Results from the participation of Switzerland to the International Cooperative Monitoring on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters)

Annual report 2008

Ufficio Protezione Aria
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Introduction

The International Cooperative Programme on Assessment and Monitoring of Acidification of 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 acidification of surface waters. The data collected should provide information on exposure/response relationships under different conditions and correlate changes in acid deposition with the physical, chemical and biological status of lakes and streams. 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 24 countries in Europe and North America are available in the database of the Programme Centre. Switzerland joined the Programme in 2000 by order of the Swiss Federal Office for the Environment.

1 Study site

The study area is located in the southern part of the Alps in the Canton of Ticino in Switzerland. Precipitation in this region is mainly determined by warm, humid air masses originating from the Mediterranean Sea, passing over the Po Plain and colliding with the Alps. The lithology of the north-western part of Canton Ticino is dominated by base-poor rocks especially gneiss. As a consequence soils and freshwaters in this region are sensitive to acidification. In order to assess the impact of long-range transboundary air pollution, 20 lakes (21 from 2006) and 3 rivers have been monitored. In addition, wet deposition has been monitored at 9 sampling stations distributed over all Canton Ticino. The lake's watersheds are constituted mainly by bare rocks with vegetation often confined to small areas of Alpine meadows. The selected Alpine lakes are situated between an altitude of 1690 m and 2580 m and are characterized by intensive irradiation, a short vegetation period, a long period of ice coverage and by low nutrient concentrations. The sampling points of the selected rivers are located at lower altitudes (610-918 m), implying larger catchment areas and therefore less sensitivity toward acidification than lakes. The geographic distribution of lakes, rivers and wet deposition sampling sites are shown in Fig. 1.1, while their main geographic and morphometric parameters are resumed in Tab. 1.1, 1.2 and 1.3.

Figure 1.1 Sampling sites

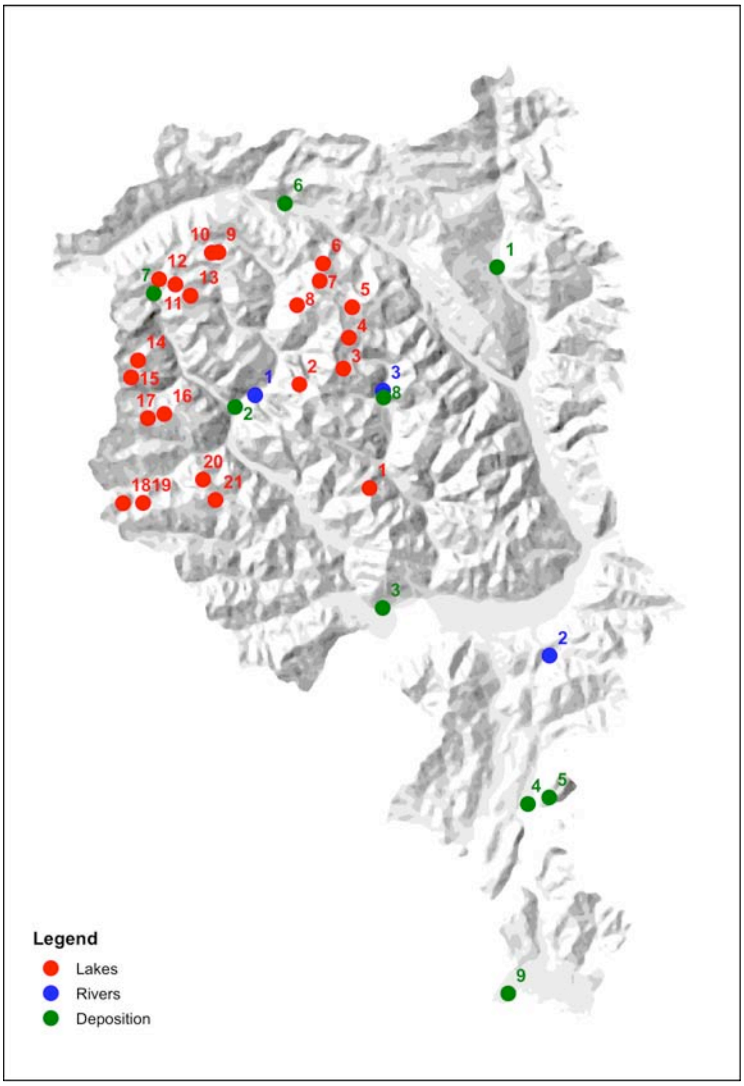


Table 1.1 Lake parameters

Lake number	Lake name	Longitude CH m	Latitude CH m	Longitude	Latitude	Altitude m a.s.l.	Catchment area ha	Lake area ha	Max depth m
1	Lago del Starlaresc da 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			
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
22	Lago di Valsabbia	686350	148675	8°33'48''	46°29'02''	2396	79	1.8	

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

2.2 Sampling methods

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

From 2000 to 2005 lake surface water was sampled twice a year (1 at beginning of summer, 1 in autumn). In 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. Weakly sampling of rainwater with wet-only samplers started in 1988.

2.3 Analytical methods

Measured parameters, conservation methods, analytical methods and quantification limits are resumed in Tab 2.1. The quality of the data was assured by participating regularly at national and international intercalibration tests. In addition, data were accepted only if the calculation of the ionic balance and the comparison of the measured with the calculated conductivity corresponded to the quality requests indicated by the programme manual of ICP Forest (ICP Forest, 2006). 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

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

The amount of monthly precipitation at each sampling site is reported in Fig. 2.1, while seasonal variations of monthly mean rainwater concentrations and deposition rates of the main chemical parameters during 2008 are shown in Fig. 2.2. Concentrations of especially nitrate and ammonia but also of sulphate behaved similar throughout the year at most sampling stations concentrations of sulphate, nitrate and ammonia peaked in February/March when concentrations of SO_2 and NOx in the air where high (UPA, 2009) and precipitation low. Interestingly, concentrations of the same pollutants were low (January, November, December) when concentrations of SO_2 and NOx in the air where high (UPA, 2009) and the amount of precipitation was average. Although concentrations of acid anions reached their minima during the winter months, acidity was highest and pH lowest in January, November and December. Lowest acidity and highest pH (Fig. 2.3) were reached during the summer months May to September, when concentrations of acid anions were also high, indicating that during summer concentrations of base cations must have increased more than acid anions. In fact, concentrations of base cations and bicarbonate suggest that during spring-summer alkaline rain events rich in minerals tend to appear more frequently. The particularly high concentrations of bicarbonate at the end of May were caused by deposition of Saharan dust (http://www.meteoschweiz.admin.ch/web/de/wetter/wetterereignisse/foehnsturm_27__...30.5.2008).

For what concerns wet deposition the amount of monthly precipitation results to be the main parameter influencing deposition of chemical parameters. In fact, wet deposition of sulphate, nitrate, ammonia, base cations and bicarbonate were highest during summer, when precipitation reached its maximum. Due to the occurrence of alkaline rain events, during summer wet deposition of acidity became very low and values were mostly negative.

In general, ion concentrations of anthropogenic origin (sulphate, nitrate, ammonia) were highest at sampling sites with low latitudes like Lugano, Monte Brè and Stabio and lowest at high latitude like Acquarossa, Bignasco, Piotta, Robiei, Sonogno. The correlation with latitude reflects the influence of long-range transboundary air pollution moving along a south to north gradient from the Po plain toward the Alps. 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. During 2008 highest deposition rates of ammonia, nitrate and sulphate were measured at Lugano, while lowest rates occurred at Acquarossa and Piotta.

For bicarbonate and acidity on average highest and lowest values, respectively, occurred at Lugano and Stabio. In fact, from May to October acidity was always negative. However, highest bicarbonate and therefore lowest acidity values were measured at Robiei, Bignasco and Piotta in May/June as a consequence of the "Föhnstorm" of 26-28 May.

Figure 2.1 Monthly precipitation during 2008
Data from MeteoSwiss

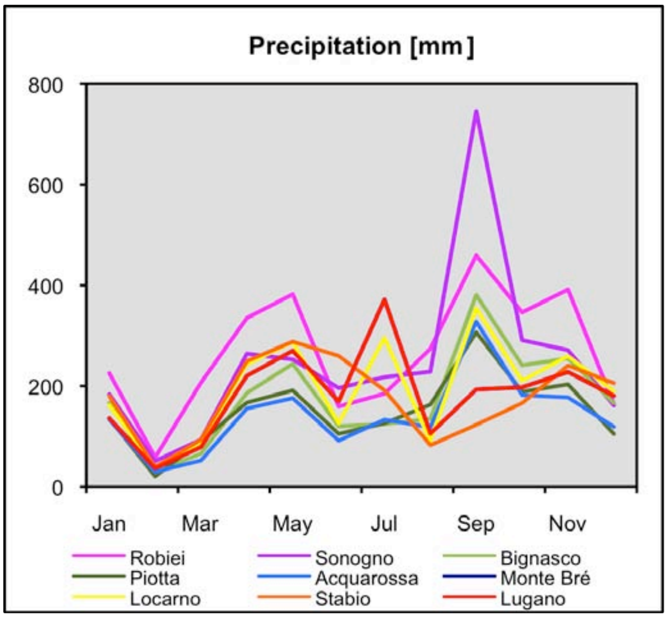
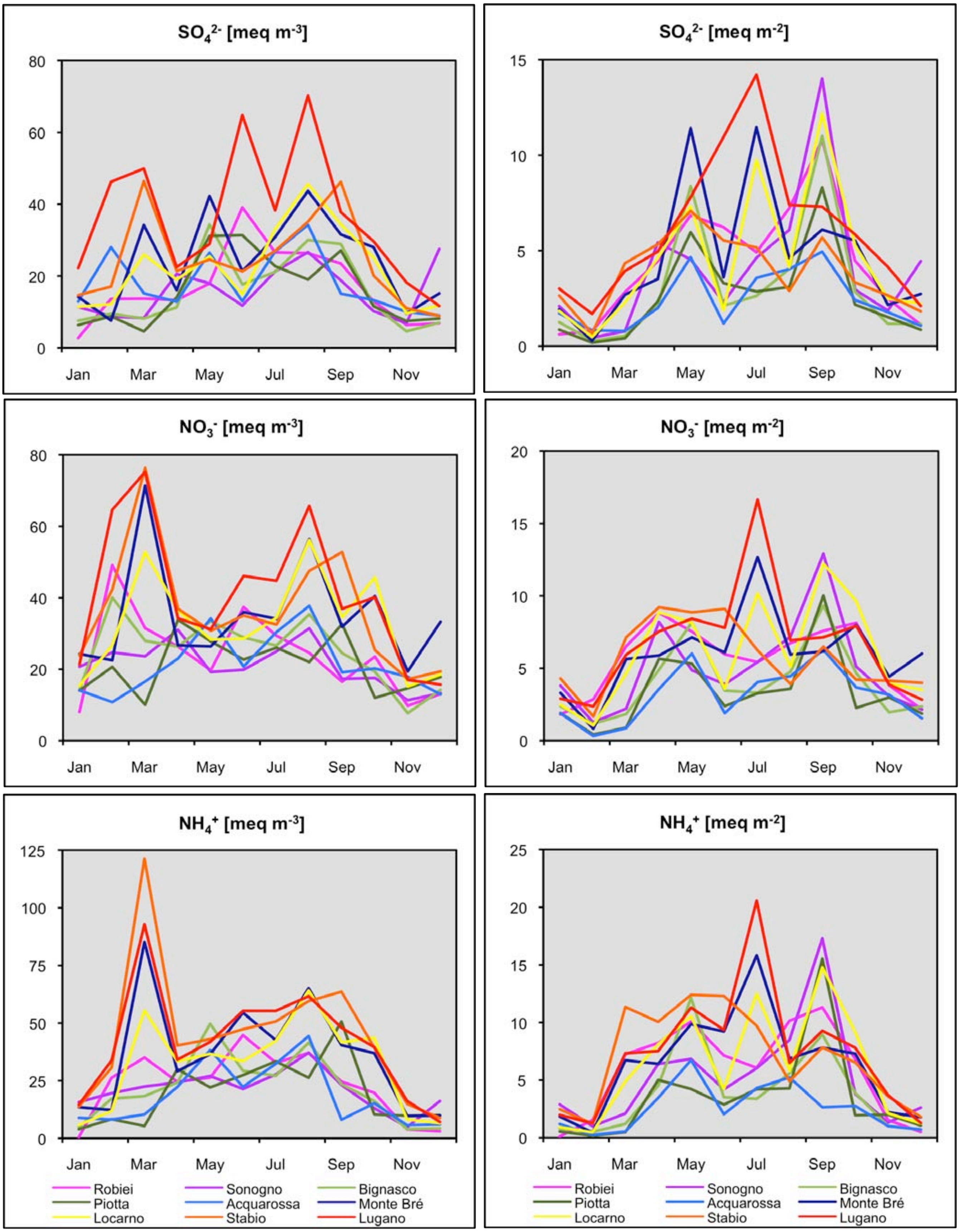
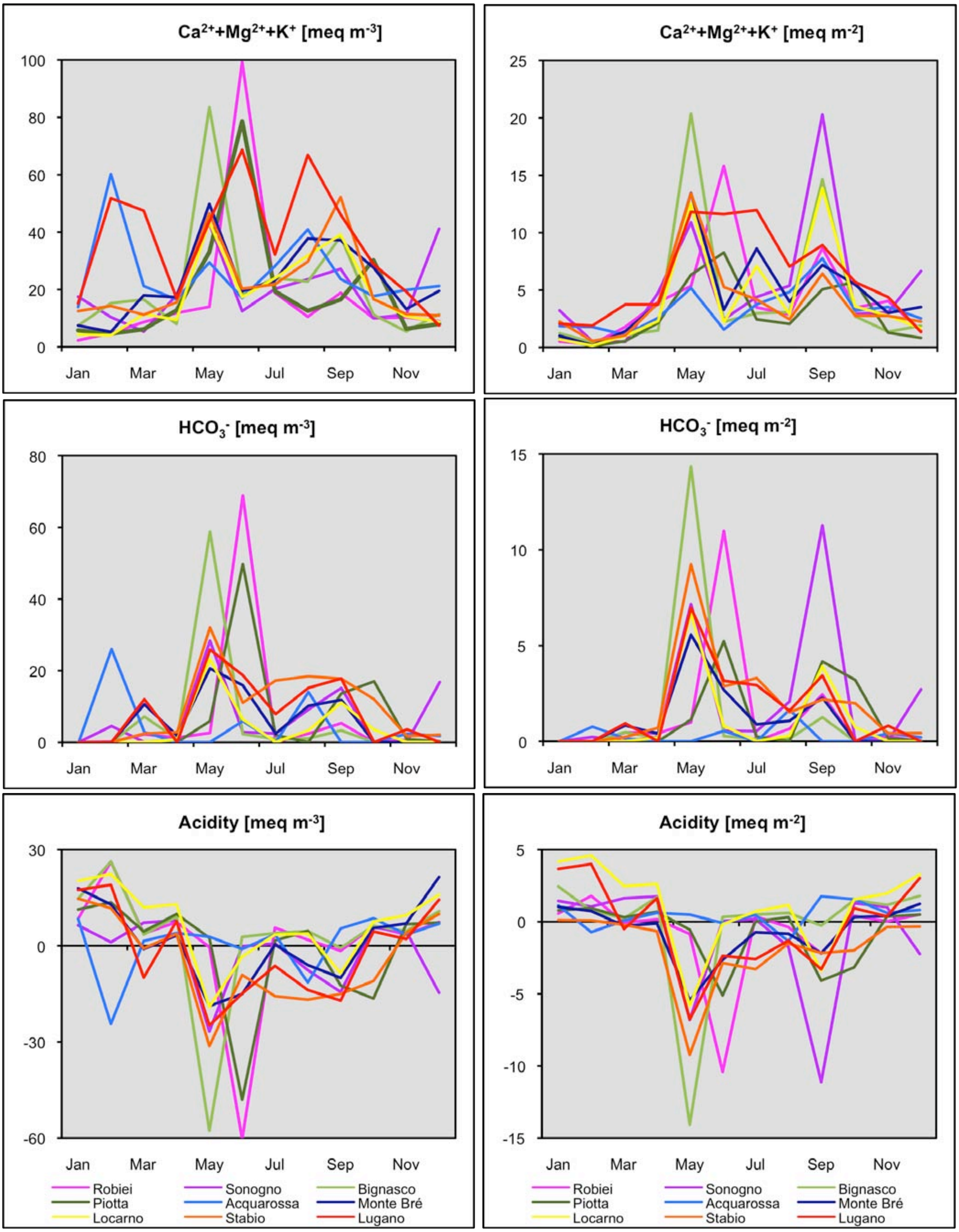


Figure 2.2 Seasonal variations of monthly average rain water concentrations and deposition rates during 2008

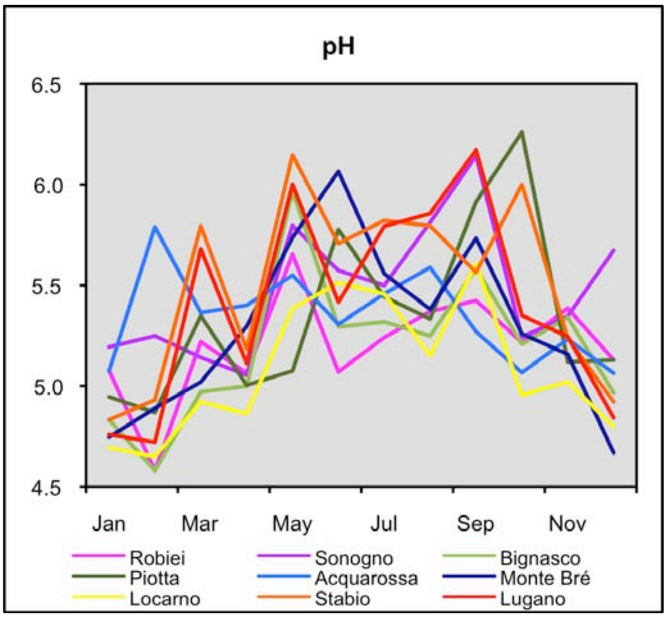
Base cations correspond to non sea salt base cations (calcium, magnesium and potassium)





Ca2+ + Mg2+ + K+ [meq m-3]
Ca2+ + Mg2+ + K+ [meq m-2]
HCO3- [meq m-3]
HCO3- [meq m-2]
Acidity [meq m-3]
Acidity [meq m-2]
Jan
Mar
May
Jul
Sep
Nov
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Monte Bré
Locarno
Stabio
Lugano

Figure 2.3 Seasonal variations of monthly average rain water pH during 2008



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

The amount of yearly precipitation at each sampling site is reported in Fig. 2.4, while variation of yearly average rainwater concentrations and deposition rates of the main chemical parameters during time are shown in Fig. 2.5. For some parameters temporal trends seem to exist. Sulphate concentrations decreased from 1980's, reflecting the decrease in sulphur dioxide emissions after 1980. Between 1988 and 2008 at Lugano and Locarno Monti sulphate concentrations decreased by around 60-72%. For nitrate and ammonia concentrations a slight decrease between 1990 and 1995 seems to have had occurred but afterwards concentrations did not decrease further. On the contrary during particularly dry years like 2003 and 2005 concentrations peaked probably because of a concentration effect. Acidity, that can be calculated as the difference between acid anions and base cations and ammonia, decreased after 1988 from values around 30-40 meq/m^3 to values around 0 meq/m^3 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). We remember that both events lead to floods in the region. When and why such events appear is still not clear. Rogora et al. (2004) observed an increased frequency of alkaline rain events especially during the last decade, many of them caused by deposition of Saharan dust. It is possible that rain rich years increase the chance of the occurrence of alkaline rain events. In addition the reduction of sulphate concentrations during the last 2 decades probably decreased the capacity of rainwater to neutralize alkaline rain events making them more observable in rainwater chemistry. If climate change may also influence the occurrence of alkaline rain events by increased long distance transport of dust is not known. In summary, decreasing sulphur emissions and increasing number of alkaline rain events generated a decrease of acidity and an increase of pH (Fig. 2.6). From the end of 1980's to the beginning of this millennium yearly average rainwater pH at Locarno Monti and Lugano increased from 4.3 to 5.1/5.3.

Trends in deposition of sulphate, nitrate, ammonia, base cations, bicarbonate and acidity were similar to those observed for concentrations with the difference that the firsts are more influenced by the amount of precipitation. In fact, the increase observed in 2008 for most analysed parameters is due to an increase of annual mean precipitation after 5 rain poor years (2003-2007).

Table 2.2 Yearly mean rain water concentrations and deposition rates during 2008

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	1696	1033	8	5.2	16	28	5	9	3	6	1	2	17	29	3	5	16	27	21	36	4	6	3	5
Bignasco	2114	2078	10	5.2	20	43	4	8	8	17	2	4	23	48	8	16	19	39	24	51	8	19	1	2
Locarno Monti	2346	2151	12	5.1	17	41	3	8	7	16	1	3	32	76	5	13	24	55	32	74	7	16	3	7
Lugano	2188	1687	14	5.3	25	54	6	14	10	22	2	5	40	88	9	20	33	72	36	79	8	18	-1	-1
Monte Brè	2188	1935	12	5.2	19	41	5	10	8	18	2	5	34	73	6	13	26	57	32	71	9	21	-4	-9
Piotta	1803	1532	10	5.3	16	28	4	6	11	19	1	3	25	45	9	15	19	33	23	41	10	19	-4	-6
Robiei	3188	3021	9	5.2	19	60	2	8	4	11	1	3	24	75	10	31	18	58	22	71	4	12	-4	-11
Sonogno	2957	2453	8	5.5	17	50	3	10	7	21	2	7	21	64	9	26	17	51	20	60	7	22	-5	-15
Stabio	2121	1966	12	5.3	15	33	4	8	9	19	3	6	40	84	11	23	22	47	32	68	9	20	-6	-13

Figure 2.4 Yearly precipitations
Data from MeteoSwiss

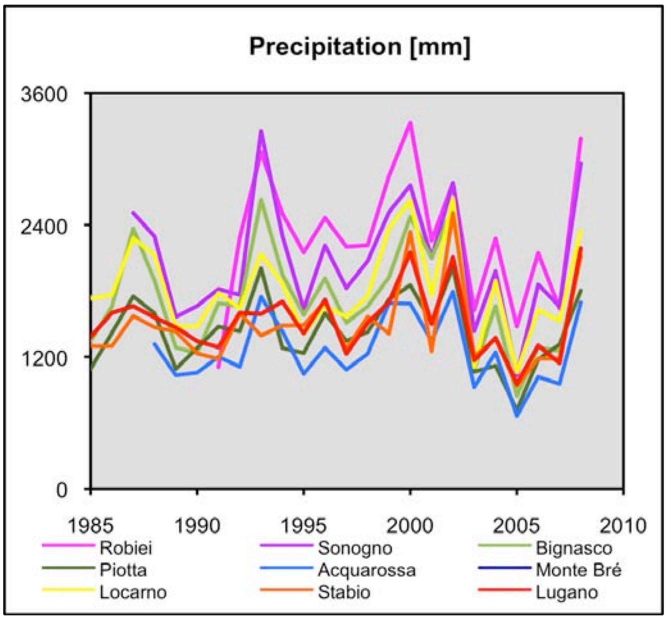
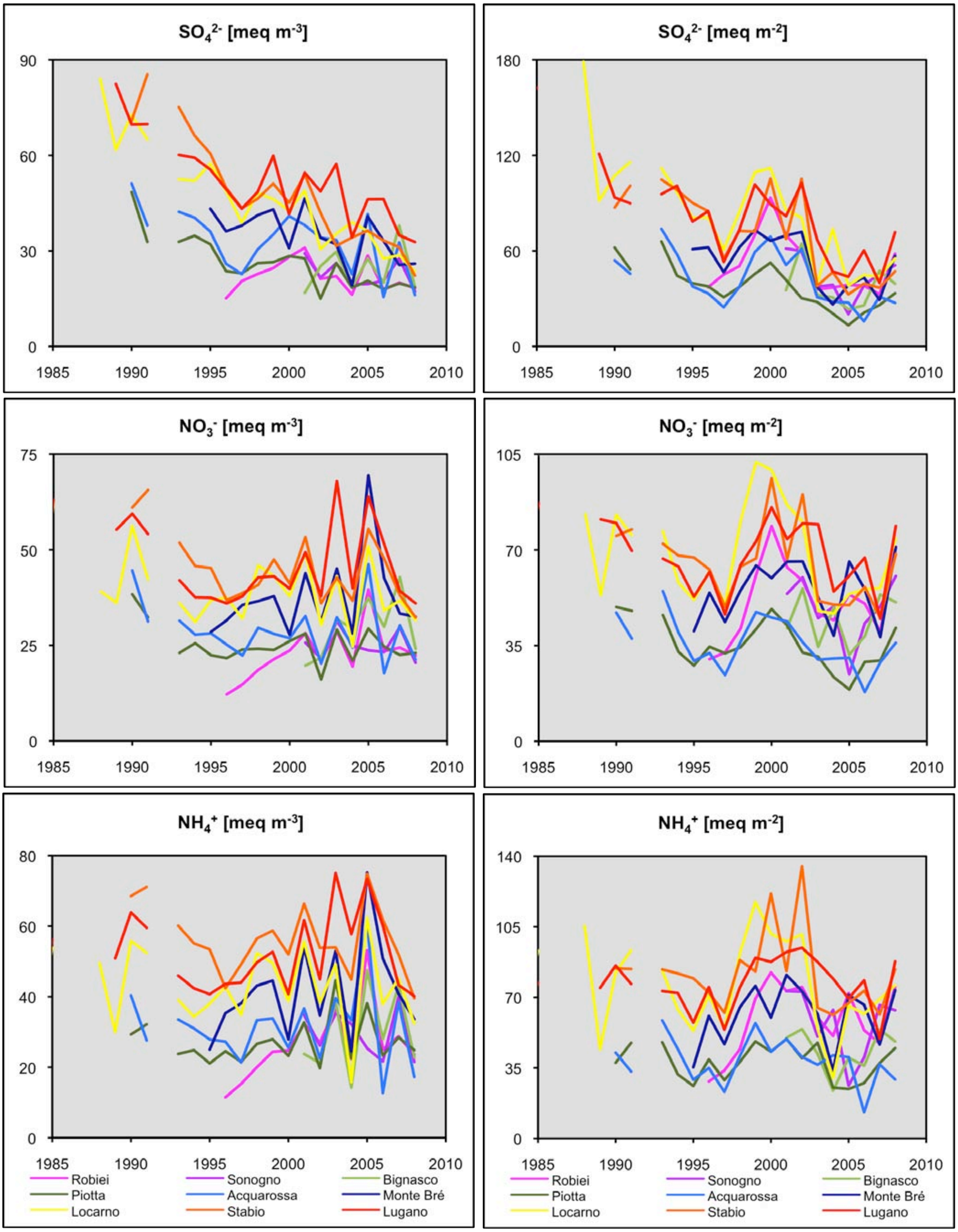
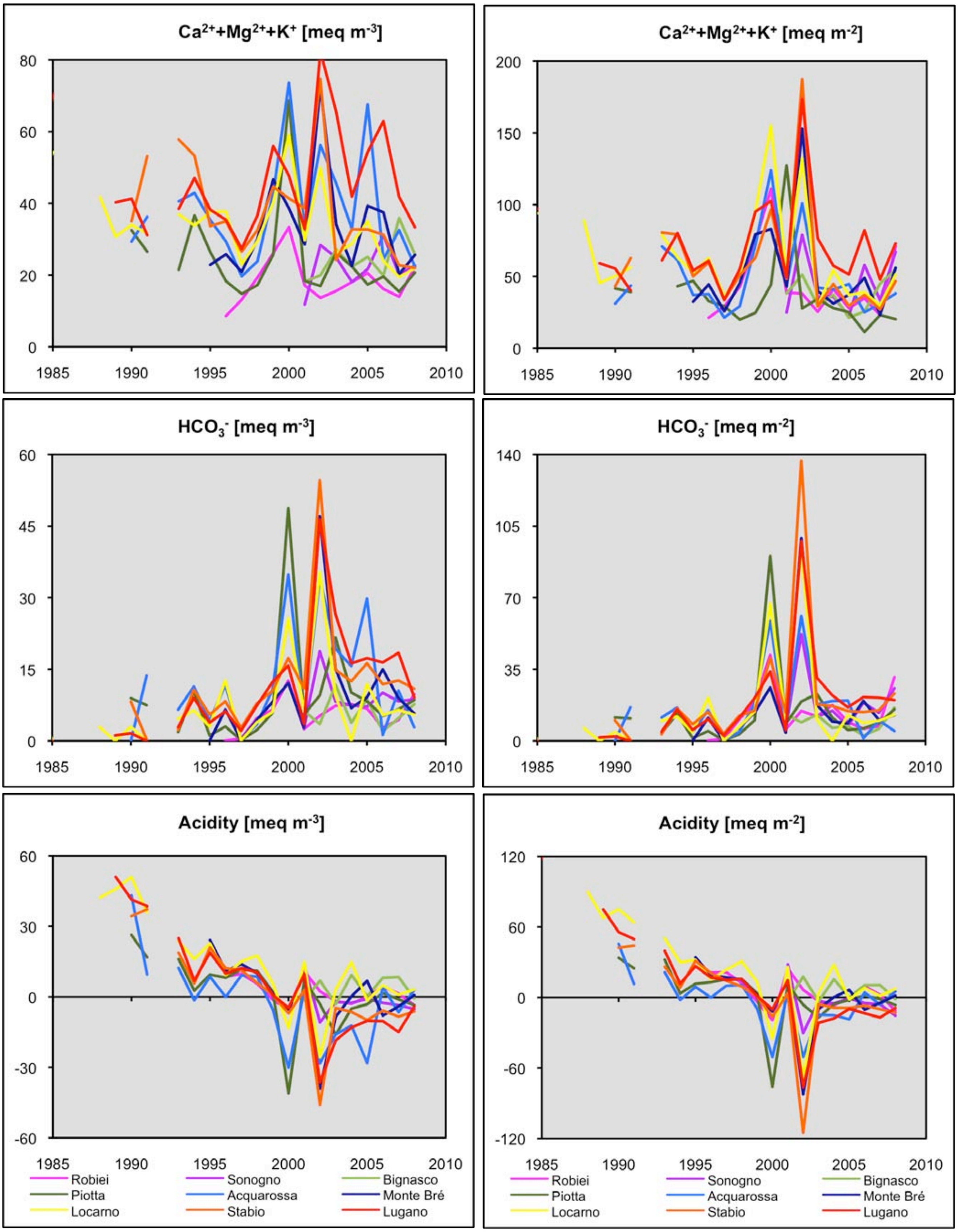


Figure 2.5 Temporal variations of annual mean rain water concentrations and deposition rates

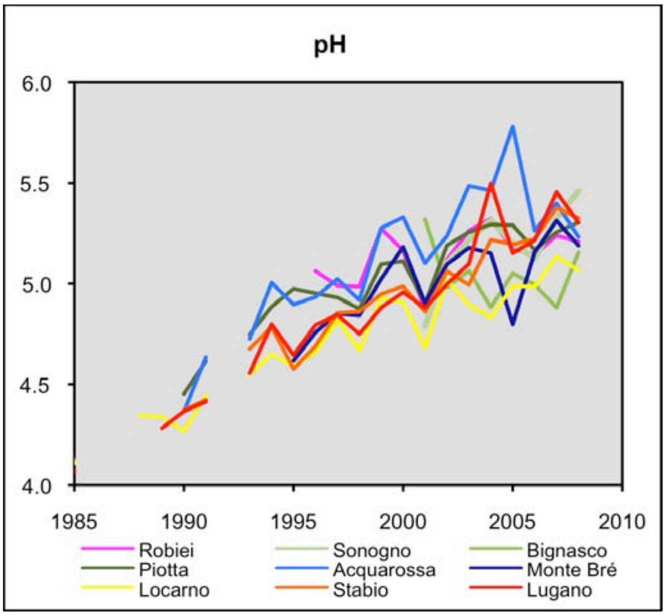
Base cations correspond to non sea salt base cations (calcium, magnesium and potassium)





Ca2+ + Mg2+ + K+ [meq m-3]
Ca2+ + Mg2+ + K+ [meq m-2]
HCO3- [meq m-3]
HCO3- [meq m-2]
Acidity [meq m-3]
Acidity [meq m-2]
1985 1990 1995 2000 2005 2010
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Monte Bré
Locarno
Stabio
Lugano

Figure 2.6 Temporal variations of annual mean pH of rain water



2.4.2 Alpine lake

Yearly mean concentrations of the main chemical parameters measured in lake surface water during 2008 are presented in Tab. 2.3. 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 7.6 and 20.0 $\mu S\ cm^{-1}$, alkalinity between -4 and 81 $\mu eq\ l^{-1}$, pH between 5.3 and 7.0, sulphate between 0.94 and 3.76 mg l^{-1}, nitrate between 0.12 and 0.38 mg N l^{-1}, dissolved organic carbon between 0.18and 0.88 mg C l^{-1}, reactive dissolved silica between 0.83 and 2.78 mg $SiO_2\ l^{-1}$ and total dissolved aluminium between 0.7 and 90.7 $\mu g\ l^{-1}$.

Table 2.3 Average lake surface water concentrations during 2008

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

Lake name	Conductivity 25°C. (µS cm^{-1})	pH	Alkalinity (µeq l^{-1})	Ca^{2+} (mg l^{-1})	Mg^{2+} (mg l^{-1})	Na^{+} (mg l^{-1})	K^{+} (mg l^{-1})	NH_4^{+} (mg N l^{-1})	SO_4^{2-} (mg l^{-1})	NO_3^{-} (mg N l^{-1})	Cl^{-} (mg l^{-1})	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	10.1	5.5	-1	0.59	0.10	0.32	0.18	0.033	1.44	0.33	0.18	0.88	1.46	90.7	99.5	<0.2	<0.2	5.6	5.8
Lago di Tomè	9.0	5.7	2	0.82	0.07	0.28	0.14	0.006	1.46	0.33	0.13	0.30	1.57	22.4	34.7	<1.0	<1.1	6.1	7.2
Lago dei Porchieirsc	20.0	6.8	64	2.79	0.14	0.43	0.44	0.009	3.76	0.29	0.11	0.19	2.78	0.7	1.5	<0.2	<0.2	2.3	3.0
Lago Barone	9.2	6.1	12	1.04	0.07	0.24	0.18	0.022	1.68	0.26	1.68	0.26	1.25	2.4	3.1	<0.2	<0.2	3.7	4.4
Laghetto Gardiscio	8.0	5.3	-4	0.52	0.09	0.16	0.21	0.020	1.58	0.18	0.10	0.18	0.83	46.6	56.0	<1.2	<1.4	4.2	5.1
Lago Leit	13.8	6.4	23	1.41	0.23	0.30	0.38	0.010	3.44	0.19	0.09	0.29	1.61	1.6	4.1	<0.2	<1.1	2.0	3.8
Lago di Morghirolo	11.9	6.6	35	1.39	0.17	0.29	0.40	0.008	2.23	0.21	0.10	0.22	1.52	0.7	1.9	<0.2	<0.2	1.0	1.7
Lago di Mognòla	16.7	6.8	53	1.96	0.25	0.53	0.48	0.009	3.17	0.25	0.11	0.25	2.69	2.3	4.6	<0.2	<0.2	1.2	1.9
Laghetto Inferiore	9.5	6.5	27	1.12	0.10	0.26	0.34	0.007	1.40	0.26	0.09	0.32	1.34	5.6	6.6	<0.2	<0.2	4.6	4.9
Laghetto Superiore	8.9	6.4	26	1.04	0.09	0.24	0.31	0.008	1.25	0.26	0.10	0.37	1.19	5.0	7.3	<0.2	<0.2	2.8	3.2
Lago Nero	15.7	6.9	60	2.09	0.16	0.33	0.40	0.013	2.77	0.19	0.10	0.32	1.04	1.1	1.2	<0.2	<0.2	2.5	3.2
Lago Bianco	92.1	7.6	491	15.12	1.02	0.41	0.84	0.007	7.67	0.16	8.12	0.23	1.84	4.7	6.4	<0.2	<0.2	1.2	1.6
Lago della Froda	10.8	6.7	38	1.60	0.08	0.22	0.21	0.016	1.80	0.17	0.08	0.39	1.20	2.2	4.4	<0.2	<0.2	3.3	4.1
Lago d'Antabia	12.5	6.8	60	1.84	0.07	0.37	0.26	0.013	1.15	0.33	0.11	0.28	2.13	1.5	3.0	<0.2	<0.2	1.9	2.4
Lago della Crosa	7.6	6.3	17	0.91	0.06	0.22	0.15	0.015	0.94	0.30	0.11	0.25	1.26	2.1	3.1	<0.2	<0.2	4.4	4.8
Lago d'Orsalìa	9.7	6.4	26	1.24	0.08	0.27	0.16	0.009	1.17	0.38	0.12	0.25	1.46	5.8	9.3	<0.2	<0.2	1.8	2.2
Schwarzsee	12.1	6.7	44	1.69	0.10	0.30	0.24	0.008	1.69	0.30	0.10	0.24	1.91	2.8	6.7	<0.2	<0.2	1.3	1.6
Laghi dei Pozzöi	8.9	6.6	33	1.09	0.10	0.33	0.16	0.008	1.37	0.12	0.12	0.64	2.10	11.7	29.5	<0.2	<0.2	1.9	2.1
Lago di Sfille	9.3	6.5	31	1.13	0.10	0.34	0.12	0.010	1.54	0.14	0.14	0.54	1.67	13.5	21.4	<0.2	<0.2	2.1	2.5
Lago di Sascòla	9.9	6.1	13	0.89	0.13	0.30	0.32	0.011	1.64	0.36	0.14	0.55	1.83	19.5	26.8	<0.2	<0.2	3.4	4.2
Lago d'Alzasca	16.9	7.0	81	2.16	0.21	0.48	0.46	0.012	2.21	0.25	0.15	0.69	2.66	4.1	6.9	<0.2	<0.2	0.7	1.0

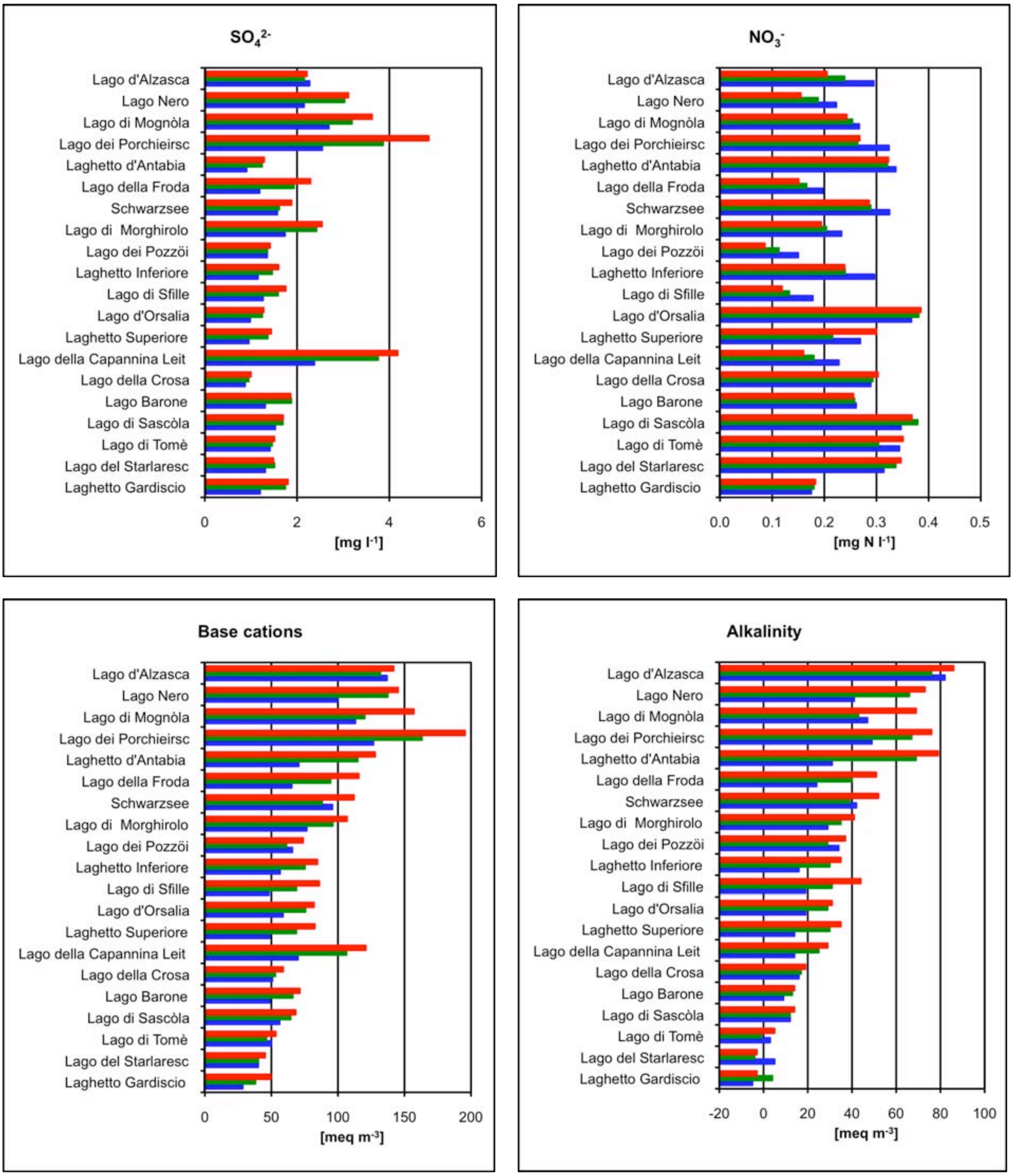
In order to better compare chemistry of lakes with low alkalinities, measured values of the main parameters are shown graphically in Fig. 2.7.

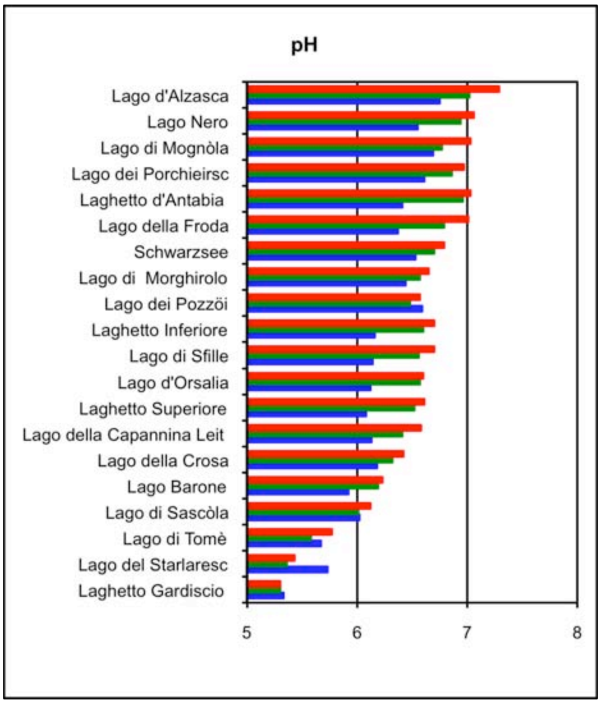
During 2008 alkalinities below 0 µeq l^{-1} were detected in 3 lakes (Laghetto Gardiscio and Lago del Starlaresc da Sgiof during 2 occasions and Lago di Tomè during one occasion). Only one lake had alkalinities always above 50 µeq l^{-1} (Lago d'Alzasca) and was therefore not sensitive to acidifications. All other 16 lakes were at least temporary sensitive to acidification (50 <alkalinity <200 µeq l^{-1}). It also immediately appears that alkalinity correlates well with pH and concentrations of aluminium. Lakes with lowest alkalinities had also lowest pH and highest concentrations of aluminium. Particularly high concentrations of aluminium were measured in lakes with pH's <= 6 like Lago del Starlaresc da Sgiof, Lago, Laghetto Gardiscio, Lago di Tomè and Lago di Sascòla where concentrations of aluminium ranged between 15 and 96 µg l^{-1}. In general concentrations of non sea salt 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. Moreover, since for the studied lakes, atmospheric deposition of sulphate and nitrate probably does not differ greatly, it is reasonable to suppose that catchments of lakes with particularly high sulphate concentrations (Lago dei Porchieirsc, Lago della Capannina Leit, Lago di Mognòla, Lago Nero) are rich in geogenic sulphate. Differences in nitrate concentrations among lakes should be more related to differences in nitrogen retention capacity of the catchment.

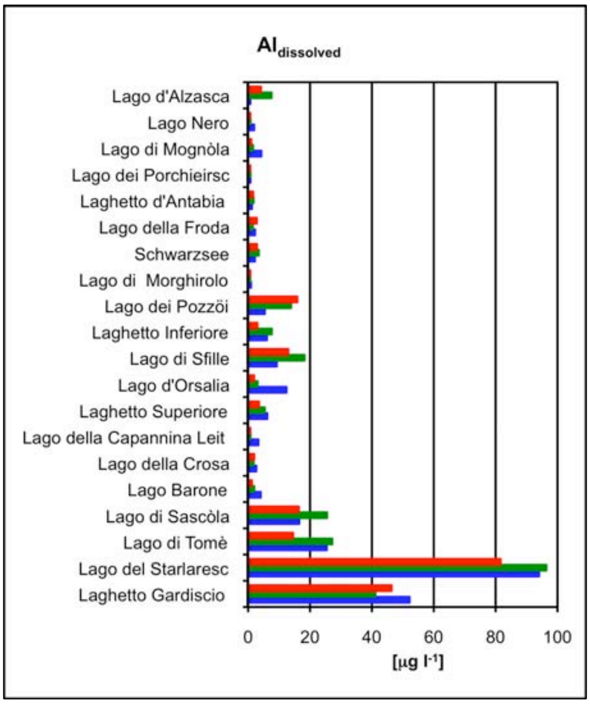
Fig. 2.7 also shows some seasonal differences. During 2008 in most lakes alkalinity and pH and concentrations of sulphate, base cations, and silica were lower in June than in September and October, while for nitrate the opposite can be observed. The same phenomena occurred in rivers (see next paragraph), where it seems correlated with the river discharge: lower concentrations of alkalinity, pH and concentrations of sulphate and base cations during high flow in May/June and November and higher concentrations of nitrate in June. For lakes it can also be observed that highest differences in concentrations of sulphate and base cations concentrations between summer and fall occurred in lakes that in June had still large part of their surface iced (data not shown), suggesting that the low sulphate and base cations concentrations were caused by dilution of lake water with melt water from the ice cover. Differently, peaks of nitrate concentrations in June were not dependent on ice cover percentage. We think that concentration peaks of nitrate in June could be the result of snow melt that was still in process. As a result of increased nitrate concentrations, alkalinity and pH were also lower in samples from June with respect to November and October.

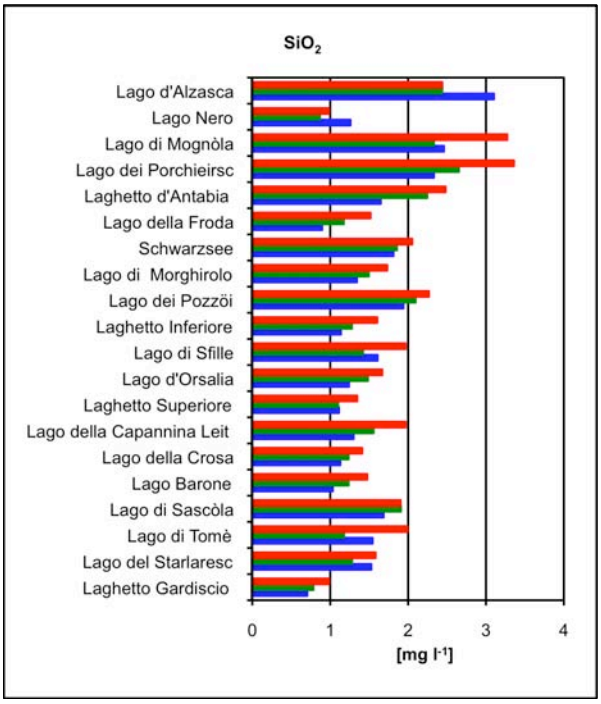
Figure 2.7 Annual average concentrations of the main chemical parameters in 20 Alpine lakes during 2008

Blue: 25.6.08, green: 22.9.08, red: 21.10.08; base cations correspond to non sea salt base cations (calcium, magnesium and potassium)




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

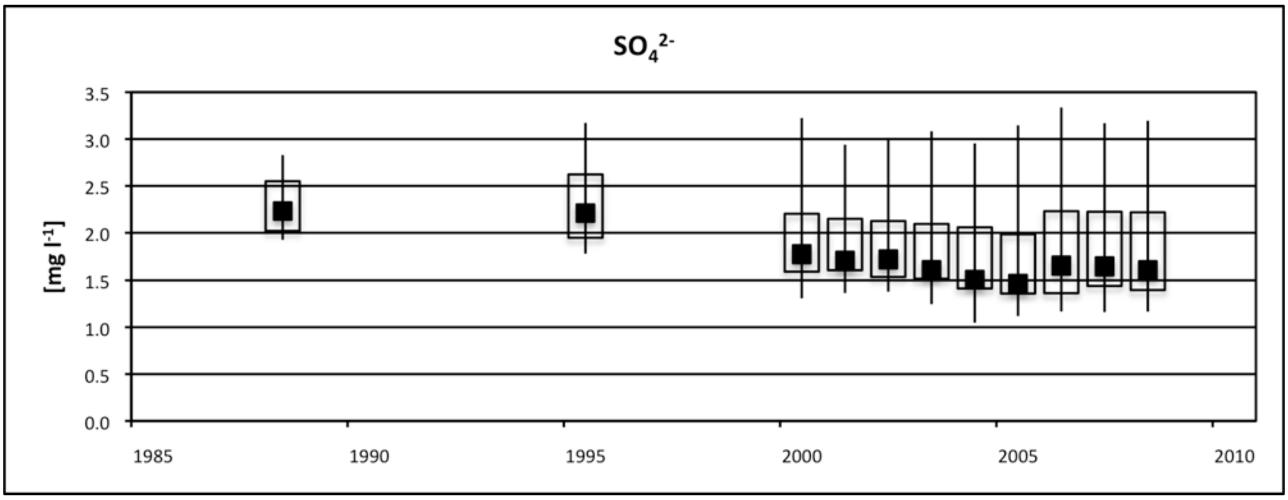

$Al_{dissolved}$
Lago d'Alzasca
Lago Nero
Lago di Mognòla
Lago dei Porchieirsc
Laghetto d'Antabia
Lago della Froda
Schwarzsee
Lago di Morghirolo
Lago dei Pozzöi
Laghetto Inferiore
Lago di Sfille
Lago d'Orsalia
Laghetto Superiore
Lago della Capannina Leit
Lago della Crosa
Lago Barone
Lago di Sascòla
Lago di Tomè
Lago del Starlaresc
Laghetto Gardiscio
0
20
40
60
80
100
[$\mu g\ l^{-1}$]

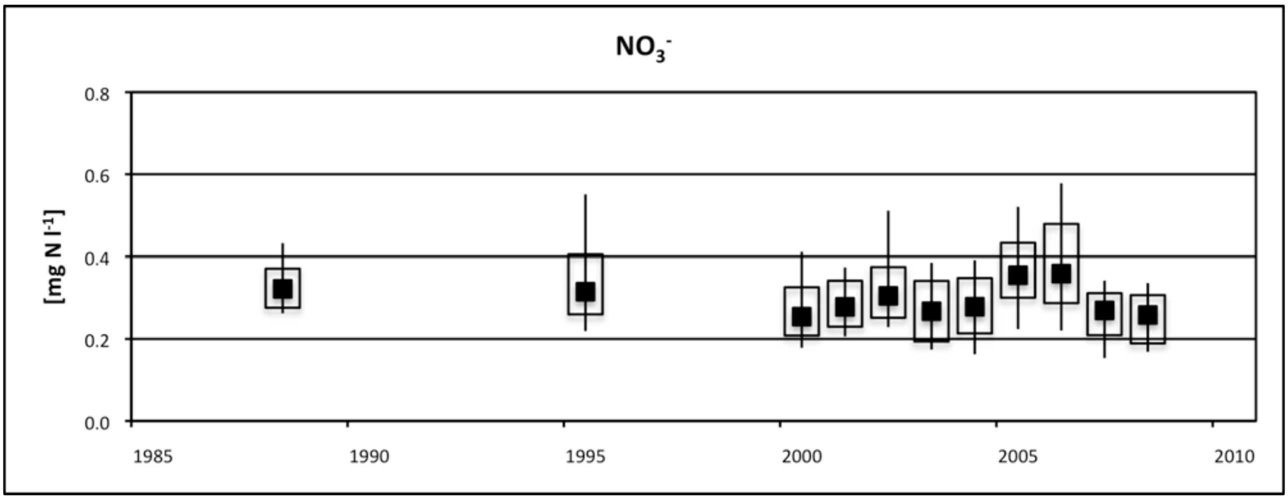

SiO_2
Lago d'Alzasca
Lago Nero
Lago di Mognòla
Lago dei Porchieirsc
Laghetto d'Antabia
Lago della Froda
Schwarzsee
Lago di Morghirolo
Lago dei Pozzöi
Laghetto Inferiore
Lago di Sfille
Lago d'Orsalia
Laghetto Superiore
Lago della Capannina Leit
Lago della Crosa
Lago Barone
Lago di Sascòla
Lago di Tomè
Lago del Starlaresc
Laghetto Gardiscio
0
1
2
3
4
[$mg\ l^{-1}$]

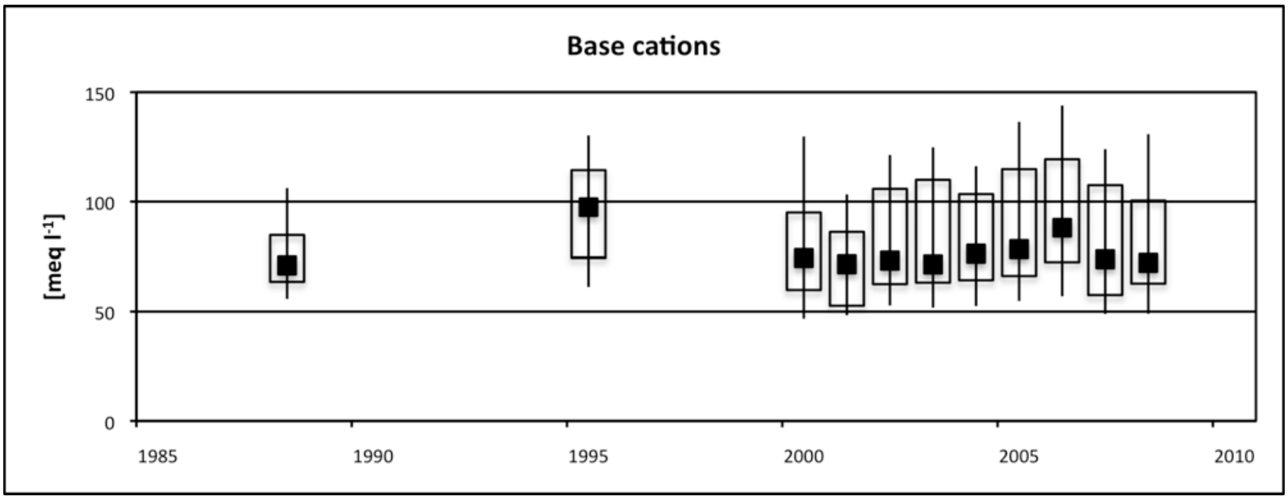
In order to show temporal variations of lake quality, annual median values of pH, alkalinity and concentrations of non sea salt base cations, sulphate and nitrate of all lakes with their 10th, 25th, 75th and 90th percentile values are represented in Fig. 2.8. In order to detect variations with time only years, where all 20 alpine lakes have been monitored were chosen. As already discussed in Steingruber and Colombo (2006), after 1980's sulphate concentrations decreased, mainly because of the reduction of the sulphur content in heating oils and the partial substitution of sulphur rich carbon with other fossil fuels. As a consequence lake alkalinity and pH increased, while concentrations of dissolved aluminium decreased. For base cations and nitrate concentrations no trend can be observed.

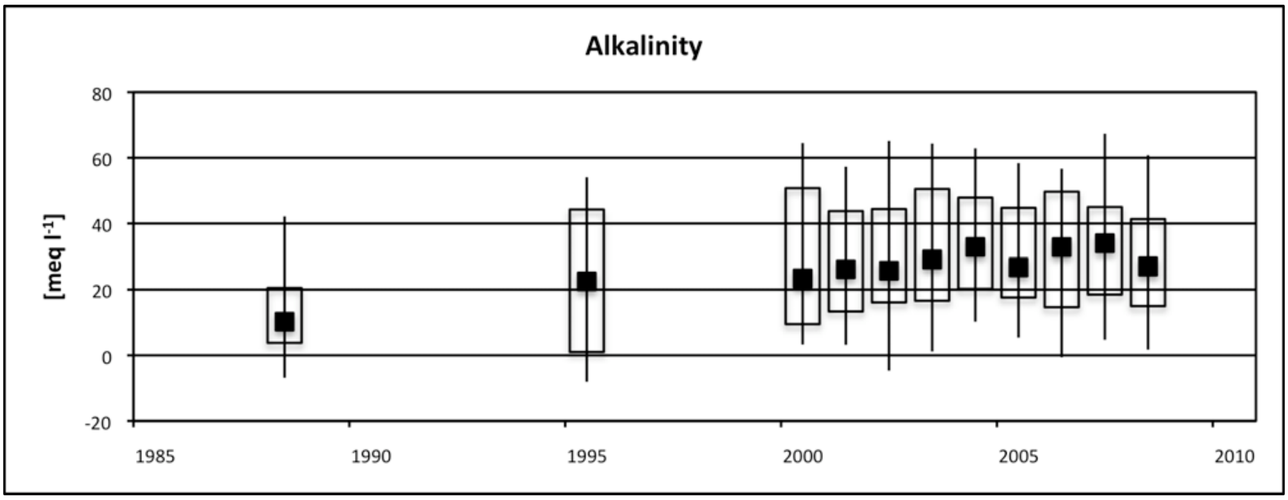
Figure 2.8 Temporal variations of annual median values and their 10th, 25th, 75th, 90th percentiles of parameters measured in 20 Alpine lakes from 1988 to 2008

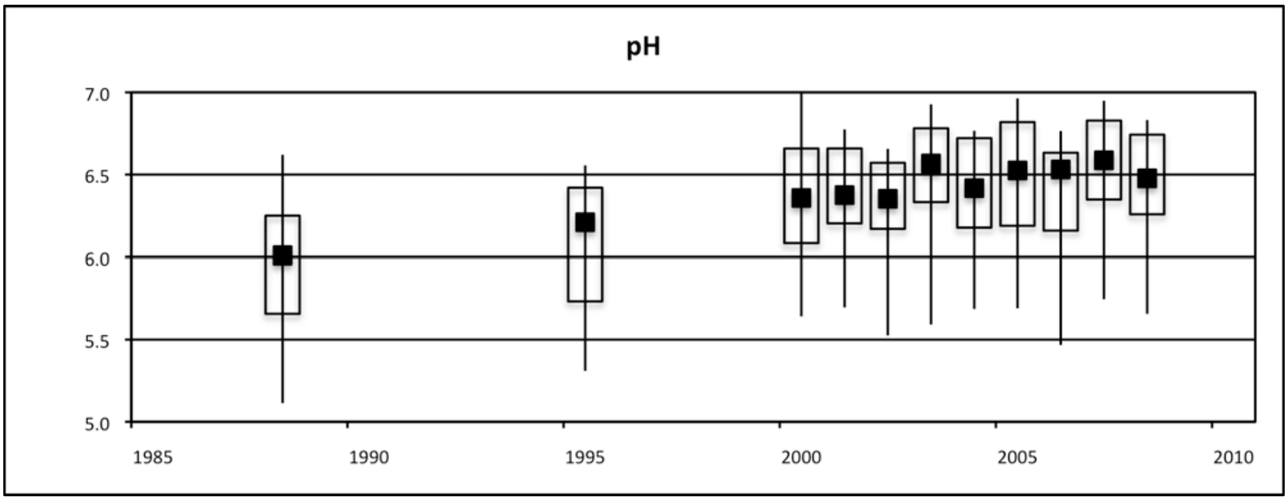
Base cations correspond to non sea salt base cations (calcium, magnesium and potassium)

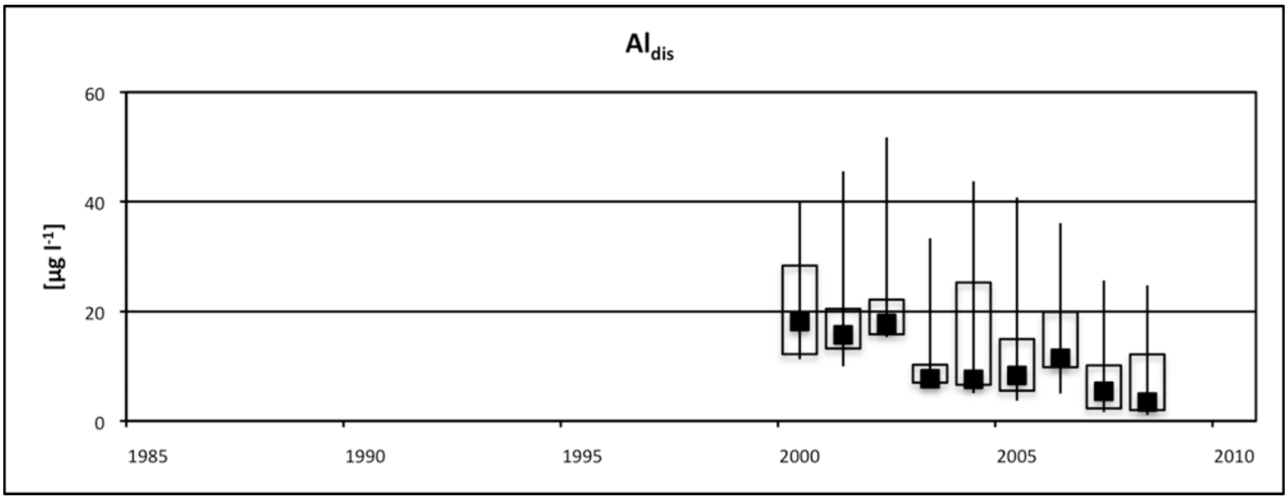


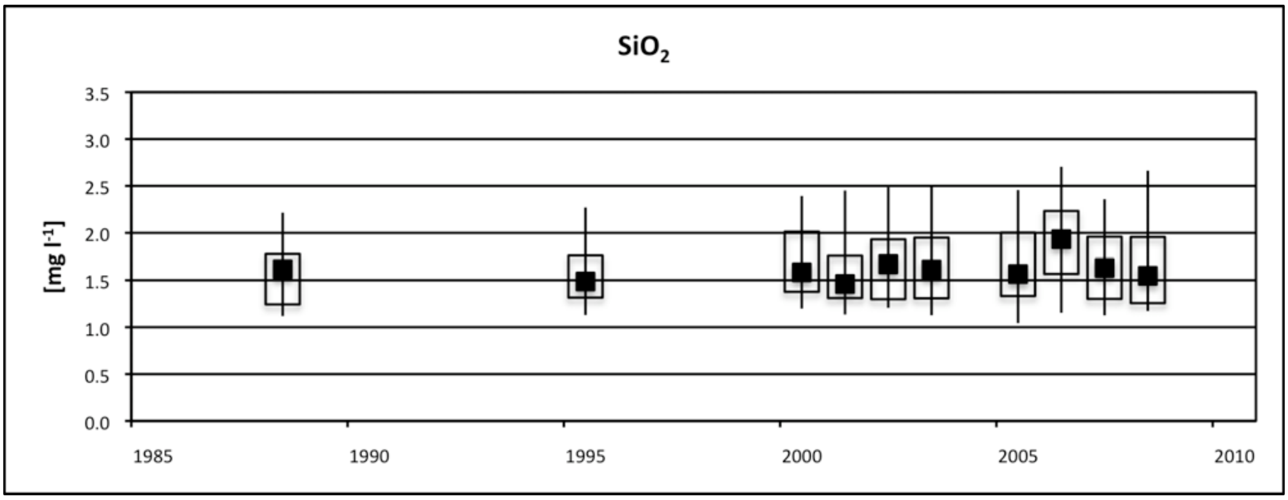





Alkalinity
[meq l-1]
80
60
40
20
0
-20
1985
1990
1995
2000
2005
2010


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


Aldis
[µg l-1]
60
40
20
0
1985
1990
1995
2000
2005
2010


SiO2
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
[mg l-1]
1985
1990
1995
2000
2005
2010

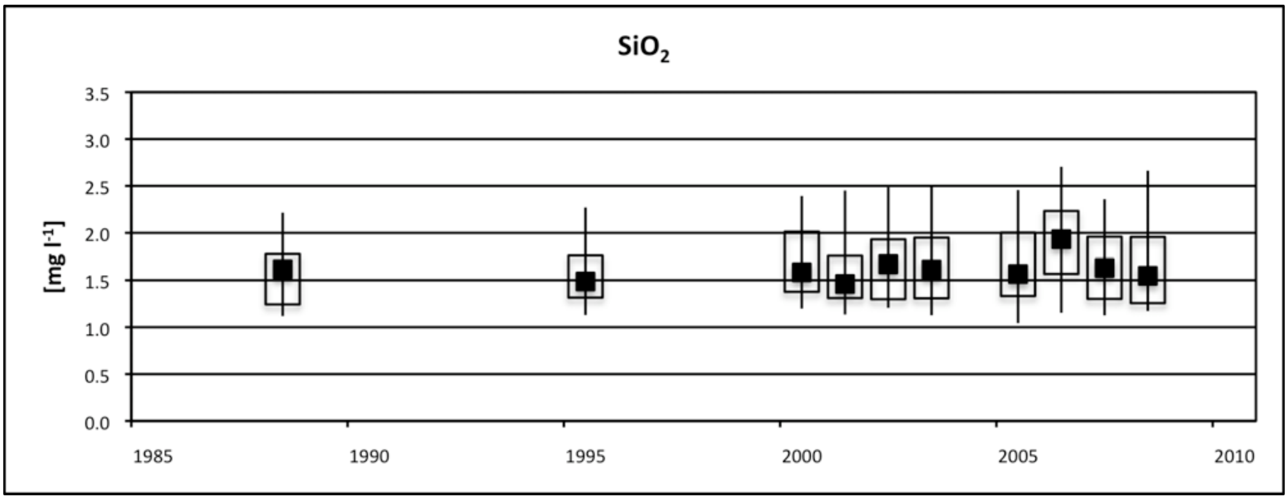
2.4.3 Alpine rivers

Annual mean concentrations of the chemical parameters measured in river Maggia, Vedeggio and Verzasca during 2008 are shown in Tab. 2.4. 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.

Table 2.4 Average concentrations in river water during 2008.

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

River name	Year	pH	Conductivity 25°C (µS cm^{-1})	Alkalinity (µeq l^{-1})	Ca^{2+} (mg l^{-1})	Mg^{2+} (mg l^{-1})	Na^{+} (mg l^{-1})	K^{+} (mg l^{-1})	NH_4^+ (mg N l^{-1})	SO_4^{2-} (mg l^{-1})	NO_3^- (mg N l^{-1})	Cl^- (mg l^{-1})	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	2008	7.4	67.4	301	8.61	0.71	1.87	1.59	<0.012	9.98	0.63	1.60	0.54	5.07	7.5	8.6	<0.2	<0.2	<0.6	<0.8
Vedeggio	2008	7.1	46.5	166	5.00	0.96	1.71	0.59	<0.006	6.49	0.99	1.02	0.55	6.83	5.5	6.7	<0.2	<0.2	0.7	0.9
Verzasca	2008	6.9	24.8	71	3.01	0.23	0.73	0.56	<0.006	3.80	0.70	0.19	0.38	3.66	6.9	7.7	<0.2	<0.2	0.4	0.5



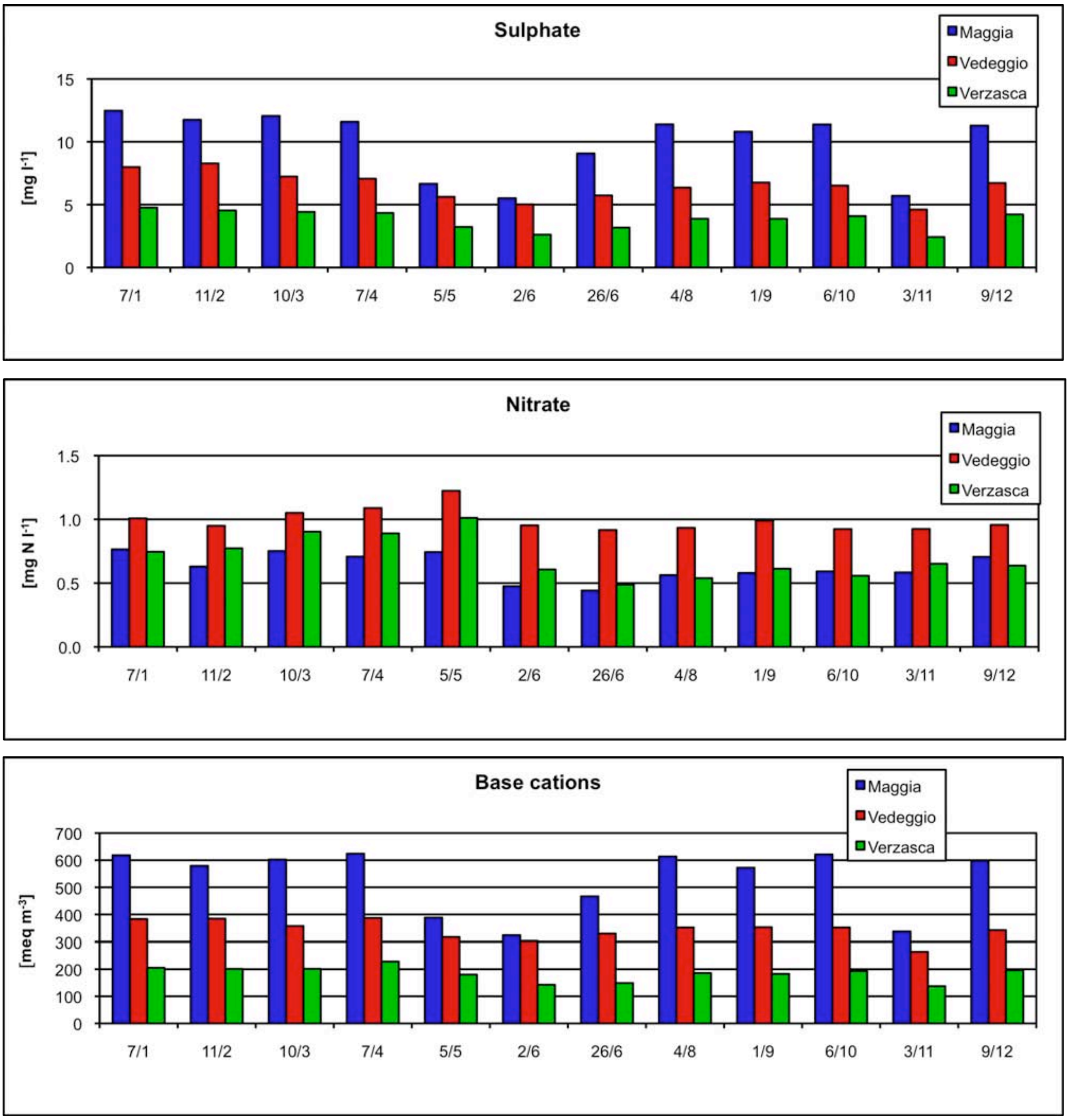
During 2008 average alkalinity was 301 µeq l^{-1} in river Maggia, 166 µeq l^{-1} in river Vedeggio and 71 µeq l^{-1} in river Verzasca. Based on these data River Verzasca and river Vedeggio have low alkalinities (50-200 µeq l^{-1}), but no river is sensitive to acidification. The same is suggested by their minimum alkalinities that were always > 0 µeq l^{-1}. Average pH was 7.4 in river Maggia, 7.1 in river Vedeggio and 6.9 in river Verzasca. Their minimum pH's were not much lower (Maggia: 7.1, Vedeggio: 7.0, Verzasca: 6.6). As a consequence of the relatively high pH's, dissolved aluminium concentrations were on average low (≤ 8 µg l^{-1}). However, higher aluminium concentrations up to 37, 25, 54 µeq l^{-1} in river Maggia, Vedeggio and Verzasca, respectively occurred in November during high flow.

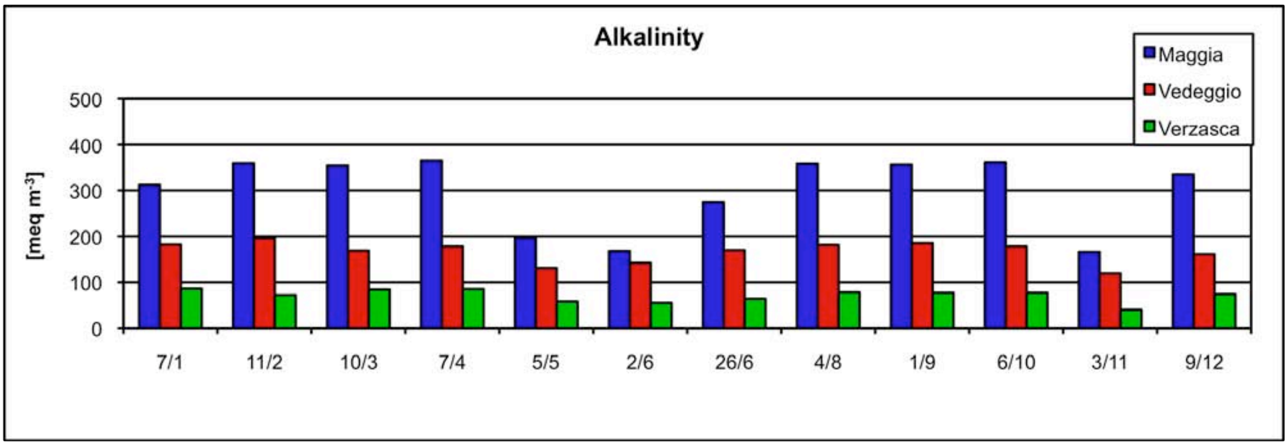
Fig. 2.9 shows the variations of the concentrations of sulphate, nitrate, base cations, alkalinity, pH and dissolved aluminium during 2008. It can be observed that the temporal variation of these parameters is the same in all 3 rivers. For sulphate, base cations, alkalinity and pH lowest values were measured in May/June and November. Differently, highest nitrate concentrations occurred in April and May.

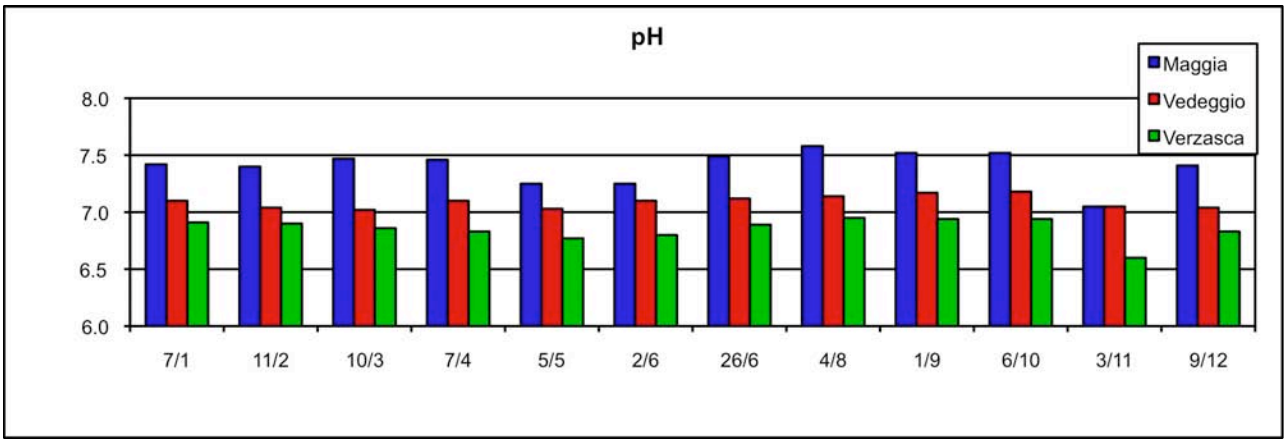
Comparing the seasonality of concentrations during 2008 with the temporal variations of the river discharge (Fig. 2.10, for river Maggia without the influence of hydropower production), it can be observed that discharge maxima overlap with concentrations minima of sulphate, base cations, alkalinity and pH. Because water quality of surface waters and rain differ greatly, Steingruber and Colombo (2006) suggested the following mechanisms occurring during rain events: a dilution of sulphate and base cations and a combination of dilution and consumption of alkalinity. Because of rain acidity river pH clearly decreases during rain events. Differently, aluminium concentrations seem to reach its highest concentrations during high flow events (May/June/November, probably due to leakage from soil. For nitrate concentrations the river discharge seems not to be the only parameter determining its intensity. In fact, during 2008, nitrate concentration peaked in April/May overlapping therefore with the snow melt period with probably low photosynthetic activity.

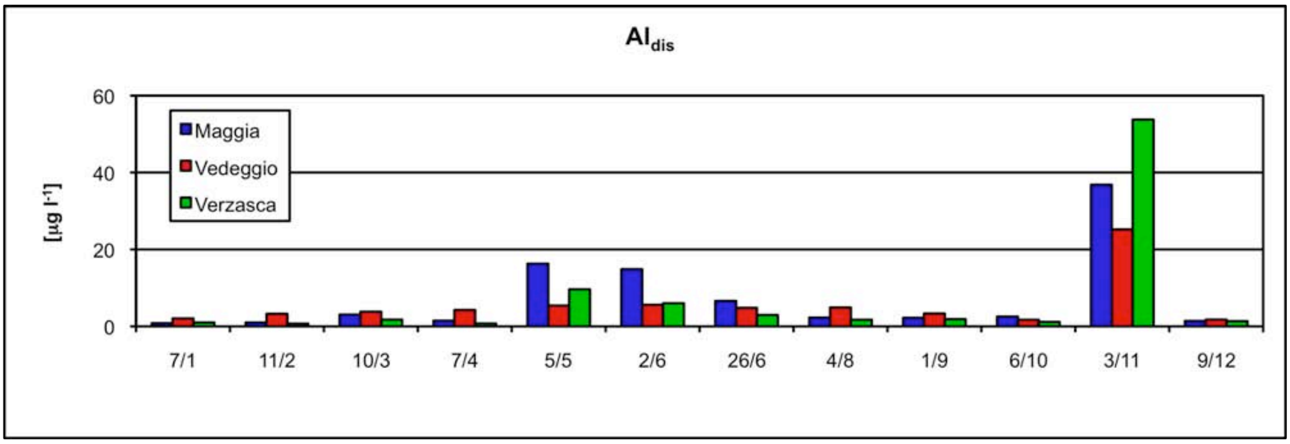
Figure 2.9 Concentrations of the main chemical parameters in river water during 2008

Base cations correspond to non-sea salt base cations (calcium, magnesium and potassium)




Alkalinity
Maggia
Vedeggio
Verzasca
[meq m-3]
500
400
300
200
100
0
7/1
11/2
10/3
7/4
5/5
2/6
26/6
4/8
1/9
6/10
3/11
9/12


pH
Maggia
Vedeggio
Verzasca
8.0
7.5
7.0
6.5
6.0
7/1
11/2
10/3
7/4
5/5
2/6
26/6
4/8
1/9
6/10
3/11
9/12


Al dis
Maggia
Vedeggio
Verzasca
[µg l-1]
60
40
20
0
7/1
11/2
10/3
7/4
5/5
2/6
26/6
4/8
1/9
6/10
3/11
9/12

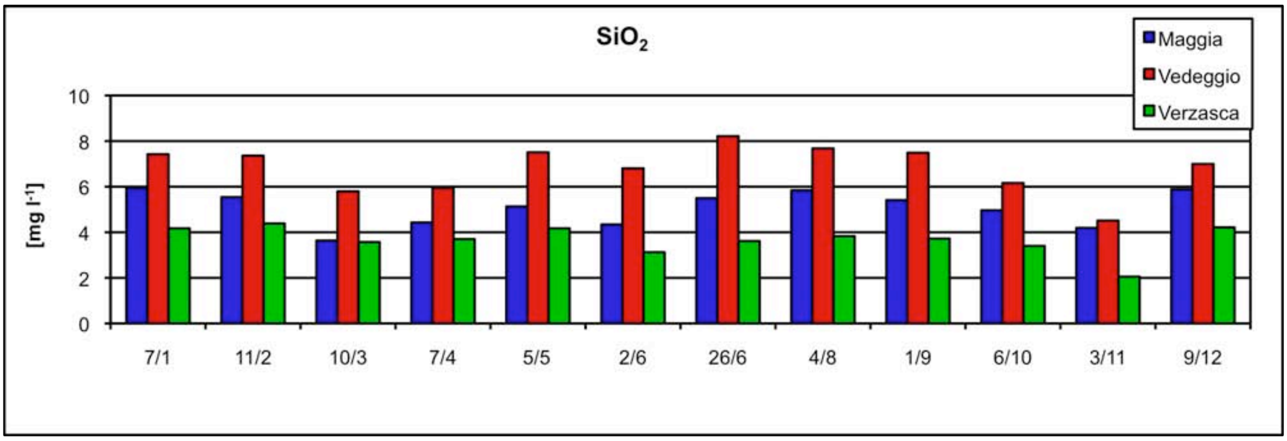
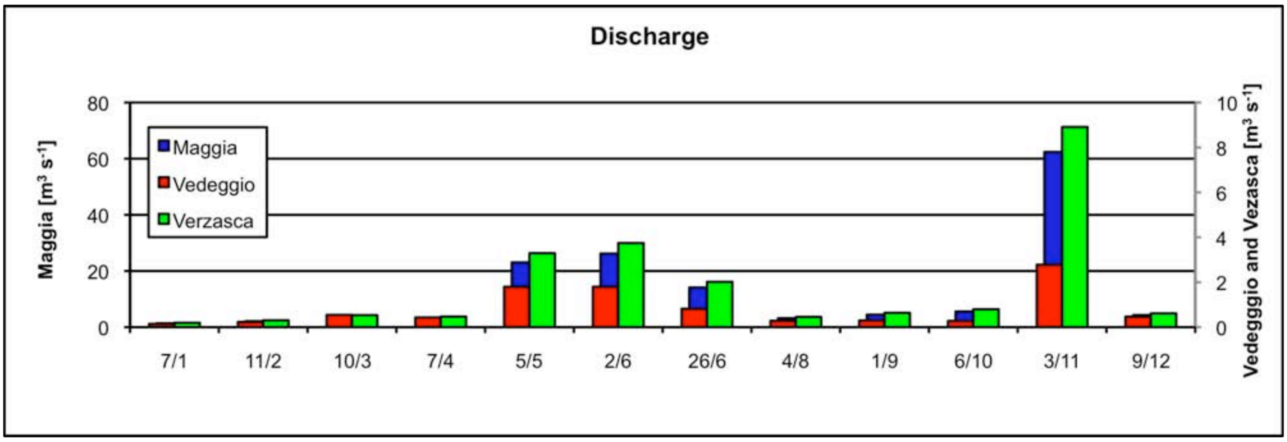

SiO2
Maggia
Vedeggio
Verzasca
[mg l-1]
10
8
6
4
2
0
7/1
11/2
10/3
7/4
5/5
2/6
26/6
4/8
1/9
6/10
3/11
9/12

Figure 2.10 Daily average discharge during sampling days in 2008

Discharge of river Vedeggio at Isone is measured by IST (2009), while discharge of river Verzasca at Sonogno and Maggia at Bignasco (without influence of hydropower production) were estimated by discharge values of Verzasca at Lavertezzo published by BAFU (2009).



In order to detect time trends, annual mean concentrations of sulphate, nitrate, base cations, alkalinity, pH and dissolved aluminium from 2000 to 2008 are presented graphically in Fig. 2.11. For river chemistry after 2000 no trend can be observed.

Figure 2.11 Annual mean concentrations of the main chemical parameters in river water from 2000 to 2008
Base cations correspond to non-sea salt base cations (calcium, magnesium and potassium)

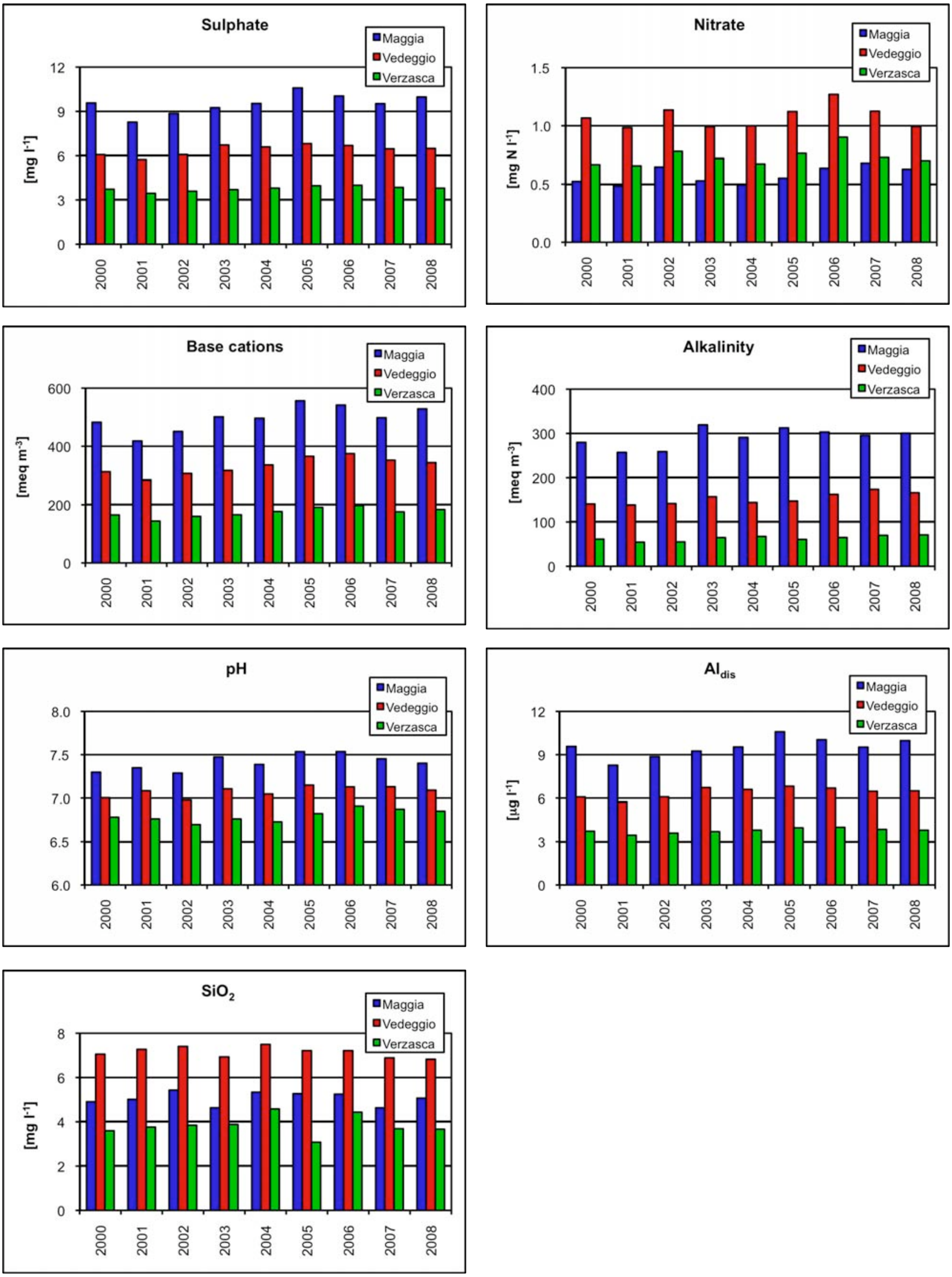
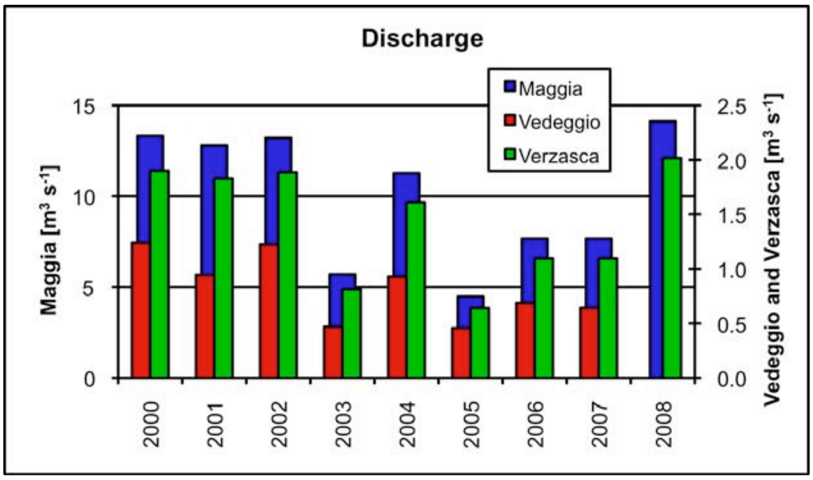


Figure 2.12 Yearly mean discharge of river Maggia, Vedeggio and Verzasca from 2000 to 2008

Discharge of river Vedeggio at Isone was measured by IST (2001-2008). Discharge of river Verzasca at Sonogno and Maggia at Bignasco (without influence of hydropower production) were estimated by discharge values of Verzasca at Lavertezzo published by BAFU (2001-2008).



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 (NIVA, 1996). 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, during 2008, thanks to the collaboration with the Institute of Ecosystem Studies in Pallanza, we started to determine *Chironomidae* down to genus and eventually species level. 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 EPT index (=number of families from the orders *Ephemeroptera, Plecoptera, Trichoptera*) were calculated. Both the taxa richness and the EPT index 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. This categorisation system permits to evaluate and assess the acidity of rivers on the basis of macroinvertebrate populations. For high altitude 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 describe the temporal evolution of the composition of macroinvertebrate populations with regard to acid sensitiveness by applying indexes from acid classification systems (Braukmann and Biss, 2004) to single taxa and omitting to attribute a specific acidification category to the entire sample. Until 2007 *Chironomidae* were only determined at the family level, during 2008 we started to determine *Chironomidae* down to genus and eventually species level.

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, during 2008 in the littoral of all lakes *Diptera* was the dominant order (average: 67%), followed by *Oligochaeta* (average: 19%)

and *Others* (average: 12%). In the emissaries other orders like *Plecoptera* were also important. The species diversity (=E.B.I. taxa number) was usually higher in the emissary than in the littoral. Similarly, behaved the EPT index.

Variations in macroinvertebrate population among lakes are probably influenced mainly by differences in water acidity. Average pH during 2008 was 7.6, 6.5, 6.4, 5.7, 5.5 in Lago Bianco, Laghetto Inferiore, Superiore Inferiore, Lago di Tomè and Lago del Starlaresc da Sgiof, respectively. In samples from the emissary the E.B.I taxa number and the EPT index were highest in Lago Bianco followed by the other lakes. Differently for the littoral, the E.B.I. taxa number and EPT index were not higher in samples from the alkaline Lago Bianco compared to the other lakes. We assume that its particular littoral morphology (very small grain size) might be the reason. Interestingly, the E.B.I. taxa number and EPT index of Lago di Tomè did not much differ from those of Laghetto Inferiore and Superiore, not reflecting the pH difference. Differences in the relative abundances of the main macroinvertebrate groups were irrelevant in samples from the littoral. Most taxa belonged to the order *Diptera* followed by *Oligochaeta*. Only in Laghetto Inferiore the presence of numerous individuals of the class *Nematoda* caused an increase of the distribution group "*Others*" on account of "*Diptera*" and "*Oligochaeta*". In samples from the outlets differences were more significant. The distribution of the main macroinvertebrate groups was similar in Lago Bianco, Laghetto Superiore and Laghetto Inferiore with *Diptera* and *Oligochaeta* being the dominant orders. Interestingly, in the emissary of the more acid lakes Lago di Tomè and Lago del Starlaresc da Sgiof *Oligochaeta* were almost absent and the percentage of *Diptera* was even higher, particularly 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 absent in Lago di Tomè, one organism of it was found for the first time in Lago del Starlaresc da Sgiof and only few organisms of it (Baetidae) were present in the emissary of Laghetto Inferiore (*Ecdyonurus sp.*), Laghetto Superiore (*Ecdyonurus sp.*) and Lago Bianco (*Baetis sp.*). Because of its wetland characteristics, Lago del Starlaresc da Sgiof is the only lake that is inhabited by *Odonata* (=*Others*). Heteroptera and Megaloptera were also only found in Lago di Tomè and Lago del Starlaresc da Sgiof.

For what concerns temporal variations it seems that after 1991 an increase of the E.B.I taxa number and the EPT index has occurred in the emissary of Laghetto Inferiore and Laghetto Superiore. However, this increase is accompanied by an increase of the sampled organisms that can be caused by a real increase of the number of organisms but also by a more effective sampling procedure and can therefore not be directly compared. In fact, it is known that as higher the number of sampled organisms as higher generally results the species number. A similar trend can be observed in the emissary of Lago di Tomè and Lago del Starlaresc da Sgiof after 2002. In the emissary of Laghetto Superiore after 1991 a decrease of the relative abundance of *Diptera* and an increase of the relative abundance of *Oligochaeta* can be observed. In the emissary of Lago di Tomè after 2002 an increase of the relative abundance of *Diptera* on account of *Plecoptera* seemed to occur.

Table 3.1 Number of samples, organisms, taxa, and EPT index and average abundances of the main macroinvertebrate groups in the littoral and in the emissary of 5 Alpine lakes during form 1991 to 2008

Lakes	Parameters	Littoral							Emissary							
		2002	2003	2004	2005	2006	2007	2008	1991	2002	2003	2004	2005	2006	2007	2008
Laghetto Inferiore	no. of samples	3	3	3	3	2	2	2	1	3	3	3	3	2	2	2
	no. organisms	199	1272	1453	5223	3228	2556	6869	64	293	1217	2004	8338	6086	7714	10519
	no. taxa E.B.I.	8	12	13	18	10	13	13	5	11	19	18	18	17	17	15
	EPT index	1	4	3	6	3	3	3	1	3	9	8	10	9	7	6
	Ephemeroptera	0%	0%	0%	0%	0%	0%	0%	0%	0%	2%	2%	1%	1%	1%	1%
	Plecoptera	1%	2%	3%	2%	4%	1%	2%	19%	33%	23%	16%	12%	13%	5%	5%
	Trichoptera	0%	1%	1%	0%	1%	2%	0%	0%	1%	3%	3%	3%	1%	0%	1%
	Diptera	59%	81%	74%	74%	76%	75%	57%	47%	44%	44%	33%	45%	43%	58%	52%
	Coleoptera	2%	1%	3%	1%	1%	1%	0%	0%	0%	0%	0%	0%	0%	0%	0%
	Oligochaeta	35%	13%	18%	17%	12%	14%	7%	30%	11%	25%	36%	30%	35%	30%	23%
	Others	3%	1%	1%	5%	6%	8%	33%	5%	12%	2%	10%	8%	7%	5%	19%
Laghetto Superiore	no. of samples	3	3	3	3	2	2	2	1	3	3	3	3	2	2	2
	no. organisms	332	1605	2055	8705	4491	4243	7204	47	150	1549	1748	6631	5742	5348	4991
	no. taxa E.B.I.	11	11	12	13	9	12	16	5	12	18	18	17	15	14	15
	EPT index	1	4	3	6	3	3	3	1	3	9	8	10	9	7	6
	Ephemeroptera	0%	0%	0%	0%	0%	0%	0%	0%	0%	9%	7%	1%	0%	0%	0%
	Plecoptera	5%	6%	4%	4%	3%	3%	3%	15%	38%	29%	17%	11%	10%	3%	5%
	Trichoptera	4%	3%	1%	1%	3%	4%	1%	0%	1%	4%	3%	1%	1%	1%	1%
	Diptera	31%	71%	65%	70%	55%	51%	78%	66%	50%	34%	49%	47%	38%	30%	29%
	Coleoptera	1%	1%	3%	1%	1%	1%	1%	0%	0%	0%	0%	0%	0%	0%	0%
	Oligochaeta	57%	15%	14%	11%	8%	10%	12%	6%	6%	21%	20%	38%	50%	64%	64%
	Others	3%	3%	13%	14%	30%	30%	5%	13%	5%	2%	4%	1%	1%	2%	0%

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

Lakes	Parameters	Littoral			Emissary		
		2006	2007	2008	2006	2007	2008
Lago Bianco	no. of samples	2	2	2	2	2	2
	no. organisms	4898	6030	6944	6195	5910	6056
	no. taxa E.B.I.	6	5	8	15	19	22
	EPT index	1	1	2	7	9	8
	Ephemeroptera	0%	0%	0%	4%	1%	1%
	Plecoptera	0%	0%	0%	7%	9%	13%
	Trichoptera	0%	0%	0%	1%	1%	0%
	Diptera	78%	56%	47%	39%	38%	54%
	Coleoptera	0%	0%	0%	0%	0%	0%
	Oligochaeta	10%	31%	47%	45%	50%	31%
	Others	12%	13%	5%	4%	1%	1%

Tab. 3.2 presents the number of taxa for the five “Braukmann and Biss” indexes from 2002 to 2008, whereas the smallest index refers to the most acid sensitive taxas. It can be observed that samples from the emissary of Laghetto Inferiore, Laghetto Superiore and Lago Bianco contained regularly taxa with “Braukmann and Biss indexes” ≥ 2. Differently, in lago di Tomè taxa with “Braukmann and Biss indexes” ≥ 2 appear seldom and in Lago del Starlaresc da Sgiof and in the littoral of all lakes only taxa with “Braukmann and Biss indexes” ≥ 4 existed. Tab. 3.3 shows for every lake the organisms with the lowest “Braukmann and Biss index”. A temporal trend cannot be observed. In Laghetto Inferiore and Laghetto Superiore organisms with “Braukmann and Biss index” = 2 seem to have appeared after 2002. However, this result may be connected with the greater number of organisms sampled after 2002 (Steingruber and Colombo, 2006).

In general, lake acidity seems to influence the population of macroinvertebrates. In fact, the higher pH’s of Lago Bianco, Laghetto Inferiore and Laghetto Superiore compared to Lago di Tomè and Lago del Starlaresc da Sgiof seem to get reflected in a higher taxa richness, EPT index and the presence of organisms with lower “Braukmann and Biss indexes” in emissary samples. Important differences regarding the macroinvertebrate population between the alkaline Lago Bianco and the low acid lakes (Laghetto Inferiore, Laghetto Superiore) were not observed. This seems to agree with the fact that toxic effects on macroinvertebrate occur below pH 6 because of increased dissolution of aluminium (Vesely et al. 1985). Differences in macroinvertebrate population between outlets and littorals are evidently due to their unique ecosystem characteristics and not because of different water quality. Because of the short monitoring period, observations about time trends are not yet possible.

Table 3.2 Number of taxa in 5 Alpine lakes for each “Braukmann and Biss index” from 1991 to 2008

The gray colored areas indicate the absence of samples

Lakes	Braukmann and Biss index	Littoral							Emissary							
		2002	2003	2004	2005	2006	2007	2008	1991	2002	2003	2004	2005	2006	2007	2008
Laghetto Inferiore	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	2	0	0	0	0	0	0	0	0	0	3	4	5	4	5	2
	3	0	0	0	0	0	0	0	0	0	3	2	3	4	1	0
	4	0	1	0	1	0	0	0	1	1	4	5	4	4	2	2
	5	1	2	2	2	3	3	4	1	4	5	4	4	6	5	5
Laghetto Superiore	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	2	0	0	0	0	0	0	0	0	0	5	7	4	3	4	1
	3	0	0	0	0	0	0	0	0	0	4	1	1	2	0	1
	4	0	0	0	0	0	0	0	1	0	4	2	3	3	3	2
	5	2	4	2	4	3	4	3	1	6	6	5	5	5	6	7
Lago Tomè	1	0	0	0	0	0	0	0		0	0	0	0	0	0	0
	2	0	0	0	0	0	0	0		0	0	0	1	0	1	2
	3	0	0	0	0	0	0	0		0	0	0	0	0	0	0
	4	1	1	1	2	4	0	0		1	2	2	4	5	4	3
	5	2	3	2	5	3	3	5		3	3	2	5	5	5	7
Lago del Starlaresc da Sgiof	1	0	0	0	0	0	0	0		0	0	0	0	0	0	0
	2	0	0	0	0	0	0	0		0	0	0	0	0	0	0
	3	0	0	0	0	0	0	0		0	0	0	0	0	0	0
	4	1	1	2	2	2	2	1		1	1	0	2	2	2	1
	5	1	0	0	0	0	0	0		1	2	1	1	2	1	4
Lago Bianco	1					0	0	0						0	0	0
	2					0	0	0						6	6	5
	3					0	0	0						2	2	1
	4					0	0	0						3	2	2
	5					2	1	1						4	6	4

Table 3.3 Macroinvertebrate species with lowest “Braukmann and Biss index” in 5 Alpine lakes from 1991 to 2008
X refers to the emissary and (X) to the littoral. The gray colored areas indicate the absence of samples

Lakes	Taxa	Index	1991	2000	2001	2002	2003	2004	2005	2006	2007	2008
Laghetto Inferiore	Ecdyonurus sp.	2						x	x	x	x	x
	Ecdyonurus helveticus-Gr.	2					x	x	x	x	x	
	Perlodes sp.	2						x			x	
	Perlodes intricatus	2						x	x		x	x
	Philopotamus lucidificatus	2					x		x	x		
	Protonemoura nimborum	2		x					x	x	x	
	Rhitrogena sp.	2					x					
Laghetto Superiore	Baetis alpinus	2					x	x		x		
	Ecdyonurus sp.	2					x	x	x	x	x	x
	Ecdyonurus helveticus-Gr.	2					x		x		x	
	Ecdyonurus parahelveticus	2						x				
	Perlodes sp.	2						x				
	Perlodes intricatus	2						x	x		x	
	Perlodes microcephalus	2					x					
	Protonemoura nimborum	2						x	x	x	x	
	Rhitrogena sp.	2						x				
Lago Tomè	Perla grandis	1			x							
	Protonemura nimborum	2							x			x
	Rhyacophila tristis	2									x	
	Odontocerum albicorne	4								x	x	
	Potamophylax cingulatus	4							x	x		
	Protonemura meyeri	4			x							
	Ryacophila (Ryacophila) sp.	4					x	x	x	x	x	x
	Ryacophila sensu stricto-Gr.	4							x	x	x	x
	Sialis sp.	4				x	x					
	Sialis fuliginosa	4						x	x	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
	Sialis sp.	4						(x)	(x)	(x)		
	Sialis fuliginosa	4									(x)	
Lago Bianco	Alainites muticus	2								x		
	Baetis alpinus	2								x	x	x
	Ecdyonurus sp.	2								x		x
	Perlodes sp.	2								x	x	x
	Perlodes intricatus	2								x	x	x
	Philopotamus ludificatus	2									x	
	Protonemura nimborum	2								x	x	x
	Rhithrogena sp.	2									x	

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, organisms, taxa, the EPT index and the relative abundances of the main macroinvertebrate groups in river Maggia, Vedeggio and Verzasca from 2000 to 2008 are shown in Tab. 3.4. The number of E.B.I. taxa and the EPT index were generally highest in river Maggia and Vedeggio, followed by river Verzasca. The main orders were *Ephemeroptera*, *Diptera, Plecoptera* and *Coleoptera*.

Table 3.4 Number of samples, organisms, taxa, average abundances of the main macroinvertebrate groups and EPT index in 3 Alpine rivers from 2000 to 2008.

Rivers	Parameters	2000	2001	2002	2003	2004	2005	2006	2007	2008
Maggia	no. of samples	8	6	6	6	5	4	4	4	4
	no. organisms	2247	1507	2833	5320	5120	9857	11904	19126	16855
	no. taxa E.B.I.	31	30	32	38	35	40	36	44	41
	EPT index	14	12	13	18	17	17	16	17	19
	Ephemeroptera	35%	20%	31%	23%	12%	16%	15%	16%	22%
	Plecoptera	35%	19%	33%	23%	16%	12%	13%	5%	5%
	Trichoptera	4%	1%	4%	4%	8%	3%	7%	2%	3%
	Diptera	19%	39%	8%	25%	24%	35%	36%	37%	36%
	Coleoptera	4%	7%	7%	5%	12%	9%	13%	12%	10%
	Oligochaeta	0%	0%	0%	1%	0%	2%	1%	4%	0%
	Others	2%	4%	1%	3%	3%	4%	4%	5%	6%
Vedeggio	no. of samples	8	6	6	6	5	4	4	4	4
	no. organisms	1578	1934	1789	3687	3081	7246	11672	9442	16588
	no. taxa E.B.I.	35	39	30	34	34	40	39	42	44
	EPT index	14	16	12	16	14	20	19	18	19
	Ephemeroptera	35%	39%	31%	18%	31%	16%	23%	27%	32%
	Plecoptera	28%	28%	38%	44%	22%	24%	17%	28%	31%
	Trichoptera	11%	6%	8%	15%	14%	15%	10%	6%	3%
	Diptera	16%	9%	9%	21%	23%	36%	31%	23%	23%
	Coleoptera	8%	18%	12%	2%	9%	6%	14%	13%	10%
	Oligochaeta	0%	0%	0%	0%	1%	1%	1%	1%	1%
	Others	1%	1%	1%	0%	1%	3%	3%	2%	1%
Verzasca	no. of samples	8	6	6	6	5	4	4	4	4
	no. organisms	1574	2258	2570	3761	4269	12901	15019	21054	20239
	no. taxa E.B.I.	26	32	29	29	25	28	30	30	35
	EPT index	12	13	12	14	11	12	14	12	17
	Ephemeroptera	46%	45%	37%	42%	55%	45%	36%	41%	38%
	Plecoptera	18%	18%	24%	18%	11%	14%	16%	12%	17%
	Trichoptera	3%	4%	3%	3%	2%	2%	2%	1%	1%
	Diptera	12%	8%	10%	21%	12%	19%	20%	22%	23%
	Coleoptera	18%	22%	23%	13%	18%	16%	24%	19%	17%
	Oligochaeta	0%	1%	1%	0%	0%	1%	0%	3%	1%
	Others	3%	2%	2%	2%	1%	4%	2%	2%	3%

All rivers were characterized by the existence of organisms with “Braukmann and Biss index” =1 (Tab. 3.5). However, looking at the number of organisms with “Braukmann and Biss index” = 1-2, it appears that river Vedeggio and Maggia had more acid sensitive species than river Verzasca. Tab. 3.6 shows for every lake the organisms with the lowest “Braukmann and Biss index”. 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 river based on the presence of acid sensitive species. However, the higher total number of taxa, the EPT index and the number of acid sensitive taxa 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 Number of taxa in 3 Alpine rivers for each “Braukmann and Biss index” from 2000 to 2008

River	Braukmann and Biss index	2000	2001	2002	2003	2004	2005	2006	2007	2008
Maggia	1	4	3	2	3	4	4	4	4	4
	2	14	8	11	11	13	15	13	14	13
	3	5	6	3	5	5	7	3	6	5
	4	3	1	5	8	6	5	6	5	6
	5	4	4	5	3	2	3	2	4	4
Vedeggio	1	5	2	2	2	2	4	2	3	4
	2	11	13	12	13	14	17	16	15	18
	3	6	7	4	5	5	8	7	6	6
	4	3	5	3	4	6	6	8	6	5
	5	9	4	3	5	5	4	4	3	3
Verzasca	1	3	2	2	2	2	2	2	2	2
	2	7	6	8	8	8	8	11	8	11
	3	5	6	4	7	5	5	6	5	6
	4	4	3	5	6	5	6	7	6	7
	5	5	4	3	4	3	3	3	3	3

Table 3.6 Macroinvtebrate species with lowest “Braukmann and Biss index” in 3 Alpine rivers from 2000 to 2008

River	Taxa	Index	2000	2001	2002	2003	2004	2005	2006	2007	2008
Maggia	Habroleptoides confusa	1	x	x			x	x	x	x	x
	Perla sp.	1	x		x	x	x	x	x	x	x
	Perla grandis	1	x	x	x	x	x	x	x	x	x
	Serratellalla ignita	1	x	x		x	x	x	x	x	x
Vedeggio	Habroleptoides confusa	1	x					x		x	x
	Perla sp.	1	x	x	x	x	x	x	x	x	x
	Perla bipunctata	1	x								
	Perla grandis	1	x	x	x	x	x	x	x	x	x
	Serratella ignita	1	x					x		x	x
Verzasca	Perla sp.	1	x	x	x	x	x	x	x	x	
	Perla grandis	1	x	x	x	x	x	x	x	x	
	Serratella ignita	1	x								

Table 3.7 “Braukmann and Biss categories” and their relative river sample number from 2000 to 2008

Rivers	Category	2000	2001	2002	2003	2004	2005	2006	2007	2008
Maggia	1	0%	0%	0%	0%	40%	0%	0%	0%	0%
	2	100%	100%	100%	100%	60%	100%	100%	75%	50%
Vedeggio	1	0%	0%	50%	0%	0%	0%	0%	0%	0%
	2	100%	100%	50%	100%	100%	100%	75%	50%	75%
Verzasca	1	0%	0%	0%	0%	0%	0%	0%	0%	0%
	2	100%	100%	100%	100%	100%	100%	100%	75%	100%

4 Persistent organic pollutants (POP's) and metals in fish muscle

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). Concentrations of POP's and metals have been measured in fish muscle from 2 Alpine lakes since 2000.

4.2 Methods

Fish were angled in autumn in Laghetto Inferiore (2074 m) and Laghetto Superiore (2128 m). All fish were measured for length and weight and aged by scale analysis. For every sampling site 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).

4.3 Results and discussion

4.3.1 Fish population characteristics

In Laghetto Inferiore and Laghetto Superiore only rainbow trouts (*Oncorhynchus mykiss*) were sampled. Fish number, average weight, length, conditioning index (CI) and age are shown in Tab. 4.1. A CI above 1 stands for a good physical condition.

Table 4.1 Number of fish and average weight, length and conditioning index (C.I.) in samples from 2000 to 2008.

	Year	Fish number	Weight (g)	Length (cm)	C.I.	Age [months]
Laghetto Inferiore	2000	26	92.6	20.9	0.99	41
	2001	40	52.5	17.5	0.94	36
	2002	22	76.3	19.6	1.02	32
	2003	17	72.4	19.2	0.99	31
	2004	16	71.6	19.0	1.01	35
	2005	21	87.7	20.4	1.02	39
	2007	17	82.7	19.5	1.06	36
	2008	17	79.6	19.6	1.01	37
Laghetto Superiore	2000	15	103.3	21.5	1.03	40
	2001	29	86.6	20.8	0.92	35
	2002	19	62.2	19.2	0.85	33
	2003	22	56.5	18.3	0.92	31
	2004	20	60.1	18.6	0.94	34
	2005	23	84.7	20.3	1.01	40
	2007	11	136.2	21.8	1.22	40
	2008	14	133.9	23.3	1.03	48

4.3.2 DDT's in fish muscle

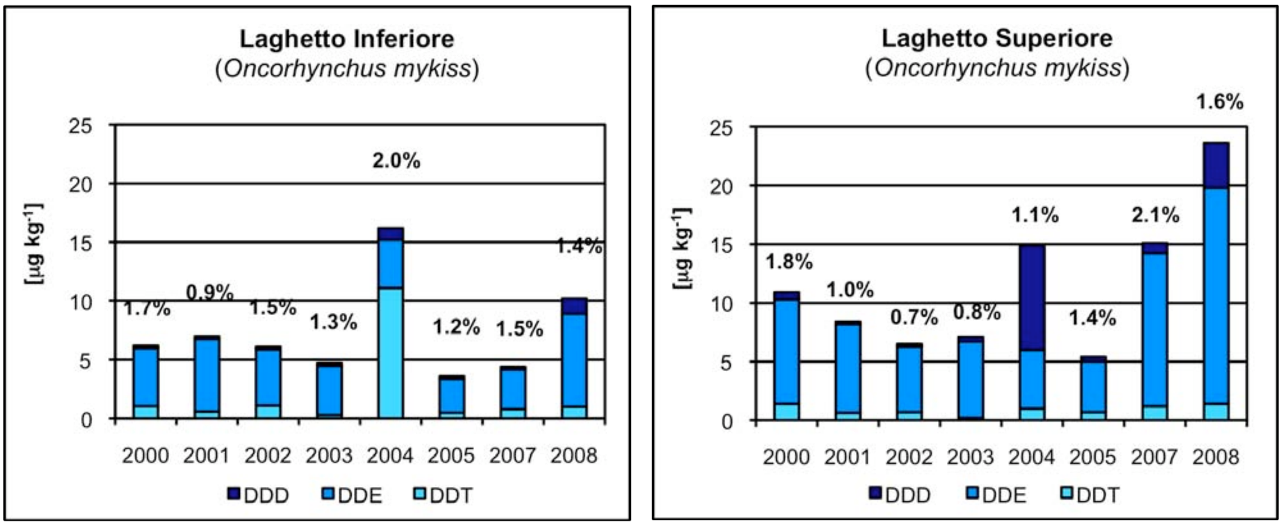
Most DDT found in the Southern part of the Swiss Alps probably origins from a contaminated site situated along the shore of Lago Maggiore, where until 1996 a factory has produced DDT. In fact, elevated total DDT concentrations (8-308 μg kg^{-1}) are still measured in fish from Lago Maggiore (Cipais, 2007).

Fish sampled in Lago Inferiore and Superiore at the end of 2008 were characterized by total DDT concentrations of 10.2 μg kg^{-1} and 23.6 μg kg^{-1} and DDE was as usual the main component (77% in Laghetto Inferiore and 78% in Laghetto Superiore). DDE is a metabolite of DDT. Values are therefore below the Swiss edibility limit for total DDT (1 mg kg^{-1}).

Comparing the data with results former years (Fig. 4.1), it appears that concentrations of DDT in Laghetto Superiore are always higher than in Laghetto Inferiore. The phenomena can be explained by the fact that the two lakes are connected and that Laghetto Superiore is situated in the drainage basin of Laghetto Inferiore, so that part of the DDT falling over the watershed of Laghetto Inferiore is retained in the sediments of Laghetto Superiore. In addition, because of their different morphology the water column of Laghetto Superiore gets regularly completely mixed while in Laghetto Inferiore the deepest layer does not participate to the spring and fall overturn (Pradella, 2001). As a consequence, in Laghetto Inferiore DDT that reaches the bottom has the tendency to remain there. However, the difference between the two lakes was particularly pronounced in 2007 and 2008. The presence of particularly large (26-27 cm), fat (190-244 g) and old fish (45-69 months), 3 in 2007 and 3 in 2008, that could absorb DDT for a longer period, may also have influenced the result.

Figure 4.1 Concentrations of DDT's in fish muscle of Laghetto Inferiore and Laghetto Superiore between 2000 and 2008

The percentage value refers to the lipid content.



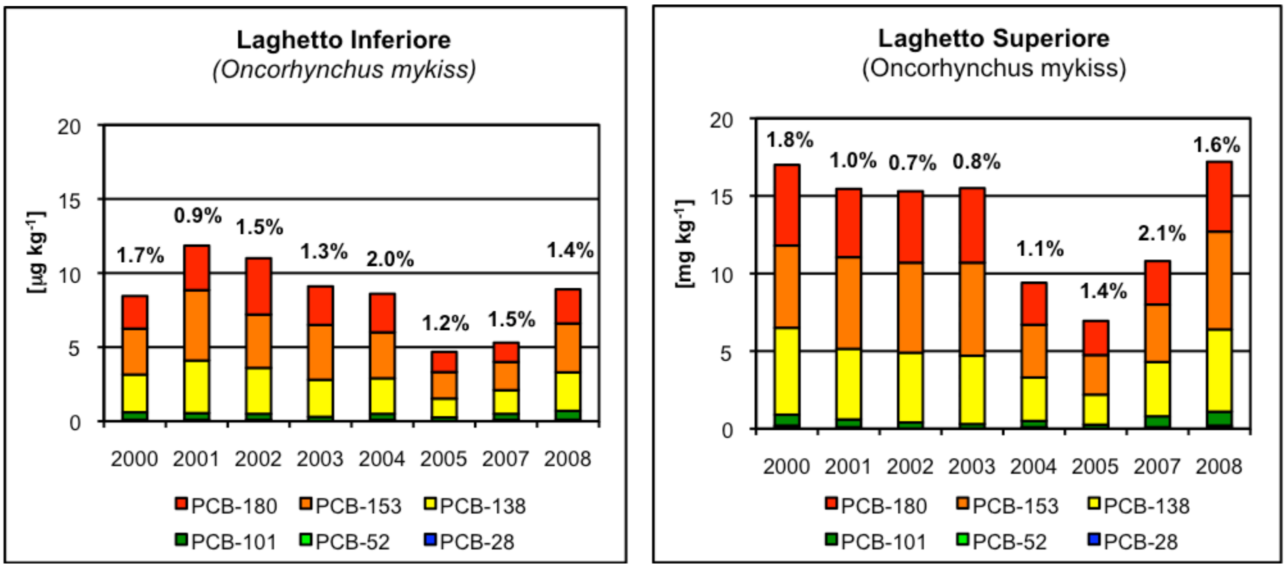
4.3.3 PCB's in fish muscle

Total PCB concentrations in fish samples from 2008 were 8.9 µg kg^{-1} in Laghetto Inferiore and 17.2 µg kg^{-1} and as usual the 3 heavier isotopes PCB-138, PCB-153, PCB-181 were the main cogeners. The Swiss edibility limit of PCB in fish (1 mg kg^{-1}) was therefore not exceeded.

Similarly to what observed for DDT, Looking at the time series of PCB concentrations in Laghetto Inferiore and Laghetto Superiore (Fig. 4.2), it appears that concentrations are always higher in the latter. The reasons were already explained in the former paragraph and are connected with the fact that Laghetto Superiore is situated in the watershed of Laghetto Inferiore and the meromixis of Laghetto Inferiore. However, the high concentrations in Lago Superiore in 2007-2008 cannot be explained only by these phenomena. As already discussed for DDT the presence of long, fat and old fish may have influenced the results, as well.

Interestingly, without considering concentrations of DDT in Laghetto Inferiore and Superiore in 2004, temporal variations of DDT and PCB are very similar, indicating that they are probably controlled by the same factors.

Figure 4.2 Concentrations of PCB's in fish muscle of Laghetto Inferiore and Laghetto Superiore between 2000 and 2008
The percentage value refers to the lipid content.



4.3.4 HCB and HCH's in fish muscle

Besides DDT and PCB, HCB and HCH concentrations were also quantified in fish muscle. Concentrations of HCB and total HCH in fish from Laghetto Inferiore and Laghetto Superiore measured in 2008 were lower than 1 µg kg^{-1} (edibility limit: 100 µg kg^{-1}).

4.3.5 Metals in fish muscle

Metals concentrations in fish muscle sampled in 2008 were very similar between Laghetto Inferiore and Superiore (Tab. 4.2). For the most dangerous metals Pb, Cd and Hg, also subject of the Aahrus Protocol 1998 on heavy metals (Convention on long-range transboundary air pollution), concentrations were below the Swiss edibility limits for fish (Pb: 0.4 mg kg^{-1}, Cd: 0.05 mg kg^{-1}, Hg: 1.0 mg kg^{-1}). After 2004 with exception of mercury all metals seemed to decrease. This trend is in agreement with the decrease in concentrations of aluminium observed in Alpine lake water. Interestingly, aluminium concentrations in fish from Laghetto Inferiore and Superiore correlate quite well with aluminium concentrations in the water column (Fig. 4.4).

Table 4.2 Metal concentrations in fish muscle (mg^{-1} kg wet weight) measured in 2008

	Laghetto Inferiore (Oncorhynchus mykiss)	Laghetto Superiore (Oncorhynchus mykiss)
Zn	6.44	5.74
Al	0.35	0.33
Cu	0.30	0.29
Cr	0.30	0.064
Ni	<0.023	0.026
Pb	0.03	0.027
Cd	0.012	0.009
Hg	0.034	0.041

Figure 4.3 Metal concentrations in fish muscle (mg^{-1} kg wet weight) from 2000 to 2008

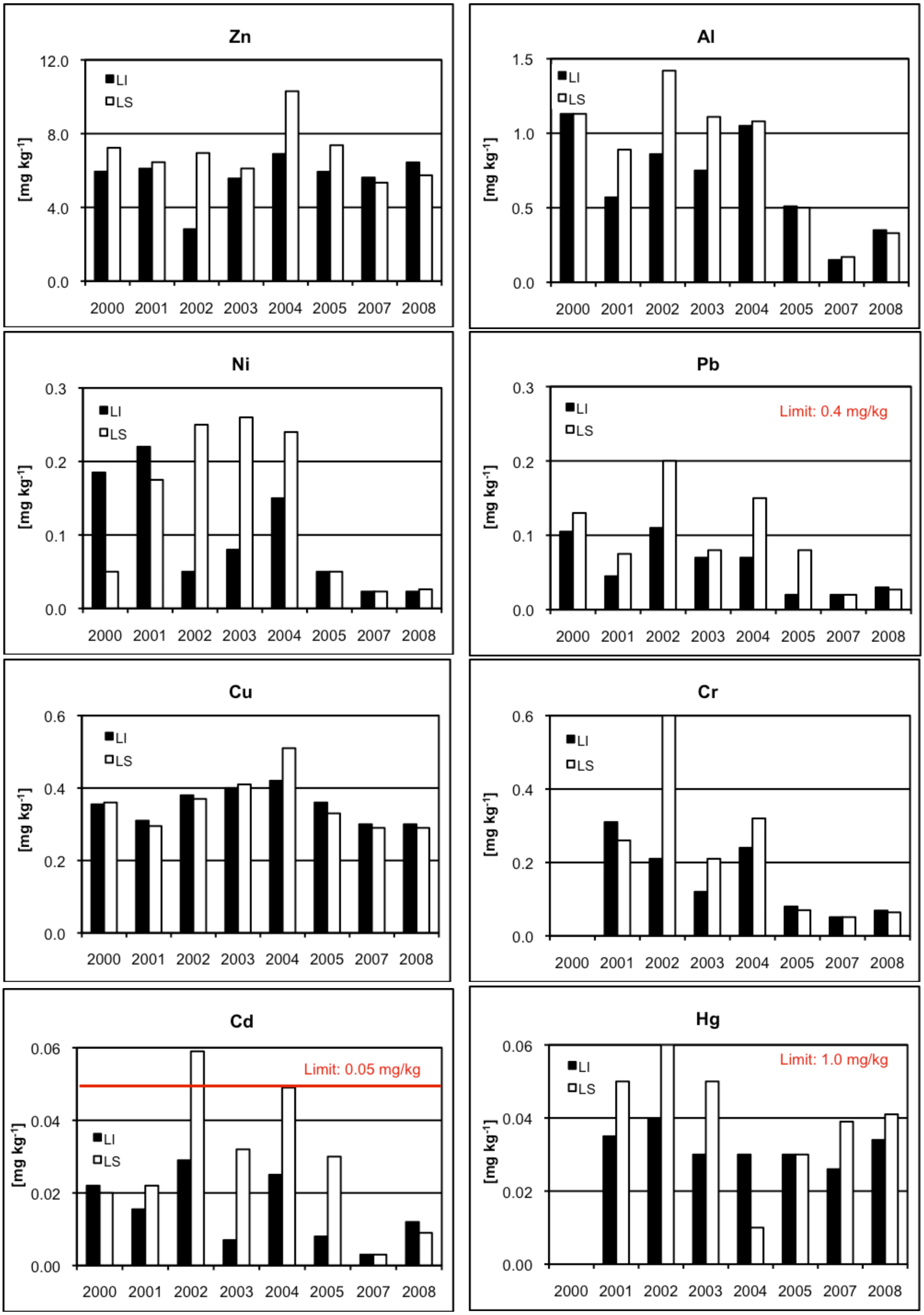
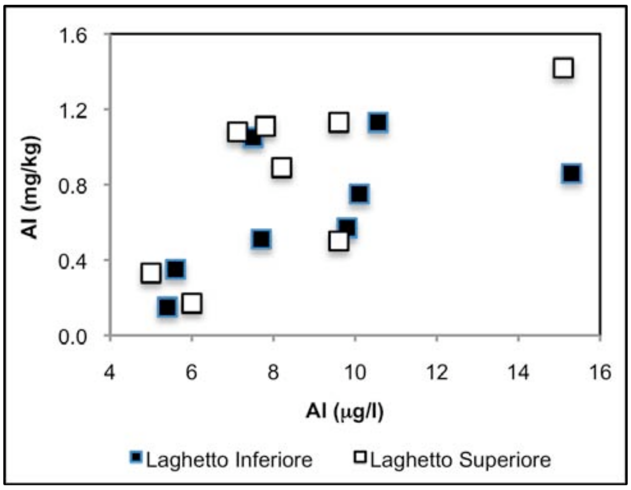


Figure 4.4 Aluminium concentrations in fish vs aluminium concentrations in lake water ion Laghetto Inferiore and Laghetto Superiore from 2000 to 2008.



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