Starlaresc da Sgiof.

Table 3.2 shows acid sensitive species are almost absent in all lakes, but moderately acid sensitive species are common in emissaries of lakes with pH>6 (Bianco, Inferiore, Superiore) with 6-7 species each, although their relative abundance is small (Tab. 3.3). In the more acidic Lago Tomè only 3 moderately acid sensitive species have up to now been observed and in Lago del Starlaresc da Sgiof any. In the first 6 acid-resistant and 7 very acid-resistant species have been found and in the second 3 acid-resistant and 5 very acid-resistant species.

Interpretations of temporal variations are difficult because during the sampling period the number of individuals per sample and the number of samples during the years changed greatly and it is known that if the number of sampled organisms increases the number of detected species also increases. In order to avoid that species appearing for the first time during the monitoring period, simply because of the higher probability to find them, are misinterpreted as a result of changing species composition over time, each sample should be "downweighted" to the smallest sample size. In this way species with few individuals present only in large samples disappear. A detailed trend analysis has been by Steingruber and Colombo (2011) for the period 2002-2009, but no significant change of biology over time could be observed, even not in the more acidic Lago Tomè and Lago del Starlaresc da Sgiof, whose pH's increased and concentrations of aluminium decreased significantly during the last decade (see Fig. 2.12).

Table 3.1 Number of samples, individuals, taxa, EPT families and relative abundances of the main macroinvertebrate groups in the littoral and in the emissary of 5 Alpine lakes during form 1991 to 2011

Lakes	Parameters	Littoral									Emissary									
		2002	2003	2004	2005	2006	2007	2008	2009	2011	1991	2002	2003	2004	2005	2006	2007	2008	2009	2011
Laghetto Inferiore	no. of samples	3	3	3	3	2	2	2	2	2	1	3	3	3	3	2	2	2	2	2
	no. individuals	199	1272	1453	5223	3228	2556	6869	2945	1050	64	293	1217	2004	8338	6086	7714	10519	5255	958
	no total taxa	7	16	15	23	15	14	18	15	9	8	11	23	21	24	22	20	17	17	13
	no. taxa E.B.I.	8	12	13	18	10	13	13	9	9	5	11	19	18	18	17	17	15	13	10
	no. EPT families	1	4	3	6	3	3	3	3	4	1	3	9	8	10	9	7	6	7	5
	Ephemeroptera	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	2%	2%	1%	1%	1%	1%	0%	0%
	Plecoptera	1%	2%	3%	2%	4%	1%	2%	3%	4%	19%	33%	23%	16%	12%	13%	5%	5%	6%	6%
	Trichoptera	0%	1%	1%	0%	1%	2%	0%	0%	0%	0%	1%	3%	3%	3%	1%	0%	1%	1%	1%
	Diptera	59%	81%	74%	74%	76%	75%	57%	69%	92%	47%	44%	44%	33%	45%	43%	58%	52%	60%	92%
	Coleoptera	2%	1%	3%	1%	1%	1%	0%	0%	1%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
	Oligochaeta	35%	13%	18%	17%	12%	14%	7%	22%	0%	30%	11%	25%	36%	30%	35%	30%	23%	23%	0%
	Others	3%	1%	1%	5%	6%	8%	33%	6%	3%	5%	12%	2%	10%	8%	7%	5%	19%	9%	2%
Laghetto Superiore	no. of samples	3	3	3	3	2	2	2	2	2	1	3	3	3	3	2	2	2	2	2
	no. individuals	332	1605	2055	8705	4491	4243	7204	3925	239	49	150	1549	1748	6631	5742	5348	4991	5474	963
	no. total taxa	10	14	15	18	13	14	23	11	10	6	10	21	22	21	19	17	20	19	12
	no. taxa E.B.I.	11	11	12	14	9	12	16	11	8	5	12	18	18	17	15	14	15	11	11
	no. EPT families	3	3	3	4	3	3	3	3	3	1	3	9	8	8	8	7	6	5	7
	Ephemeroptera	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	9%	7%	1%	0%	0%	0%	0%	1%
	Plecoptera	5%	6%	4%	4%	3%	3%	5%	3%	4%	15%	38%	29%	17%	11%	10%	3%	6%	21%	13%
	Trichoptera	4%	3%	1%	1%	3%	4%	2%	0%	3%	0%	1%	4%	3%	1%	1%	1%	1%	1%	2%
	Diptera	31%	71%	65%	70%	55%	51%	65%	71%	87%	66%	50%	34%	49%	47%	38%	30%	49%	49%	81%
	Coleoptera	1%	1%	3%	1%	1%	1%	0%	1%	2%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
	Oligochaeta	57%	15%	14%	11%	8%	10%	18%	15%	0%	6%	6%	21%	20%	38%	50%	64%	43%	29%	1%
	Others	3%	3%	13%	14%	30%	30%	9%	11%	4%	13%	5%	2%	4%	1%	1%	2%	2%	1%	3%

Lakes	Parameters	Littoral									Emissary								
		2002	2003	2004	2005	2006	2007	2008	2009	2011	2002	2003	2004	2005	2006	2007	2008	2009	2011
Lago di Tomè	no. of samples	2	2	2	2	2	2	2	2	2	2	1	2	2	2	2	2	2	2
	no. individuals	227	393	466	1581	1527	1668	3432	1619	533	157	347	351	2160	3066	4007	4606	3771	230
	no. total taxa	10	14	11	16	17	13	16	15	9	10	17	11	19	20	20	21	22	6
	no. taxa E.B.I.	10	9	11	12	10	9	11	11	7	10	11	7	13	15	14	17	14	6
	no. EPT families	4	3	3	5	5	3	4	4	3	4	5	3	5	6	5	6	6	2
	Ephemeroptera	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
	Plecoptera	3%	1%	2%	1%	1%	0%	1%	2%	4%	60%	56%	56%	13%	35%	34%	8%	10%	3%
	Trichoptera	7%	16%	4%	5%	7%	6%	4%	6%	7%	2%	4%	1%	2%	2%	1%	1%	1%	1%
	Diptera	54%	66%	37%	71%	64%	58%	73%	58%	72%	28%	33%	39%	83%	57%	64%	86%	86%	95%
	Coleoptera	2%	2%	3%	0%	2%	2%	0%	1%	1%	1%	3%	0%	0%	0%	0%	0%	0%	1%
	Oligochaeta	33%	10%	51%	15%	16%	28%	15%	29%	14%	7%	1%	0%	0%	0%	0%	1%	1%	0%
	Others	1%	4%	3%	8%	10%	7%	7%	5%	1%	3%	3%	4%	2%	5%	1%	5%	2%	0%
Lago del Starlaresc da Sgiof	no. of samples	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
	no. individuals	206	471	277	1489	2353	2760	3781	1272	135	709	896	511	2730	6293	3487	4028	3028	604
	no total taxa	7	11	12	14	13	13	12	11	4	9	13	12	18	21	20	20	20	10
	no. taxa E.B.I.	9	7	7	9	6	10	6	6	4	6	9	9	13	11	12	13	11	10
	no. EPT families	1	1	1	1	1	1	1	0	0	2	3	1	3	4	4	5	3	1
	Ephemeroptera	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
	Plecoptera	0%	0%	0%	0%	0%	0%	0%	0%	0%	2%	2%	5%	1%	1%	9%	8%	12%	1%
	Trichoptera	4%	0%	0%	0%	0%	0%	0%	0%	0%	5%	4%	0%	0%	0%	1%	1%	1%	0%
	Diptera	75%	78%	78%	73%	88%	90%	79%	72%	98%	85%	88%	62%	86%	95%	84%	84%	68%	95%
	Coleoptera	0%	0%	0%	0%	0%	0%	0%	0%	0%	2%	0%	0%	0%	0%	0%	0%	0%	1%
	Oligochaeta	16%	8%	3%	16%	5%	4%	13%	17%	0%	0%	1%	3%	3%	1%	0%	2%	8%	0%
	Others	5%	14%	19%	11%	7%	6%	8%	11%	2%	6%	5%	30%	9%	2%	5%	5%	11%	2%

Lakes	Parameters	Littoral					Emissary				
		2006	2007	2008	2009	2011	2006	2007	2008	2009	2011
Lago Bianco	no. of samples	2	2	2	2		2	2	2	2	2
	no. individuals	4898	6030	6944	4642	2269	6195	5910	6056	4122	1158
	no total taxa	10	10	11	11	6	24	25	25	20	13
	no. taxa E.B.I.	6	5	7	9	3	15	19	21	14	9
	no. EPT families	1	1	2	1	2	7	9	8	6	6
	Ephemeroptera	0%	0%	0%	0%	0%	4%	1%	1%	0%	0%
	Plecoptera	0%	0%	0%	0%	0%	7%	9%	13%	2%	15%
	Trichoptera	0%	0%	0%	0%	0%	1%	1%	0%	0%	1%
	Diptera	78%	56%	47%	36%	92%	39%	38%	54%	60%	80%
	Coleoptera	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
	Oligochaeta	10%	31%	47%	54%	1%	45%	50%	31%	36%	3%
	Others	12%	13%	5%	10%	7%	4%	1%	1%	1%	1%

Table 3.2 Macroinvertebrate species with lowest “Braukmann and Biss index” in emissaries of 5 Alpine lakes from 1991 to 2011
X refers to the emissary and (X) to the littoral. The gray coloured areas indicate the absence of samples

Lakes	Taxa	Index	1991	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2011
	Ecdyonurus helveticus-Gr.	2					x	x	x	x	x			
	Ecdyonurus sp.	2						x	x	x	x	x	x	x
	Perlodes intricatus	2						x	x		x	x		
	Perlodes sp.	2						x			x			
	Philopotamus lucidificatus	2					x		x	x				
	Protonemoura nimborum	2		x					x	x	x		x	
	Rhithrogena sp.	2					x							
Laghetto Superiore	Baetis alpinus	2					x	x		x				
	Ecdyonurus helveticus-Gr.	2					x	x	x		x			
	Ecdyonurus sp.	2					x	x	x	x	x	x		x
	Perlodes intricatus	2						x	x		x			
	Perlodes microcephalus	2					x							
	Perlodes sp.	2						x						
	Protonemoura nimborum	2						x	x	x	x		x	
	Rhithrogena sp.	2						x						
Lago Tomè	Perla grandis	1			x									
	Perlodes sp.	2										x		
	Protonemura nimborum	2							x			x	x	
	Rhyacophila tristis	2									x			
	Crenobia alpina	(3)								x	x	x	x	
	Odontocerum albicorne	4								x	x		x	
	Potamophylax cingulatus	4							x	x				
	Protonemura meyeri	4			x									
	Rhyacophila (Ryacophila) sp.	4							x	x	x	x	x	
	Rhyacophila sp.	4					x	x	x	x	x	x	x	
	Sialis fuliginosa	4						x	x	x	x	x	x	
	Sialis sp.	4				x	x						x	
Lago del Starlaresc da Sgiof	Allogamus uncatus	4							x	x	x			
	Oligotricha striata	4			x	x	x	(x)	x	x	x	x	x	
	Sialis fuliginosa	4									(x)			
	Sialis sp.	4						(x)	(x)	(x)			x	
Lago Bianco	Alainites muticus	2								x				
	Baetis alpinus	2								x	x	x		
	Ecdyonurus sp.	2								x		x		
	Perlodes intricatus	2								x	x	x	x	
	Perlodes sp.	2								x	x	x	x	x
	Philopotamus ludificatus	2									x			
	Protonemura nimborum	2								x	x	x	x	
	Rhithrogena sp.	2									x			

Table 3.3 Relative abundance for taxa with "Braukmann and Biss index" = 1 to 5 in the emissaries from 2000 to 2011

River	Braukmann and Biss index	1991	2002	2003	2004	2005	2006	2007	2008	2009	2011
Laghetto Inferiore	1	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
	2	0%	0%	2%	3%	2%	4%	2%	1%	2%	0%
	3	5%	9%	6%	11%	9%	6%	5%	11%	8%	0%
	4	9%	1%	3%	2%	1%	1%	0%	0%	1%	0%
	5	27%	31%	18%	15%	11%	9%	3%	4%	4%	6%
Laghetto Superiore	1	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
	2	0%	0%	10%	13%	1%	2%	1%	0%	0%	1%
	3	13%	5%	4%	4%	1%	1%	2%	1%	1%	0%
	4	4%	0%	2%	3%	1%	0%	0%	0%	1%	1%
	5	19%	39%	25%	11%	7%	9%	2%	6%	1%	13%
Lago Tomè	1		0%	0%	0%	0%	0%	0%	0%	0%	0%
	2		0%	0%	0%	0%	0%	0%	0%	0%	0%
	3		0%	0%	0%	0%	0%	0%	0%	0%	0%
	4		2%	1%	1%	1%	1%	1%	0%	1%	0%
	5		57%	57%	56%	13%	31%	23%	2%	3%	6%
Lago del Starlaresc da Sgiof	1		0%	0%	0%	0%	0%	0%	0%	0%	0%
	2		0%	0%	0%	0%	0%	0%	0%	0%	0%
	3		0%	0%	0%	0%	0%	0%	0%	0%	0%
	4		1%	2%	0%	0%	0%	1%	0%	0%	0%
	5		5%	3%	5%	1%	1%	0%	1%	9%	1%
Lago Bianco	1						0%	0%	0%	0%	0%
	2						3%	1%	2%	0%	1%
	3						7%	1%	1%	0%	0%
	4						1%	0%	0%	0%	0%
	5						5%	8%	9%	2%	6%

3.3.2 Rivers

Compared to the previously discussed Alpine lakes, the monitored rivers are situated at much lower altitudes, having therefore larger catchments areas, that are responsible for higher average weathering rates. As a consequence these rivers are richer in nutrient concentrations and have higher average pH's than lakes (see chapter 2). However, during high flow pH of river Verzasca and Vedeggio can decrease close to average pH values of lakes.

The number of samples, individuals, taxa, EPT families and the relative abundances of the main macroinvertebrate groups in river Maggia, Vedeggio and Verzasca from 2000 to 2011 are shown in Tab. 3.4. The number of E.B.I. taxa and the EPT index were generally similar in river Maggia and Vedeggio but smaller in river Verzasca. The main orders were *Ephemeroptera*, *Plecoptera, Diptera* and *Coleoptera*.

Table 3.4 Number of samples, individuals, taxa, EPT families and relative abundances of the main macroinvertebrate groups in 3 Alpine rivers from 2000 to 2011.

Rivers	Parameters	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2011
Maggia	no. of samples	8	6	6	6	5	4	4	4	4	4	4
	no. organisms	2247	1507	2833	5320	5120	9857	11904	19126	16855	13596	6173
	no. taxa	40	35	43	48	44	47	46	53	50	49	38
	no. taxa E.B.I.	31	30	32	38	35	40	36	43	40	38	32
	no. EPT families	14	12	13	18	17	17	16	17	17	16	17
	Ephemeroptera	35%	28%	50%	40%	40%	31%	23%	24%	23%	34%	28%
	Plecoptera	35%	20%	31%	23%	12%	16%	15%	16%	22%	23%	16%
	Trichoptera	4%	1%	4%	4%	8%	3%	7%	2%	3%	2%	2%
	Diptera	19%	39%	8%	25%	24%	35%	36%	37%	36%	31%	46%
	Coleoptera	4%	7%	7%	5%	12%	9%	13%	12%	10%	4%	5%
	Oligochaeta	0%	0%	0%	1%	0%	2%	1%	4%	1%	2%	0%
	Others	2%	4%	1%	3%	3%	4%	5%	5%	6%	4%	3%
Vedeggio	no. of samples	8	6	6	6	5	4	4	4	4	4	4
	no. organisms	1578	1934	1789	3687	3081	7246	11672	9442	16588	10968	4404
	no. total taxa	50	48	35	41	45	55	53	52	55	56	38
	no. taxa E.B.I.	35	39	30	34	34	40	39	42	43	39	31
	no. EPT families	14	16	12	16	14	20	19	18	18	17	16
	Ephemeroptera	35%	39%	31%	18%	31%	16%	23%	27%	32%	27%	11%
	Plecoptera	28%	28%	38%	44%	22%	24%	17%	28%	31%	41%	19%
	Trichoptera	11%	6%	8%	15%	14%	15%	10%	6%	3%	3%	6%
	Diptera	16%	9%	9%	21%	23%	36%	31%	23%	23%	22%	48%
	Coleoptera	8%	18%	12%	2%	9%	6%	14%	13%	10%	3%	10%
	Oligochaeta	0%	0%	0%	0%	1%	1%	1%	1%	1%	2%	1%
	Others	1%	1%	1%	0%	1%	3%	3%	2%	1%	1%	5%
Verzasca	no. of samples	8	6	6	6	5	4	4	4	4	4	4
	no. organisms	1574	2258	2570	3761	4269	12901	15019	21054	20239	11694	4510
	no. total taxa	35	32	34	39	35	39	42	40	46	38	32
	no. taxa E.B.I.	26	32	29	29	25	28	30	31	34	27	23
	EPT families	12	13	12	14	11	12	14	12	15	12	10
	Ephemeroptera	46%	45%	37%	42%	55%	45%	36%	41%	38%	34%	35%
	Plecoptera	18%	18%	24%	18%	11%	14%	16%	12%	17%	29%	8%
	Trichoptera	3%	4%	3%	3%	2%	2%	2%	1%	1%	2%	2%
	Diptera	12%	8%	10%	21%	12%	19%	20%	22%	23%	21%	30%
	Coleoptera	18%	22%	23%	13%	18%	16%	24%	19%	17%	8%	22%
	Oligochaeta	0%	1%	1%	0%	0%	1%	0%	3%	1%	5%	0%
	Others	3%	2%	2%	2%	1%	4%	2%	2%	3%	2%	3%

All rivers were characterized by the existence of acid sensitive species (Tab. 3.5). However, in rivers Vedeggio and Maggia more acid sensitive species and moderately acid sensitive species (5+27, 3+20) were found than in river Verzasca (5+14). Tab. 3.6 lists the acid sensitive species. A temporal trend cannot be observed. No difference between rivers can be observed with regard to their "Braukmann and Biss categories" (Tab. 3.7). Most samples ended in category 2. This category stays for predominantly neutral to episodically weakly acidic rivers (pH around 6.5-7 and rarely below 5.5).

It can therefore be concluded, that although the categorisation system of Braukmann and Biss (2004) describes well the pH range of the rivers, it is not able to distinguish the rivers based on the presence of acid sensitive species. However, the higher total number of taxa, the number of EPT families and the number of acid sensitive and moderately acid sensitive species in river Maggia and Vedeggio with respect to river Verzasca, suggests lower acid conditions in the firsts. This corresponds well with results from water chemistry analysis (chapter 2). As already observed for lakes, because of the short monitoring period, observations about time trends are still difficult. However, river data seem to be very constant over time, suggesting the absence of a time trend.

Table 3.5 Acid sensitive species according to Braukmann and Biss found in 3 Alpine rivers from 2000 to 2011

River	Taxa	Index	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2011
Maggia	Habroleptoides confusa	1	x	x			x	x	x	x	x	x	
	Habroleptoides sp.	(1)				x		x	x	x	x		x
	Perla grandis	1	x	x	x	x	x	x	x	x	x		
	Perla sp.	1	x		x	x	x	x	x	x	x	x	x
	Serratella ignita	1	x	x		x	x	x	x	x	x	x	
	Serratella sp.							x	x	x	x		
Vedeggio	Agapetus ochripes	1										x	
	Habroleptoides confusa	1	x					x		x	x	x	x
	Habroleptoides sp.	(1)				x	x	x	x		x		x
	Perla bipunctata	1	x										
	Perla grandis	1	x	x	x	x	x	x	x	x	x	x	x
	Perla sp.	1	x	x	x	x	x	x	x	x	x	x	x
	Serratella ignita	1	x					x			x		
	Serratella sp.	(1)								x			
Verzasca	Allogamus auricollis	1											x
	Perla bipunctata	1											x
	Perla grandis	1	x	x	x	x	x	x	x	x		x	x
	Perla sp.	1	x	x	x	x	x	x	x	x	x	x	x
	Serratella ignita	1	x										
	Habroleptoides sp.	(1)				x					x		

Table 3.6

Relative abundance for taxa with “Braukmann and Biss index” =1 to 5 from 2000 to 2011

River	Braukmann and Biss index	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2011
Maggia	1	3%	1%	1%	0%	7%	3%	2%	3%	2%	1%	0%
	2	26%	21%	36%	28%	22%	17%	15%	12%	9%	15%	16%
	3	6%	12%	16%	22%	17%	15%	11%	13%	8%	20%	12%
	4	4%	1%	3%	3%	6%	3%	5%	4%	8%	4%	1%
	5	18%	8%	17%	7%	4%	8%	9%	11%	4%	2%	9%
Vedeggio	1	5%	4%	11%	4%	2%	2%	1%	1%	1%	1%	1%
	2	37%	39%	37%	24%	30%	23%	16%	12%	5%	9%	7%
	3	7%	10%	5%	12%	15%	13%	22%	17%	19%	22%	6%
	4	4%	1%	3%	2%	2%	2%	3%	3%	1%	1%	2%
	5	15%	19%	14%	14%	12%	13%	7%	18%	4%	8%	16%
Verzasca	1	2%	4%	4%	2%	4%	2%	2%	1%	0%	1%	1%
	2	44%	43%	34%	30%	42%	18%	22%	12%	19%	11%	11%
	3	3%	6%	10%	19%	15%	33%	12%	32%	6%	25%	23%
	4	2%	3%	2%	3%	2%	4%	5%	5%	5%	3%	6%
	5	10%	6%	11%	9%	4%	7%	12%	6%	4%	3%	4%

Table 3.7 “Braukmann and Biss categories” and their relative river sample number from 2000 to 2011

Rivers	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2011
Maggia	1.9	2.0	2.0	2.0	1.6	2.0	2.0	2.3	2.5	2.0	2.0
Vedeggio	2.0	2.0	1.5	2.0	2.0	2.0	2.3	2.5	3.0	2.5	2.5
Verzasca	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.3	2.0	2.3	2.5

4 Persistent organic pollutants (POP's), mercury and stable isotopes in fish muscle of rainbow trout in

4.1 Introduction

Persistent organic pollutants (POP's) are chemical substances that persist in the environment, bioaccumulate through the food web and can have negative effects to human health and the environment. POP's 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. "Concentrations of POP's and metals in fish are influenced by the contamination level of lake water and sediment. However, it is likely that food web structure and biological factors, as longevity and growth, are important variables explaining the observed variability (Cabana and Rasmussen, 1996; Kidd et L. 1998). Fish are opportunistic feeders whose diets change as they grow. The diet can vary significantly among individuals of the same species (Kidd et al. 1995). Generally, there is a significant enrichment of the heavy isotope of nitrogen (^{15}N) relative to the light isotope (^{14}N) through the food web (on average 3.5 +/- 1‰ per level; Meili et al. 1993). Hence the ratio ($\delta^{15}N$) provide a time-integrated and continuous measure of the relative trophic position of consumers (Kiriluk et al., 1995). The fractionation of ^{13}C in the food chain is much less (about 1 +/- 1‰; Meili et al. 1993) and the ratio ($\delta^{13}C$) is more indicative of the carbon sources of the assimilated diet than the trophic position (De Niro and Epstein, 1978; Fry and Sherr 1984; Estep and Vigg, 1985; France 1995)."(Rognerud et al. 2002) In fact, "due to the high diffusion of CO_2 in water, plants with well-defined boundary layers will assimilate otherwise normally discriminated ^{13}C. Therefore, under conditions of decreased water turbulence and consequently higher diffusive boundary-layer resistance, primary producers should become enriched in ^{13}C relative to ^{12}C. As a result, on a global basis, benthic algae in both lakes and oceans are enriched in ^{13}C by $\approx$ 7‰ compared to planktonic algae measured as POM (particulate organic matter). Because carbon undergoes little further fractionation with food assimilation, the observed difference in $\delta^{13}C$ between benthic and planktonic algae can often be substantial enough to be reflected by differences in the $\delta^{13}C$ signatures by consumers." (France, 1995)

From 2000 to 2009 concentrations of POP's (mainly DDT and PCB) and metals have been measured in homogenized samples of muscle flesh from rainbow trouts fished in 2 alpine mountain lakes (Laghetto Superiore and Laghetto Inferiore). In 2010, because of the very small fish population in Laghetto Inferiore, only fish from Laghetto Superiore could be analysed. However, differently to the previous years, analysis ware performed for each fish individually and next to the most important POP's, mercury and stable isotopes ($\delta^{15}N$, $\delta^{13}C$) were also measured.

4.2 Methods

Fish were angled in autumn. All fish were measured for length and weight and aged by scale analysis. From 2000 to 2009 for each lake (Laghetto Superiore and Laghetto Inferiore) homogenized samples of fish muscle were prepared. Concentrations of POP's (DDT, PCB, HCB, HCH) and metals in fish muscle were determined as described in Steingruber and Colombo (2006). Fish muscle samples from 2010 were prepared as described by the ICP waters Programme Manual (ICP Waters Programme Centre, 2010) and sent for the analysis of POP's, mercury and stable isotopes to laboratories in Norway.

Analysis of mercury and stable isotopes were carried out in the Environmental Chemistry Section of the Department of Plant and Environmental Sciences (IPM) and the Isotope Laboratory, respectively of the Norwegian University of Life Sciences. Analysis of POP's were carried out at the Laboratory of Norwegian

Institute for Agricultural and Environmental Research (Bioforsk), Norway. Methods are descrive in Sharma et al. (2009).

4.3 Results and discussion

4.3.1 Fish population characteristics

In Laghetto Superiore only rainbow trouts (*Oncorhynchus mykiss*) were sampled. Fish number, average weight, length, age and coefficient of condition are shown in Tab. 4.1. A coefficient of condition above 1 stands for a good physical condition. In samples from 2010 weight ranged from 58 to 150 g, length from 18 to 25 cm, age from 33 to 57 months and coefficient of condition from 0.7 to 1.1. Fig. 4.1 shows that both length and weight increase with age.

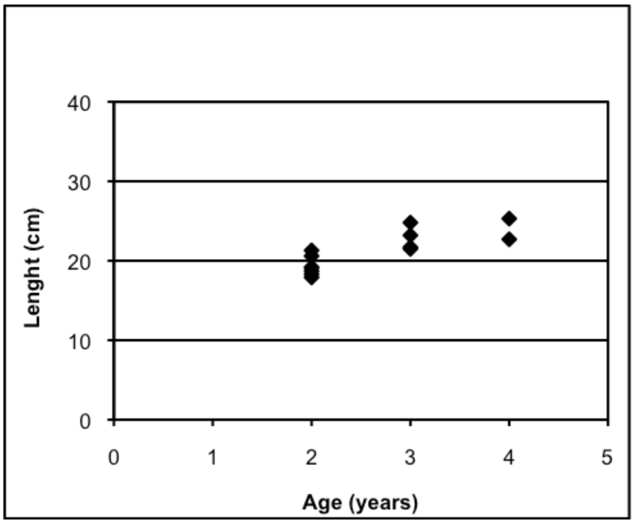
The $\delta^{15}N$ signal in fish samples from 2010 was on average 5.2‰ and typical for non-piscivorous population (Meili et al. 1993). $\delta^{15}N$ in individuals ranged from 3.5 to 7.1‰ suggesting that all the fish were probably within the same trophic level (Fig. 4.2). The $\delta^{13}C$ values ranged from -28 to -22‰. According to Rognerud et al. (2002), an enrichment of ^{13}C above -20‰ implies a significant contribution from littoral sources, values depleted below -25‰ suggest incorporation of planktonic and terrestrial organic carbon and values in the mid-range (-25 to -20), as measured in Laghetto Superiore, indicate approximately equal assimilation of both sources. However, in order to interpret more precisely fish stable isotope values, normally primary producers, zooplankton and zoobenthos should also be included in the analysis.

Interestingly, a few smaller individuals seem to have preferred food more enriched with ^{15}N, while for carbon, $\delta^{13}C$ values in fish seem to increase with age/weight/length (Fig. 4.3). The correlation of $\delta^{13}C$ with fish size may be explained by the fact that some of the youngest specimens are feeding in the more deeper waters (plankton and/or profundal invertebrates). The higher $\delta^{15}N$ values may be related to a preference for carnivorous zooplankton and/or invertebrate.

Table 4.1 Number of fish and average weight, length, age and coefficient of condition in samples from Laghetto Superiore.

Year	Fish number	Weight (g)	Length (cm)	Age (months)	Coefficient of condition
2000	15	103.3	21.5	40	1.03
2001	29	86.6	20.8	35	0.92
2002	19	62.2	19.2	33	0.85
2003	22	56.5	18.3	31	0.92
2004	20	60.1	18.6	34	0.94
2005	23	84.7	20.3	40	1.01
2007	11	136.2	21.8	40	1.22
2008	14	133.9	23.3	48	1.03
2009	17	106.8	21.8	41	1.01
2010	15	87.3	20.8	39	0.95

Figure 4.1 Relationships between length, weight and age of rainbow trout sampled in Laghetto Superiore in 2010.



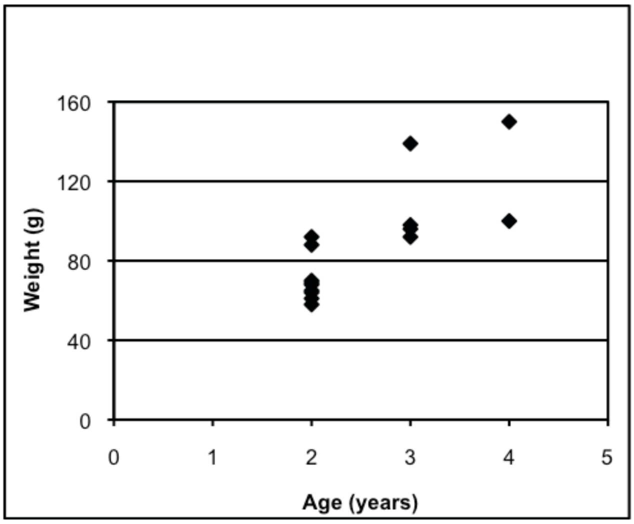


Figure 4.2 Relationship between stable-carbon and –nitrogen isotope ratios of individual fish from Laghetto Superiore in 2010.

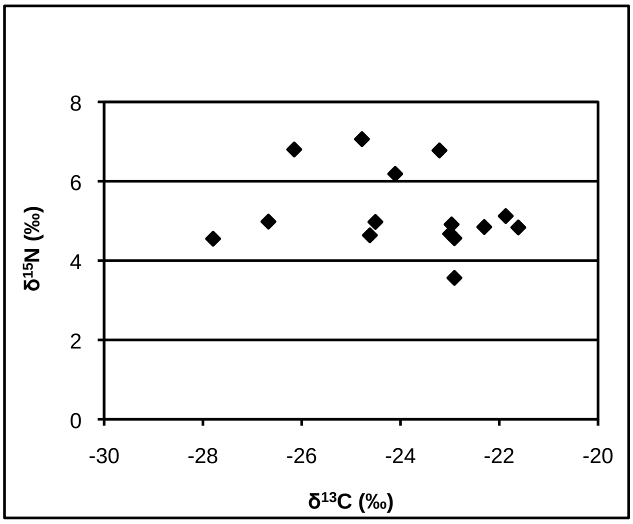
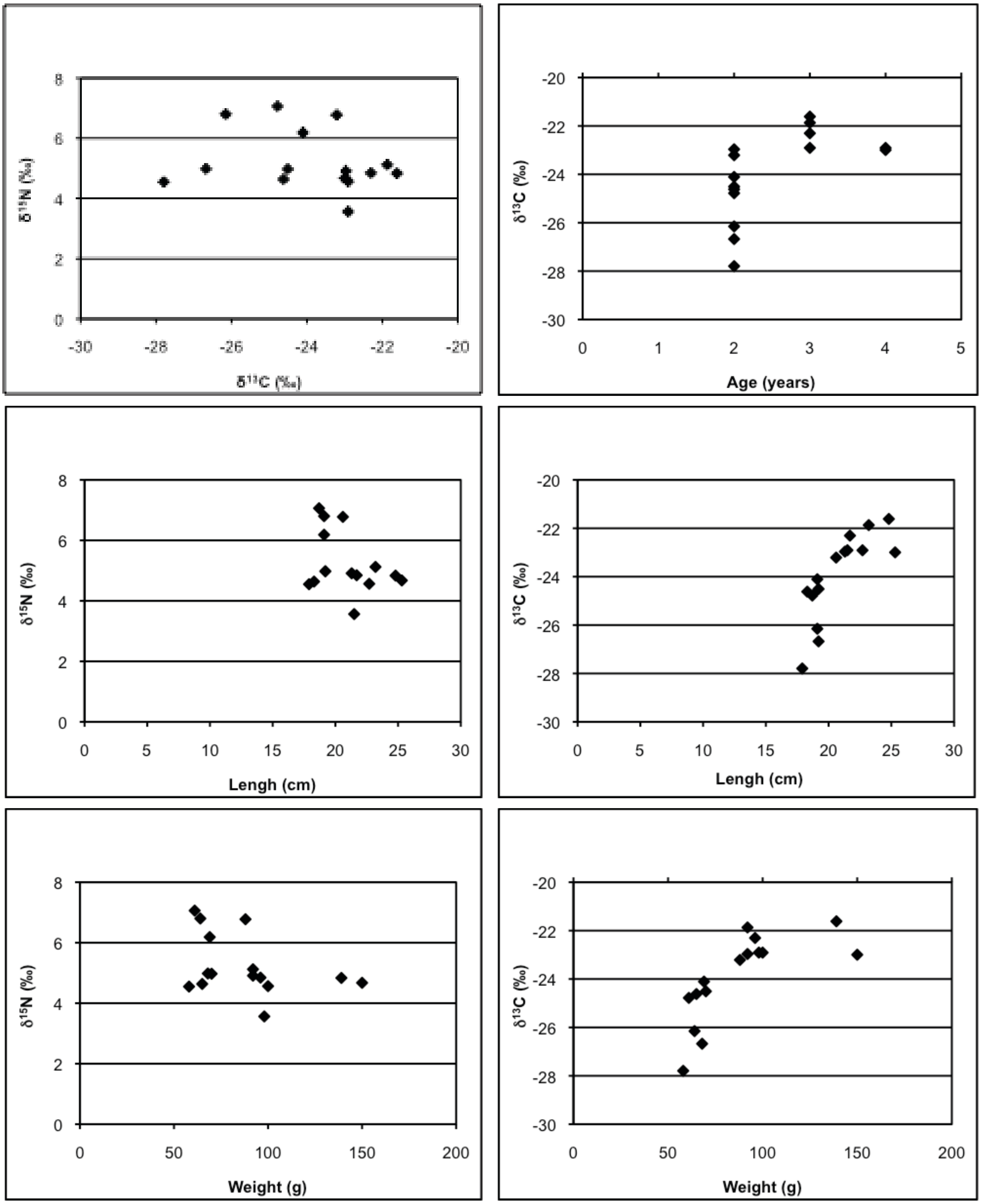


Figure 4.3 Relationship between stable isotope ratios and age/length/weight of individual fish from Laghetto Superiore in 2010.



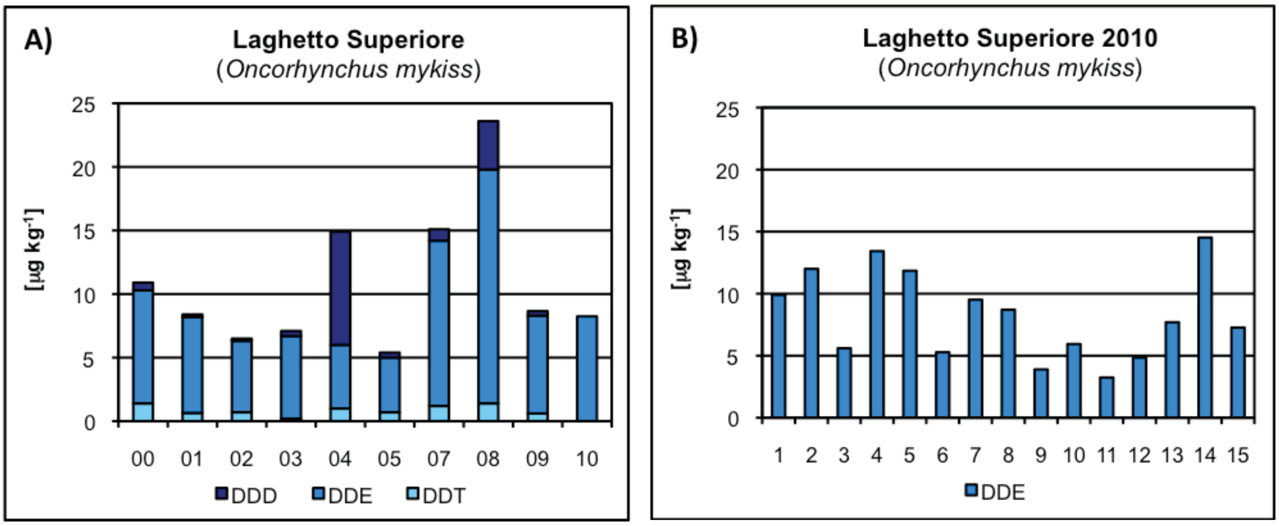
4.3.2 DDT's in fish muscle

Most DDT found in the Southern part of the Swiss Alps probably origins from a contaminated site situated along the shore of Lago Maggiore, where until 1996 a factory has produced DDT. In fact, elevated total DDT concentrations (ca. 5-72 µg kg^{-1}) are still measured in fish from Lago Maggiore (CIPAIS, 2009).

Concentrations of total DDT, PCB and Hg in fish sampled in Laghetto Superiore at the end of 2010 varied between 3 and 15 µg kg^{-1}, 3 and 30 µg kg^{-1}, 0.03 and 0.08 mg kg^{-1}, respectively (Fig. 4.4A) and were always below the Swiss edibility limit (1 mg kg^{-1}). The calculated mean value of 2010 (DDT_{tot}: 8.2 µg kg^{-1}, PCB_{tot}: 10 µg kg^{-1}, Hg: 0.05 mg kg^{-1} were similar to the measured mean values from 2000 to 2009 (Fig. 4.4B). As already observed in the former years DDE was the main component, the main PCB cogeners were the heavier isotopes PCB-138, PCB-153, PCB-181. For concentrations of total DDT and Hg no temporal trend can be observed. Differently, concentrations of total PCB seem to have decreased after 2003.

For the studied age range no bioaccumulation of DDT with age can be observed (Fig. 4.7).

Figure 4.4 Concentrations of DDT's in fish muscle samples from Laghetto Superiore between 2000 and 2010. A: average values from 2000 to 2010. B: values in individuals from 2010.

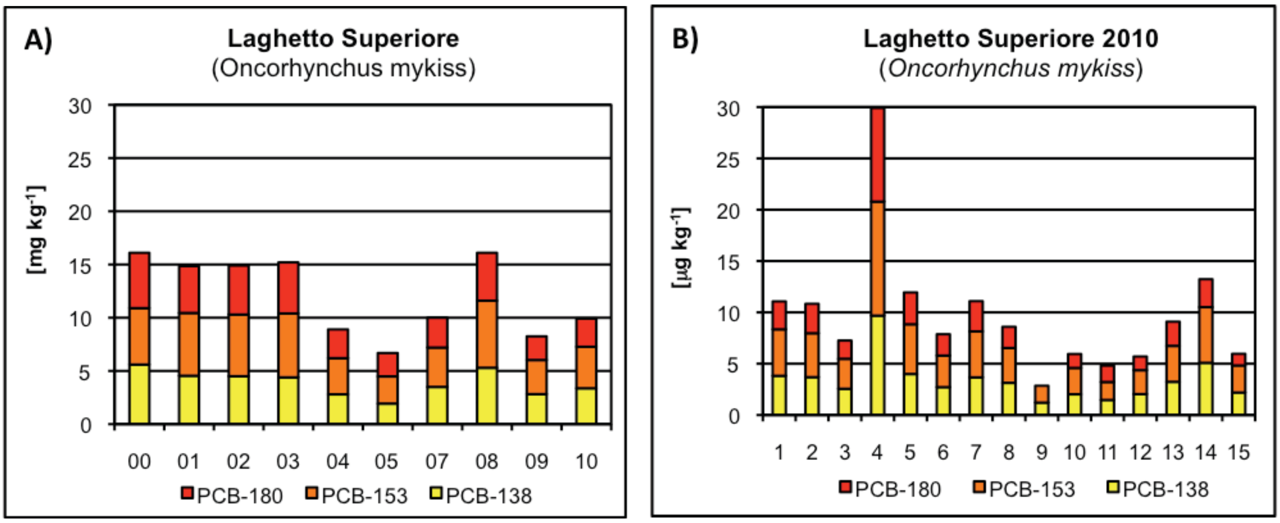


4.3.3 PCB's in fish muscle

Total PCB concentrations in fish sampled in Laghetto Superiore at the end of 2010 varied between 3 and 30 µg kg^{-1} (Fig. 4.5A) The Swiss edibility limit of PCB in fish (1 mg kg^{-1}) was therefore not exceeded. The calculated mean value of 2010 (10 µg kg^{-1}) was similar to the measured mean values from 2000 to 2009 (Fig. 4.5B). The main cogeners were the heavier isotopes PCB-138, PCB-153, PCB-181. Concentrations of total PCB seem to have decreased after 2003.

For the studied age range no bioaccumulation of PCB's with age can be observed (Fig. 4.7).

Figure 4.5 Concentrations of PCB's in fish muscle samples from Laghetto Superiore between 2000 and 2010. A: average values from 2000 to 2010. B: values in individuals from 2010.



4.3.4 Mercury in fish muscle

Concentrations of mercury in fish sampled at the end of 2010 varied between 0.03 and 0.08 mg kg^{-1} (Fig. 4.6A) and were therefore always below the Swiss edibility limits for fish (1.0 mg kg^{-1}). The calculated mean value (0.05 mg kg^{-1}) was in the same range as concentrations measured between 2001 and 2009 (Fig. 4.6B). A temporal trend in mercury concentrations can not be observed.

For the studied age range no bioaccumulation of mercury with age can be observed (Fig. 4.7).

Figure 4.6 Concentrations of mercury in fish muscle samples from Laghetto Superiore between 2000 and 2010. A: average values from 2000 to 2010. B: values in individuals from 2010.

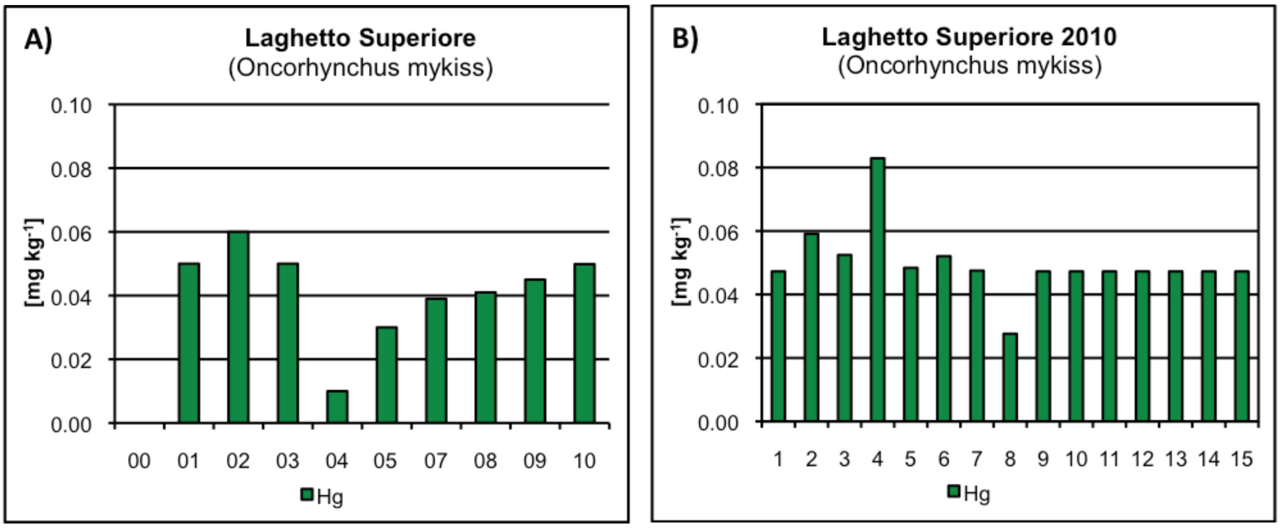
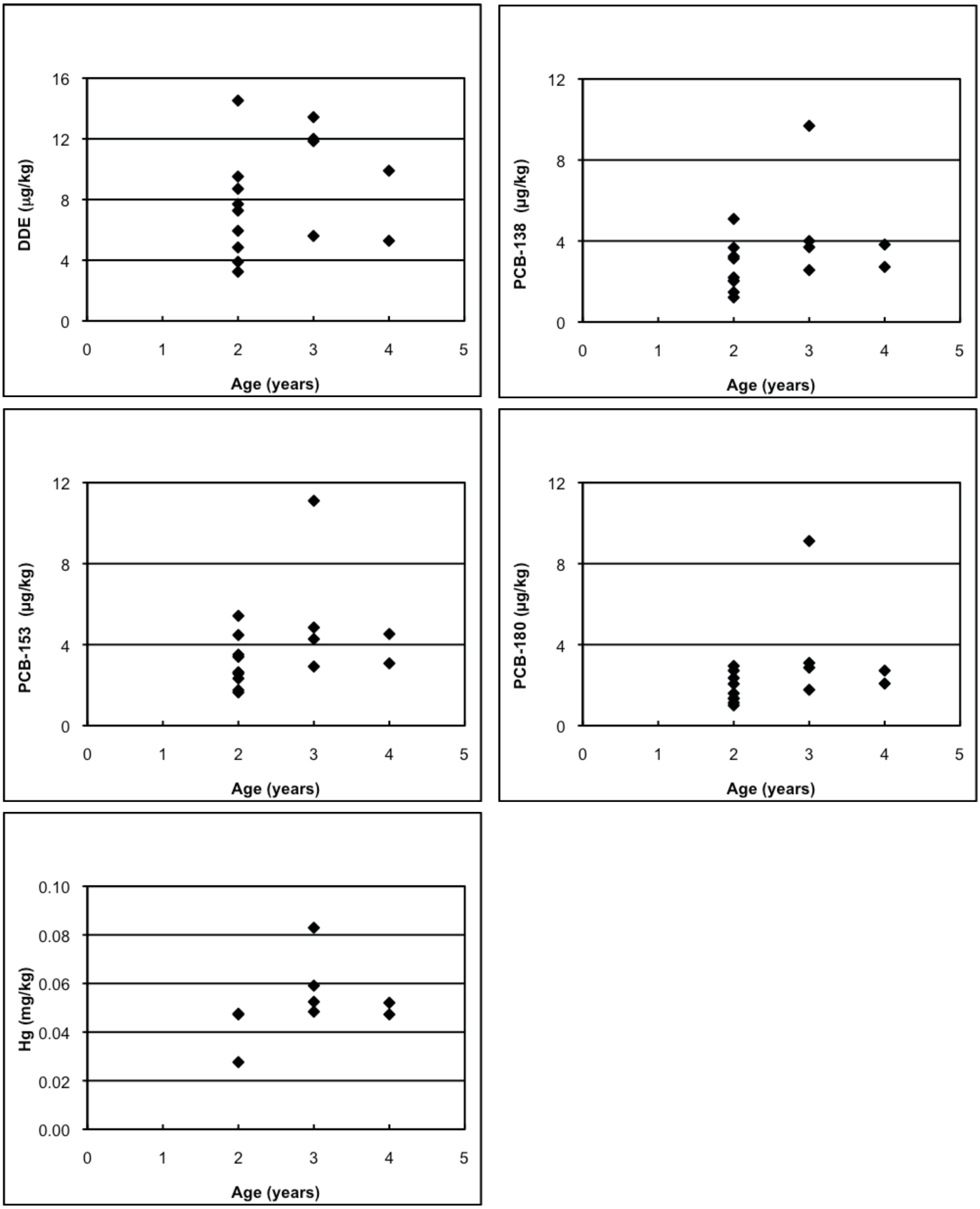


Figure 4.7 Dependence of the concentrations of DDE, PCB's and Hg on fish from 2010 on age.



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