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 2009

Ufficio dell’Aria, del Clima e delle Energie Rinnovabili
Sezione della Protezione del’Aria, deéé’Acqua e del Suolo
Divisione Ambiente
Dipartimento del Territorio

Authors:	Sandra Steingruber and Luca Colombo Ufficio aria, clima e energie rinnovabili, SPAAS Via C. Salvioni 2a 6500 Bellinzona
Chemical analysis:	Germano Righetti, Manuela Simoni-Vassalli Laboratorio, SPAAS Via Mirasole 22 6500 Bellinzona
Chemical sampling:	Corinna Beffa, Luca Colombo, David Fontana, Valerio Fumagalli, Germano Righetti, Dario Rezzonico , Claudia Gervasoni, Sandra Steingruber Laboratorio e Ufficio aria, clima e energie rinnovabili, SPAAS Via C. Salvioni 2a 6500 Bellinzona
Sampling and identification of macroinvertebrates:	Chiara Pradella 6956 Lopagno
Sampling and identification of Chironomidae and Oligochaetae:	Angela Boggero C.N.R. Istituto per lo Studio degli Ecosistemi 28922 Pallanza-Verbania (I)
Fish sampling and biometrical analysis :	Bruno Polli Ufficio caccia e pesca Via S. Franscini 17 6500 Bellinzona
Fish muscle analysis:	Nicola Solcà Laboratorio Cantonale Via Mirasole 22 6500 Bellinzona

Content

Introduction

The International Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP Waters) was established under the United Nations Economic Commission for Europe's Convention on Long-Range Transboundary Air Pollution (LRTAP) in 1985, when it was recognised that acidification of freshwater systems provided some of the earliest evidence of the damage caused by sulphur emissions. The monitoring programme is designed to assess, on a regional basis, the degree and geographical extent of the impact of atmospheric pollution, in particular acidification on surface waters. The monitoring data provide a basis for documenting effects of long-range transboundary air pollutants on aquatic chemistry and biota. An additional important programme activity is to contribute to quality control and harmonisation of monitoring methods. The Programme is planned and coordinated by a Task Force under the leadership of Norway. Up to now chemical and site data from more than 200 catchments in 16 countries in Europe and North America are available in the database of the Programme Centre. Switzerland joined the Programme in 2000 by order of the Swiss Federal Office for the Environment.

1 Study site

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

Figure 1.1 Sampling sites

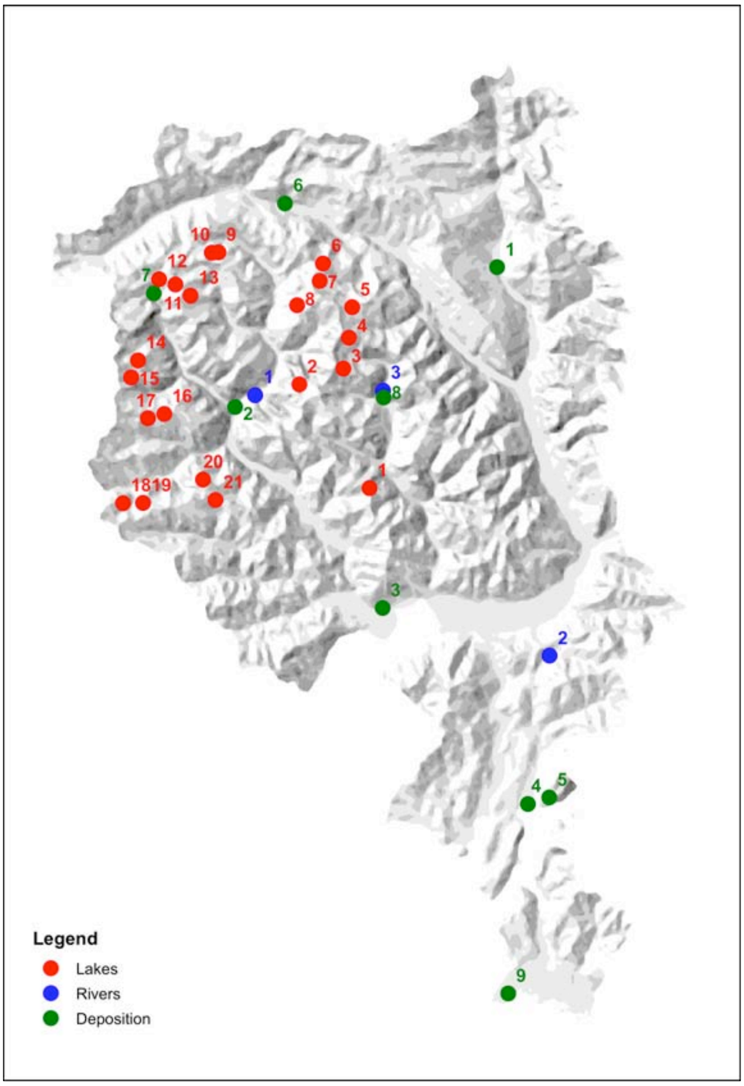


Table 1.1 Lake parameters

Lake number	Lake name	Longitude CH m	Latitude CH m	Longitude	Latitude	Altitude m a.s.l.	Catchment area ha	Lake area ha	Max depth m
1	Lago del Starlaresc da 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 $\mu eq\ l^{-1}$, 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). 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. 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 (UNECE, 2009). Furthermore, the data were checked for outliers. If available, as for metals, dissolved concentrations were compared with total concentrations.

Table 2.1 Measured parameters, conservation methods, analytical methods, accuracy and quantification limits
CA, PC, GF, PP stay for cellulose acetate, polycarbonate, glass fibre and polypropylene, respectively. ICP-OES for inductively coupled plasma atomic-emission spectroscopy.

Parameter	Filtration	Conservation	Method	Accuracy
pH	No	No	potentiometry	0.02
conductivity	No	No	Kolrausch bridge (20°C)	0.5 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 Statistical methods used for trend analysis

For the period 2000-2009 we utilized the Mann-Kendall test to detect temporal trends in precipitation, lake and river chemistry (Dietz and Kileen, 1981). For precipitation, a seasonal partial Mann-Kendall (Libiseller and Grimvall, 2002) was performed on monthly mean values and the amount of monthly precipitation. The latter was added as covariate in order to include meteorological influences in the study. For both concentrations and precipitation volumes the test statistics were summed over before conditioning. For lake chemistry a seasonal Mann-Kendall test was performed. Two seasons were chosen: season 1 (June-July) and season 2 (September-November). Similarly to precipitation, for river chemistry a seasonal partial Mann-Kendall test (Libiseller and Grimvall, 2002) was perfomed. As covariate was included the average daily discharge of the sampling day.

The two sided test for the null hypothesis that no trend is present was rejected for p-values below 0.05. In addition we quantified trends with the method of Sen (Sen, 1968). However, for precipitation instead of a median slope a mean slope was calculated. The reason is that, especially for parameters related to alkaline rain events (bicarbonate, base cations), the observed trends are not related to a general increase/decrease of concentrations during each event through time, but an increase/decrease of the number of events with increased/decreased concentrations. A median rate would therefore underestimate the increase/decrease of average concentrations through time.

2.5 Results and discussion

2.5.1 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 2009 are shown in Fig. 2.2. Concentrations of nitrate, ammonia, sulphate but also of base cations were in general higher during summer months and lower during winter months. This phenomena can be explained with the precipitation volume. In fact, at low precipitation volume concentrations decrease with increasing rain water volume, while at high precipitation volume concentrations tend to increase with increasing rain water volume (data not shown). Since highest precipitation volume usually occur during warmer months (storm season), concentrations of anthropogenic pollutants tend also to be higher then. Differently, acidity was highest in winter and lowest in summer. Knowing that acidity can be expressed as the sum of base cations and ammonia minus acid anions, the seasonality of acidity can be explained by the fact the concentrations of ammonia increase percentually more during summer months, probably because of increased evaporation of ammonia, than acid anions. As a consequence of decreased acidity during summer, concentrations of bicarbonate and pH values were highest during summer.

Depositions behaved similar to concentrations, with the difference that rain water volume gained further importance. Highest concentrations of acid anions, base cations, ammonia, bicarbonate and lowest concentrations of acidity were measured in July when rain water volume peaked.

In general, ion concentrations of anthropogenic origin (sulphate, nitrate, ammonia) were highest at sampling sites with low latitudes like Locarno, 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. Highest concentrations of base cations occurred at Lugano and Monte Brè lowest at Bignasco, Piotta and Robiei. As a consequence of high concentrations of base cations and ammonia, highest concentrations of bicarbonate and lowest concentrations of acidity were measured at Lugano. On the contrary, low concentrations of base cations and ammonia produced low concentrations of bicarbonate and high conentrations of acidity at Bignasco, Piotta 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. During 2009 highest deposition rates of ammonia, nitrate, sulphate and base cations were measured at Lugano and Locarno while lowest rates occurred at Acquarossa, Bignasco, Piotta and Robiei. Similar to what observed for concentrations, high depositions of base cations and ammonia caused highest depositions of bicarbonate and lowest depositions of acidity at Lugano, while low depositions of base cations and ammonia produced low depositions of bicarbonate and high depositions of acidity at Bignasco, Piotta and Robiei.

Figure 2.1 Monthly precipitation during 2009

Data from MeteoSwiss

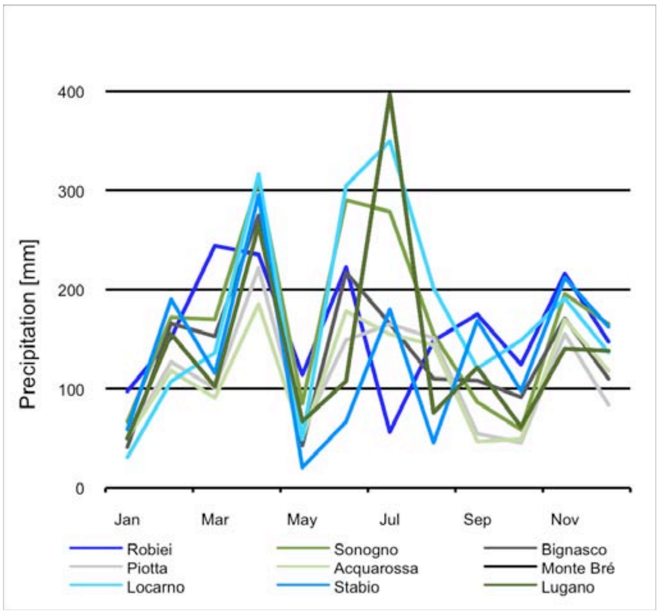
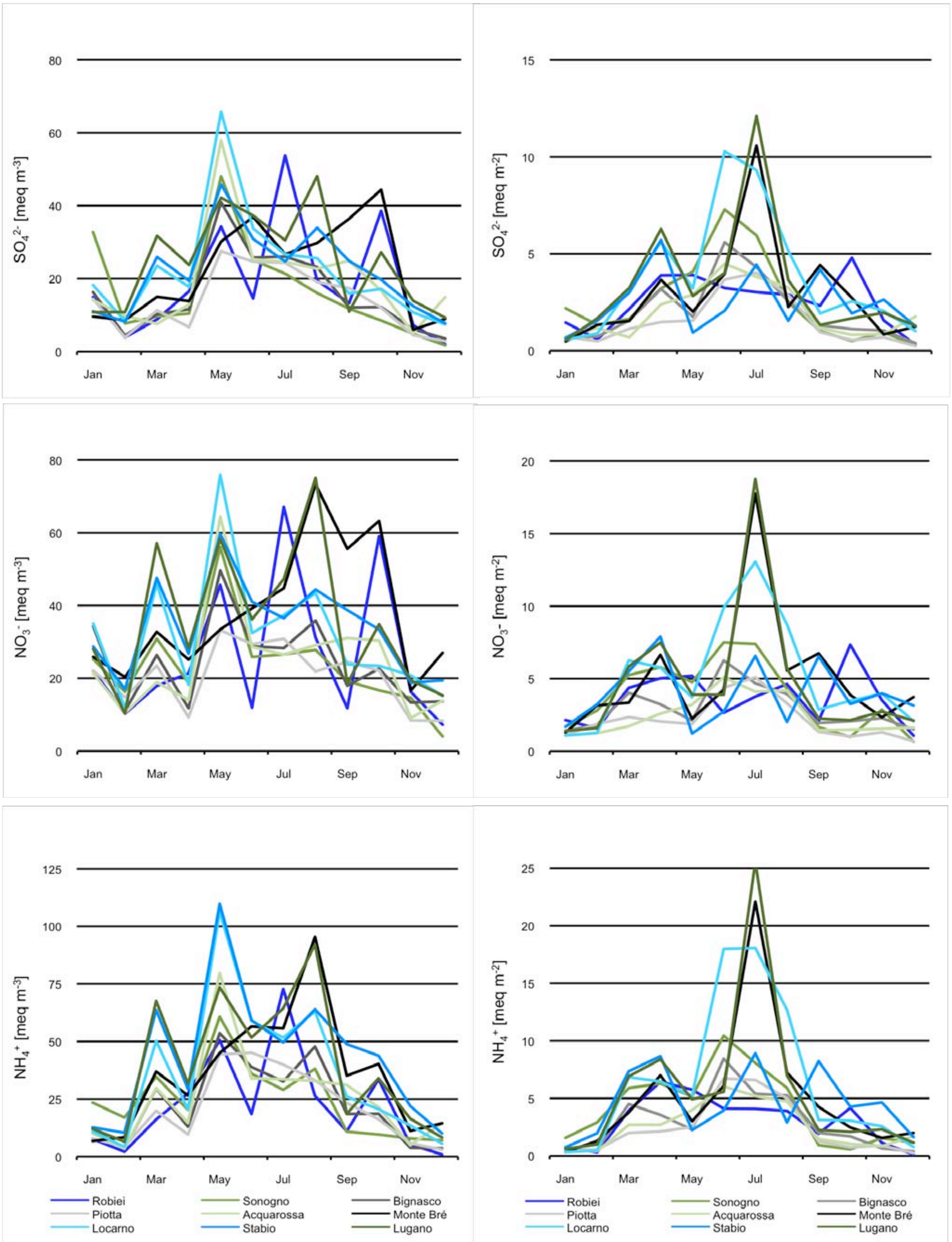


Figure 2.2 Seasonal variations of monthly average rain water concentrations and deposition rates during 2009
Base cations correspond to the sum of calcium, magnesium, sodium and potassium.



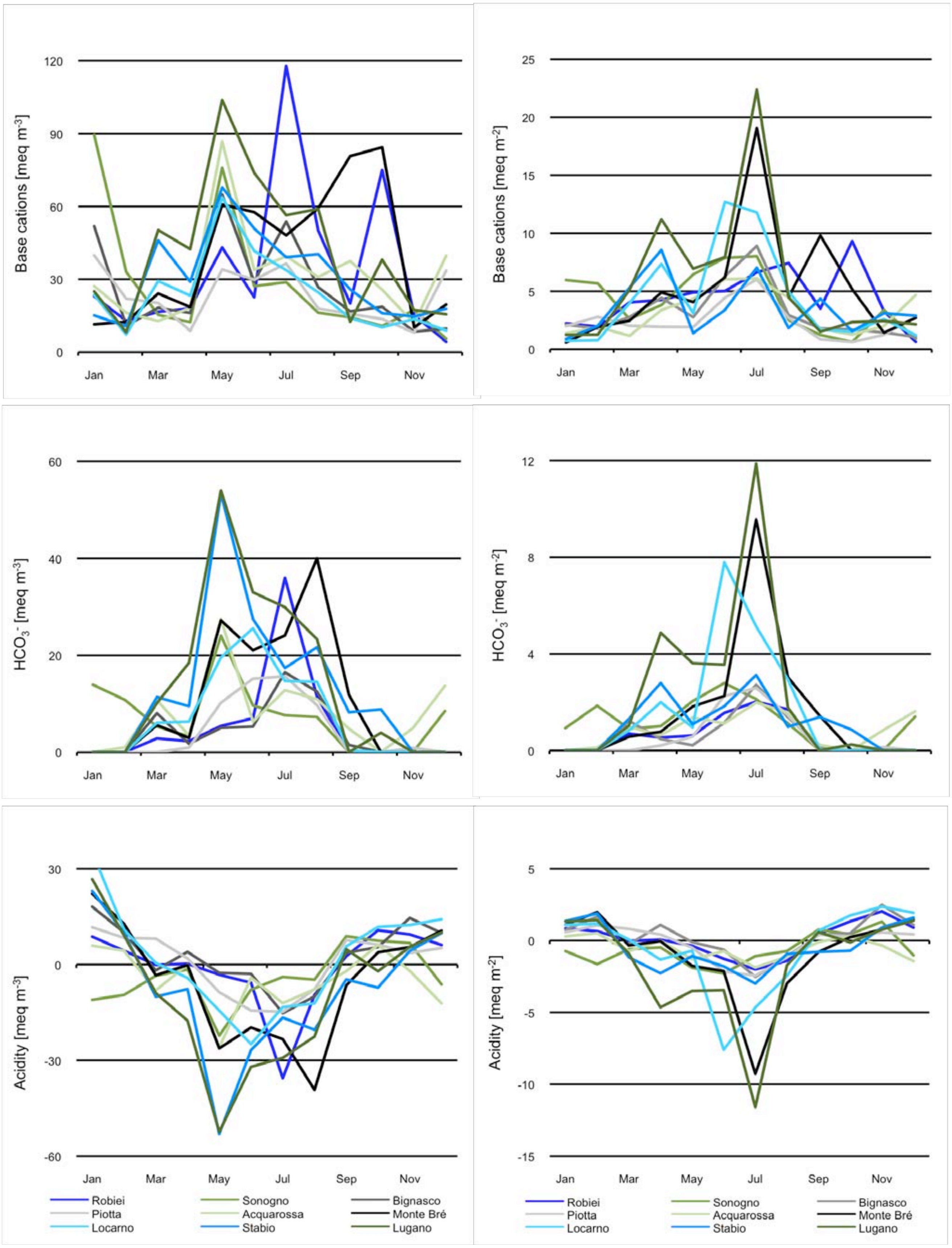
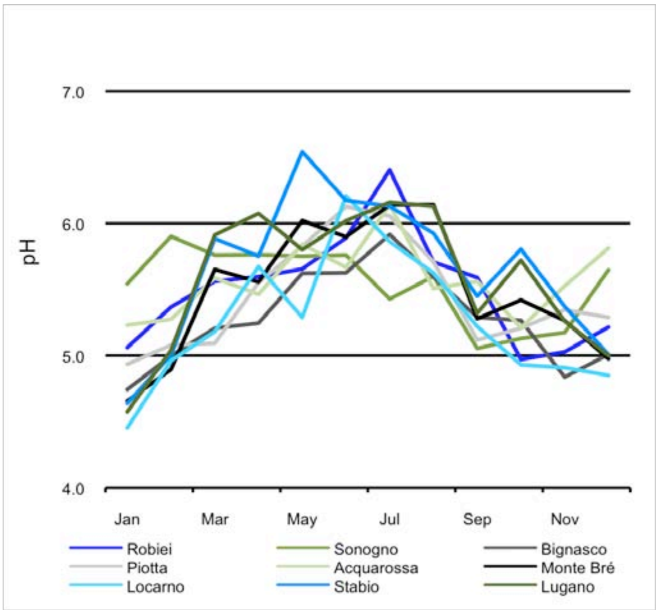

Base cations [meq m-3]
Base cations [meq m-2]
HCO3- [meq m-3]
HCO3- [meq m-2]
Acidity [meq m-3]
Acidity [meq m-2]
Jan
Mar
May
Jul
Sep
Nov
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Monte Bré
Locarno
Stabio
Lugano

Figure 2.3 Seasonal variations of monthly average rain water pH during 2009



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. 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).

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 concentratio
ns and deposition rates during 2009

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	1355	1233	8	5.6	18	24	6	8	3	5	1	2	23	32	8	11	18	24	22	29	4	5	-5	-7
Bignasco	1650	1723	9	5.2	11	19	2	3	7	11	3	4	21	34	4	7	14	24	21	35	6	11	2	3
Locarno Monti	2093	1959	11	5.2	15	32	3	6	5	11	1	3	36	76	9	19	22	45	29	62	5	11	-3	-7
Lugano	1680	1234	12	5.4	25	42	5	8	6	11	2	4	39	65	15	24	23	39	33	56	7	11	-11	-18
Monte Brè	1680	1328	11	5.3	21	35	5	8	6	10	3	5	31	52	10	17	19	32	33	55	7	11	-5	-8
Piotta	1360	1215	8	5.4	11	15	2	3	7	10	1	2	22	29	5	7	14	18	19	26	7	10	-1	-2
Robiei	1932	956	6	5.5	15	28	2	3	3	5	1	2	16	31	3	6	11	22	18	34	5	9	0	1
Sonogno	2033	1940	8	5.5	14	29	3	6	6	12	2	5	25	50	7	14	15	31	23	46	6	13	-4	-6
Stabio	1613	1601	11	5.3	14	22	4	6	8	13	2	3	36	57	9	15	19	31	30	49	8	13	-5	-7

Figure 2.4 Yearly precipitations
Data from MeteoSwiss

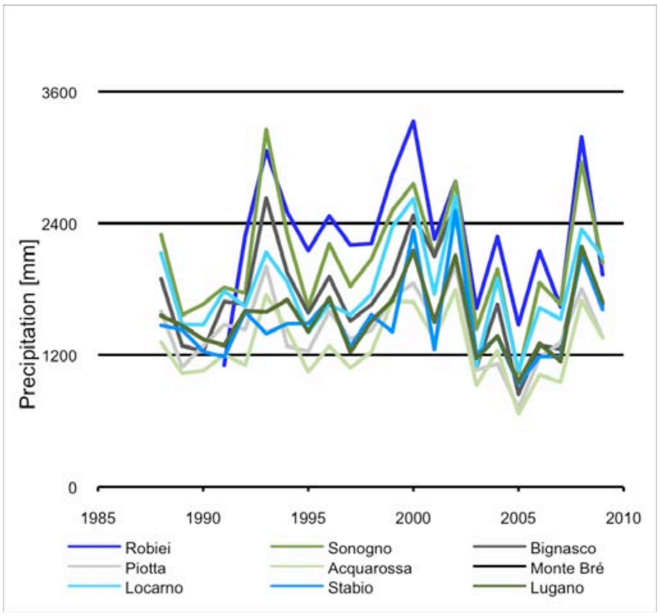
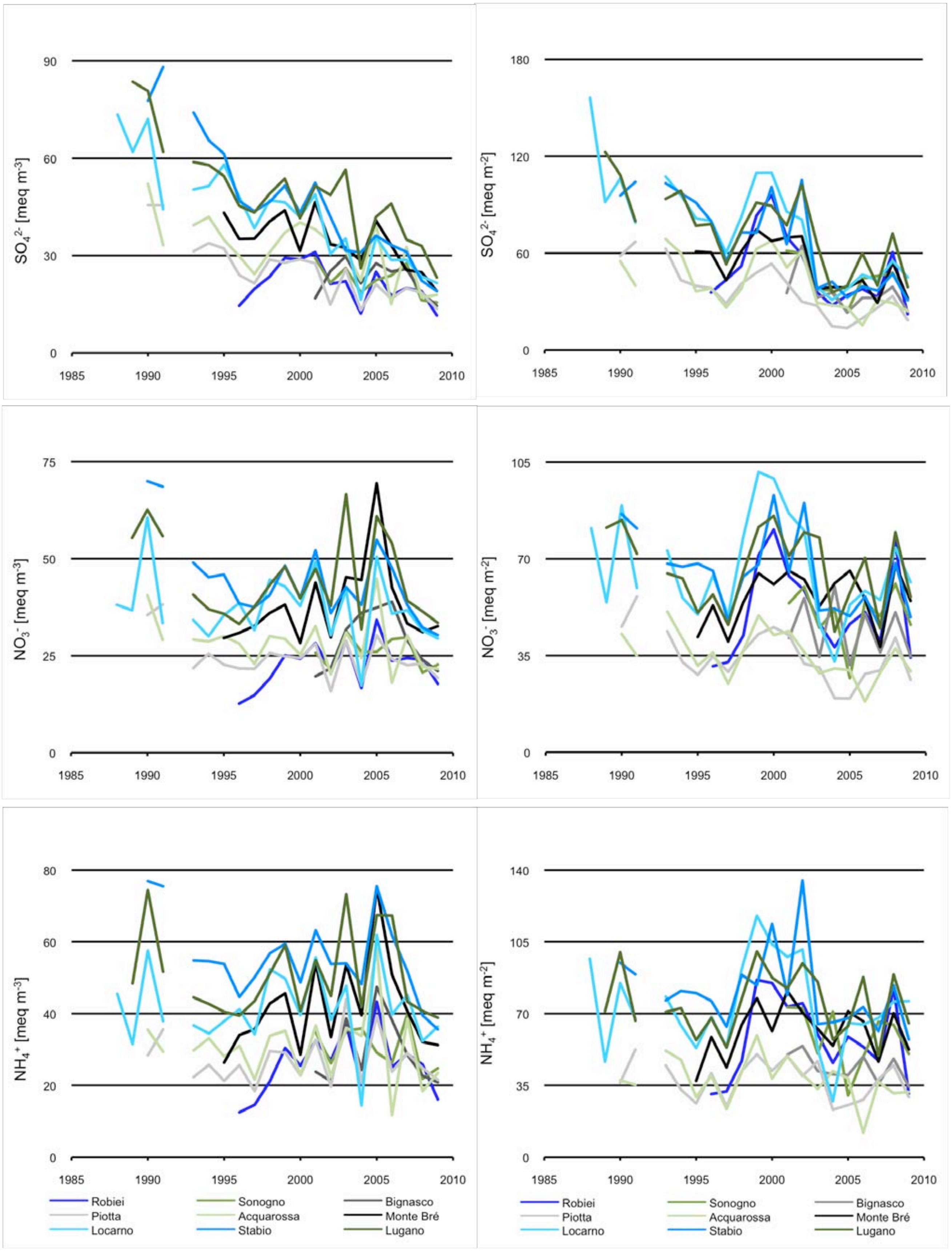


Figure 2.5 Temporal variations of annual mean rain water concentrations and deposition rates
Base cations correspond to the sum of calcium, magnesium, sodium and potassium.



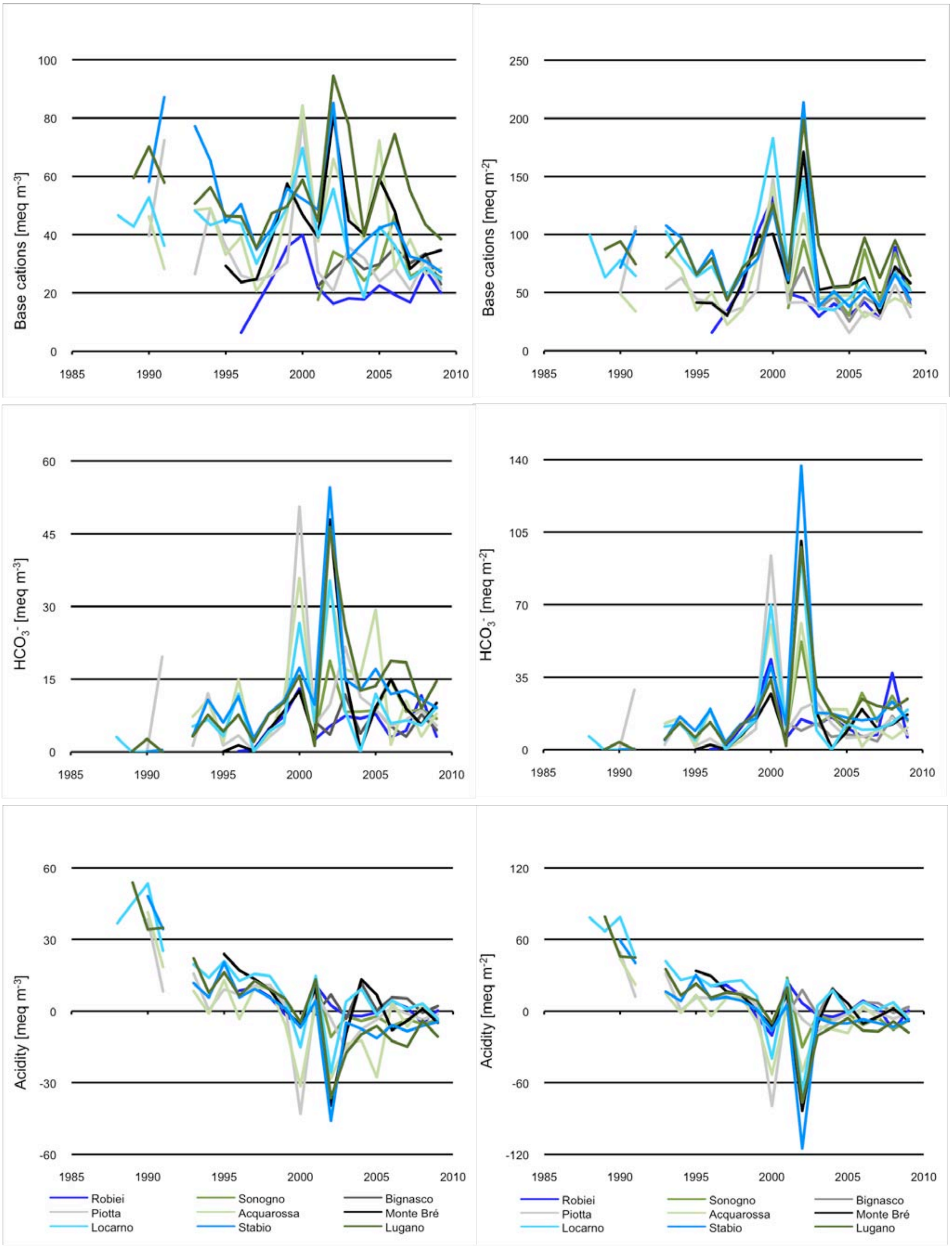
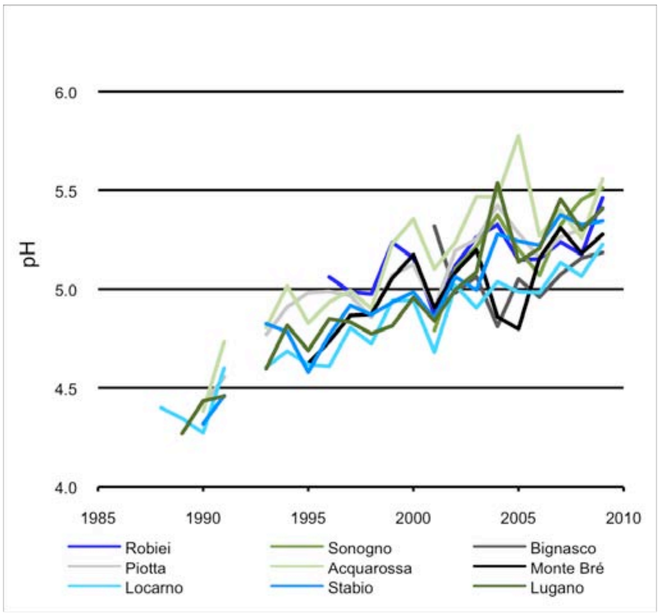

Base cations [meq m-3]
Base cations [meq m-2]
HCO3- [meq m-3]
HCO3- [meq m-2]
Acidity [meq m-3]
Acidity [meq m-2]
1985
1990
1995
2000
2005
2010
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Monte Bré
Locarno
Stabio
Lugano

Figure 2.6 Temporal variations of annual mean pH of rain water



A detailed trend analysis was performed for the last 10 years (2000-2009). In order to better understand trends in atmospheric chemistry, trends in rain water volume were subtracted from trends in rain water concentrations (partial Mann-Kendall test, see chapter 2.4). The results are presented in Tab. 2.3. p-values < 0.05 are marked in red and indicate a significant trend. Interestingly, even after 2000 sulphate concentrations decreased significantly at all sampling stations. Highest rates occurred at Lugano, Locarno Monti and Stabio where concentrations were also higher. A significant reduction of nitrate concentrations can be observed only at Locarno Monti and Piotta. At Locarno Monti, Piotta, Robiei and Sonogno also concentrations of ammonia decreased significantly. Also base cations decreased significantly at 3 sites: Acquarossa, Locarno Monti and Stabio. The overall decrease in concentrations of sulphate lead to a significant decrease in acidity only at Stabio. At most other sites the decrease in acid anions was probably compensated by a simultaneous decrease in ammonia and base cations. On the contrary, a significant decrease of pH could be observed for Locarno Monti, Lugano and Piotta. In order to better understand the correlation between trends in deposition and trends in surface water chemistry, a Mann-Kendall trend analysis on monthly mean deposition (in this case the precipitation volume was not added as a covariate (Tab. 2.4). However, results did not differ greatly from the trend analysis performed on monthly mean concentration.

Table 2.3 Results from trend analyses (significant trends in red) performed on mean monthly concentrations weighted with the precipitation volume during the period 2000-2009.
p corresponds to the probability level obtained with the Mann-Kendall test and the rate (meq m^{-3} yr^{-1}) to the Sen's slope

Station		Acquarossa	Bignasco	Monte Brè	Locarno Monti	Lugano	Piotta	Robiei	Sonogno	Stabio
SO_4^{2-}	p	0.007	0.045	0.006	0.006	0.030	0.014	0.007	0.019	0.011
	rate	-4.00	-1.66	-3.30	-5.56	-7.61	-2.00	-1.70	-1.53	-5.40
NO_3^-	p	0.070	0.092	0.324	0.029	0.298	0.018	0.213	0.341	0.113
	rate	-2.35	-1.75	-3.45	-8.66	-9.13	-1.91	-0.82	-1.34	-6.43
Cl^-	p	0.017	0.251	0.621	0.015	0.196	0.164	0.583	0.111	0.834
	rate	-0.22	0.08	-0.15	-0.40	-0.44	-0.24	0.17	0.16	-0.01
HCO_3^-	p	0.131	0.947	0.099	0.702	0.461	0.170	0.458	0.844	0.068
	rate	-1.58	-1.00	-0.05	-0.89	-0.52	-1.31	-0.17	-0.63	-0.41
NH_4^+	p	0.129	0.121	0.306	0.013	0.251	0.041	0.011	0.045	0.055
	rate	-2.23	-2.32	-4.20	-8.75	-9.50	-2.12	-1.82	-2.15	-7.43
Base cations	p	0.038	0.403	0.327	0.026	0.230	0.121	0.238	0.066	0.017
	rate	-4.83	-1.31	-1.11	-3.77	-5.71	-2.38	-0.04	-0.82	-2.67
H^+	p	0.568	0.734	0.018	0.027	0.047	0.027	0.165	0.270	0.004
	rate	-0.92	-0.63	-1.91	-3.43	-3.23	-1.16	-0.67	-0.50	-2.33
Acidity	p	0.529	0.941	0.017	0.083	0.111	0.229	0.571	0.928	0.004
	rate	0.66	0.38	-1.86	-2.54	-2.70	0.15	-0.50	0.12	-1.92
Acidity=H^+-HCO_3^-	rate	0.66	0.37	-1.86	-2.54	-2.71	0.15	-0.50	0.13	-1.92
Acidity=AA-C	rate	0.49	0.30	-2.65	-2.10	-1.97	0.35	-0.49	0.26	-1.74

Table 2.4 Results from trend analyses (significant trends in red) performed on mean monthly deposition during the period 2000-2009.
p corresponds to the probability level obtained with the Mann-Kendall test and the rate (meq m^{-2} yr^{-1}) to the Sen's slope

Station		Acquarossa	Bignasco	Monte Brè	Locarno Monti	Lugano	Piotta	Robiei	Sonogno	Stabio
SO_4^{2-}	p	0.006	0.492	0.089	0.036	0.025	0.091	0.058	0.235	0.035
	rate	-0.35	-0.15	-0.30	-0.57	-0.58	-0.24	-0.48	-0.20	-0.61
NO_3^-	p	0.070	0.589	0.643	0.258	0.170	0.243	0.2145	0.666	0.096
	rate	-0.12	-0.01	-0.10	-0.45	-0.45	-0.16	-0.27	-0.11	-0.45
Cl^-	p	0.074	0.089	0.620	0.371	0.229	0.314	0.848	0.981	0.717
	rate	-0.03	0.06	-0.02	-0.06	-0.06	-0.02	-0.01	0.06	-0.05
HCO_3^-	p	0.121	0.873	0.089	0.835	0.468	0.186	0.414	0.889	0.399
	rate	-0.24	-0.01	-0.08	-0.28	-0.11	-0.44	-0.14	-0.12	-0.32
NH_4^+	p	0.067	0.711	0.411	0.184	0.042	0.107	0.031	0.321	0.068
	rate	-0.13	-0.13	-0.17	-0.47	-0.48	-0.15	-0.42	-0.23	-0.61
Base cations	p	0.016	0.292	0.459	0.126	0.162	0.373	0.764	0.638	0.160
	rate	-0.57	0.07	-0.25	-0.75	-0.57	-0.60	-0.36	-0.08	-0.69
H^+	p	0.642	0.883	0.062	0.091	0.089	0.117	0.183	0.129	0.014
	rate	-0.04	-0.02	-0.08	-0.20	-0.16	-0.10	-0.15	-0.10	-0.15
Acidity	p	0.509	0.785	0.090	0.124	0.229	0.965	0.801	0.417	0.118
	rate	0.20	0.00	0.00	0.08	-0.05	0.34	0.00	0.02	0.17
Acidity=H^+-HCO_3^-	rate	0.20	0.00	0.00	0.08	-0.05	0.34	0.00	0.02	0.17
Acidity=AA-C	rate	0.19	-0.04	0.00	0.15	-0.04	0.33	0.02	0.05	0.20

2.5.2 Alpine rivers

Annual mean concentrations of the chemical parameters measured in river Maggia, Vedeggio and Verzasca during 2009 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.

Table 2.5 Average concentrations in river water during 2009.

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	2009	7.4	57.0	257	7.52	0.61	1.55	1.31	0.012	8.42	0.55	1.22	0.42	4.51	6.9	10.2	<0.2	<0.2	<0.8	<0.9
Vedeggio	2009	7.1	42.6	148	4.74	0.88	1.56	0.49	0.012	5.92	0.99	0.93	0.68	6.35	8.5	10.9	<0.2	<0.3	1.0	1.1
Verzasca	2009	6.8	23.7	65	2.90	0.23	0.69	0.53	0.012	3.79	0.65	0.18	0.24	3.50	24.1	46.4	<0.2	<0.2	<1.3	<2.0

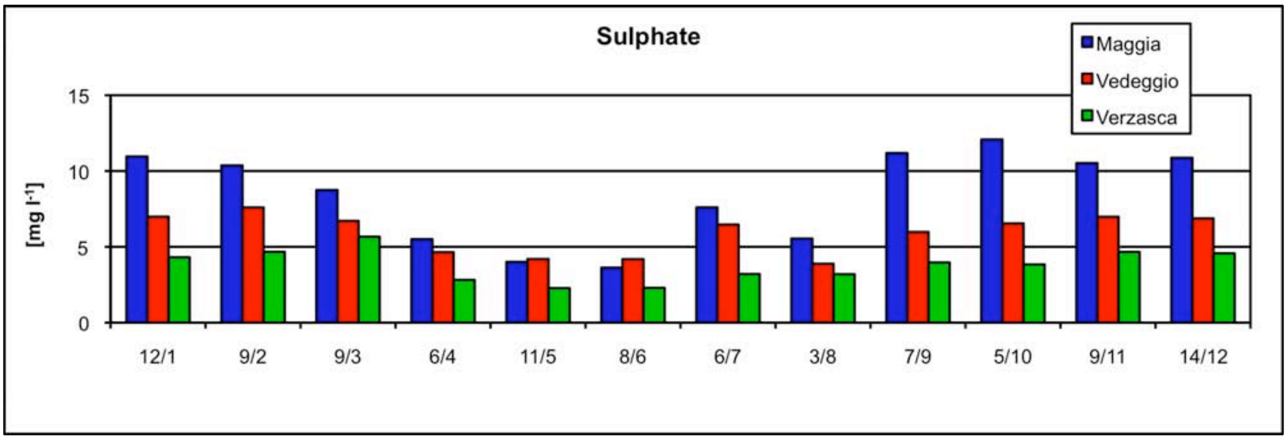
During 2009 average alkalinity was 257 μeq l^{-1} in river Maggia, 148 μeq l^{-1} in river Vedeggio and 65 μeq l^{-1} in river Verzasca. Based on these data River Verzasca and river Vedeggio have low alkalinities (50-200 μeq l^{-1}), but no river is sensitive to acidification. The same is suggested by their minimum alkalinities that were always > 0 μeq l^{-1}. Average pH was 7.4 in river Maggia, 7.1 in river Vedeggio and 6.8 in river Verzasca. Their minimum pH's were not much lower (Maggia: 7.1, Vedeggio: 7.0, Verzasca: 6.4). As a consequence of the relatively high pH's, dissolved aluminium concentrations were on average low. However, higher aluminium concentrations up to 19 μeq l^{-1} in river Maggia and 34 μeq l^{-1} in river Vedeggio occurred during high flow events in April-June and August. Extremely high concentrations of aluminium were measured in river Verzasca during one occasion in May, when a landslip occurred before the sampling point.

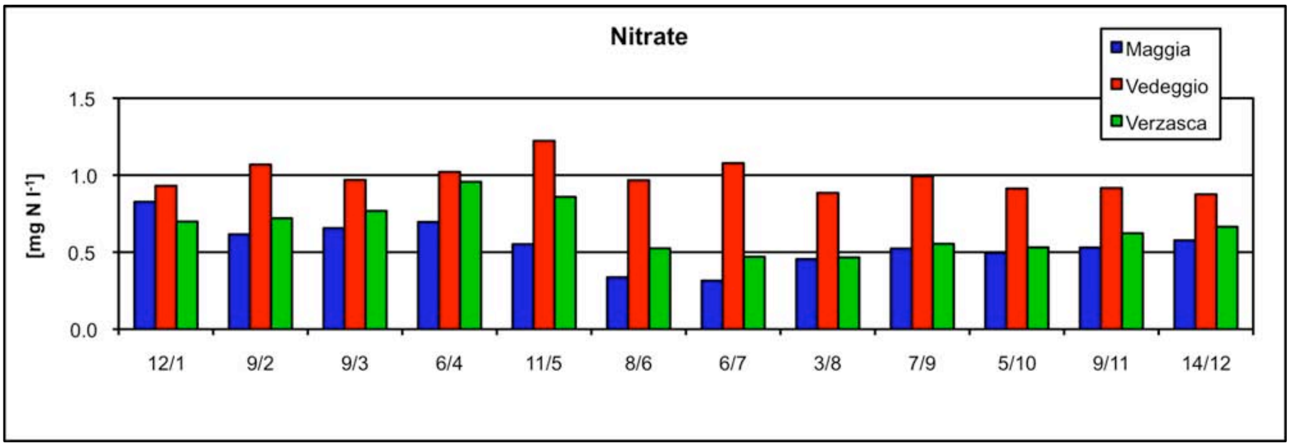
Fig. 2.9 shows the variations of the concentrations of sulphate, nitrate, base cations, alkalinity, pH and dissolved aluminium during 2009. It can be observed that the temporal variation of these parameters is more or less the same in all 3 rivers. For sulphate, base cations, alkalinity and pH lowest values were measured in May/June. On the contrary, during the same period nitrate concentrations were relatively high.

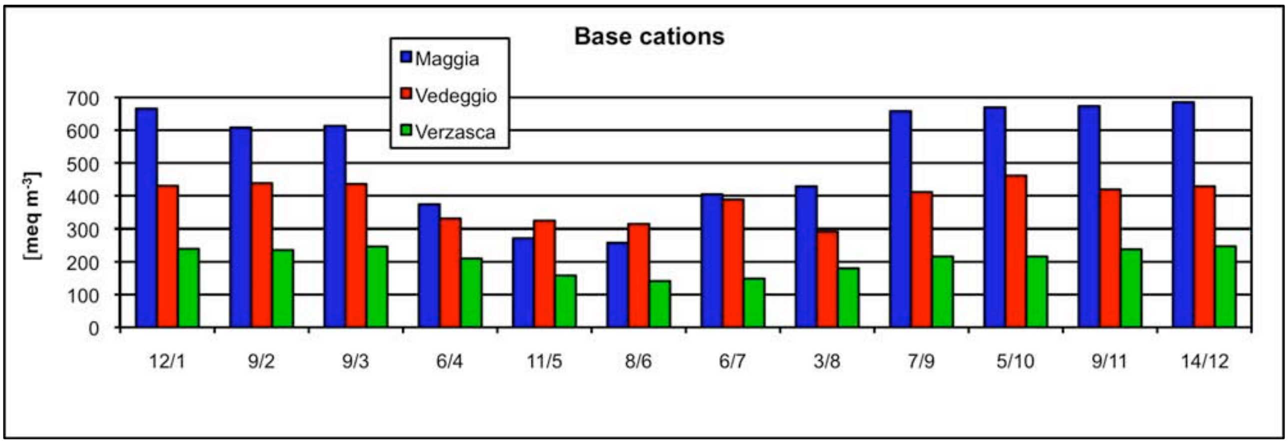
Comparing the seasonality of concentrations during 2009 with the temporal variations of the river discharge (Fig. 2.10, for river Maggia without the influence of hydropower production), it can be observed that discharge maxima overlap with concentrations minima of sulphate, base cations, alkalinity, pH and silica. 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, silica 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/August, 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 2009, high concentrations of nitrate occurred during periods with high flow like May/June, suggesting either leakage from the soils either nitrate peaks in precipitation/snow. However, high concentrations of nitrate could be observed for the entire winter-spring period (January to June) overlapping with the period with poor photosynthetic activity, suggesting that concentrations of nitrate are determined by more than one factor.

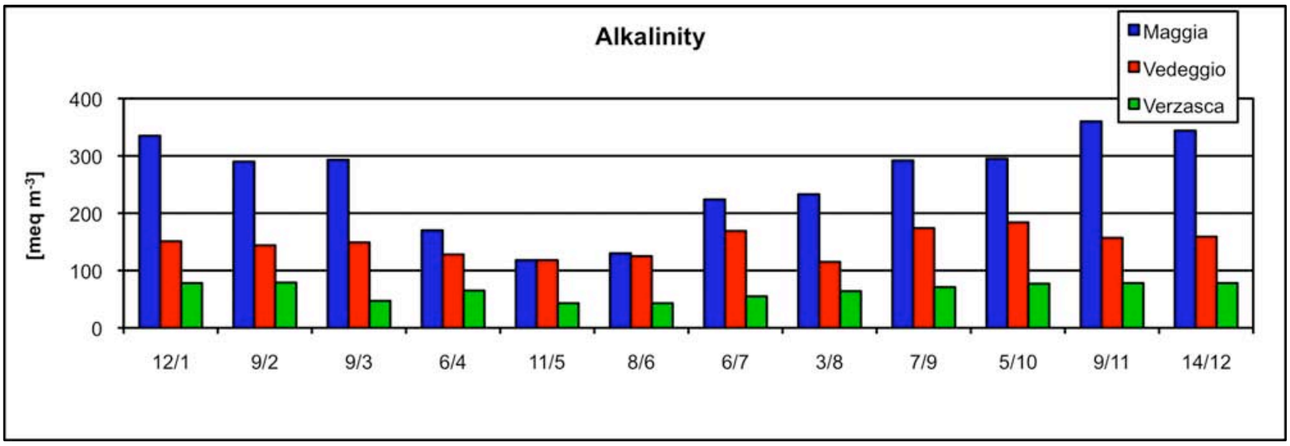
Figure 2.9 Concentrations of the main chemical parameters in river water during 2009

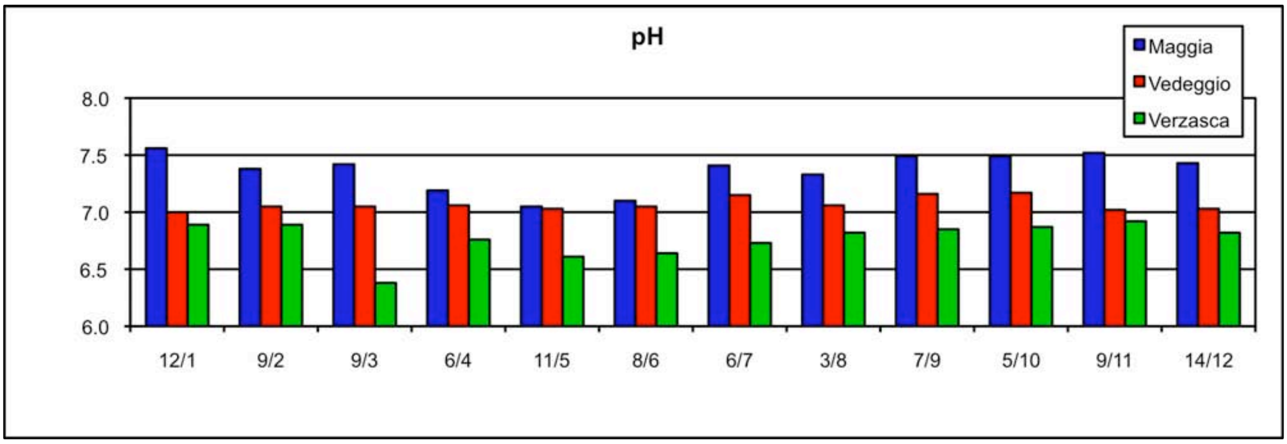
Base cations correspond to the sum of calcium, magnesium, sodium and potassium.

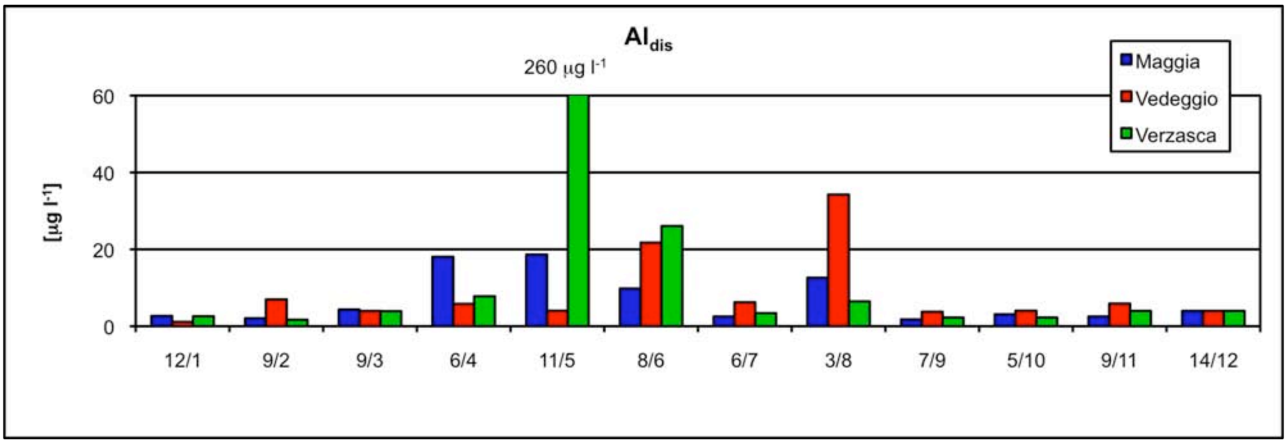







Alkalinity
[meq m-3]
400
300
200
100
0
12/1
9/2
9/3
6/4
11/5
8/6
6/7
3/8
7/9
5/10
9/11
14/12
Maggia
Vedeggio
Verzasca


pH
8.0
7.5
7.0
6.5
6.0
12/1
9/2
9/3
6/4
11/5
8/6
6/7
3/8
7/9
5/10
9/11
14/12
Maggia
Vedeggio
Verzasca


Al dis
260 µg l-1
[µg l-1]
60
40
20
0
12/1
9/2
9/3
6/4
11/5
8/6
6/7
3/8
7/9
5/10
9/11
14/12
Maggia
Vedeggio
Verzasca

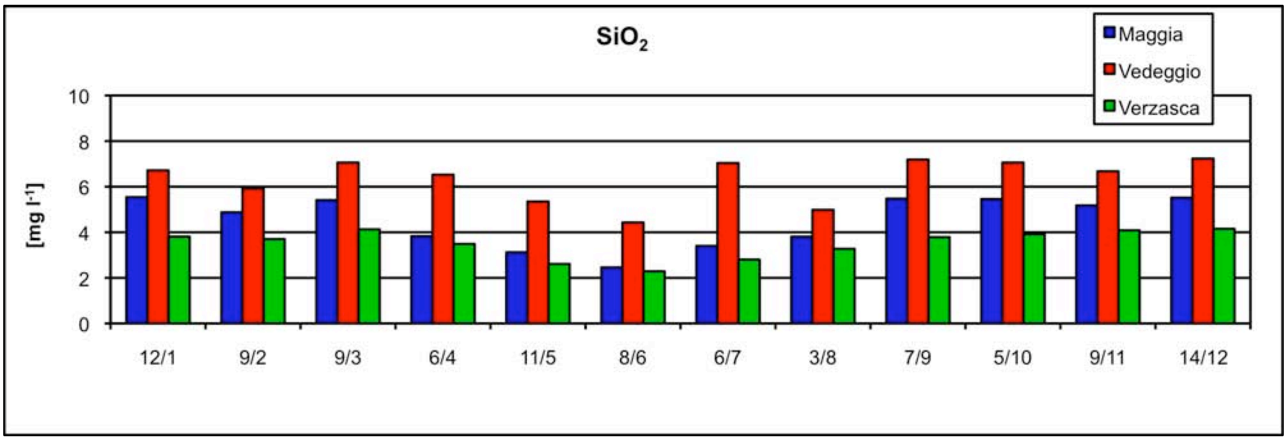
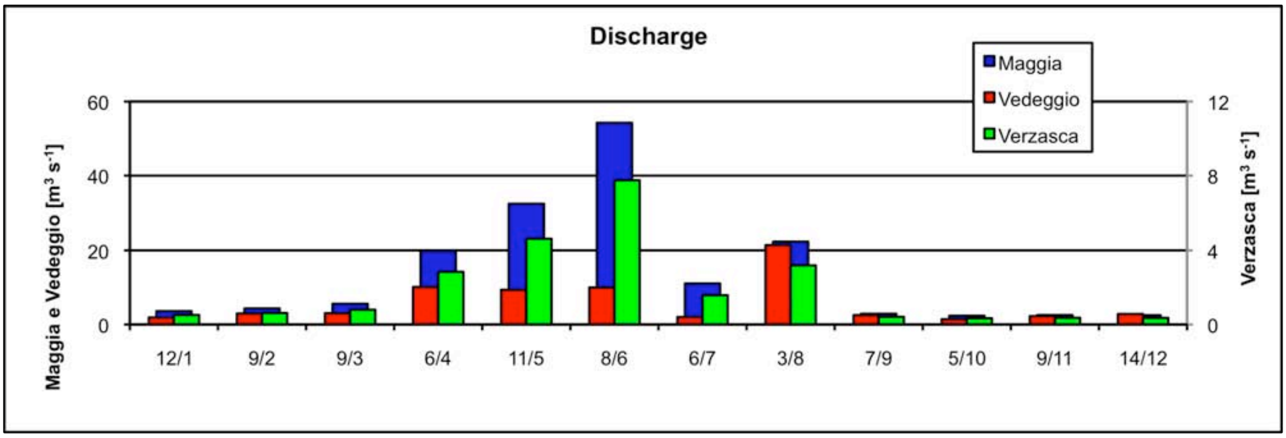

SiO2
[mg l-1]
10
8
6
4
2
0
12/1
9/2
9/3
6/4
11/5
8/6
6/7
3/8
7/9
5/10
9/11
14/12
Maggia
Vedeggio
Verzasca

Figure 2.10 Daily average discharge during sampling days in 2009

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 2009 are presented graphically in Fig. 2.11. 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. This is also the reason why we performed a partial Mann-Kendall test for the period 2000-2009 with concentrations as response variables and discharge as explanatory variable. Results of the trend analysis are shown in Tab. 2.6. Differently than what observed for precipitation, sulphate concentrations in river water did not decrease significantly during the last 10 years. The same can be observed for nitrate and base cations. On the contrary, a significant increase in concentrations of base cations seemed to have occurred in river Maggia and Verzasca. This increase caused in river Verzasca and increase in alkalinity as well.

Figure 2.11 Annual mean concentrations of the main chemical parameters in river water from 2000 to 2009

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

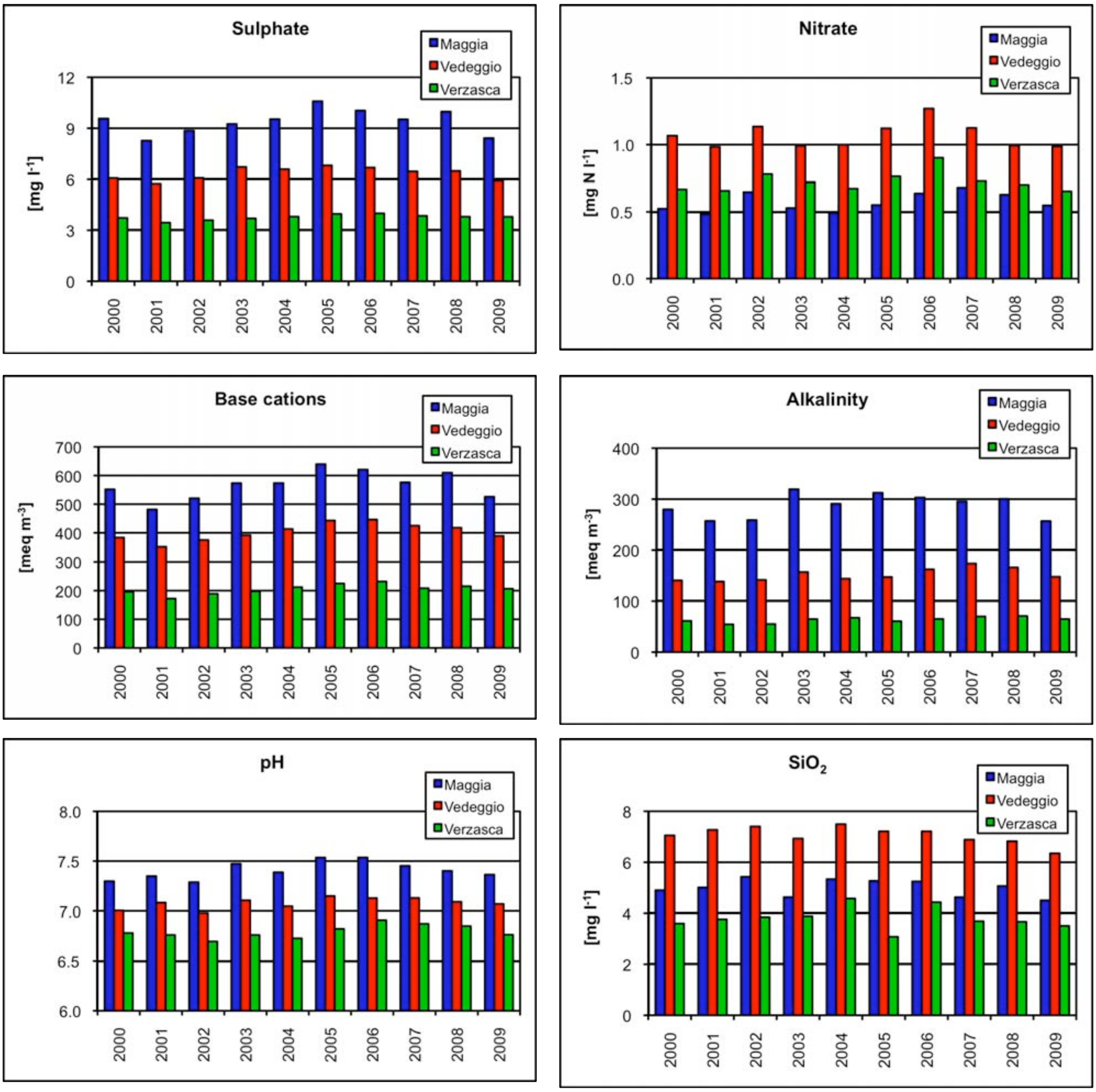


Figure 2.12 Yearly mean discharge of river Maggia, Vedeggio and Verzasca from 2000 to 2009

Discharge of river Vedeggio at Isone was measured by IST (2001-2009). Discharge of river Verzasca at Sonogno and Maggia at Bignasco (without influence of hydropower production) were estimated by discharge values of Verzasca at Lavertezzo published by BWG (2001-2004) and BAFU (2005-2010).

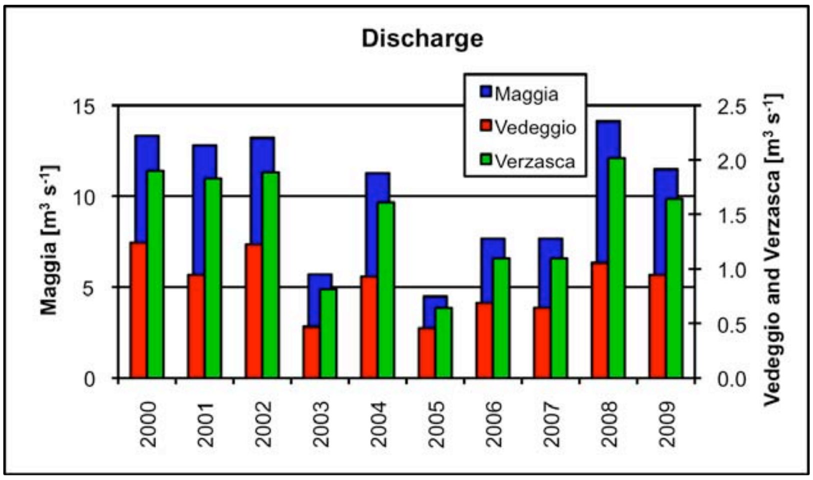


Table 2.6 Results from trend analyses (significant trends in red) during the period 2000-2009.

p corresponds to the probability level obtained with the Mann-Kendall test and the rate (meq m^{-3} yr^{-1}) to the Sen's slope

River	SO_4^{2-}		NO_3^-		Cl^-		Base cations		H^+		Alcalinity		SiO_2	
	p	rate	p	rate	p	rate	p	rate	p	rate	p	rate	p	rate
Maggia	0.328	1.315	0.050	0.742	0.003	1.912	0.049	8.784	0.113	-9.26E--4	0.141	2.247	0.230	-0.023
Vedeggio	0.279	0.918	0.819	-0.193	0.344	0.000	0.075	6.583	0.358	-8.55E-4	0.064	2.685	0.016	-0.080
Verzasca	0.044	0.795	0.490	0.000	0.168	-0.167	0.010	4.345	0.201	-4.58E-3	0.036	1.549	0.267	-0.013

2.5.3 Alpine lake

Yearly mean concentrations of the main chemical parameters measured in lake surface water during 2009 are presented in Tab. 2.7. 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 7.7 and 19.1 µS cm^{-1}, alkalinity between -4 and 76 µeq l^{-1}, pH between 5.3 and 6.9, sulphate between 0.94 and 4.42 mg l^{-1}, nitrate between 0.08 and 0.33 mg N l^{-1}, dissolved organic carbon between 0.11 and 0.65 mg C l^{-1}, reactive dissolved silica between 0.72 and 2.75 mg SiO_2 l^{-1} and total dissolved aluminium between 0.9 and 71.1 µg l^{-1}.

Table 2.7 Average lake surface water concentrations during 2009

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	8.5	5.5	-1	0.85	0.07	0.27	0.14	0.008	1.38	0.29	0.14	0.47	1.29	45.0	51.9	<0.2	<0.4	3.9	4.3
Lago di Tomè	8.8	5.8	9	0.82	0.07	0.28	0.14	0.006	1.40	0.33	0.11	0.19	1.53	16.1	19.5	<0.5	<0.7	2.9	3.1
Lago dei Porchieirsc	19.1	6.8	60	2.39	0.12	0.37	0.37	0.007	3.32	0.30	0.09	0.12	2.51	1.6	1.9	<0.2	0.4	0.4	0.4
Lago Barone	9.0	6.0	12	0.93	0.06	0.21	0.15	0.024	1.56	0.24	0.10	0.17	1.09	3.0	1.2	<0.2	<0.2	0.9	1.1
Laghetto Gardiscio	8.3	5.3	-4	0.49	0.09	0.17	0.22	0.021	1.65	0.18	0.09	0.11	0.72	71.1	97.2	<0.2	<0.2	2.3	2.8
Lago Leit	17.2	6.4	24	1.73	0.23	0.30	0.37	0.010	4.42	0.17	0.08	0.22	1.68	1.7	3.1	<0.2	<0.2	0.9	1.2
Lago di Morghirolo	12.8	6.6	36	1.37	0.17	0.29	0.39	<0.010	2.37	0.18	0.08	0.21	1.63	1.1	2.1	<0.2	<0.2	0.7	0.7
Lago di Mognòla	17.9	6.9	53	1.90	0.25	0.53	0.45	0.013	3.45	0.23	0.10	0.18	2.63	2.0	3.1	<0.2	<0.2	0.8	0.8
Laghetto Inferiore	10.2	6.6	31	1.16	0.09	0.28	0.33	0.007	1.39	0.22	0.08	0.21	1.30	3.7	6.9	<0.2	<0.2	1.6	1.8
Laghetto Superiore	8.6	6.4	25	0.98	0.08	0.22	0.26	0.007	1.08	0.20	0.08	0.23	1.03	4.8	8.1	<0.2	<0.2	0.9	0.9
Lago Nero	15.5	6.7	55	1.96	0.15	0.32	0.38	0.009	2.59	0.17	0.09	0.18	1.19	0.9	1.8	<0.2	<0.2	0.5	0.6
Lago Bianco	73.7	7.6	397	11.25	0.72	0.30	0.66	0.007	10.58	0.15	0.11	0.23	1.52	5.3	6.5	<0.2	<0.2	0.5	0.6
Lago della Froda	13.4	6.7	46	1.94	0.09	0.24	0.21	0.007	2.12	0.20	0.08	0.18	1.25	2.0	4.2	<0.2	<0.2	0.6	0.6
Lago d'Antabia	11.7	6.8	50	1.63	0.06	0.35	0.21	0.011	1.07	0.28	0.10	0.16	1.94	1.8	4.5	<0.2	<0.2	0.6	0.7
Lago della Crosa	7.7	6.4	19	0.89	0.06	0.23	0.15	0.009	0.94	0.28	0.10	0.16	1.24	1.0	2.4	<0.2	<0.2	0.9	1.0
Lago d'Orsalìa	8.3	6.3	22	0.93	0.06	0.22	0.13	0.017	0.95	0.29	0.10	0.15	1.18	5.1	9.9	<0.2	<0.3	1.2	1.3
Schwarzsee	10.2	6.5	35	1.24	0.08	0.24	0.18	0.007	1.30	0.24	0.09	0.16	1.39	5.4	10.1	<0.2	<0.2	0.7	0.8
Laghi dei Pozzöi	8.0	6.5	33	0.94	0.09	0.28	0.15	0.007	1.10	0.08	0.10	0.65	1.60	4.6	15.5	<0.2	<0.2	0.8	1.1
Lago di Sfille	10.1	6.5	35	1.21	0.10	0.35	0.12	0.008	1.57	0.16	0.11	0.40	1.74	5.7	14.4	<0.2	<0.2	1.2	1.6
Lago di Sascòla	8.9	6.1	18	0.80	0.12	0.26	0.28	0.011	1.36	0.29	0.09	0.57	1.29	12.7	26.8	<0.2	<0.2	1.4	1.7
Lago d'Alzasca	17.6	6.8	76	2.04	0.22	0.48	0.45	0.015	2.19	0.32	0.15	0.33	2.75	1.6	2.0	<0.2	<0.2	0.4	0.5

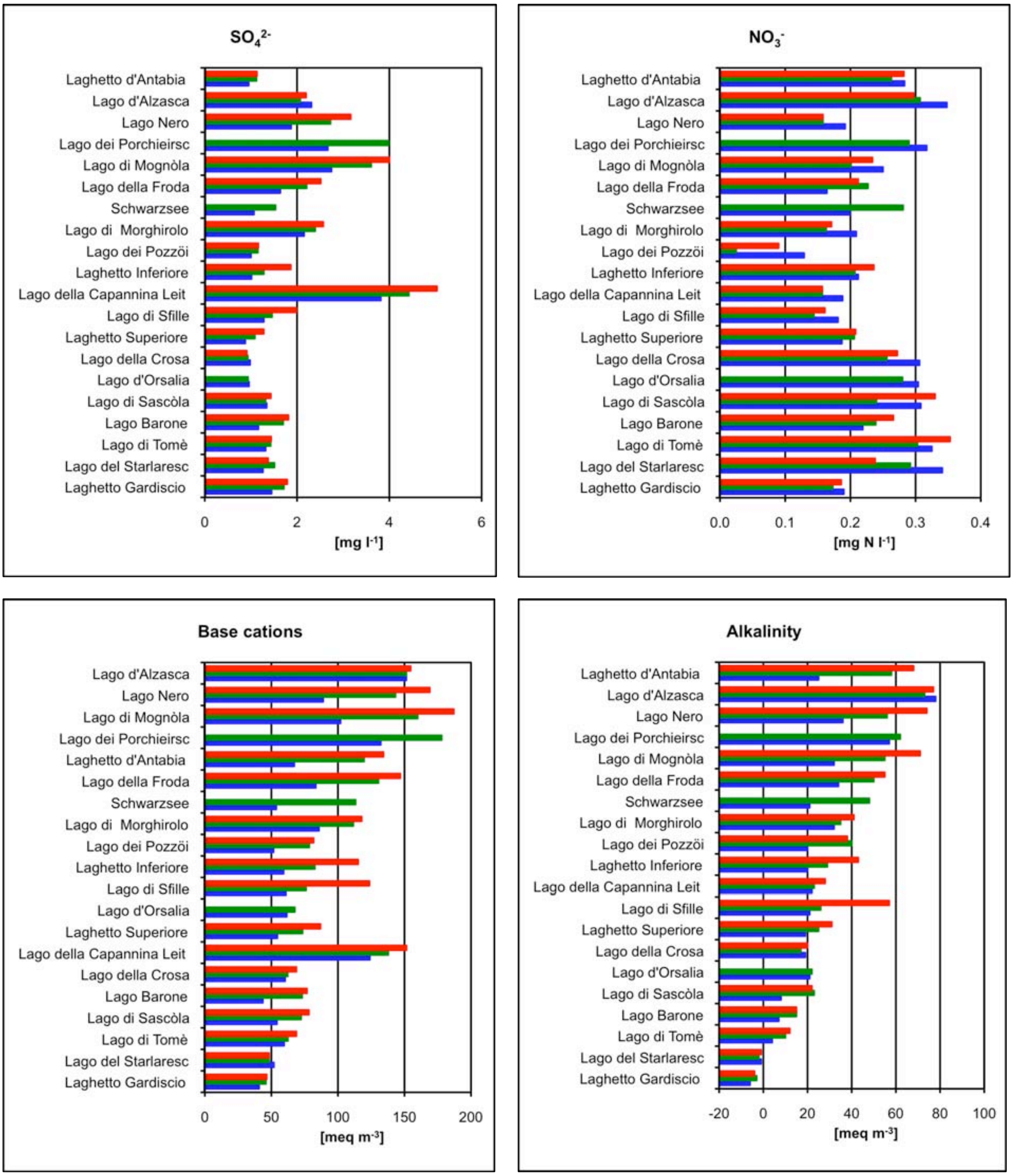
In order to better compare chemistry of lakes with low alkalinities, measured values of the main parameters are shown graphically in Fig. 2.7.

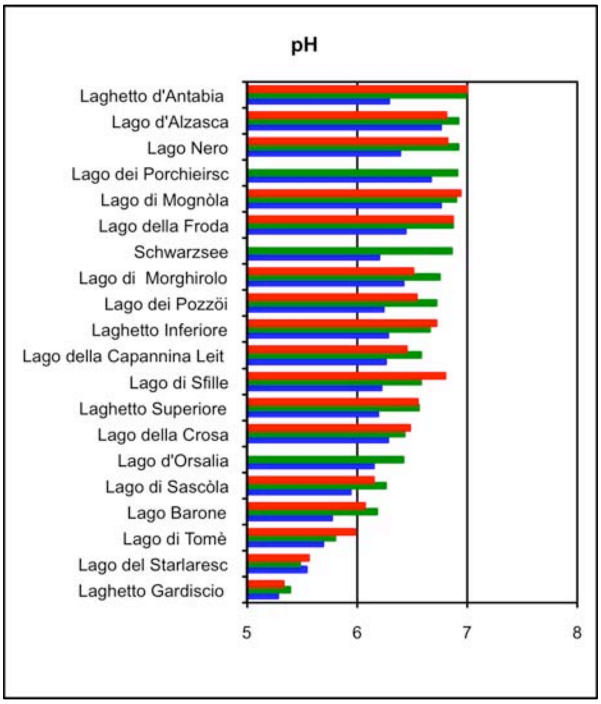
During 2009 alkalinities below 0 μeq l^{-1} were detected in 3 lakes (Laghetto Gardiscio and Lago del Starlaresc da Sgiof during 3 occasions and Lago di Tomè during one occasion). Only one lake had alkalinities always above 50 μeq l^{-1} (Lago d'Alzasca) and was therefore not sensitive to acidifications. All other 19 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 13 and 111 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.

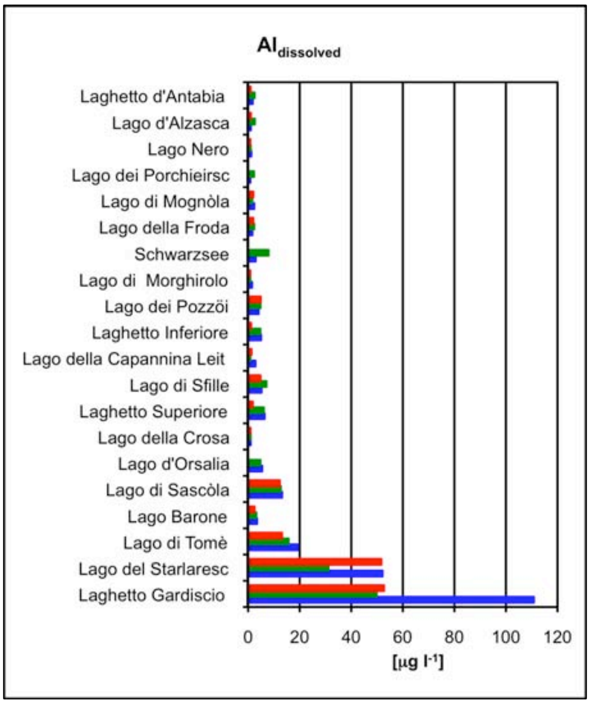
Fig. 2.7 also shows some seasonal differences. During 2009 in most lakes alkalinity and pH and concentrations of sulphate, base cations, and silica were lower in July than in September and October, while for nitrate the opposite can be observed. This result is in agreement with what observed for river chemistry, where the elevated discharge in spring caused a dilution of sulphate, base cations, silica and a combination of dilution and consumption of alkalinity. For nitrate, as discussed in the river paragraph more than one factor may be responsible for their higher concentrations at the beginning of July with respect to October and November: leakage from the soils during elevated discharge periods, nitrate peaks in precipitation/snow, period of poor photosynthetic activity.

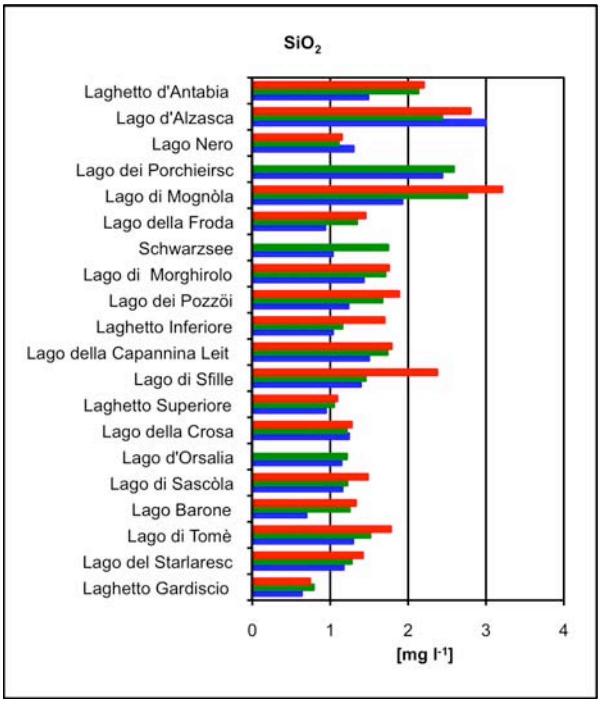
Figure 2.7 Annual average concentrations of the main chemical parameters in 20 Alpine lakes during 2009

Blue: 6.7.09, green: 14.9.09, red: 26.10.10; base cations correspond to the sum of calcium, magnesium, sodium and potassium.




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


Al dissolved
Laghetto d'Antabia
Lago d'Alzasca
Lago Nero
Lago dei Porchieirsc
Lago di Mognòla
Lago della Froda
Schwarzsee
Lago di Morghirolo
Lago dei Pozzöi
Laghetto Inferiore
Lago della Capannina Leit
Lago di Sfille
Laghetto Superiore
Lago della Crosa
Lago d'Orsalia
Lago di Sascòla
Lago Barone
Lago di Tomè
Lago del Starlaresc
Laghetto Gardiscio
0
20
40
60
80
100
120
[µg l-1]

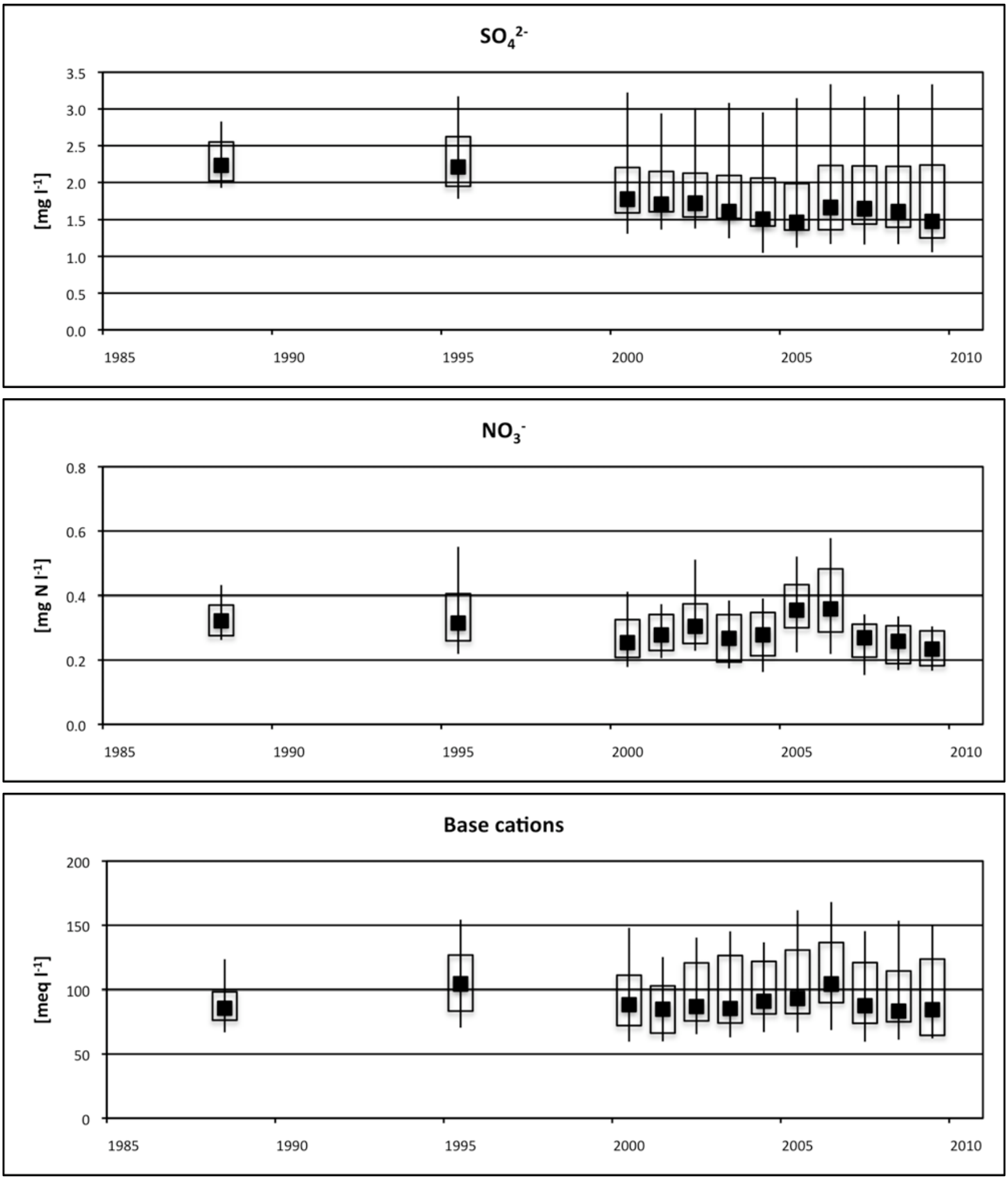

SiO2
Laghetto d'Antabia
Lago d'Alzasca
Lago Nero
Lago dei Porchieirsc
Lago di Mognòla
Lago della Froda
Schwarzsee
Lago di Morghirolo
Lago dei Pozzöi
Laghetto Inferiore
Lago della Capannina Leit
Lago di Sfille
Laghetto Superiore
Lago della Crosa
Lago d'Orsalia
Lago di Sascòla
Lago Barone
Lago di Tomè
Lago del Starlaresc
Laghetto Gardiscio
0
1
2
3
4
[mg l-1]

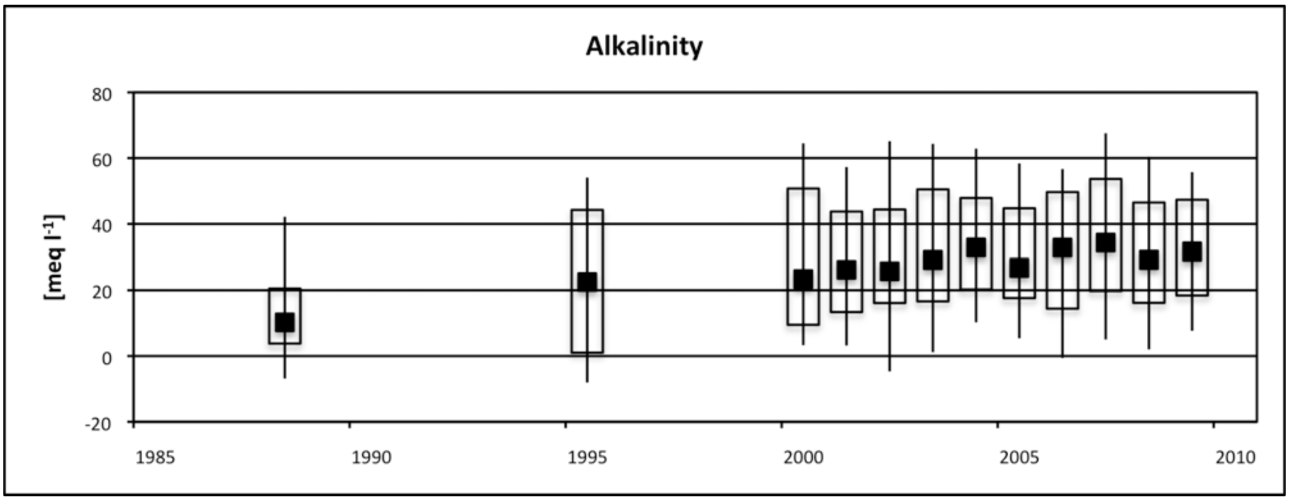
In order to show temporal variations of lake quality, annual median values of pH, alkalinity and concentrations of non sea salt base cations, sulphate and nitrate of all lakes with their 10th, 25th, 75th and 90th percentile values are represented in Fig. 2.8. Only years, where all 20 alpine lakes have been monitored were chosen. As already discussed in Steingruber and Colombo (2006), after 1980's sulphate concentrations decreased, mainly because of the reduction of the sulphur content in heating oils and the partial substitution of sulphur rich carbon with other fossil fuels. As a consequence lake alkalinity and pH increased. For base cations and nitrate concentrations no trend can be observed. Aluminium concentrations of the 3 most acidic lakes are presented in Fig. 2.9. A decrease in concentrations can be observed.

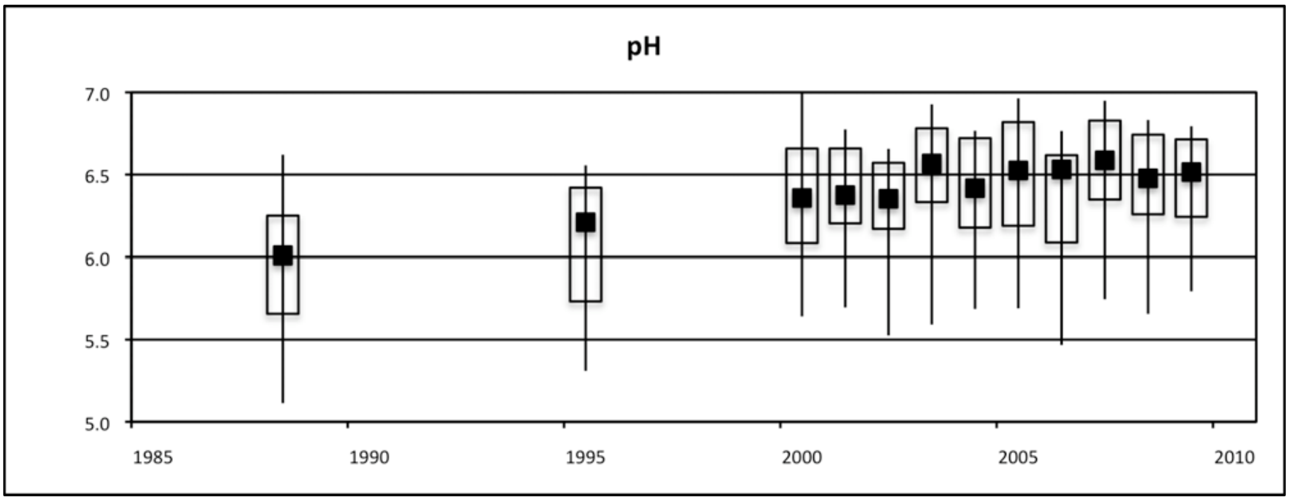
Results of a detailed trend analysis of the main parameters during the last 10 years are presented in Tab.2.8. Accordingly to what observed for rain water concentrations, in 8 lakes a significant decrease in sulphate concentrations can be observed. However, only in Lago di Sfille this decrease caused recently a significant increase in lake alkalinity. A significant increase in sulphate concentrations occurred in lakes with relatively high sulphate concentrations (Lago di Morghirolo, Lago di Mognòla, Lago Nero).

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 2009

Base cations correspond to the sum of calcium, magnesium, sodium 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

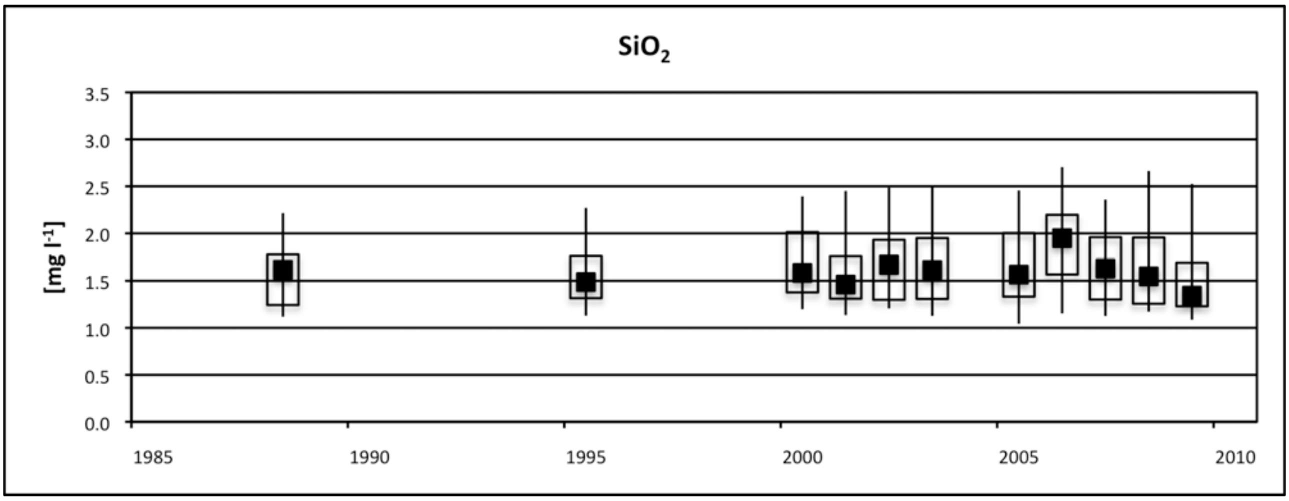

SiO2
[mg l-1]
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1985
1990
1995
2000
2005
2010

Figure 2.9 Temporal variations of dissolved aluminium in the 3 most acidic lakes from 1988 to 2009

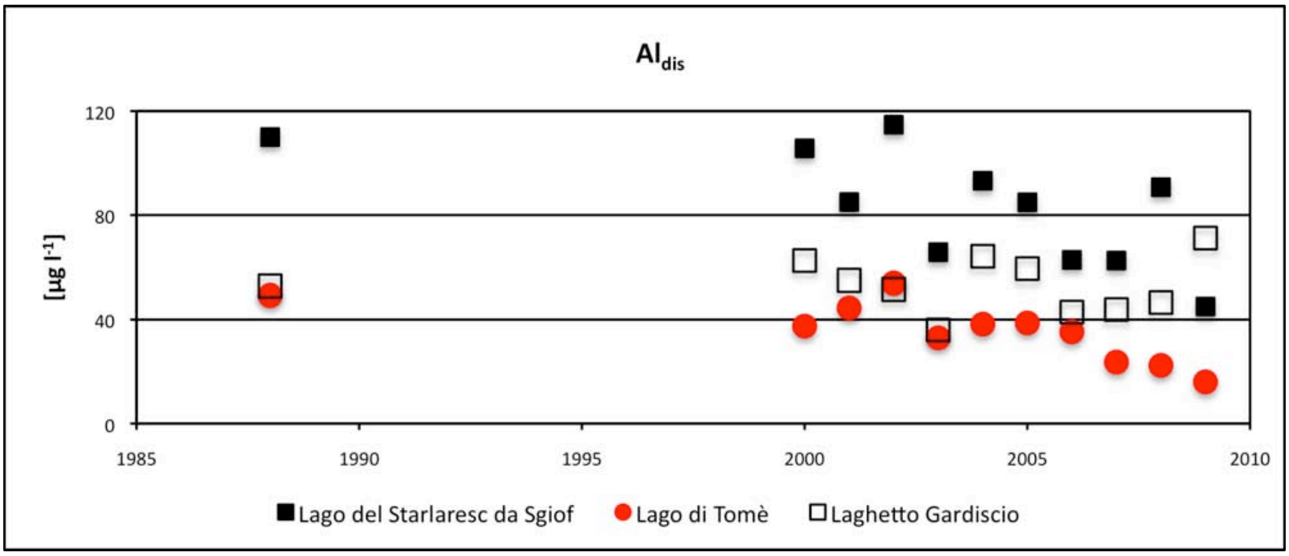


Table 2.8 Results from trend analyses (significant trends in red) during the period 2000-2009.

p corresponds to the probability level obtained with the Mann-Kendall test and the rate (meq m^{-3} yr^{-1}) to the Sen's slope

Lake	SO_4^{2-}		NO_3^-		Cl^-		Base cations		H^+		Alcalinity		SiO_2	
	p	rate	p		p	rate	p	rate	p	rate	p	rate	p	rate
Lago del Starlaresc da Sgiof	0.005	-0.67	0.136	-1.03	0.039	-0.29	0.031	-1.42	0.031	-0.54	0.058	1.31	0.551	-0.02
Lago di Tomè	0.011	-0.47	0.181	-1.61	0.169	-0.10	0.366	-0.83	0.366	-0.08	0.312	0.74	0.696	-0.01
Lago dei Porchieirsc	0.743	1.15	0.854	-0.46	0.232	-0.17	0.451	3.01	0.451	-0.01	0.443	0.78	0.496	0.02
Lago Barone	0.740	0.02	0.306	-0.53	0.067	-0.10	0.844	0.72	0.844	-0.01	0.882	0.48	0.619	-0.01
Laghetto Gardiscio	0.527	0.22	0.543	-0.30	0.129	-0.08	1.000	0.16	1.000	0.03	0.892	0.00	0.943	0.00
Lago Leit	0.107	1.46	0.253	-0.38	0.004	-0.12	0.070	3.40	0.070	-0.02	0.444	0.49	0.172	0.02
Lago di Morghirolo	0.014	0.85	0.576	-0.26	0.065	-0.14	0.147	2.63	0.147	-0.01	0.062	0.99	0.576	0.01
Lago di Mognòla	0.017	1.04	0.875	-0.37	0.298	-0.06	0.514	2.66	0.514	-0.01	0.468	0.51	0.303	0.03
Laghetto Inferiore	0.037	-0.39	0.380	-0.35	0.054	-0.10	0.605	1.19	0.605	-0.01	0.277	0.82	0.815	0.01
Laghetto Superiore	0.014	-0.53	0.149	-0.42	0.033	-0.09	0.499	1.31	0.499	-0.02	0.111	0.75	0.825	0.00
Lago Nero	0.048	1.11	0.716	-0.01	0.917	0.00	0.042	2.47	0.042	0.00	0.793	0.74	0.288	-0.03
Lago della Froda	0.744	0.62	0.585	-0.29	0.226	-0.04	0.120	3.25	0.120	-0.01	0.754	0.67	0.947	0.02
Lago d'Antabia	0.007	-0.58	0.321	-0.33	0.016	-0.11	0.949	0.95	0.949	0.00	0.337	-0.32	0.094	-0.03
Lago della Crosa	0.013	-0.52	0.064	0.16	0.115	-0.06	1.000	0.06	1.000	-0.01	0.259	0.33	0.192	-0.03
Lago d'Orsalìa	0.016	-0.54	0.309	-0.54	0.086	-0.08	0.801	0.63	0.801	-0.02	0.203	0.67	0.267	-0.01
Schwarzsee	0.323	0.16	0.196	-0.73	0.008	-0.18	0.681	1.12	0.681	-0.02	1.000	0.71	0.581	0.01
Laghi dei Pozzöi	0.076	-0.63	0.199	-0.42	0.049	-0.12	0.913	0.70	0.913	0.00	1.000	0.86	0.427	0.02
Lago di Sfille	0.030	-0.27	0.113	-0.91	0.007	-0.16	0.830	0.71	0.830	-0.02	0.026	1.34	0.615	-0.02
Lago di Sascòla	0.575	-0.16	0.180	-0.91	0.051	-0.21	0.407	-0.60	0.407	-0.03	0.181	0.67	0.777	-0.01
Lago d'Alzasca	0.674	-0.03	-0.11	-0.11	0.520	-0.05	0.157	2.23	0.157	0.00	0.161	1.57	0.652	0.01

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. The same happened for *Oligochaetae* in 2009, so that at the end of 2009 we had a detailed analysis of *Chironomidae* and *Oligochaetae* of the years 1991 and 2007. 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.

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 (=E.B.I. taxa number) was usually higher in the emissary than in the littoral. Similarly, behaved the

EPT index. During 2009 in the littoral of all lakes with exception of Lago Bianco *Diptera* was the dominant order, followed by *Oligochaeta* and *Others*. In the littoral of Lago Bianco the opposite occurred: *Oligochaeta* was the dominant order and was follwed by *Diptera* and *Others*. In the emissaries other orders like *Plecoptera* were also important.

Variations in macroinvertebrate population among lakes are probably influenced mainly by differences in water acidity. Average pH during 2009 was 7.6, 6.6, 6.4, 5.8, 5.5 in Lago Bianco, Laghetto Inferiore, Superiore Inferiore, Lago di Tomè and Lago del Starlaresc da Sgiof, respectively. During 2009 the E.B.I. taxa number and the EPT index were lowest in the most acidic lake Lago del Starlaresc da Sgiof. Among the other lakes during 2009 the two indexes did not differ significantly. Differences in the relative abundances of the main macroinvertebrate groups were mostly irrelevant in samples from the littoral. Most taxa belonged to the order *Diptera* (average 68%) followed by *Oligochaeta (average 21%)*. Only in the not acidic lake Lago Bianco, as already mentioned, *Oligochaeta* (average 54%) were more important than *Diptera (average 36%)*. In samples from the outlets *Diptera* was the main order. In the less acidic lakes Lago Bianco, Laghetto Inferiore and Laghetto Superiore *Diptera* (average 56%) were followed by *Oligochaeta (29%)*. In the more acidic lakes Lago di Tomè and Lago del Starlaresc da Sgiof *Diptera* also dominated (average 77%) but were more important with respect to *Oligochaeta* (average 5%). It therefore seems that with increasing pH in both littoral and emissary samples the relative abundance of *Diptera* decreases in favour of *Oligochaeta.*

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). During 2009 the order *Ephemeroptera*, to which belong many of the most acid sensitive species, was absent in Lago di Tomè and Lago del Starlaresc da Sgiof, one organism of it was found in Laghetto Superiore (*Ephemeroptera Fam. Gen. sp.*) and Lago Bianco (Baetis sp.) and only few organisms were present in the emissary of Laghetto Inferiore (*Ecdyonurus sp.).* 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.

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 2005. 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 from 2005 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 2009

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

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

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

Tab. 3.2 presents the number of taxa for the five “Braukmann and Biss” indexes from 1991 to 2009, 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 from 2003 and in Lago di Tomè from 2005. However, this result may be connected with the greater number of organisms sampled after 2002 in Laghetto Inferiore and Superiore and after 2004 in Lago di Tomè.

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 2009

The gray colored areas indicate the absence of samples

Lakes	Braukmann and Biss index	Littoral								Emissary								
		2002	2003	2004	2005	2006	2007	2008	2009	1991	2002	2003	2004	2005	2006	2007	2008	2009
Laghetto Inferiore	1	0	0	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	0	3	4	5	4	5	2	2
	3	0	0	0	0	0	0	0	0	0	0	3	2	3	4	1	0	1
	4	0	1	0	1	0	0	0	0	1	1	4	5	4	4	2	2	2
	5	1	2	2	2	3	3	4	3	1	4	5	4	4	6	5	5	4
Laghetto Superiore	1	0	0	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	0	5	7	4	3	4	1	1
	3	0	0	0	0	0	0	0	0	0	0	4	1	1	2	0	1	0
	4	0	0	0	0	0	0	0	1	1	0	4	2	3	3	3	2	3
	5	2	4	2	4	3	4	3	3	1	6	6	5	5	5	6	7	6
Lago Tomè	1	0	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	0	0	1	0	1	2	1
	3	0	0	0	0	0	0	0	0		0	0	0	0	0	0	0	0
	4	1	1	1	2	4	0	0	2		1	2	2	4	5	4	3	4
	5	2	3	2	5	3	3	5	4		3	3	2	5	5	5	7	8
Lago del Starlaresc da Sgiof	1	0	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	0	0	0	0	0	0	0
	3	0	0	0	0	0	0	0	0		0	0	0	0	0	0	0	0
	4	1	1	2	2	2	2	1	1		1	1	0	2	2	2	1	2
	5	1	0	0	0	0	0	0	0		1	2	1	1	2	1	4	4
Lago Bianco	1					0	0	0	0						0	0	0	0
	2					0	0	0	0						6	6	5	3
	3					0	0	0	0						2	2	1	1
	4					0	0	0	0						3	2	2	2
	5					2	1	1	1						4	6	4	4

Table 3.3 Macroinvertebrate species with lowest "Braukmann and Biss index" in 5 Alpine lakes from 1991 to 2009
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	2009
Laghetto Inferiore	Ecdyonurus sp.	2						x	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		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		x
	Rhitrogena sp.	2						x					
Lago Tomè	Perla grandis	1			x								
	Protonemura nimborum	2							x			x	x
	Rhyacophila tristis	2									x		
	Odontocerum albicorne	4								x	x		x
	Potamophylax cingulatus	4							x	x			
	Protonemura meyeri	4			x								
	Ryacophila (Ryacophila) sp.	4					x	x	x	x	x	x	x
	Ryacophila sensu stricto-Gr.	4							x	x	x	x	x
	Sialis sp.	4				x	x						x
	Sialis fuliginosa	4						x	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	x
	Sialis sp.	4						(x)	(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	x
	Perlodes intricatus	2								x	x	x	x
	Philopotamus ludificatus	2									x		
	Protonemura nimborum	2								x	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 2009 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* and *Plecoptera*.

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 2009.

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

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”. River Maggia and Vedeggio have more spieces with index=1 than river Verzasca. 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 2009

River	Braukmann and Biss index	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Maggia	1	4	3	2	3	4	4	4	4	4	3
	2	14	8	11	11	13	15	13	14	12	12
	3	6	6	3	5	5	7	5	7	5	8
	4	3	1	5	8	6	5	5	5	6	5
	5	4	4	5	3	2	3	2	4	4	3
Vedeggio	1	5	2	2	2	2	4	2	3	4	4
	2	11	13	12	13	14	17	16	15	17	17
	3	6	7	4	5	6	9	8	7	6	11
	4	3	5	3	4	5	5	7	6	5	7
	5	9	4	3	5	5	4	4	3	3	3
Verzasca	1	3	2	2	2	2	2	2	2	2	2
	2	7	6	8	8	8	8	11	8	11	12
	3	5	6	4	7	6	7	7	6	6	6
	4	4	3	5	6	5	6	7	6	7	5
	5	5	4	3	4	3	3	3	3	3	3

Table 3.6 Macroinvtebrate species with lowest “Braukmann and Biss index” in 3 Alpine rivers from 2000 to 2009

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

Rivers	Category	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Maggia	1	0%	0%	0%	0%	40%	0%	0%	0%	0%	0%
	2	100%	100%	100%	100%	60%	100%	100%	75%	50%	100%
Vedeggio	1	0%	0%	50%	0%	0%	0%	0%	0%	0%	0%
	2	100%	100%	50%	100%	100%	100%	75%	50%	75%	50%
Verzasca	1	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
	2	100%	100%	100%	100%	100%	100%	100%	75%	100%	75%

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 2009.

	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
	2009	16	63.9	18.2	1.00	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
	2009	17	106.8	21.8	1.01	41

4.3.2 DDT's in fish muscle

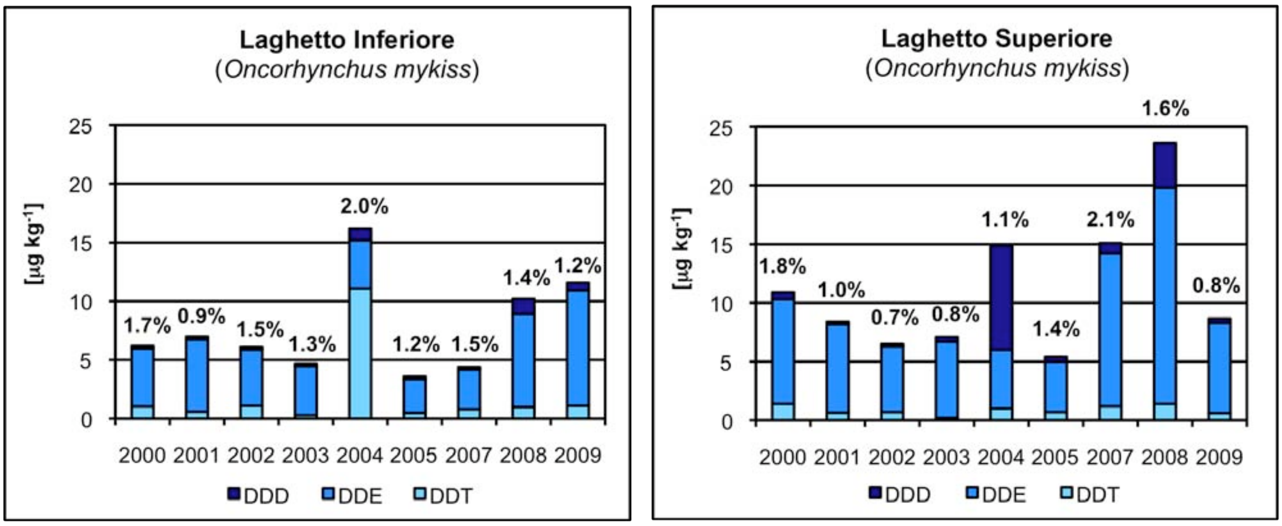
Most DDT found in the Southern part of the Swiss Alps probably origins from a contaminated site situated along the shore of Lago Maggiore, where until 1996 a factory has produced DDT. In fact, elevated total DDT concentrations (ca. 5-72 µg kg^{-1}) are still measured in fish from Lago Maggiore (Cipais,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

Fish sampled in Lago Inferiore and Superiore at the end of 2009 were characterized by total DDT concentrations of 11.6 µg kg^{-1} and 8.7 µg kg^{-1} and DDE was as usual the main component (85% in Laghetto Inferiore and 89% in Laghetto Superiore). DDE is a metabolite of DDT and is during most seasons the main component of total DDT in lake water of Lago Maggiore (CIPAIS, 2009). Values are therefore below the Swiss edibility limit for total DDT (1 mg kg^{-1}).

Normalizing the concentrations with the fat content, the data can be compared with those of fish in Lago Maggiore. With the fat content normalized concentrations of total DDT in 2009 were 967 µg kg^{-1} and 1088 µg kg^{-1} in Laghetto Inferiore and Laghetto Superiore, respectively. In fish from Lago Maggiore during 2008 values ranged between 450 µg kg^{-1} to 2667 µg kg^{-1} and were therefore in the same range as in the studied mountain lakes. However, in fish from Lago Maggiore not only DDE is important in determining totale DDT but also DDD.

Comparing the data with results former years (Fig. 4.1), it appears that concentrations of DDT in Laghetto Superiore are mostly 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) in Laghetto Superiore, 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 2009
The percentage value refers to the lipid content.



4.3.3 PCB's in fish muscle

Total PCB concentrations in fish samples from 2009 were 10.8 µg kg^{-1} in Laghetto Inferiore and 8.9 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.

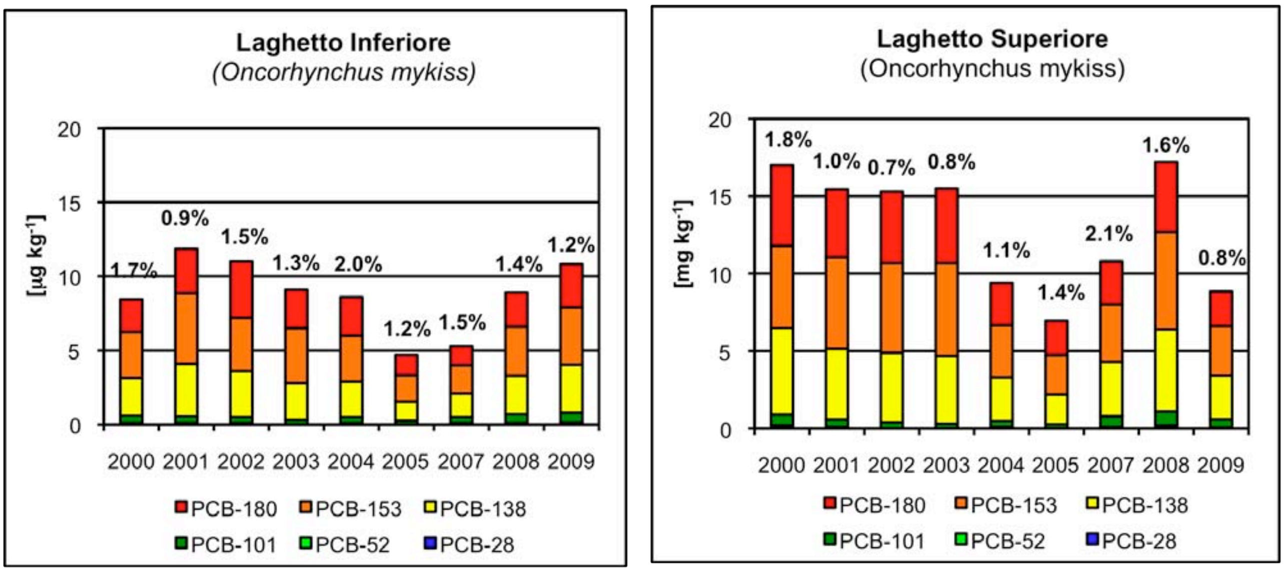
Similarly to what observed for DDT, Looking at the time series of PCB concentrations in Laghetto Inferiore and Laghetto Superiore (Fig. 4.2), it appears that concentrations are often higher in the latter. The reasons were already explained in the former paragraph and are connected with the fact that 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.

As done for DDT, with the fat content normalized concentrations of PCB in fish from Laghetto Inferiore and Laghetto Superiore can also be compared with values from Lago Maggiore. Concentrations of total PCB in 2009 were 900 µg kg^{-1} and 1113 µg kg^{-1} in Laghetto Inferiore and Laghetto Superiore, respectively. In fish from Lago Maggiore during 2008 the sum ff the same cogeners ranged between 177 µg kg^{-1} to 922 µg kg^{-1} and were therefore in the same range as in the studied mountain lakes. However, in fish from Lago Maggiore the lighter cogener PCB-101 is also quantitatively important.

Interestingly, without considering concentrations of 2004, temporal variations of DDT and PCB in Laghetto Inferior and Laghetto Superiore 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 2009

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 2009 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 2009 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	7.73	5.98
Al	0.29	0.18
Cu	0.36	0.38
Cr	0.068	0.078
Ni	<0.023	<0.023
Pb	0.043	<0.013
Cd	0.017	0.004
Hg	0.053	0.045

Figure 4.3 Metal concentrations in fish muscle (mg^{-1} kg wet weight) from 2000 to 2009

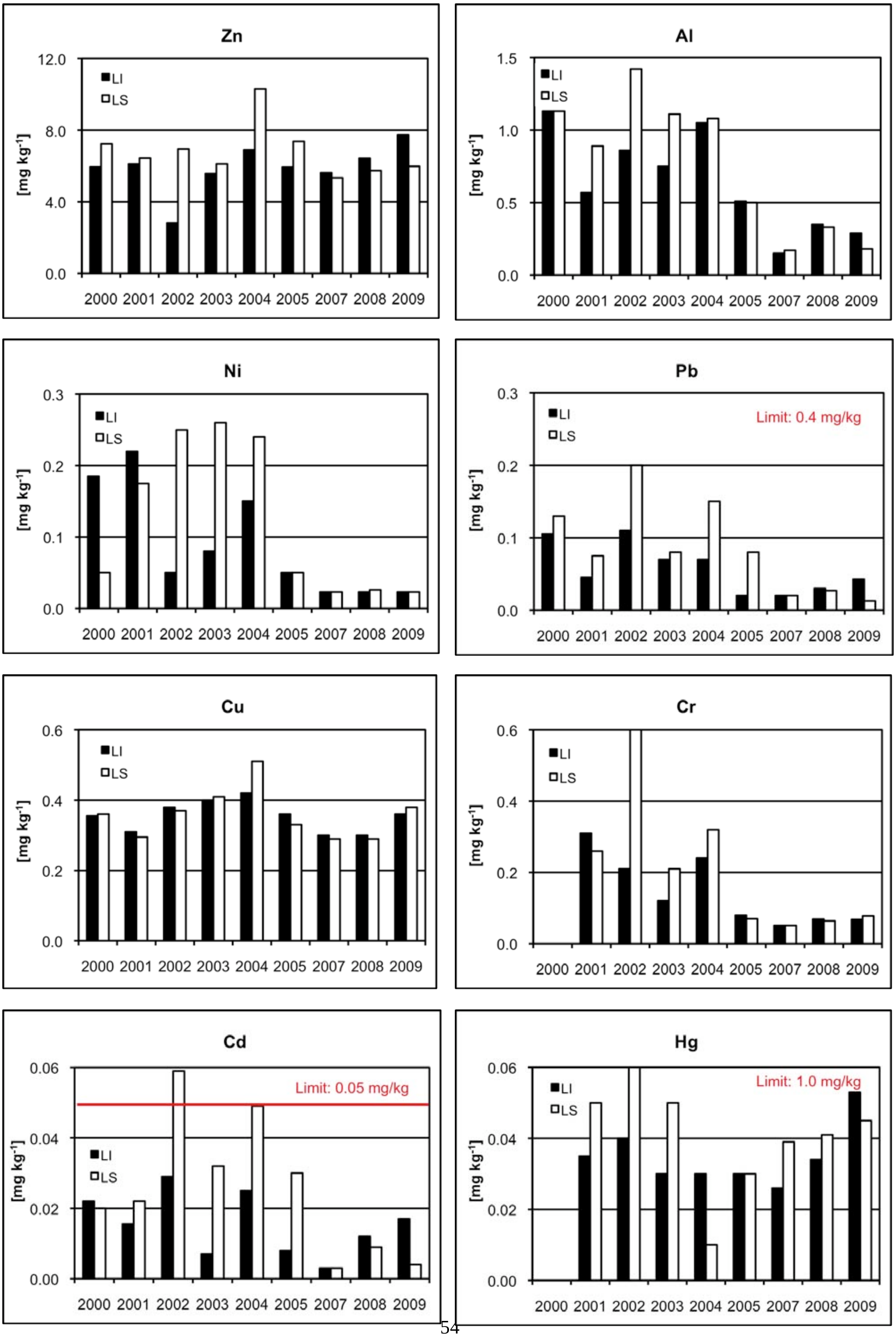
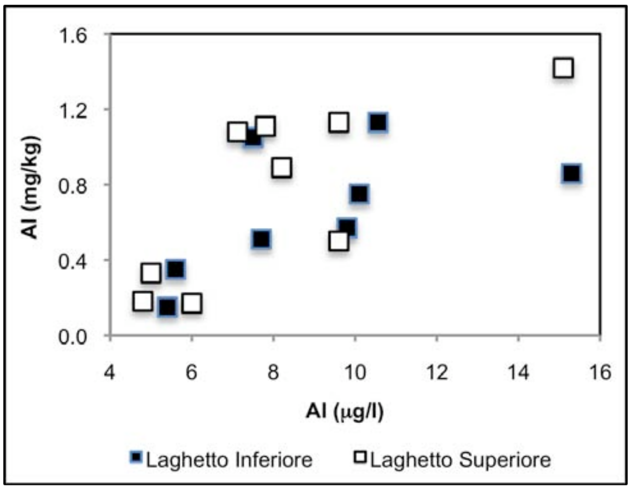


Figure 4.4 Aluminium concentrations in fish vs aluminium concentrations in lake water ion Laghetto Inferiore and Laghetto Superiore from 2000 to 2009.



Bibliography

Braukmann U. and R. Biss. 2004. Conceptual study-An improved method to assess acidification in German streams by using benthic macroinvertebrates. Limnologica 34: 433-450.

Bundesamt für Umwelt (BAFU) (Editor). 2005-2010. Hydrologisches Jahrbuch der Schweiz 2004-2009. BAFU. Bern, Schweiz.

Bundesamt für Wasser unf Geologie (BWG) (Editor). 2001-2004. Hydrologisches Jahrbuch der Schweiz 2000-2003. BWG. Bern, Schweiz.

Commissione internazionale per la protezione delle acque italo-evizzere (CIPAIS). 2009. Indagini du DDT e sostanze periocolose nell'ecosistema del Lago Maggiore. Programma 2008-2012. Rapporto annuale 2008. CIPAIS. Verbania Pallanza, Italia.

Libiseller C. and Grimvall A. 2002. Performance of partial Mann-Kendall test for trend detection in the presence of covariates. Environmetrics 13: 71-84.

Fjellheim A., A. Boggero, G.A. Halvorsen, A.M. Nocentini, M Rieradevall, G. Raddum and Ø.A. Schnell. 2000. Distribution of benthic invertebrates in relation to environmental factors. A study of European remote Alpine ecosystems. Verh. Internat. Verein. Limnol. 27: 484-488.

Ghetti P.F. 1986. I macroinvertebrati nell'analisi di qualità dei corsi d'acqua. Bertelli. Trento, Italia.

Hieber M. 2002. Alpine Fliessgewässer: vielfältige und empfindliche Oekosysteme. Eawag News 55d: 9-11.

UNECE. 2009. Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests. Part VI. Sampling and analysis of deposition. International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests, United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution, Geneva, Switzerland.

Istituto delle scienze della terra (IST) (Editor). 2001-2010. Annuario Idrologico del Canton Ticino 2000-2009. IST. Scuola Universitaria Professionale della Svizzera Italiana. Trevano, Svizzera.

Marchetto A., R. Mosello, M. Rogora, M. Manca, A. Boggero, G. Morabito, S. Musazzi, G.A. Tartari, A.M. Nocentini, A. Pugnetti, R. Bettinetti, P. Panzani, M. Armiraglio, P. Cammarano and A. Lami. 2004. The chemical and biological response of two remote mountain lakes in the Southern Central Alps (Italy) to twenty years of changing physical and chemical climate. J. Limnol. 63: 77.89.

Mosello R., A. Lami, P. Guilizzoni, M. Manca, A.M. Nocentini, A. Pugnetti, A. Boggero, A. Marchetto, G.A. Tartari, R. Bettinetti, M. Bonardi, P. Cammarano. 1993. Limnological studies on two acid sensitive lakes in the Central Alps (lakes Paione Superiore and Paione Inferiore, Italy). Mem. Ist. Ital. Idrobiol. 51: 127-146.

Norwegian Institute for Water Research (NIVA). 1996. Programme Manual. Programme Centre, NIVA, Oslo. NIVA_Report SNO 3547-96.

Pradella C. 2001. Indagini idrochimiche e biologiche su due laghetti alpini concatenati d'alta quota e stime di bilanci di massa. Tesi di laurea. Università degli Studi di Parma. Parma, Italia.

Rogora M., R. Mosello, A. Marchetto and R. Mosello. 2004. Long-term trends in the chemistry of atmospheric deposition in northwestern Italy: the role of increasing Saharan dust deposition. Tellus. 56B(5): 426-434.

Steingruber S. and L. Colombo. 2006. Impact of air pollution on Alpine lakes and rivers. Environmental studies no.UW-0619. Federal Office for the Environment. Berne, Switzerland.

Vesely J., Z. Šulcek and V. Majer. 1985. Acid-base changes in streams and their effect on the contents of heavy metals in stream sediments. J. Geol. Survey Prague 60: 9-23.