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 2007

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

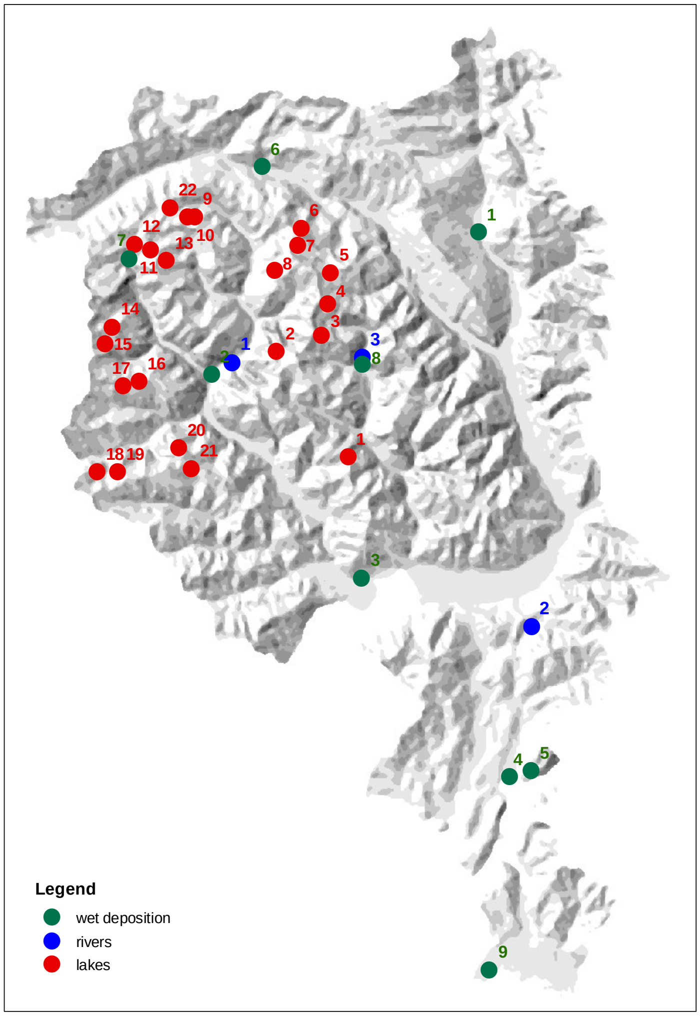


Table 1.1 Lake parameters

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 μeq l^{-1}, sensitive to acidification when 0<alkalinity<50 μeq l^{-1} and with low alkalinity but not sensitive to acidification when 50 <alkalinity <200 μeq 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 rain water 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 rain water concentrations and deposition rates of the main chemical parameters during 2007 are shown in Fig. 2.2. Concentrations of nitrate and ammonia were inversely proportional to precipitation. Concentrations were highest at the beginning of the year when precipitation was lowest, suggesting a dilution during warmer months when precipitation reached its maximum. Concentrations of sulphate and base cations behaved similarly, although a little bit more random. The fact that concentrations of acidity were also inversely proportional to the amount of precipitation implies that the decrease of acid anions during spring-summer must have been higher than that of base cations and ammonia. This indicates that dilution alone can not be the only factor influencing concentrations. The same conclusion appears from observing concentrations of bicarbonate, that were highest in the period May-September and were therefore not greatly influenced by dilution. We therefore suppose that besides dilution, during spring-summer alkaline rain events rich in minerals tend to appear more frequently influencing concentrations.

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.

Figure 2.1 Monthly precipitation during 2007

Data from MeteoSwiss

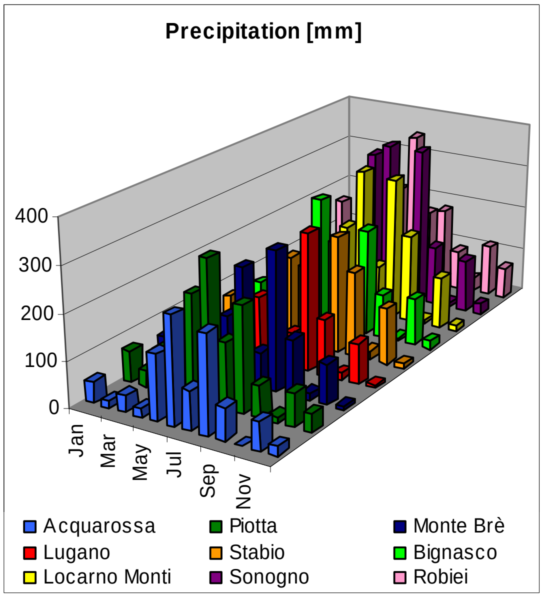
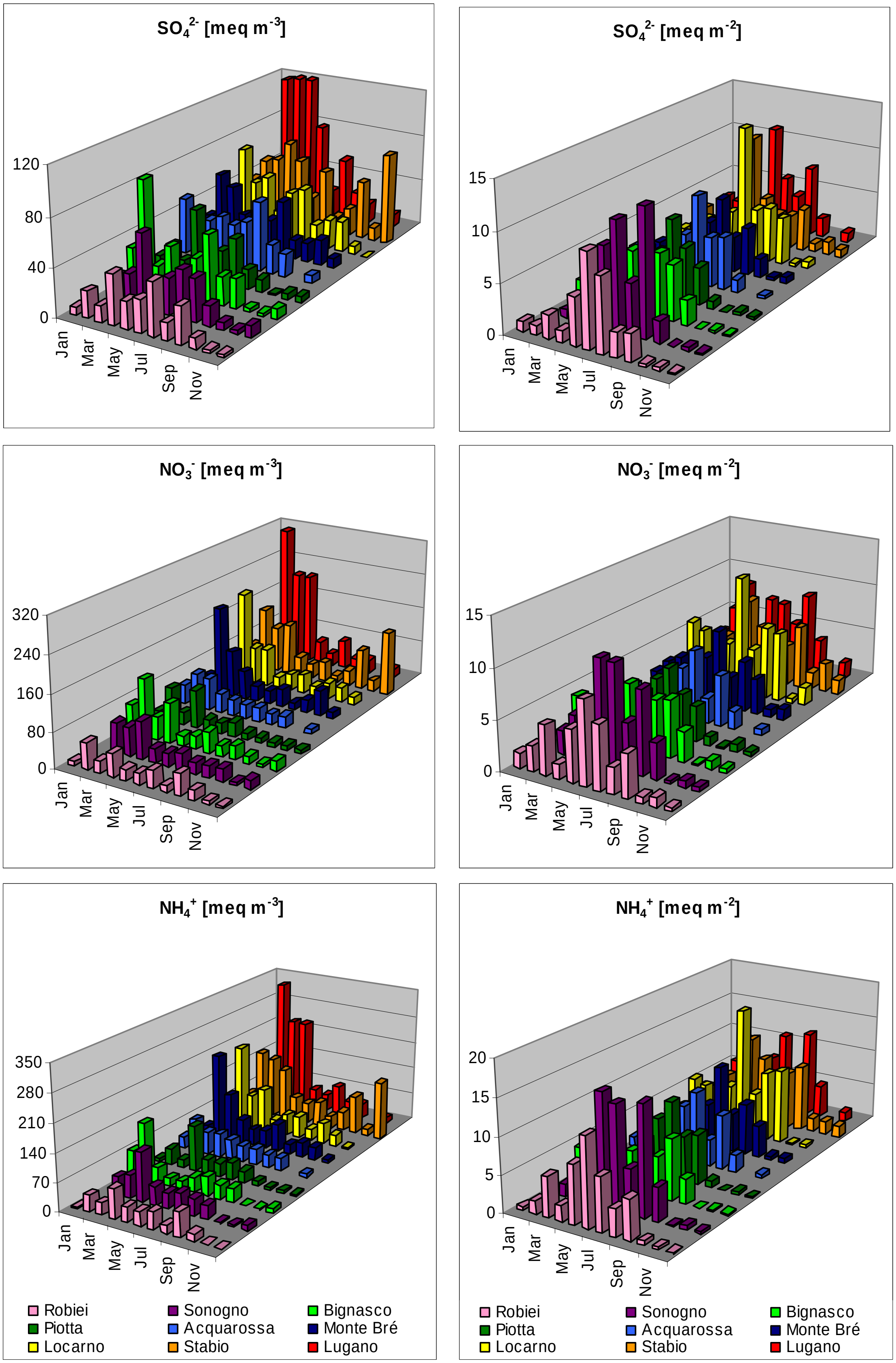
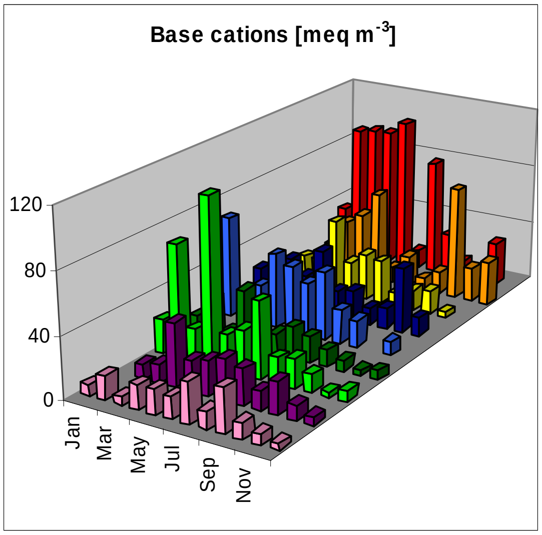
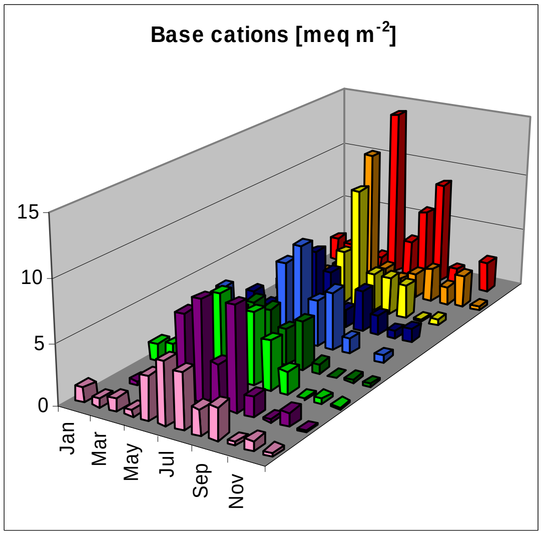


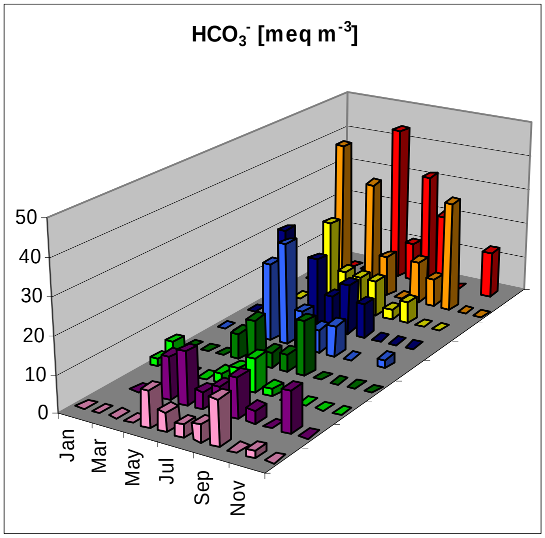
Figure 2.2 Seasonal variations of monthly average rain water concentrations and deposition rates during 2007

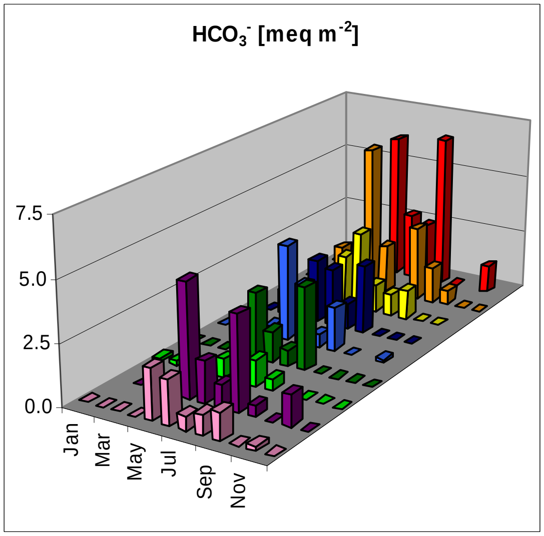
Base cations correspond to non sea salt base cations (calcium, magnesium and potassium)

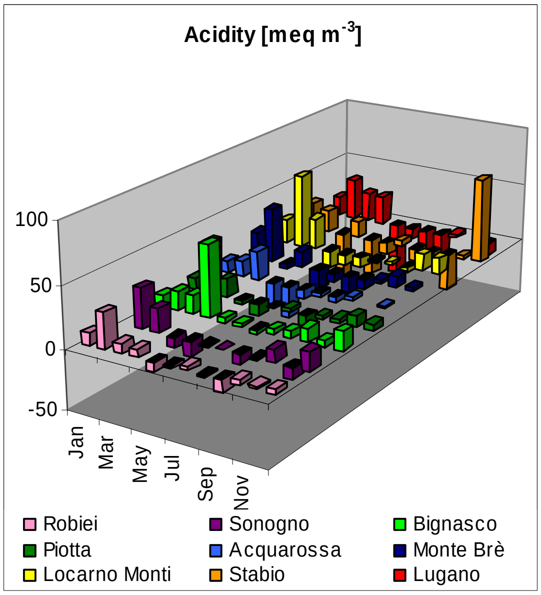


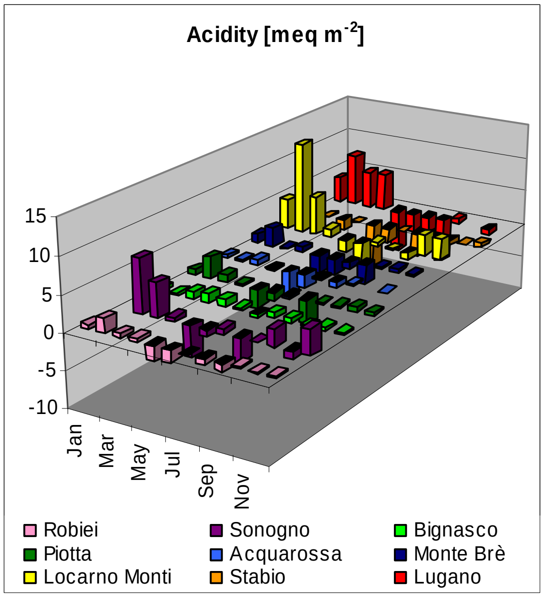

Base cations [meq m^{-3}]


Base cations [meq m^{-2}]


HCO_3^- [meq m^{-3}]


HCO_3^- [meq m^{-2}]


Acidity [meq m^{-3}]


Acidity [meq m^{-2}]

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

In general, ion concentrations of anthropogenic origin (sulphate, nitrate, ammonia) were highest at sampling sites with low altitudes and latitudes like Lugano and Stabio and lowest at sites with high altitude and latitudes like Piotta and Robiei. 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, while the decrease of concentrations with altitude reflects both the pollutants gradient from south toward north and the decrease of anthropogenic pollutants with altitude. Wet deposition of chemical parameters is also greatly influenced by the amount of precipitation. Highest precipitation occurs in the north-western part of Canton Ticino. The reason for this distribution are air masses rich in humidity that move predominantly from southwest toward the southern Alps and the particular orography of the area that causes a steep raise of the air masses to higher altitudes. It results that highest deposition rates of ammonia, nitrate and sulphate occur where both concentrations and precipitation are high. This is the case for sampling stations with average latitude and altitude as can be observed for Locarno Monti and Sonogno. Concentrations of bicarbonate increase with the number and intensity of alkaline rain event during the year and decrease with the amount of annual precipitation. It results that during 2007 highest concentrations of bicarbonate are found at stations with low latitude and altitude like Lugano and Stabio with low annual precipitation. Similar results are obtained for concentrations of base cations, although high concentrations are also measured at Acquarossa, where precipitation is lowest. Yearly mean concentrations and deposition of bicarbonate and base cations behave likewise. For what concerns concentrations and deposition of acidity lowest values are measured at Lugano, where concentrations of antropogenic pollutants, base cations and bicarbonate are highest.

The amount of yearly precipitation at each sampling site is reported in Fig. 2.3, while variation of yearly average rain water concentrations and deposition rates of the main chemical parameters during time are shown in Fig. 2.4. Since before 1988, rain water was collected with bulk samplers and after 1988 with wet-only samplers, data of these 2 periods should not be compared with each other. For some parameters temporal trends seem to exist. Sulphate concentrations and deposition rates decreased from 1980's, reflecting the decrease in sulphur dioxide emissions after 1980. Between 1988 and 2007 at Locarno Monti and Lugano sulphate concentrations decreased by around 57-66%. Instead no significant trend can be observed for ammonia and nitrate concentrations and depositions rates. Interestingly, yearly average bicarbonate concentrations and deposition seemed to increase during the monitoring period and was particularly high during the years 1999, 2000, 2002, when precipitation was higher than usual. A similar trend can be observed for base cations. This is consistent with what described by Rogora et al. (2004), who 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 rain water to neutralize alkaline rain events making them more observable in rain water chemistry. If climate change may also influence the occurrence of alkaline rain events by increased long distance transport of dust is not clear. In summary, decreasing sulphur emissions and increasing number of alkaline rain events generated a decrease of acidity and increase of pH. From the end of 1980's to the beginning of this millennium yearly average rain water pH at Locarno Monti and Lugano increased from 4.3 to 5.0/5.3. After 2000 at most sites yearly average acidity started to be negative.

It is important to observe that during the last five years precipitation was lower than usual (Fig. 2.4). As a consequence wet deposition rates of sulphate, nitrate, ammonia, base cations and bicarbonate were also smaller and should not automatically be interpreted as the result of reduced emissions into the atmosphere. However, average sulphate concentrations over the last five years are smaller than in the previous five-years period, suggesting that reduction in sulphate emissions continued. However, the recent slight increase in deposition of acidity at most sites (Acquarossa, Locarno Monti, Mont Brè, Piotta, Stabio) indicates that the decrease in deposition of base cations plus ammonia was higher than that of sulphate and nitrate, indicating that the decrease in deposition of base cations and bicarbonate was not only caused by decreased precipitation but also to less frequent rain events with alkaline characteristics. In fact, concentrations of bicarbonate and base cations were also smaller in the most recent 5-years period, despite a dry period would rather suggest increased yearly average concentrations if precipitation would be the only determining factor. It is therefore possible that reduced annual precipitation reduces the probability that alkaline rain events occur.

Table 2.2 Yearly mean rain water concentrations and deposition rates during 2007

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	954	814	12	5.4	24	23	7	6	6	6	2	2	39	37	11	10	33	31	30	29	4	4	-7	-6
Bignasco	1252	1166	12	5.1	17	21	4	5	8	9	3	3	29	37	3	4	26	25	30	37	6	8	6	7
Locarno Monti	1527	1299	14	5.1	15	23	3	5	5	8	1	2	45	69	6	10	29	44	37	56	5	7	1	1
Lugano	1143	754	15	5.5	29	33	7	8	13	15	6	7	43	50	18	21	35	40	39	45	9	10	-15	-17
Monte Brè	1143	1075	12	5.3	15	17	3	3	8	9	2	3	41	47	9	10	26	29	33	38	7	8	-4	-5
Piotta	1313	1046	10	5.3	12	16	2	3	5	7	1	2	28	37	7	9	20	26	22	30	5	7	-1	-1
Robiei	1639	1638	9	5.2	10	17	2	4	3	5	1	2	29	47	4	7	20	32	24	40	3	4	1	2
Sonogno	1659	1391	12	5.3	15	24	3	5	6	9	3	4	40	66	8	14	28	46	30	49	4	6	-4	-6
Stabio	1183	1047	14	5.4	15	18	4	5	10	11	4	4	52	61	13	15	31	37	38	45	8	9	-8	-10

Figure 2.3 Yearly precipitations

Data from MeteoSwiss

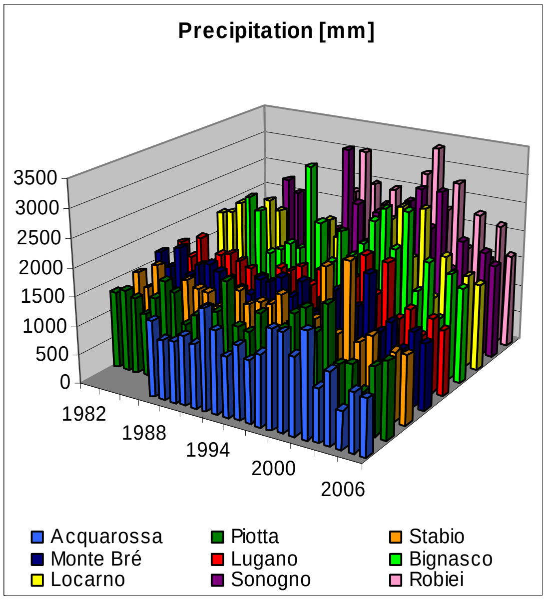
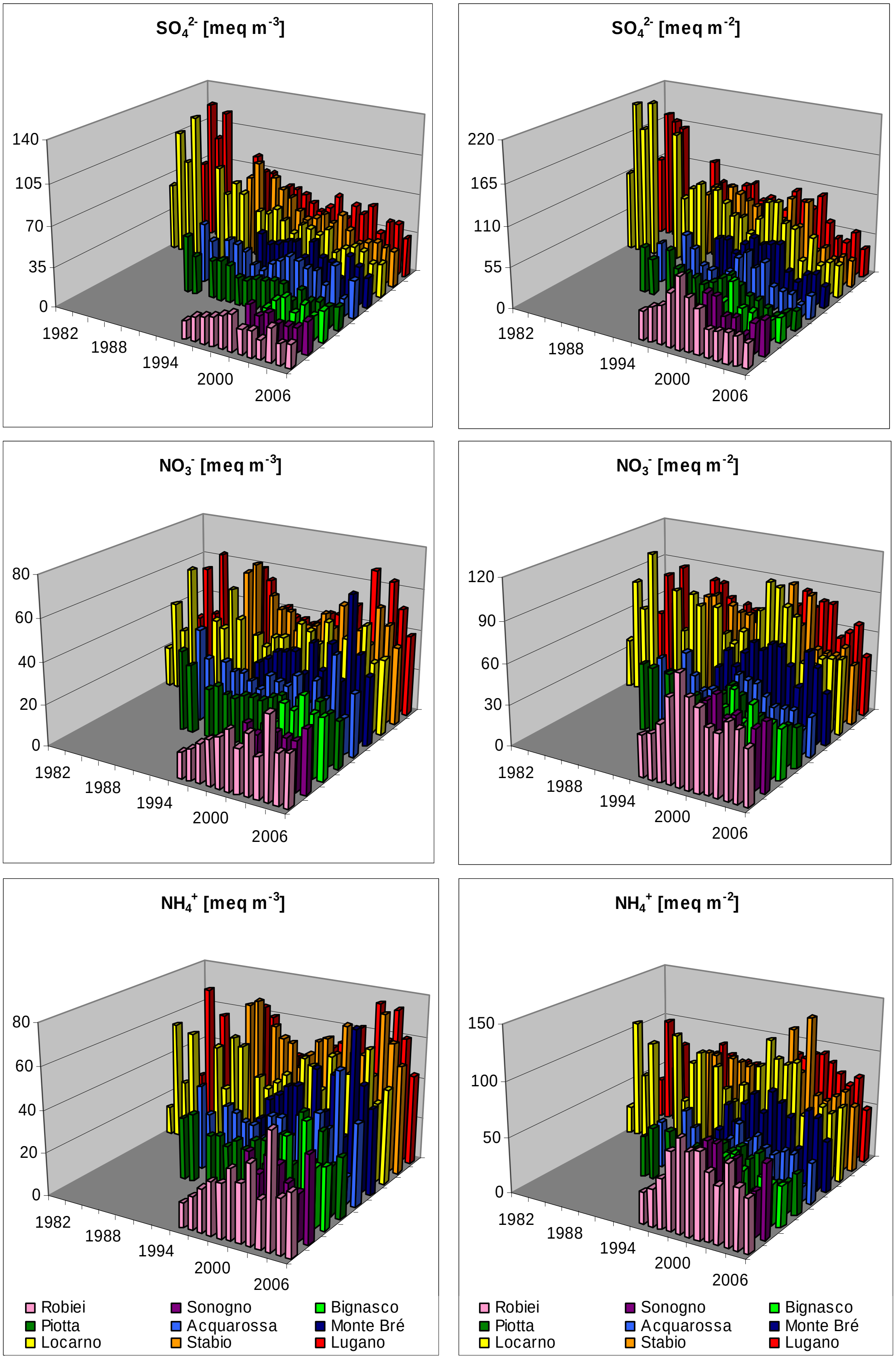
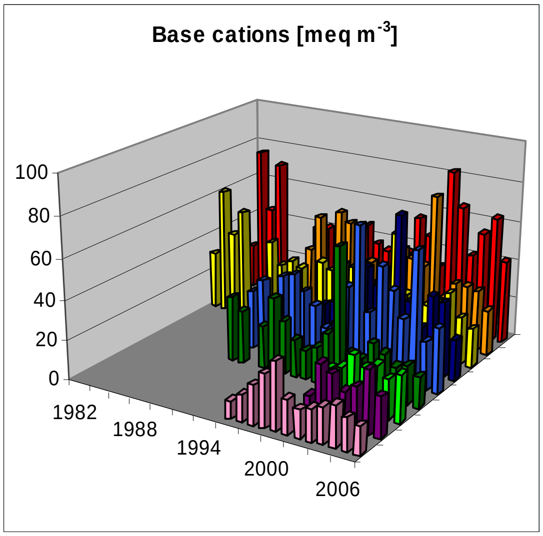


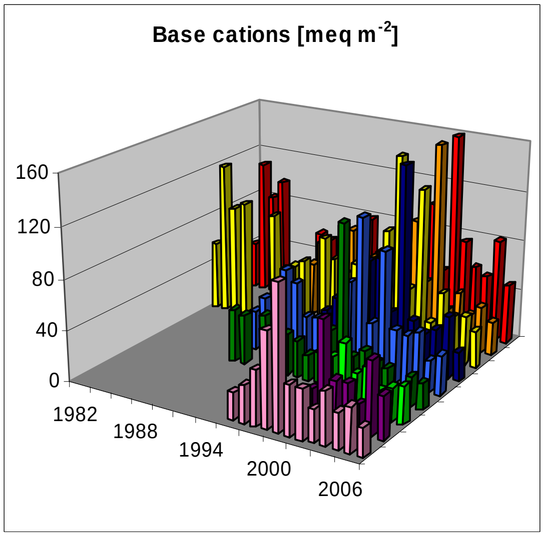
Figure 2.4 Temporal variations of annual mean rain water concentrations and deposition rates

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

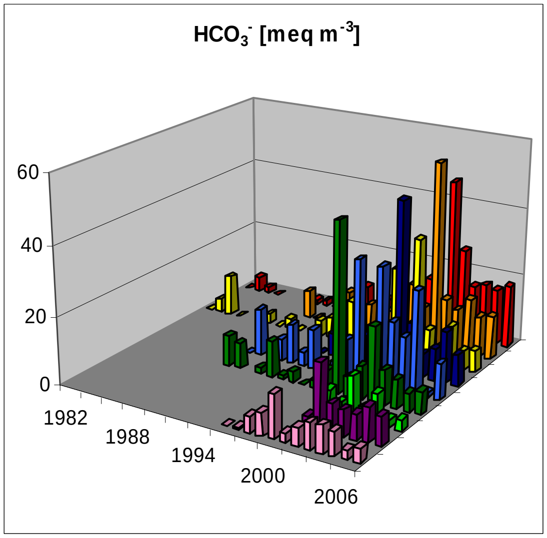




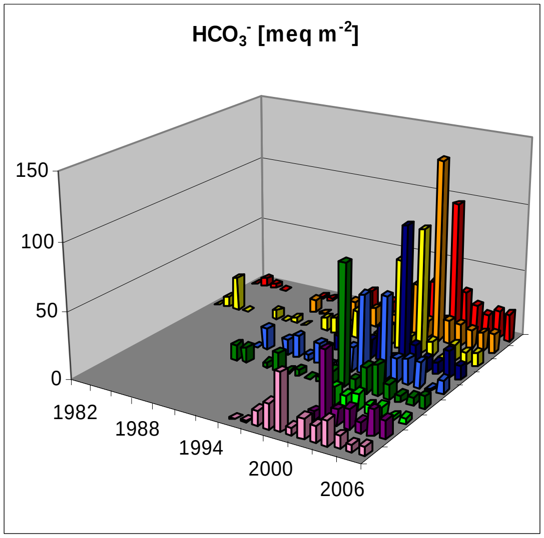
Base cations [meq m^{-3}]



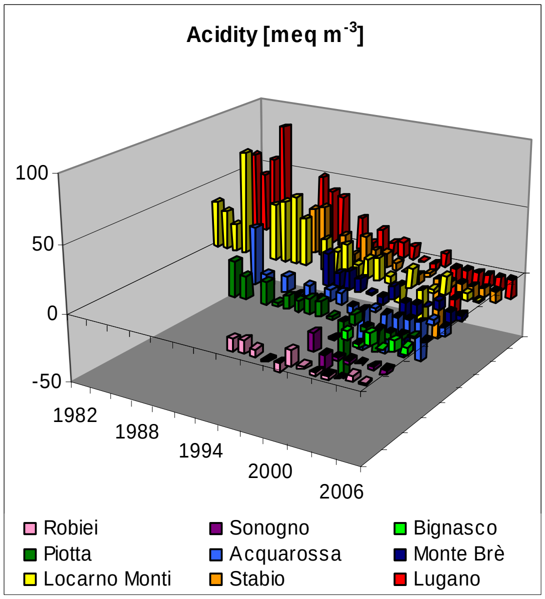
Base cations [meq m^{-2}]



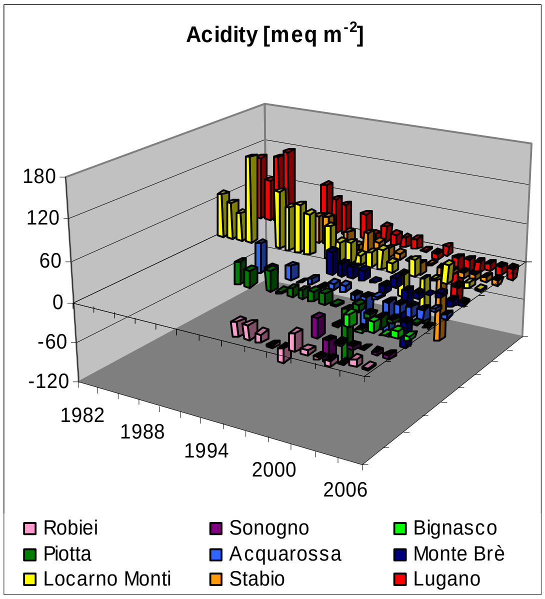
HCO$_3^-$ [meq m^{-3}]



HCO$_3^-$ [meq m^{-2}]



Acidity [meq m^{-3}]



Acidity [meq m^{-2}]

2.4.2 Alpine lake

Yearly mean concentrations of the main chemical parameters measured in lake surface water during 2007 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 7.9 and 21.5 μS cm^{-1}, alkalinity between -1 and 83 μeq l^{-1}, pH between 5.3 and 7.2, sulphate between 0.92 and 4.04 mg l^{-1}, nitrate between 0.13 and 0.39 mg N l^{-1}, dissolved organic carbon between 0.13 and 1.26 mg C l^{-1}, reactive dissolved silica between 0.85 and 2.84 mg SiO_2 l^{-1} and total dissolved aluminium between 0.9 and 62.5 μg l^{-1}.

In order to better compare chemistry of lakes with low alkalinities, average values of the main parameters are shown graphically in Fig. 2.5.

For 2007 it can be observed that only one lake had an average alkalinity below 0 μeq l^{-1} and is therefore acid (Laghetto Gardiscio) and 13 lakes are sensitive to acidification (alkalinity between 0 and 50 μeq l^{-1}). It also immediately appears that alkalinity correlates well with pH. Lowest pH's were measured in lakes with lowest alkalinities. Lago del Starlaresc da Sgiof, Lago, Laghetto Gardiscio and Lago di Tomè had an average pH below 6 and are therefore also characterized by high concentrations of dissolved aluminium (24-63 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.

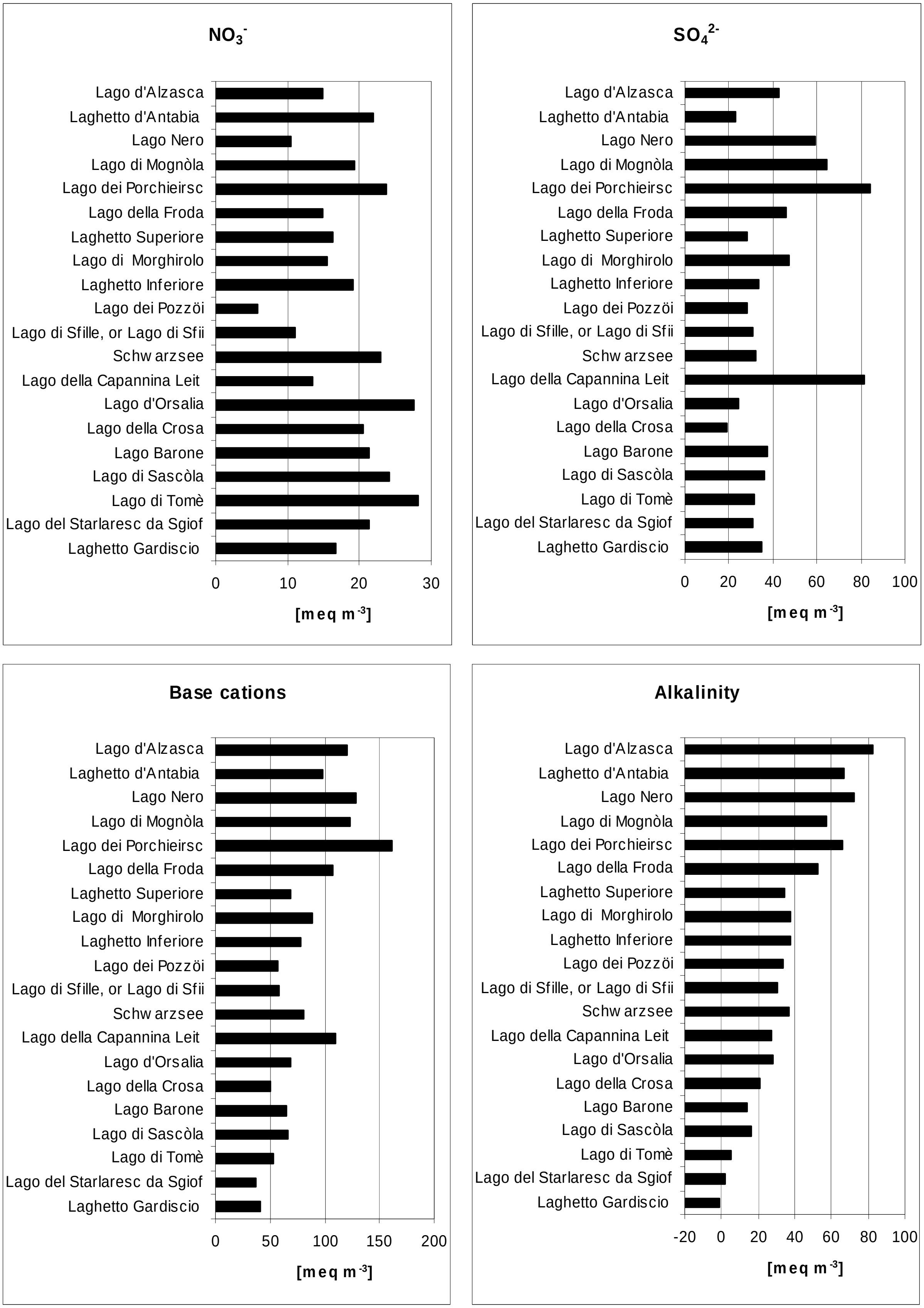
Table 2.3 Average lake surface water concentrations during 2007

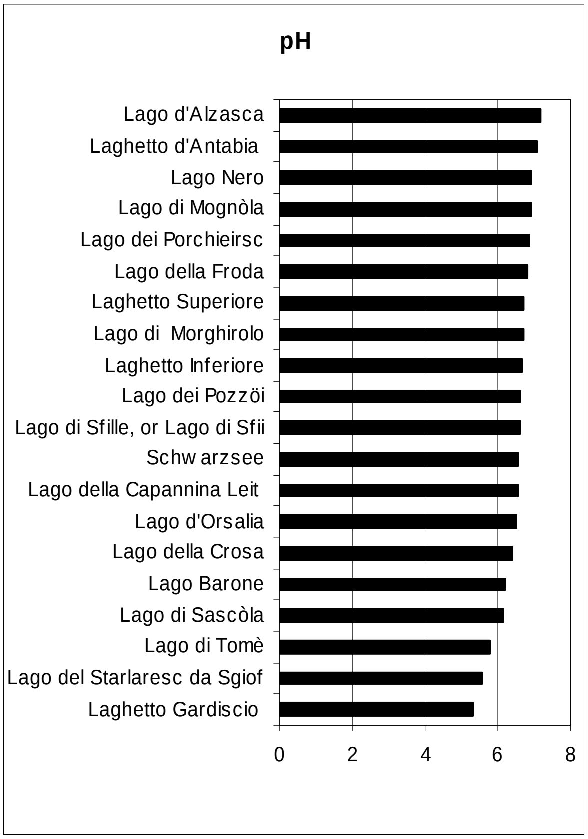
Average values with some values below the quantification limit were preceded with <

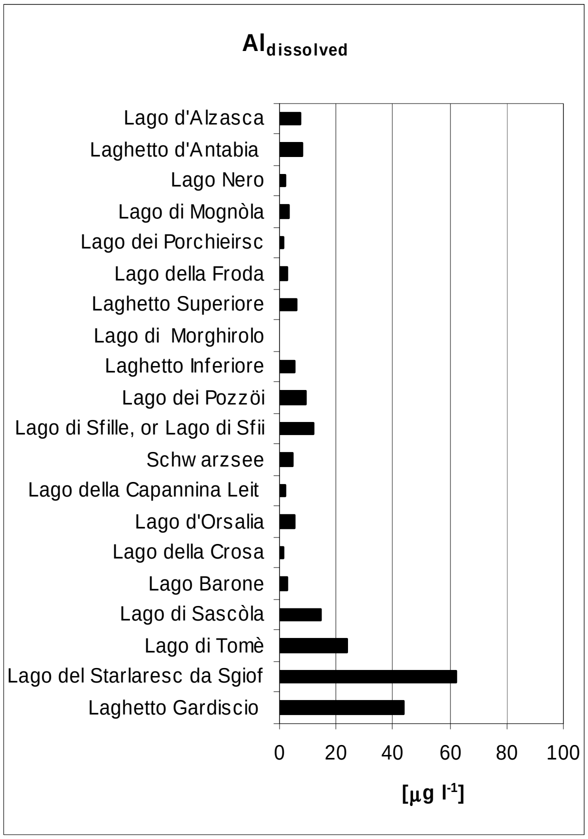
Lake name	Conductivity 25°C. (µS cm^{-1})	pH	Alkalinity (µeq l^{-1})	Ca^{2+} (mg l^{-1})	Mg^{2+} (mg l^{-1})	Na^{+} (mg l^{-1})	K^{+} (mg l^{-1})	NH_4^{+} (mg N l^{-1})	SO_4^{2-} (mg l^{-1})	NO_3^{-} (mg N l^{-1})	Cl^{-} (mg l^{-1})	DOC (mg C l^{-1})	SiO_2 (mg l^{-1})	$Al_{dissolved}$ (µg l^{-1})	Al_{tot} (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	9.3	5.6	2	0.50	0.09	0.34	0.16	0.035	1.50	0.30	0.13	0.79	1.46	62.5	76.8	<0.2	<0.3	4.4	4.6
Lago di Tomè	9.7	5.8	5	0.86	0.33	0.33	0.17	0.008	1.52	0.39	0.10	0.27	1.84	23.7	30.3	<0.2	<0.2	1.7	1.7
Lago dei Porchieirsc	21.5	6.9	66	2.73	0.15	0.49	0.50	0.008	4.04	0.33	0.11	0.24	2.84	1.4	6.0	<0.2	<0.2	0.4	0.5
Lago Barone	10.0	6.2	14	1.07	0.08	0.27	0.21	0.022	1.79	0.30	0.09	0.33	1.34	2.4	8.6	<0.2	<0.2	1.1	1.5
Laghetto Gardiscio	9.1	5.3	-1	0.53	0.10	0.20	0.26	0.029	1.69	0.23	0.09	0.13	0.85	43.9	62.7	<0.2	<0.3	2.3	2.3
Lago Leit	16.0	6.5	28	1.52	0.27	0.38	0.48	0.013	3.92	0.19	0.09	0.40	1.72	1.9	14.2	<0.2	<0.3	1.3	1.4
Lago di Morghirolo	12.6	6.7	38	1.25	0.17	0.33	0.47	<0.008	2.27	0.22	0.07	0.30	1.16	0.9	18.9	<0.2	<0.3	0.8	1.1
Lago di Mognòla	17.5	6.9	58	1.80	0.25	0.57	0.53	0.004	3.09	0.27	0.09	0.25	2.61	3.4	16.7	<0.2	<0.3	0.7	0.8
Laghetto Inferiore	11.3	6.7	37	1.19	0.10	0.34	0.42	0.006	1.61	0.27	0.08	0.34	1.44	5.4	17.6	<0.2	<0.2	1.2	1.4
Laghetto Superiore	9.9	6.7	35	1.06	0.09	0.28	0.33	0.006	1.35	0.23	0.08	0.44	1.22	6.0	12.4	<0.2	<0.2	2.0	1.5
Lago Nero	17.3	6.9	73	2.04	0.16	0.39	0.50	0.013	2.85	0.15	0.09	0.38	0.55	2.0	5.2	<0.2	<0.2	1.3	1.1
Lago Bianco	78.4	7.7	482	12.8	0.80	0.39	0.83	0.004	11.49	0.15	0.10	0.27	1.61	5.9	15.3	<0.2	<0.2	0.3	0.6
Lago della Forda	13.9	6.8	52	1.85	0.10	0.28	0.26	0.007	2.21	0.21	0.07	0.33	1.29	2.7	8.9	<0.2	<0.2	0.6	0.6
Lago d'Antabia	13.2	7.1	67	1.72	0.07	0.43	0.28	0.006	1.11	0.31	0.09	0.47	2.03	8.1	16.5	<0.2	<0.2	0.9	1.0
Lago della Crosa	7.9	6.4	21	0.81	0.06	0.25	0.17	0.012	0.92	0.29	0.10	0.28	1.31	1.7	7.8	<0.2	<0.2	1.0	1.1
Lago d'Orsalìa	10.4	6.5	28	1.15	0.08	0.31	0.19	0.008	1.17	0.39	0.10	0.33	1.54	5.4	23.3	<0.2	<0.2	1.6	1.3
Schwarzsee	11.6	6.6	37	1.33	0.10	0.32	0.26	0.004	1.53	0.32	0.10	0.28	1.86	4.8	13.9	<0.2	<0.2	1.0	1.0
Laghi dei Pozzöi	8.7	6.6	34	0.88	0.10	0.37	0.18	0.007	1.35	0.08	0.10	0.72	2.11	9.5	40.6	<0.2	<0.2	1.4	1.7
Lago di Sfille	9.4	6.6	30	0.94	0.09	0.38	0.14	0.015	1.47	0.15	0.12	0.66	1.80	12.2	28.8	<0.2	<0.3	2.0	2.1
Lago di Sascòla	10.4	6.1	16	0.83	0.19	0.34	0.34	0.012	1.73	0.34	0.08	0.60	1.91	14.4	43.0	<0.2	<0.2	2.4	1.6
Lago d'Alzasca	16.6	7.2	83	1.86	0.20	0.52	0.48	0.008	2.05	0.21	0.15	1.26	2.33	7.4	13.8	<0.2	<0.2	0.4	<0.5

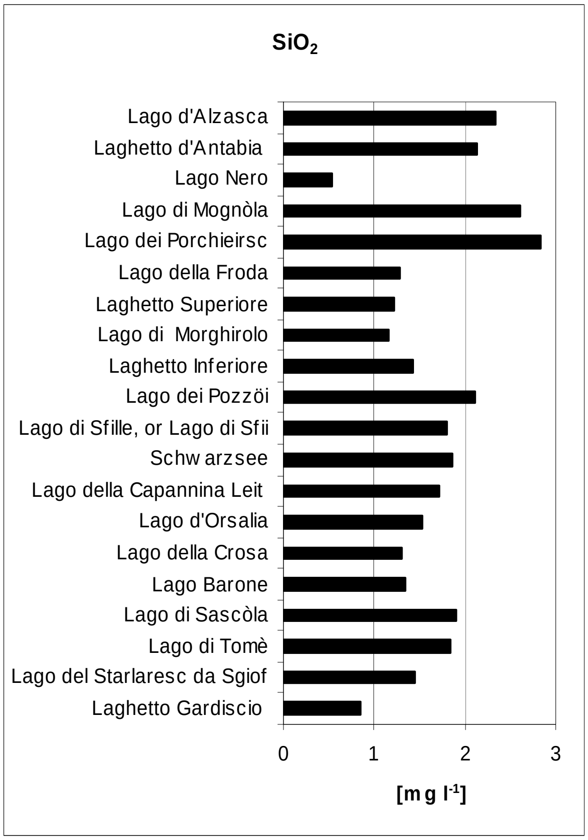
Figure 2.1 Annual average concentrations of the main chemical parameters in 20 Alpine lakes during 2007

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




pH
Lago d'Alzasca
Laghetto d'Antabia
Lago Nero
Lago di Mognòla
Lago dei Porchieirsc
Lago della Froda
Laghetto Superiore
Lago di Morghirolo
Laghetto Inferiore
Lago dei Pozzöi
Lago di Sfille, or Lago di Sfii
Schw arzsee
Lago della Capannina Leit
Lago d'Orsalia
Lago della Crosa
Lago Barone
Lago di Sascòla
Lago di Tomè
Lago del Starlaresc da Sgiof
Laghetto Gardiscio
0
2
4
6
8


$Al_{dissolved}$
Lago d'Alzasca
Laghetto d'Antabia
Lago Nero
Lago di Mognòla
Lago dei Porchieirsc
Lago della Froda
Laghetto Superiore
Lago di Morghirolo
Laghetto Inferiore
Lago dei Pozzöi
Lago di Sfille, or Lago di Sfii
Schw arzsee
Lago della Capannina Leit
Lago d'Orsalia
Lago della Crosa
Lago Barone
Lago di Sascòla
Lago di Tomè
Lago del Starlaresc da Sgiof
Laghetto Gardiscio
0
20
40
60
80
100
[µg l^{-1}]

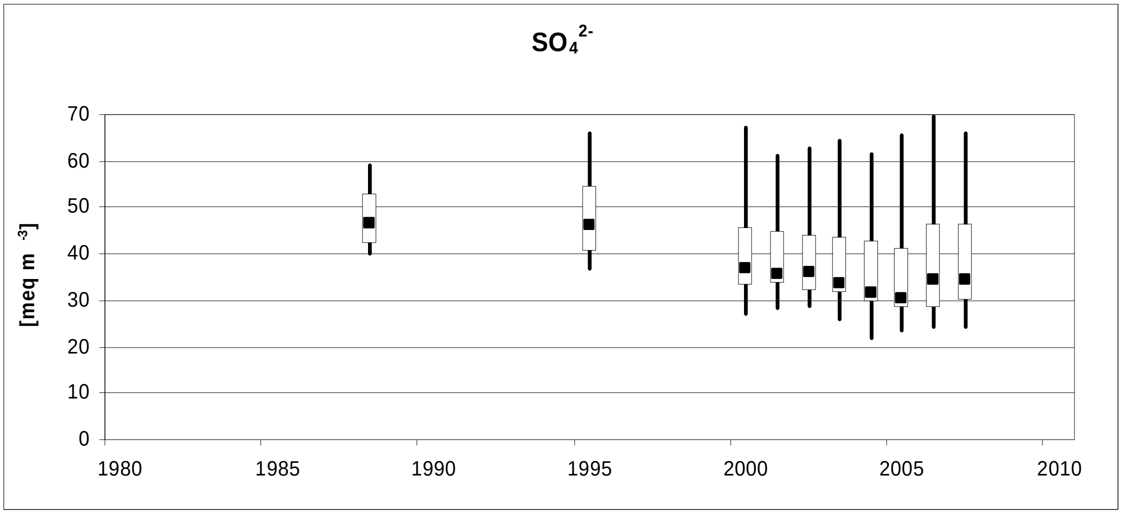

SiO_2
Lago d'Alzasca
Laghetto d'Antabia
Lago Nero
Lago di Mognòla
Lago dei Porchieirsc
Lago della Froda
Laghetto Superiore
Lago di Morghirolo
Laghetto Inferiore
Lago dei Pozzöi
Lago di Sfille, or Lago di Sfii
Schw arzsee
Lago della Capannina Leit
Lago d'Orsalia
Lago della Crosa
Lago Barone
Lago di Sascòla
Lago di Tomè
Lago del Starlaresc da Sgiof
Laghetto Gardiscio
0
1
2
3
[mg l^{-1}]

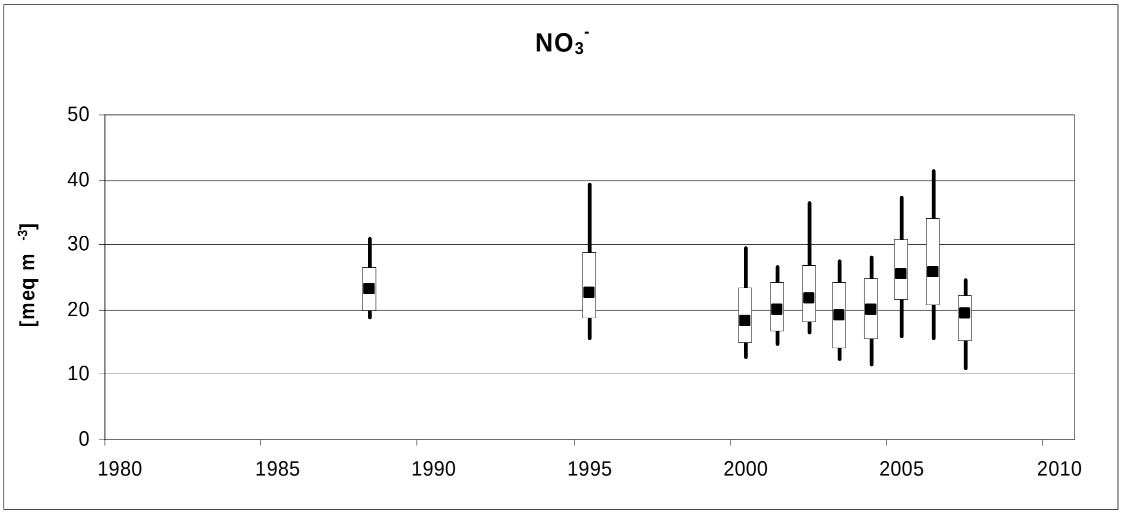
In order to show temporal variations of lake quality, annual median values of pH, alkalinity and concentrations of non sea salt base cations, sulphate and nitrate of all lakes with their 10th, 25th, 75th and 90th percentile values are represented in Fig. 2.6. In order to detect variations with time only 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 increased. For base cations and nitrate concentrations no trend can be observed.

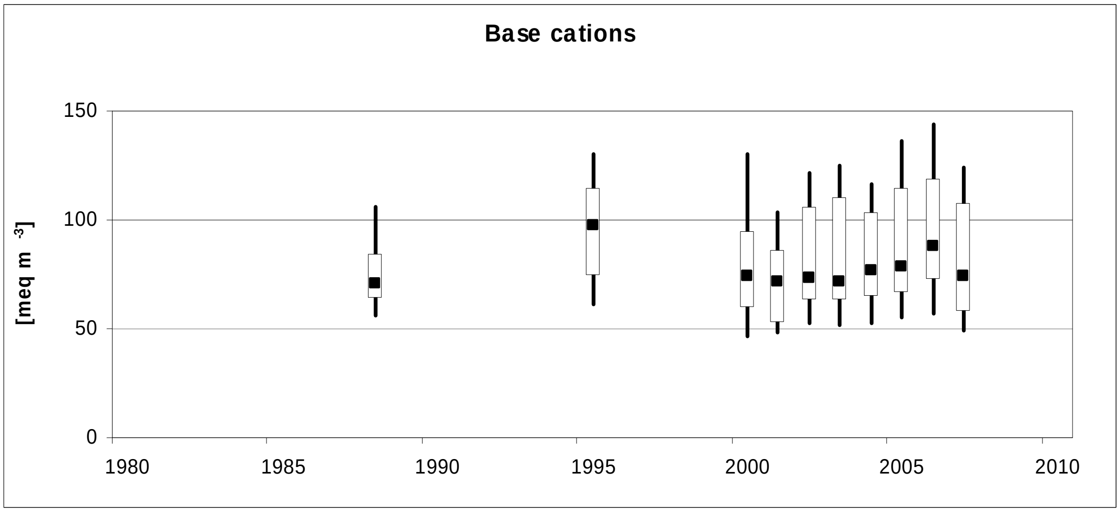
Interestingly, although wet deposition of sulphate and nitrogen decreased during the last 5 rain poor years, concentrations of nitrate, base cations and sulphate in the last 2 years seem to slightly increase in Alpine lakes. We suppose that a concentration effect (reduced dilution) might be the reason. However, since alkalinity increased as well concentrations of acid anions must have increased less than those of base cations plus ammonia, suggesting that decreased wet deposition of antropogenic pollutants must also have caused a reduction in alkalinity consumption. Furthermore, as a consequence of improved pH values also concentrations of dissolved aluminium decreased consistently after 2000.

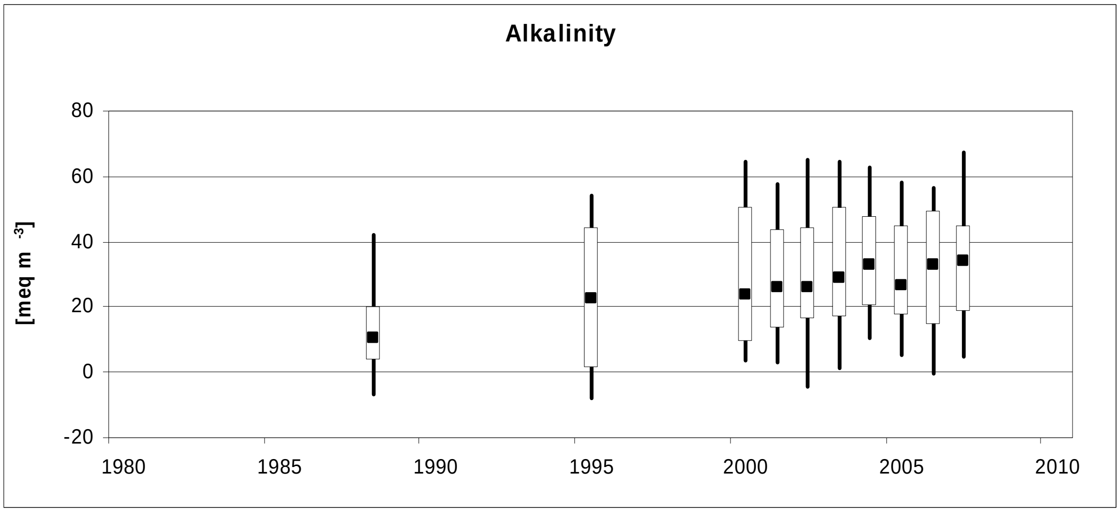
Figure 2.2 Temporal variations of annual median values and their 10th, 25th, 75th, 90th percentiles of parameters measured in 20 Alpine lakes from 1988 to 2007

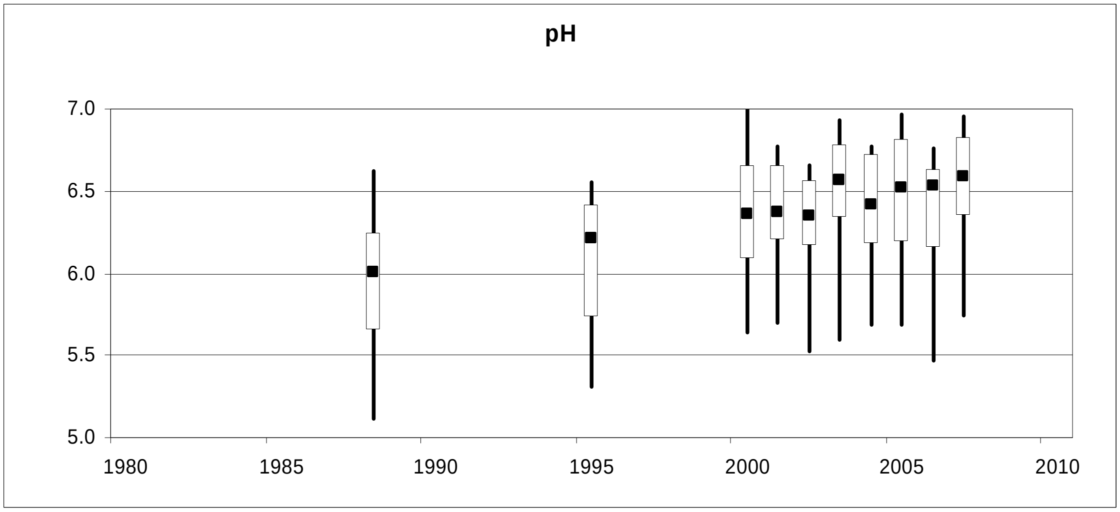
Base cations correspond to non sea salt base cations (calcium, magnesium and potassium)

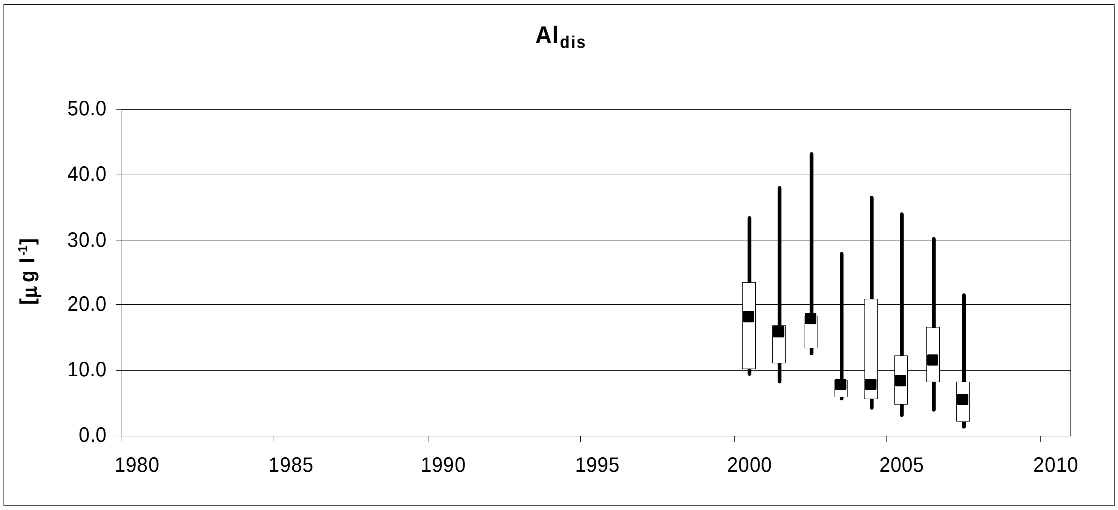







Alkalinity
80
60
40
20
0
-20
[meq m -3]
1980
1985
1990
1995
2000
2005
2010


pH
7.0
6.5
6.0
5.5
5.0
1980
1985
1990
1995
2000
2005
2010


Al$_{dis}$
50.0
40.0
30.0
20.0
10.0
0.0
[µg l-1]
1980
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 2007 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 2007.

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	2007	7.5	65.2	296	8.17	0.66	1.79	1.43	<0.012	9.52	0.68	1.48	0.47	4.63	5.9	6.8	<0.8	<1.0	<1.0	<1.7
Vedeggio	2007	7.1	48.0	174	5.08	1.00	1.68	0.62	<0.007	6.47	1.13	0.82	0.58	6.89	5.5	6.6	<0.3	<0.3	0.8	1.2
Verzasca	2007	6.9	25.0	70	2.84	0.23	0.75	0.59	<0.007	3.85	0.73	0.19	0.36	3.69	3.6	5.2	<0.2	<0.2	<0.5	<0.6

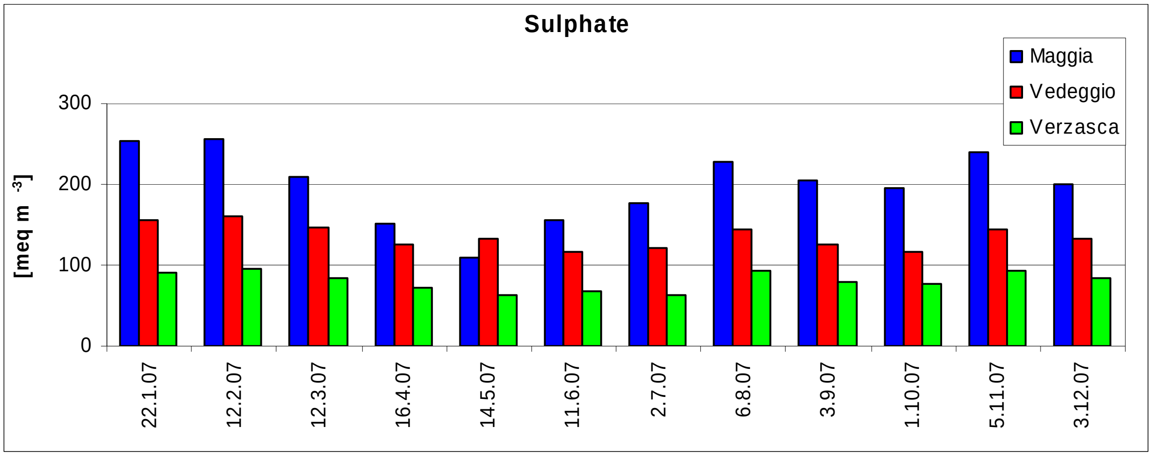
During 2007 average alkalinity was 296 µeq l^{-1} in river Maggia, 174 µeq l^{-1} in river Vedeggio and 70 µeq l^{-1} in river Verzasca. Based on these data River Verzasca and river Vedeggio have low alkalinities (50-200 µeq l^{-1}), but no river is sensitive to acidification. The same is suggested by their minimum alkalinities that were always > 0 µeq l^{-1}. Average pH was 7.5 in river Maggia, 7.1 in river Vedeggio and 6.9 in river Verzasca. Their minimum pH's were not much lower (Maggia: 7.2, Vedeggio: 7.1, Verzasca: 6.7). As a consequence of the relatively high pH's, dissolved aluminium concentrations were on average low ($\leq$ 6 µg l^{-1}). However, higher aluminium concentrations up to 13.9, 16.8, 10.7 µeq l^{-1} in river Maggia, Vedeggio and Verzasca, respectively occurred in the summer month July and August.

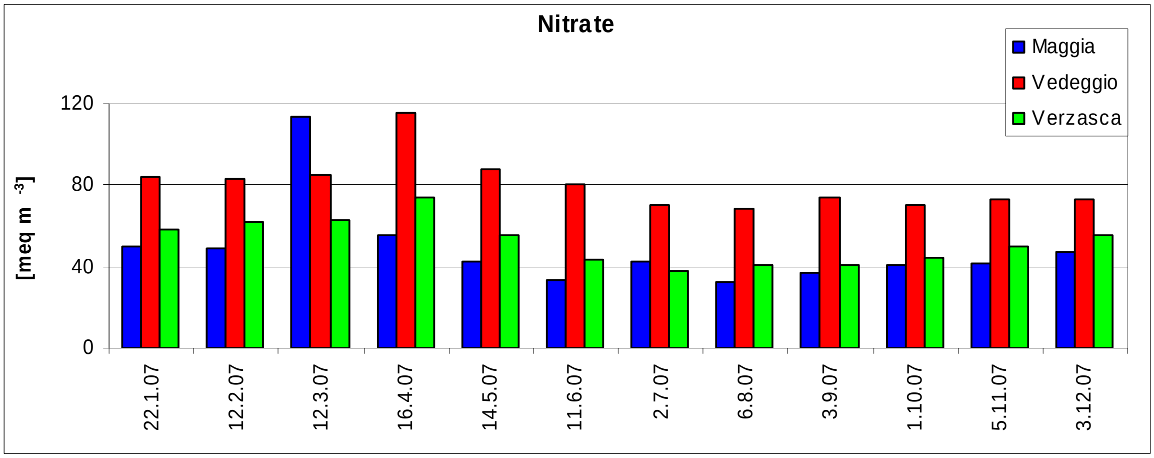
Fig. 2.7 shows the variations of the concentrations of sulphate, nitrate, base cations, alkalinity, pH and dissolved aluminium during 2007. It can be observed that the temporal variation of these parameters is the same in all 3 rivers. For sulphate, base cations, alkalinity and pH lowest values were measured in April and May. Differently, nitrate concentrations were highest during these months.

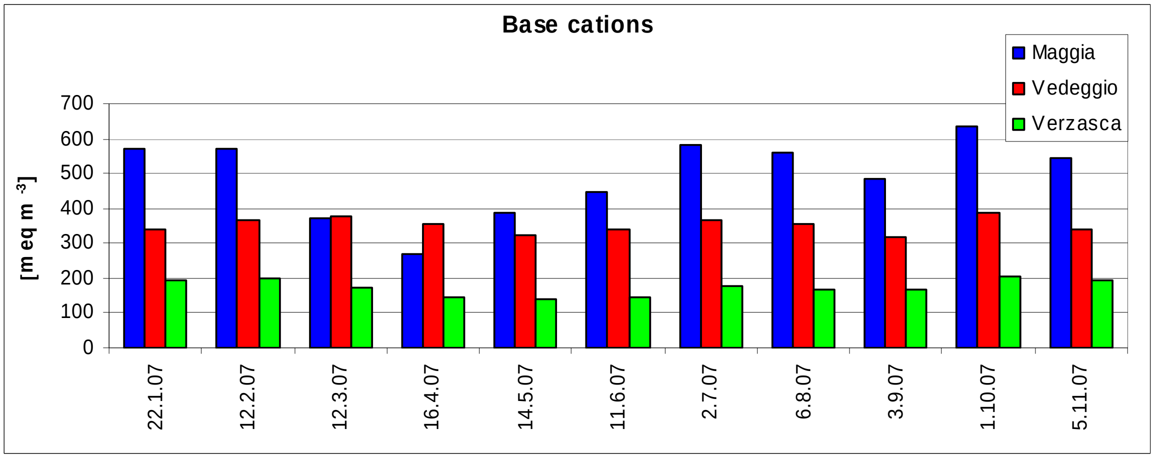
Comparing the seasonality of concentrations during 2007 with the temporal variations of the river discharge (Fig. 2.8, for river Maggia without the influence of hydropower production), it can be observed that discharge maxima overlap with concentrations minima of sulphate, base cations, alkalinity and 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, nitrate and aluminium concentrations seem to reach their highest concentrations during high flow events, probably due to leakage from soil of previously accumulated nitrate and aluminium.

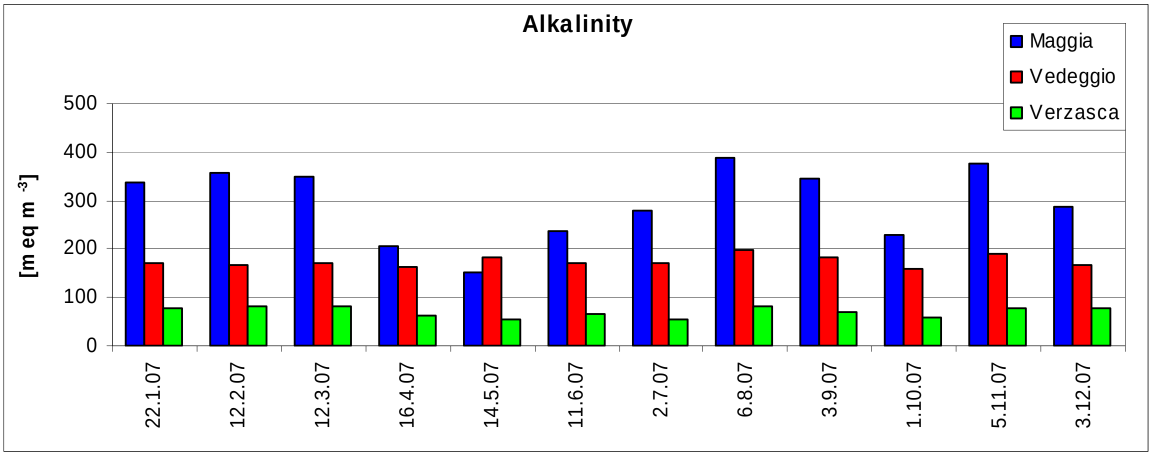
Figure 2.3 Concentrations of the main chemical parameters in river water during 2007

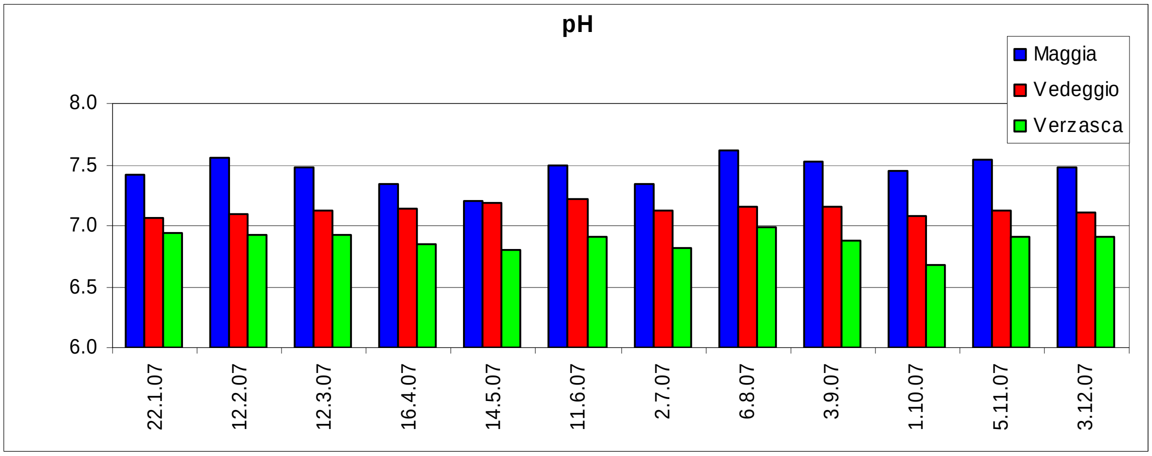
Base cations correspond to non sea salt base cations (calcium, magnesium and potassium)








Alkalinity
Maggia
Vedeggio
Verzasca
[meq m -3]
500
400
300
200
100
0
22.1.07
12.2.07
12.3.07
16.4.07
14.5.07
11.6.07
2.7.07
6.8.07
3.9.07
1.10.07
5.11.07
3.12.07


pH
Maggia
Vedeggio
Verzasca
8.0
7.5
7.0
6.5
6.0
22.1.07
12.2.07
12.3.07
16.4.07
14.5.07
11.6.07
2.7.07
6.8.07
3.9.07
1.10.07
5.11.07
3.12.07

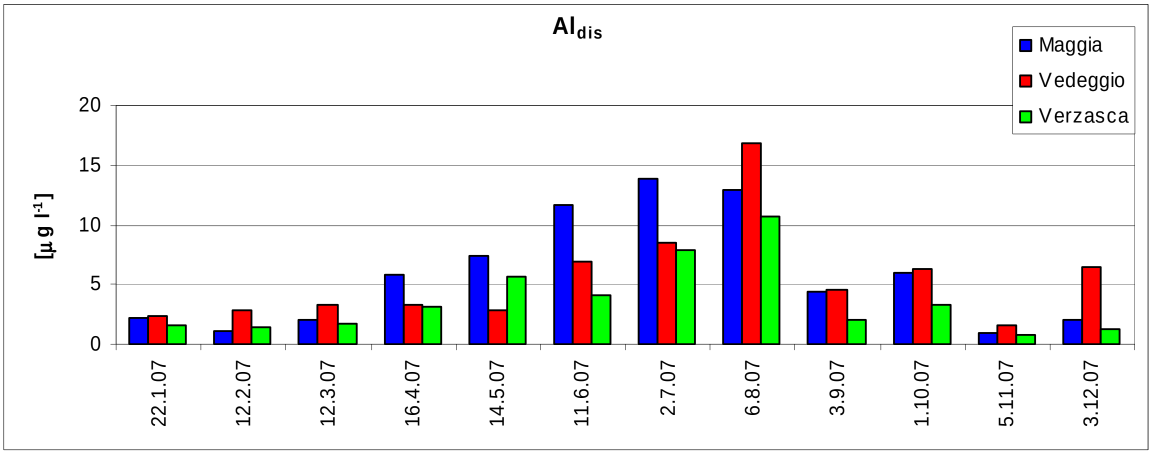
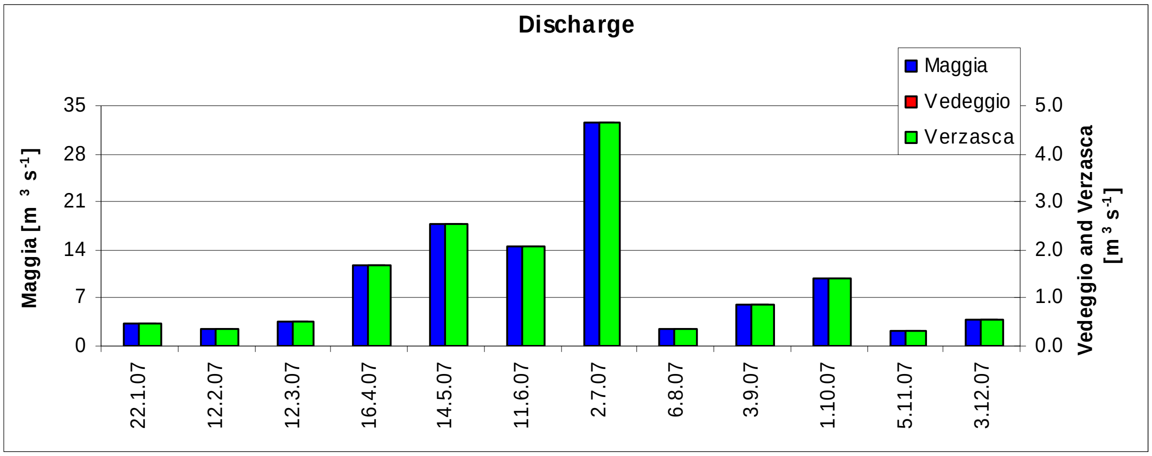

Al$_{dis}$
Maggia
Vedeggio
Verzasca
[μg l-1]
20
15
10
5
0
22.1.07
12.2.07
12.3.07
16.4.07
14.5.07
11.6.07
2.7.07
6.8.07
3.9.07
1.10.07
5.11.07
3.12.07

Figure 2.4 Daily average discharge during sampling days in 2007

Discharge of river Vedeggio at Isone is measured by IST (2008), 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 (2008).



In order to detect time trends, annual mean concentrations of sulphate, nitrate, base cations, alkalinity, pH and dissolved aluminium from 2000 to 2007 are presented graphically in Fig. 2.9.

As a consequence of the low amount of precipitation during the last 5 years and the related lower deposition rates of sulphate, nitrate, ammonia and base cations, one might expect a similar trend in river water chemistry. However, it has been shown when dicussing seasonality of river water chemistry that things are more complicated. It follows that, similarly to what observed for lake chemistry, concentrations of sulphate, nitrate and base cations tend to increase with decreasing yearly precipitation because of diminished dilution of river water, while the increase in alkalinity is caused by both concentration and decreased consumption. It follows that pH has increased as well during the last 5 years. Increasing pH and decreasing precipitation would suggest decreased dissolved aluminium concentrations. However, differently than what observed for Alpine lakes the opposite seems to occur. It seems that concentrations of aluminium have been determined not only by pH but have also been influenced by decreased dilution as a consequence of decreased precipitation.

Figure 2.5 Annual mean concentrations of the main chemical parameters in river water from 2000 to 2007

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

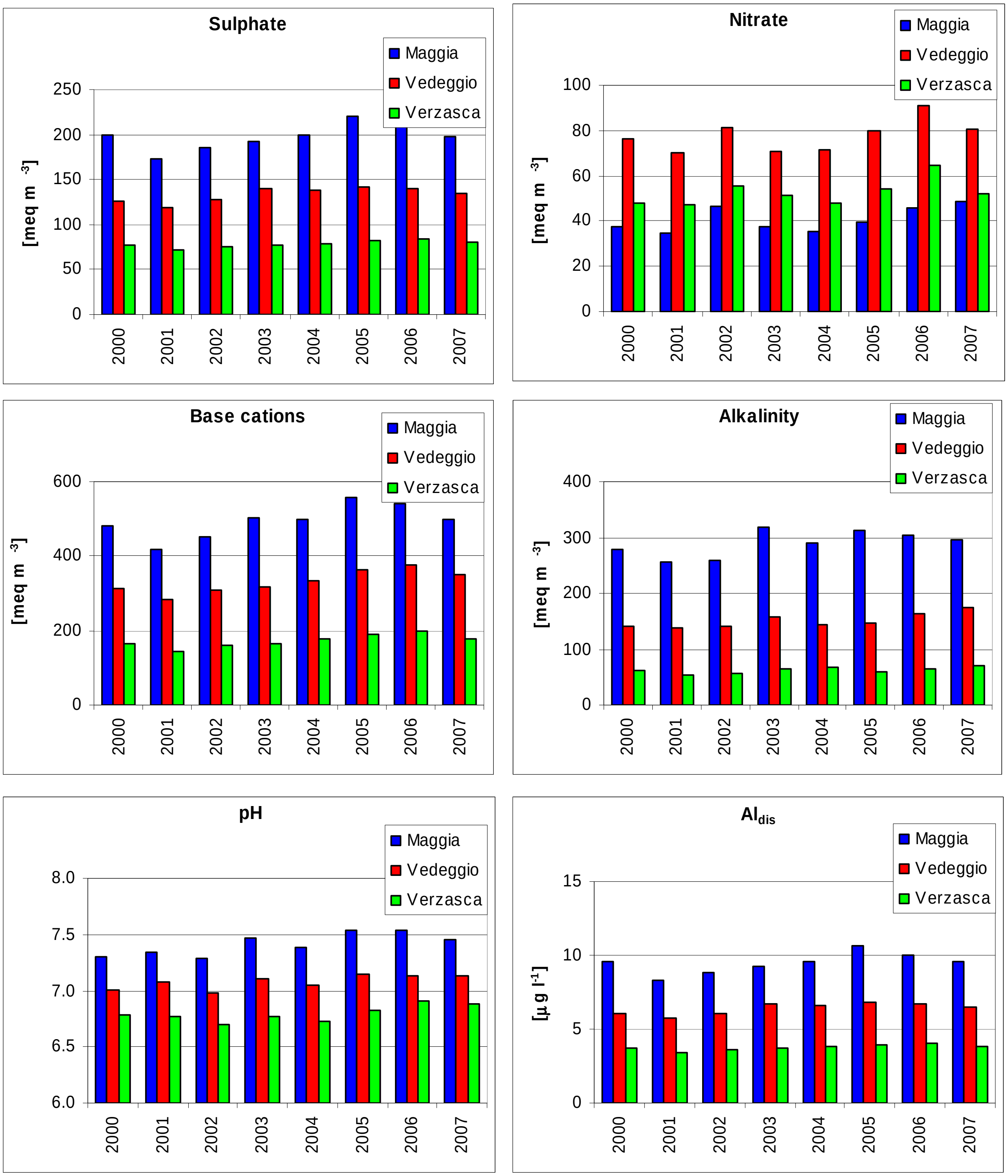
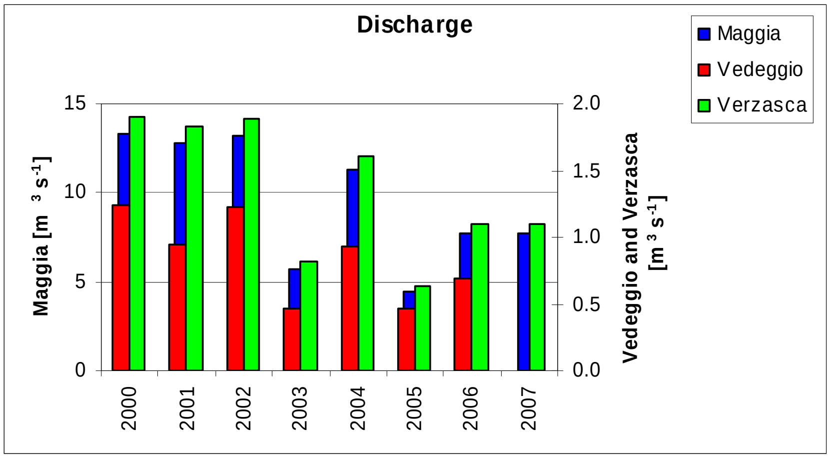


Figure 2.6 Yearly mean discharge of river Maggia, Vedeggio and Verzasca from 2000 to 2007

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.

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 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 between 2 and 3 times a year. Macroinvertebrates were conserved in 70% ethanol. 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, in the littoral of all lakes *Diptera* was the dominant order (average: 66%). followed by *Oligochaeta* (average: 17%) and *Others* (average: 12%). In the emissaries other orders like *Plecoptera* were also important. The species diversity (=E.B.I. taxa number) was higher in the emissary than in the littoral and the higher EPT index in the emissary reflects a greater abundance of the orders *Ephemeroptera*, *Plecoptera* and *Trichoptera*.

Variations in macroinvertebrate population among lakes are probably influenced by differences in water acidity. Average pH during 2007 was 7.7, 6.7, 6.7, 5.8, 5.6 in Lago Bianco, Laghetto Superiore, Laghetto

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 taxa index were highest in Lago Bianco followed by Laghetto Superiore, Laghetto Inferiore, Lago di Tomè and Lago del Starlaresc da Sgiof. A similar trend can be observed in samples from the littoral with exception of Lago Bianco, whose E.B.I. taxa number and EPT index were lowest despite its highest pH value. We assume that its particular littoral morphology (very small grain size) might be the reason. 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 Superiore 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 Starlaresca da Sgiof *Oligochaeta* were absent and the percentage of *Diptera* was even higher, particularly in Lago del Starlaresc da Sgiof. In the emissary of Lago di Tomè *Plecoptera* was the second most abundant order. In all lakes *Diptera* was mainly represented by *Chirononmidae* 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 and Lago del Starlaresc da Sgiof and only few organisms of it were found 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*).

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 2007

LI, LS, LT, LSt, LB stay for Laghetto Inferiore, Laghetto Superiore, Lago di Tomè, Lago del Starlaresc da Sgiof, Lago Bianco

	Littoral					**Emissary**				
	LI	**LS**	**LT**	**LSt**	**LB**	**LI**	**LS**	**LT**	**LSt**	**LB**
no. of samples	2	2	2	2	2	2	2	2	2	2
no. organisms	2556	4243	1668	2760	6030	7714	5348	4007	3487	5910
no. taxa E.B.I.	13	12	9	10	5	17	14	14	12	19
EPT index	3	3	3	1	1	7	7	5	4	9
Ephemeroptera	0%	0%	0%	0%	0%	1%	0%	0%	0%	1%
Plecoptera	1%	3%	0%	0%	0%	5%	3%	34%	9%	9%
Trichoptera	2%	4%	6%	0%	0%	0%	1%	1%	1%	1%
Diptera	75%	51%	58%	90%	56%	58%	30%	64%	84%	38%
Coleoptera	1%	1%	2%	0%	0%	0%	0%	0%	0%	0%
Oligochaeta	14%	10%	28%	4%	31%	30%	64%	0%	0%	50%
Others	8%	30%	7%	3%	13%	5%	2%	1%	1%	1%

Tab. 3.2 presents the number of taxa for the five "Braukmann and Biss" indexes from 2002 to 2007, 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 can not 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 seem 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 2000 to 2007

The gray colored areas indicate the absence of samples

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

Table 3.3 Macroinvertebrate species with lowest "Braukmann and Biss index" in 5 Alpine lakes from 2000 to 2007

X refers to the emissary and (X) to the littoral. The gray colored areas indicate the absence of samples

Lakes	Taxa	Index	2000	2001	2002	2003	2004	2005	2006	2007
Laghetto Inferiore	Ecdyonurus sp.	2					x	x	x	x
	Ecdyonurus helveticus-Gr.	2				x	x	x	x	x
	Isoperla rivuloruum	2							x	x
	Perlodes sp.	2					x			x
	Perlodes intricatus	2					x	x		x
	Philopotamus lucidificatus	2				x		x	x	
	Protonemoura nimborum	2	x					x	x	x
	Rhitrogena semicolorata-Gr.	2				x				
Laghetto Superiore	Baetis alpinus	2				x	x		x	
	Ecdyonurus sp.	2				x	x	x	x	x
	Ecdyonurus gr. helveticus	2				x		x		x
	Ecdyonurus parahelveticus	2					x			
	Isoperla rivulorum	2				x	x			
	Perlodes sp.	2					x			
	Perlodes intricatus	2					x	x		x
	Perlodes microcephalus	2				x				
	Protonemoura nimborum	2						x	x	x
	Rhitrogena gr. semicolorata	2					x			
Lago Tomè	Perla grandis	1	▨	x						
	Protonemura nimbrorum	2	▨					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
	Ryacophila sensu stricto-Gr.	4	▨					x	x	x
	Sialis sp.	4	▨		x	x				
	Sialis fuliginosa	4	▨				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
	Sialis sp.	4	▨				(x)	(x)	(x)	
	Sialis fuliginosa	4	▨							(x)
Lago Bianco	Alainites muticus	2	▨	▨	▨	▨	▨	▨	x	
	Baetis alpinus	2	▨	▨	▨	▨	▨	▨	x	x
	Ecdyonurus sp.	2	▨	▨	▨	▨	▨	▨	x	
	Perlodes sp.	2	▨	▨	▨	▨	▨	▨	x	x
	Perlodes intricatus	2	▨	▨	▨	▨	▨	▨	x	x
	Philopotamus ludificatus	2	▨	▨	▨	▨	▨	▨		x
	Protonemura nimborum	2	▨	▨	▨	▨	▨	▨	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 during 2007 are shown in Tab. 3.4. The number of E.B.I. taxa and the EPT index were highest in river Maggia and Vedeggio, followed by river Verzasca. The main orders were *Ephemeroptera* (average: 31%), *Diptera* (average: 27%), *Plecoptera* (average: 19%) and *Coleoptera* (average: 15%).

Table 3.4 Number of samples, organisms, taxa, average abundances of the main macroinvertebrate groups and EPT index in 3 Alpine rivers during 2007.

	Maggia	Vedeggio	Verzasca
no. of samples	4	4	4
no. organisms	19126	9442	21054
no. taxa E.B.I.	43	42	30
EPT index	17	18	12
Ephemeroptera	24%	27%	41%
Plecoptera	16%	28%	12%
Trichoptera	2%	6%	1%
Diptera	37%	23%	22%
Coleoptera	12%	13%	19%
Oligochaeta	4%	1%	3%
Others	5%	2%	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". A temporal trend can not 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 2007

River	Braukmann and Biss index	2000	2001	2002	2003	2004	2005	2006	2007
Maggia	1	4	3	2	3	4	4	4	4
	2	19	12	16	14	16	16	16	17
	3	4	5	2	5	5	7	4	6
	4	3	1	5	8	6	6	8	6
	5	3	1	5	8	6	6	8	4
Vedeggio	1	5	2	2	2	2	4	2	3
	2	16	17	18	18	17	18	19	18
	3	5	6	3	5	5	8	7	6
	4	3	5	3	4	6	7	10	6
	5	9	4	3	5	5	4	4	3
Verzasca	1	3	2	2	2	3	2	2	2
	2	12	11	12	11	11	12	14	11
	3	5	5	3	7	5	5	6	5
	4	4	3	5	6	5	6	8	6
	5	5	4	3	4	3	3	3	3

Table 3.6 Macroinvtebrate species with lowest “Braukmann and Biss index” in 3 Alpine rivers from 2000 to 2007

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

Table 3.7 “Braukmann and Biss categories” and their relative river sample number from 2000 to 2006

Rivers	Category	2000	2001	2002	2003	2004	2005	2006	2007
Maggia	1	0%	0%	0%	0%	40%	0%	0%	0%
	2	100%	100%	100%	100%	60%	100%	100%	75%
Vedeggio	1	0%	0%	50%	0%	0%	0%	0%	0%
	2	100%	100%	50%	100%	100%	100%	75%	50%
Verzasca	1	0%	0%	0%	0%	0%	0%	0%	0%
	2	100%	100%	100%	100%	100%	100%	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 fall 2007 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. 6.1. The CI above 1 indicates a good physical condition of the fish in both lakes, particularly in Laghetto Superiore.

Table 4.1 Number of fish and average weight, length and conditioning index (C.I.) in samples from 2007.

	Altitude (m a.s.l.)	Species	Fish number	Weight (g)	Length (cm)	C.I.	Age [months]
Laghetto Inferiore	2074	*Oncorhynchus mykiss*	17	82.7	19.5	1.06	36
Laghetto Superiore	2128	*Oncorhynchus mykiss*	11	136.2	21.8	1.22	40

4.3.2 DDT's in fish muscle

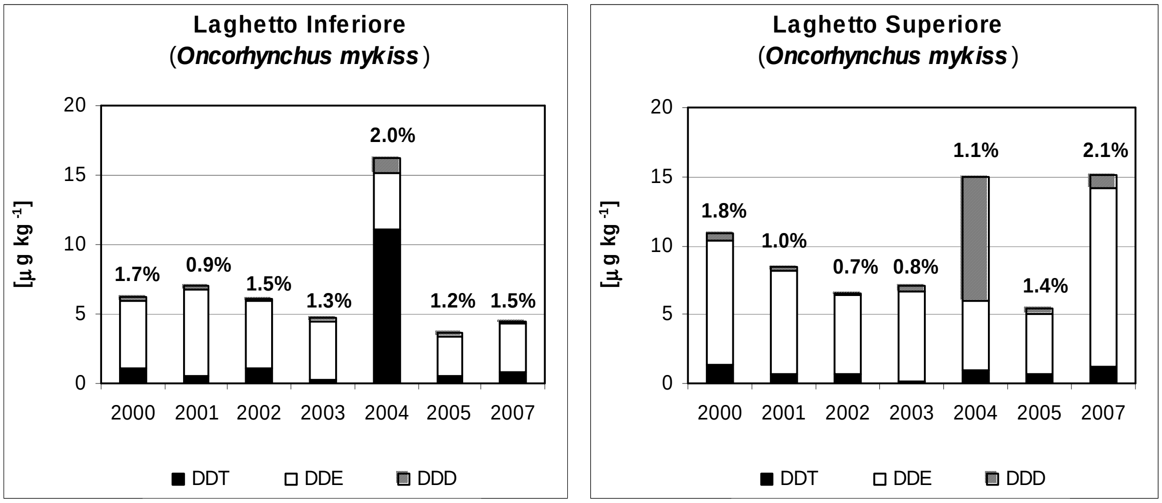
Most DDT found in the Southern part of the Swiss Alps probably origins from a contaminated site situated along the shore of Lago Maggiore, where until 1996 a factory has produced DDT. In fact, elevated total DDT concentrations (8-308 μg kg^{-1}) are still measured in fish from Lago Maggiore (Cipais,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

Fish samples from Lago Inferiore and Superiore were characterized by total DDT concentrations of 4.4 μg kg^{-1} and 15.1 μg kg$^{-1,}$ respectively and DDE was as usual the main component (80% in Laghetto Inferiore and 86% 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. The presence of 2 particularly large (26 cm), fat (200-244 g) and old fish (57-69 months), that could absorbed DDT for a longer period, may also have influenced the result.

Compared to 2005, DDT concentrations in fish muscle seemed to increase again in 2007. This might be explained with higher precipitation and therefore DDT deposition in 2006. In fact, precipitation measured by MeteoSuisse at Robiei was 1476 mm in 2005 and 2146 mm in 2007 and deposition of total DDT at Robiei has shown to be higher in 2006 with respect to 2005 (Cipais, 2007).

Figure 4.1 Concentrations of DDT's in fish muscle of Laghetto Inferiore and Laghetto Superiore between 2000 and 2007
The percentage value refers to the lipid content.



Laghetto Inferiore
(***Oncorhynchus mykiss***)

Laghetto Superiore
(***Oncorhynchus mykiss***)

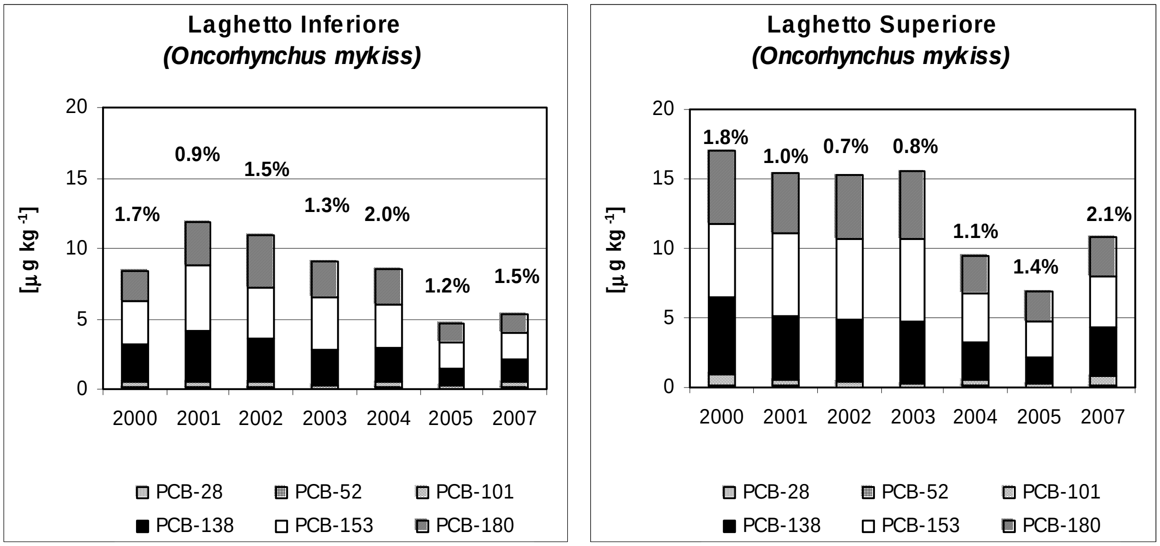
4.3.3 PCB's in fish muscle

Total PCB concentrations in fish samples from 2007 were 5.3 μg kg^{-1} in Laghetto Inferiore and 10.8 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 can not be explained only by these phenomena. As already discussed for DDT the presence of 2 long, fat and old fish may have influenced the results, as well. Also for PCB an increase of concentrations in 2007 can be observed.

Interestingly, without considering concentrations of DDT in Laghetto Inferiore and Superiore in 2004 and in Laghetto Superiore in 2007, temporal variations of DDT and PCB are very similar and a decreasing trend seem to occur, suggesting that the mechanisms determining concentrations in fish muscle must be the same. This results seems to contradict increased wet deposition of DDT and PCB after 2003 at Robiei (Cipais, 2007). It follows that concentrations of DDT and PCB in fish muscle are not directly related to atmospheric deposition, but are controlled by other factors as well.

Figure 4.2 Concentrations of PCB's in fish muscle of Laghetto Inferiore and Laghetto Superiore between 2000 and 2007
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 2007 was lower than 1 µg kg^{-1} (edibility limit: 100 µg kg^{-1}).

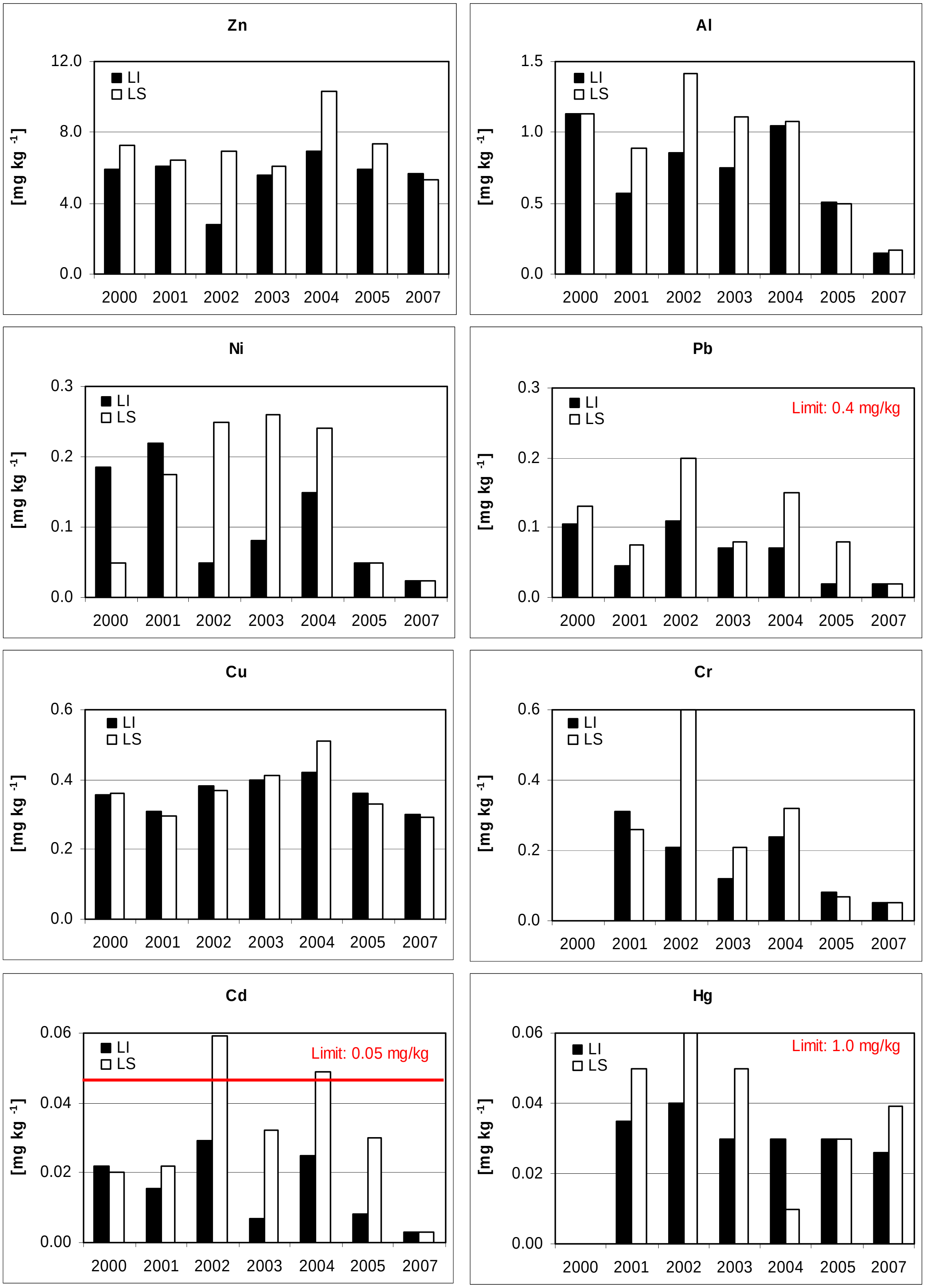
4.3.5 Metals in fish muscle

Metals concentrations in fish muscle sampled in 2007 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.

Table 4.2 Metal concentrations in fish muscle (mg^{-1} kg wet weight) measured in 2007

	Laghetto Inferiore (*Oncorhynchus mykiss*)	**Laghetto Superiore** (*Oncorhynchus mykiss*)
Zn	5.62	5.34
Al	0.15	0.17
Cu	0.30	0.29
Cr	0.051	0.051
Ni	<0.023	<0.023
Pb	<0.020	<0.020
Cd	0.003	0.003
Hg	0.026	0.039

Figure 4.3 Metal concentrations in fish muscle (mg^{-1} kg wet weight) measured in 2005



Conclusion

During the last five years precipitation was lower than usual. Although concentrations of sulphate in rain water continued to decrease, reflecting reduction in emissions into the atmosphere, a slight increase of concentrations and deposition of acidity at most sites is observed. A reduction in the frequency of the occurrence of alkaline rain events is probably the main reason of this trend.

Interestingly, although wet deposition of sulphate and nitrogen decreased during the last 5 rain poor years, concentrations of nitrate, base cations and sulphate in the last 2 years seem to slightly increase in Alpine lakes. We suppose that a concentration effect (reduced dilution) might be the reason. However, since alkalinity increased as well concentrations of acid anions must have increased less than those of base cations plus ammonia, suggesting that decreased wet deposition of antropogenic pollutants must also have caused a reduction in alkalinity consumption. Furthermore, as a consequence of improved pH values also concentrations of dissolved aluminium decreased consistently after 2000.

During the same time period concentrations of sulphate, nitrate and base cations in river water tended to increase with decreasing yearly precipitation because of diminished dilution of river water, while the increase in alkalinity is caused by both concentration and decreased consumption. It follows that pH has increased as well during the last 5 years. Increasing pH and decreasing precipitation would suggest decreased dissolved aluminium concentrations. However, the opposite seems to occur. It seems that concentrations of aluminium have been determined not only by pH but have also been influenced by decreased dilution as a consequence of decreased precipitation.

It can be concluded, that hydrology highly influences quality of atmospheric deposition, alpine lakes and rivers. As a consequence, seasonal variations and long term trends in concentrations and deposition should not be discussed separately from hydrology.

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