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 2005-2006

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Content

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.

1 Study site

The study area is located at 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 regularly since 2000. 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

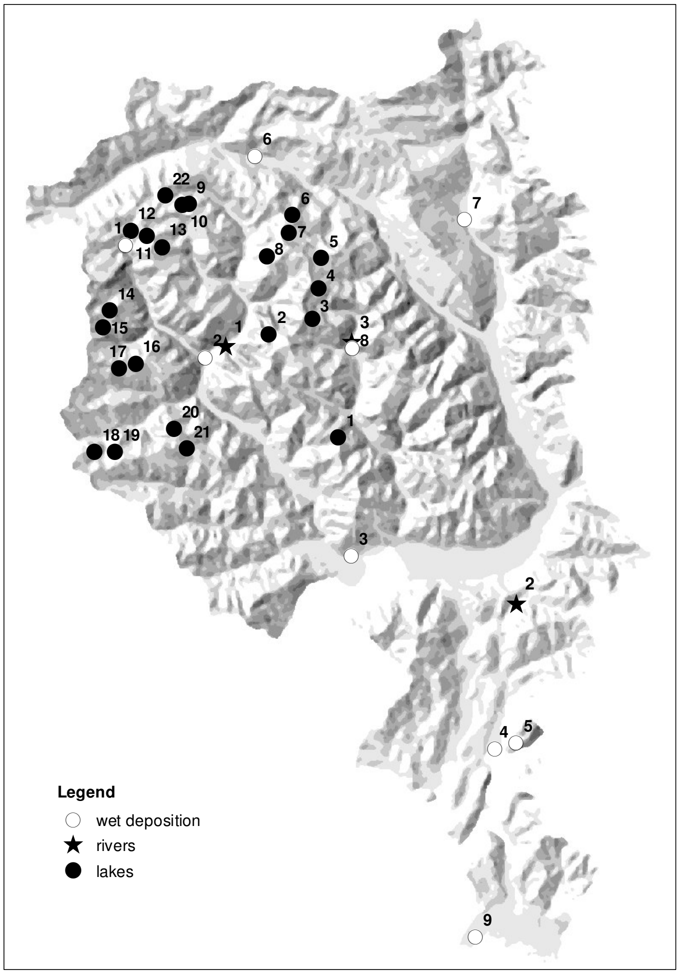


Table 1.1 Lake parameters

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, we monitored the amount of wet deposition and water chemistry of 20 Alpine lakes (21 from 2006) and 3 rivers (Maggia, Vedeggio, Verzasca).

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. 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

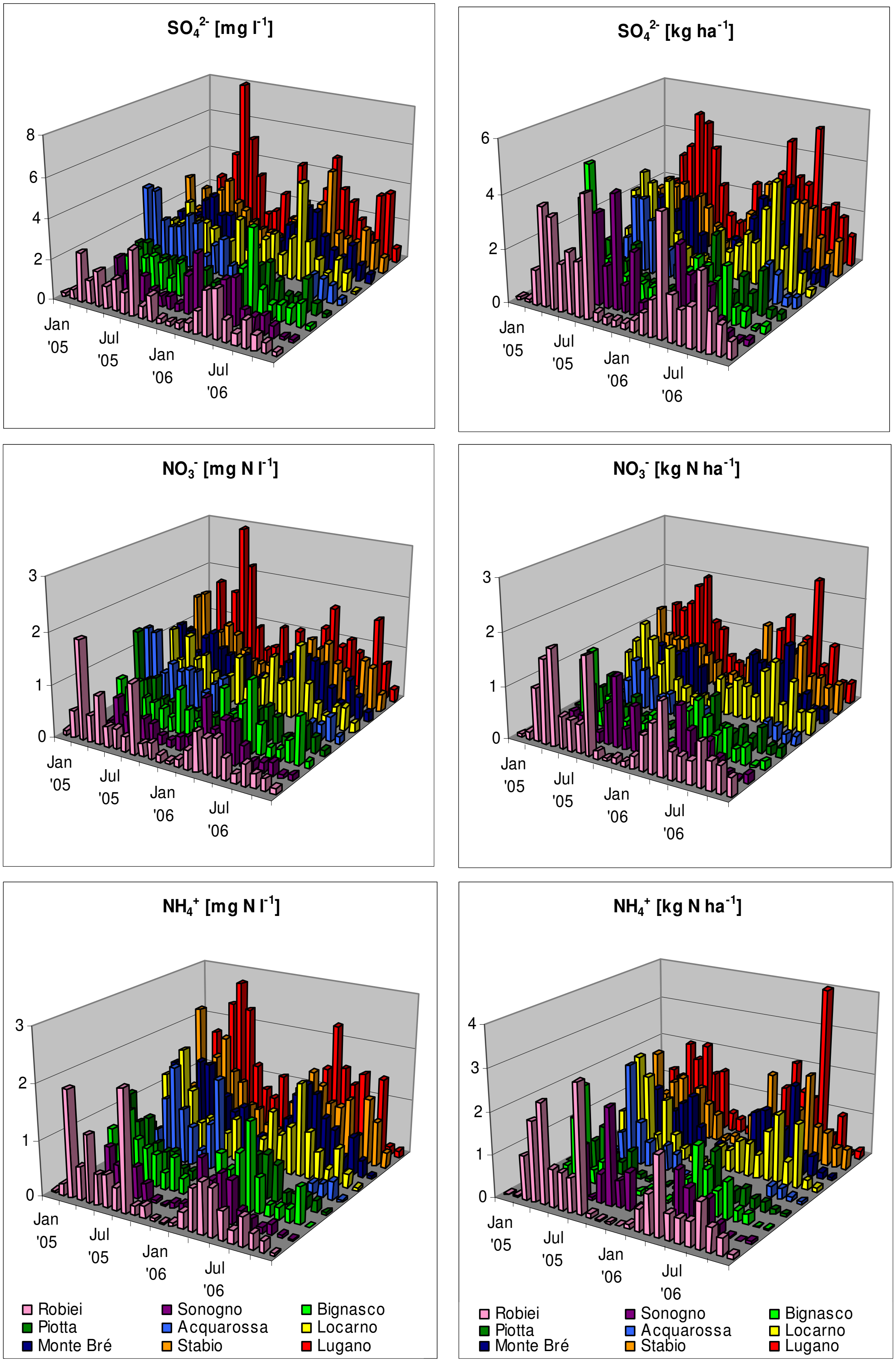
2.4.1 Wet deposition

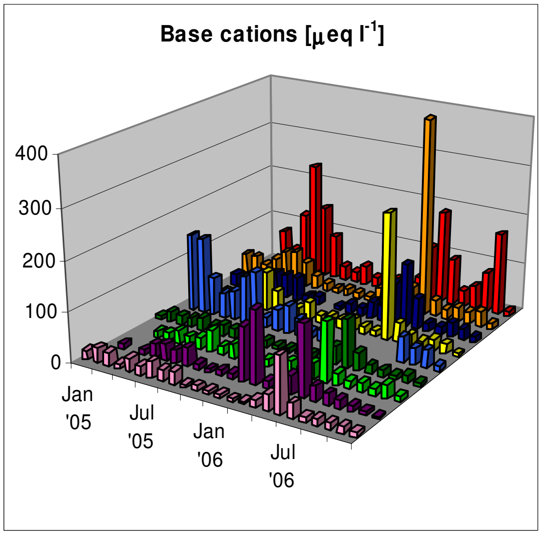
Monthly and yearly mean concentrations in precipitation were calculated by weighting weekly concentrations with the precipitation volume, while monthly and yearly wet deposition were calculated by multiplying monthly and yearly concentrations with the precipitation volume. To estimate precipitation volumes, data from MeteoSwiss were used. 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.

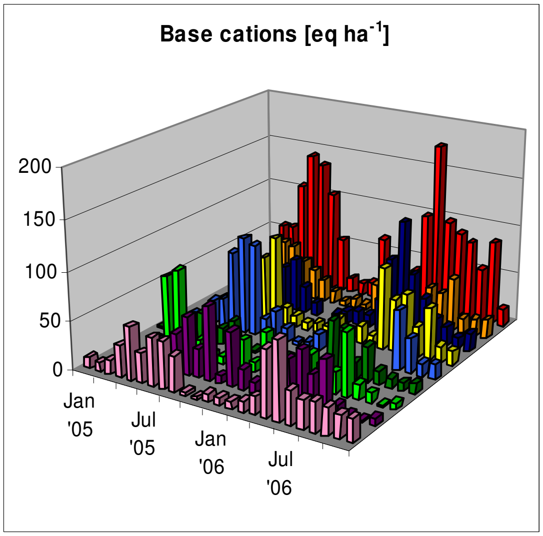
Seasonal variations of monthly mean rain water concentrations and deposition rates of the main chemical parameters during 2005 and 2006 are shown in Fig. 2.1. In general, no seasonal trend in rain water concentrations can be observed. However, because of increased precipitation during warmer month (Fig. 2.2), wet deposition was also higher during summer months. Interestingly, both concentrations and deposition rates of acidity varied much from month to month without a seasonal trend. As a consequence, rain water quality fluctuated irregularly from acid to alkaline.

Figure 2.1 Seasonal variations of monthly average rain water concentrations and deposition rates during 2005 and 2006

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




Base cations [μeq l^{-1}]
400
300
200
100
0
Jan '05
Jul '05
Jan '06
Jul '06


Base cations [eq ha^{-1}]
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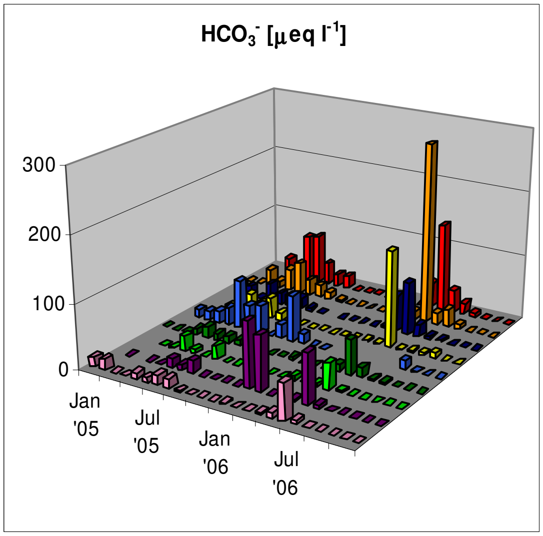
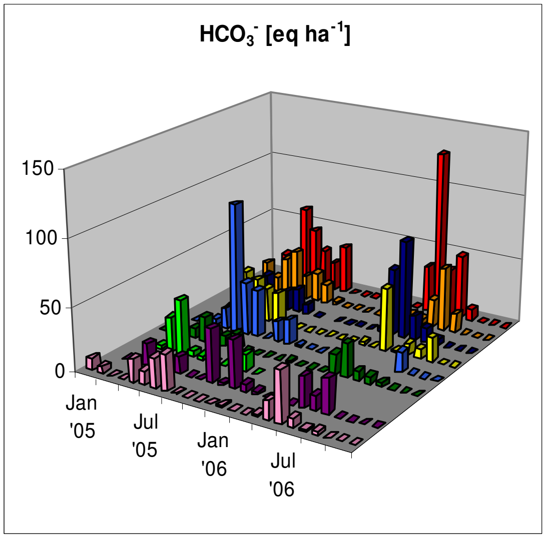
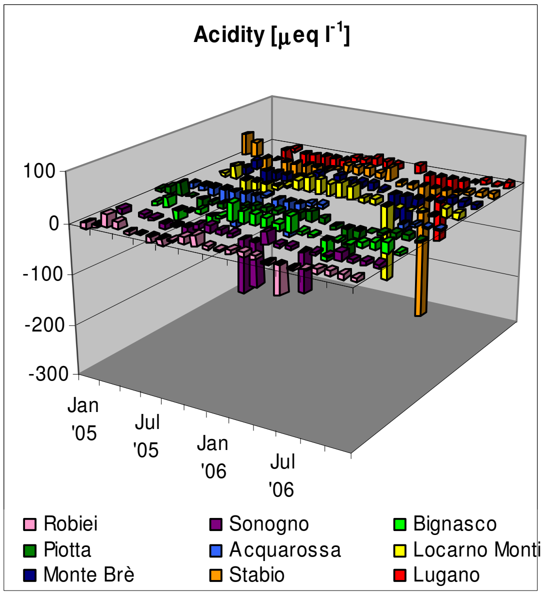
150
100
50
0
Jan '05
Jul '05
Jan '06
Jul '06


HCO$_3^-$ [μeq l^{-1}]
300
200
100
0
Jan '05
Jul '05
Jan '06
Jul '06


HCO$_3^-$ [eq ha^{-1}]
150
100
50
0
Jan '05
Jul '05
Jan '06
Jul '06


Acidity [μeq l^{-1}]
100
0
-100
-200
-300
Jan '05
Jul '05
Jan '06
Jul '06
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Locarno Monti
Monte Brè
Stabio
Lugano

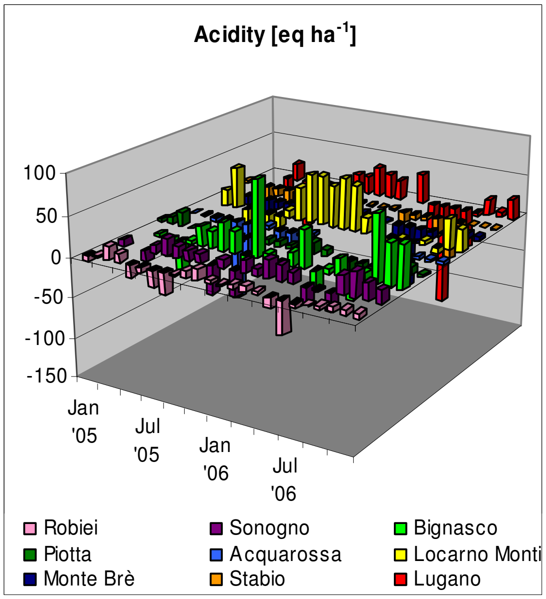
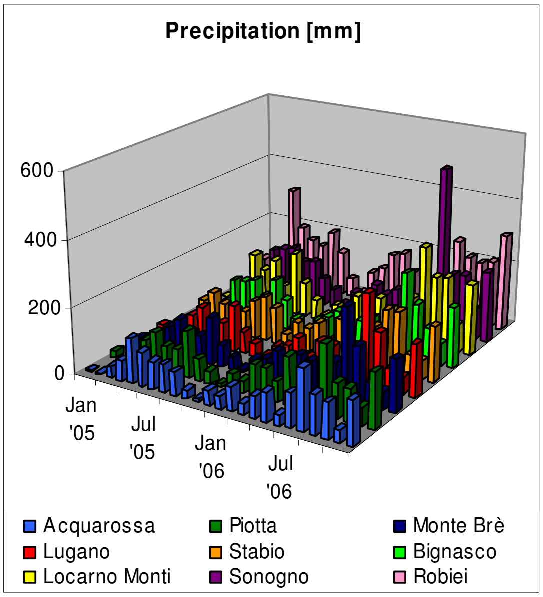

Acidity [eq ha^{-1}]
100
50
0
-50
-100
-150
Jan '05
Jul '05
Jan '06
Jul '06
Robiei
Sonogno
Bignasco
Piotta
Acquarossa
Locarno Monti
Monte Brè
Stabio
Lugano

Figure 2.2 Monthly precipitation during 2005 and 2006

Data from MeteoSwiss



Annual average rain water concentrations of the main chemical parameters and their yearly deposition rates during 2005 and 2006 are shown in Tab. 2.2. Because of technical problems of the sampling engine, rain samples could not be sampled at Acquarossa between March and August 2006. As a consequence, annual average values of 2006 at this sampling site are not representative and are therefore not discussed further.

In general, ion concentrations of anthropogenic origin (sulphate, nitrate, ammonia) were highest at sampling sites with low latitudes like Lugano, Monte Brè and Stabio. On the contrary, concentrations were lowest at sites with high latitudes like Bignasco, Piotta, Robiei and 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. Because of its highest precipitations, highest deposition rates of ammonia, nitrate and sulphate were measured at Robiei, although it is situated at high longitude and altitude.

During 2005-2006 lowest average acidity and highest concentrations of base cations and bicarbonate were measured at Lugano, Stabio, Monte Brè and Acquarossa.

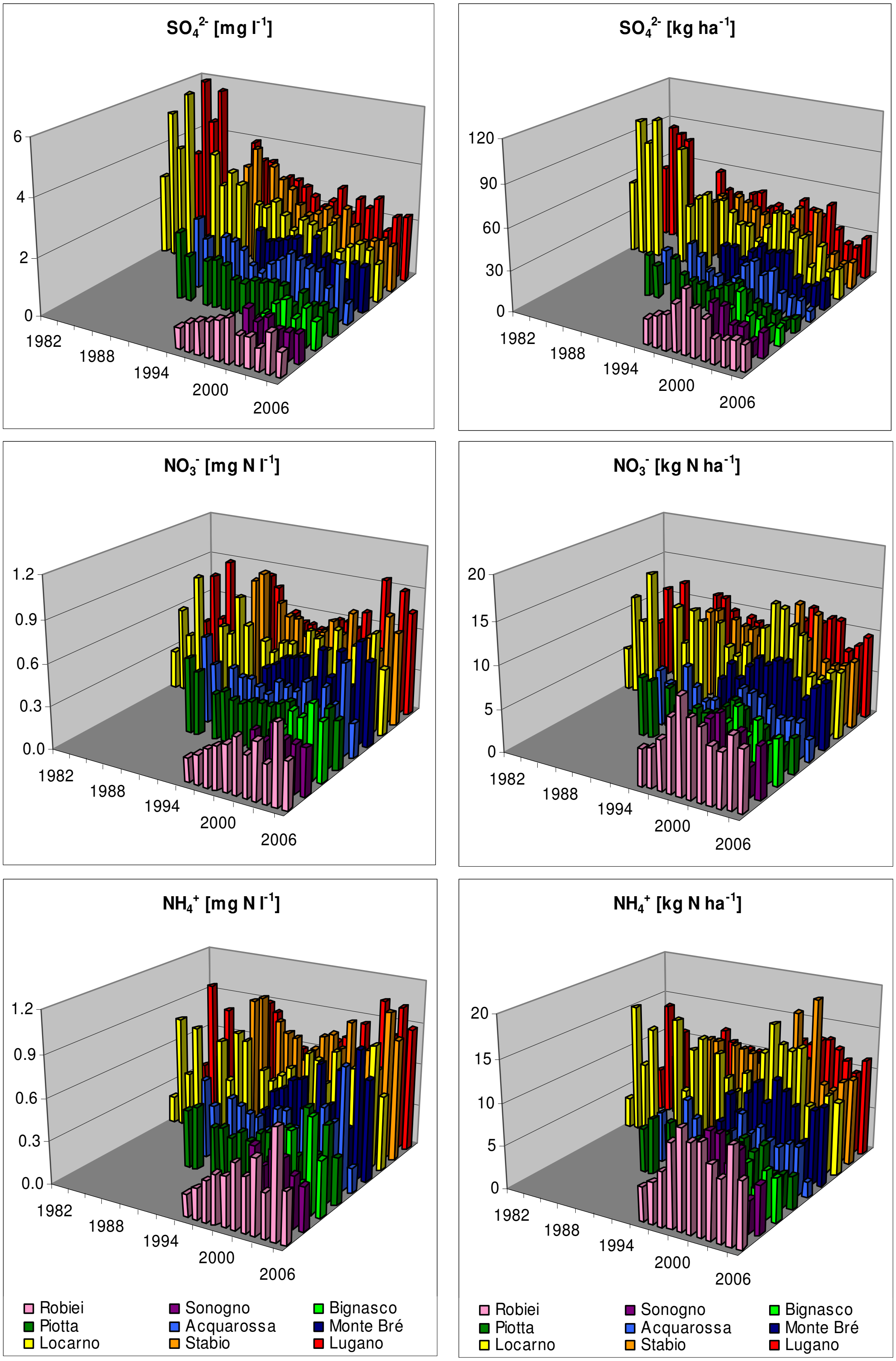
Variation of yearly average rain water concentrations and deposition rates of the main chemical parameters during time are shown in Fig. 2.3. Since before 1988, rain water was collected with bulk samplers and after 1988 with wet-only samplers, data of these 2 periods should not be compared with each 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. Instead no significant trend can be observed for ammonia and nitrate concentrations and deposition rates. Interestingly, yearly average bicarbonate concentrations increased during the monitoring period. 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 causing by deposition of Saharan dust. Decreasing sulphate concentrations and increasing bicarbonate concentrations generated an increase of pH. From the end of 1980's to the beginning of this millennium yearly average rain water pH at Locarno Monti, Lugano and Stabio increased from around 4.3 to 5.1. As a consequence of decreasing H^+ and increasing bicarbonate concentrations, yearly average acidity (acidity=H^+-HCO_3^-) also decreased. In fact, after 2000 at most sites yearly average acidity started to be negative.

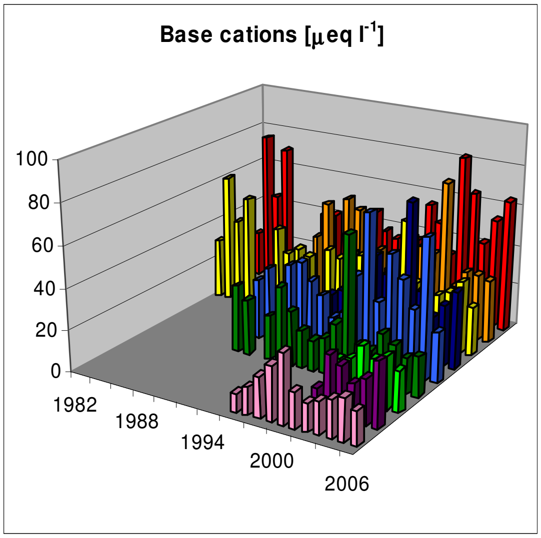
Table 2.2 Yearly mean rain water concentrations and deposition rates during 2005 and 2006

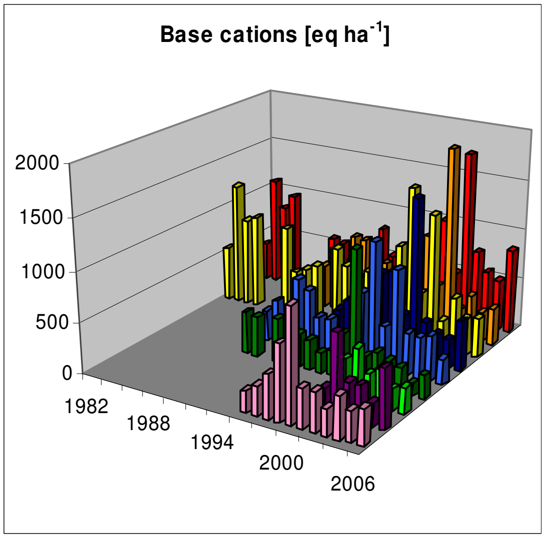
Sampling site	Year	Precipitation (mm)	Analysed precipitation	Conductivity 25°C (µS cm^{-1})	pH	Ca^{2+}		Mg^{2+}		Na^{+}		K^{+}		NH$_4^+$		HCO$_3^-$		SO$_4^{2-}$		NO$_3^-$		Cl$^-$		Acidity = H$^+$– HCO$_3^-$	
						Concentration (mg l^{-1})	Deposition (kg ha^{-1})	Concentration (mg l^{-1})	Deposition (kg ha^{-1})	Concentration (mg l^{-1})	Deposition (kg ha^{-1})	Concentration (mg l^{-1})	Deposition (kg ha^{-1})	Concentration (mg N l^{-1})	Deposition (kg N ha^{-1})	Concentration (µeq l^{-1})	Deposition (eq ha^{-1})	Concentration (mg l^{-1})	Deposition (kg ha^{-1})	Concentration (mg N l^{-1})	Deposition (kg N ha^{-1})	Concentration (mg l^{-1})	Deposition (kg ha^{-1})	Concentration (µeq l^{-1})	Deposition (eq ha^{-1})
Acquarossa	2005	662	76%	18.0	5.8	0.98	6.5	0.17	1.1	0.14	0.9	0.19	1.3	0.85	5.7	30	197	1.99	13.2	0.65	4.3	0.18	1.2	-28	-186
	2006	1018	35%	8.0	5.3	0.34	3.5	0.07	0.7	0.11	1.1	0.05	0.5	0.18	0.2	1	13	0.74	7.5	0.25	2.5	0.13	1.3	4	43
Bignasco	2005	844	92%	14.5	5.1	0.40	3.4	0.04	0.3	0.11	0.9	0.07	0.6	0.66	5.6	9	73	1.33	11.2	0.52	4.4	0.15	1.3	0	2
	2006	1287	85%	12.4	5.0	0.30	3.8	0.04	0.5	0.20	2.6	0.07	0.9	0.39	5.0	2	26	0.96	12.4	0.42	5.4	0.20	2.5	8	104
Locarno Monti	2005	1058	89%	19.0	5.0	0.57	6.0	0.05	0.5	0.19	2.0	0.10	1.0	0.87	9.2	12	126	1.74	18.4	0.71	7.6	0.19	2.0	-2	-17
	2006	1629	78%	14.6	5.0	0.37	6.0	0.04	0.7	0.53	4.1	0.07	1.2	0.53	8.6	5	86	1.32	21.5	0.48	7.8	0.29	4.6	5	80
Lugano	2005	952	60%	22.0	5.2	0.82	7.8	0.10	0.9	0.25	2.4	0.21	2.0	1..03	9.8	17	165	2.22	21.1	0.89	8.5	0.34	3.2	-10	-98
	2006	1304	60%	21.7	5.2	0.91	11.8	0.16	2.1	0.37	4.9	0.24	3.1	0.88	11.5	17	225	2.29	29.8	0.75	9.8	0.62	8.1	-11	-145
Monte Brè	2005	952	84%	17.7	5.1	0.46	4.4	0.05	0.5	0.15	1.5	0.08	0.8	0.91	8.7	10	94	1.63	15.5	0.73	6.9	0.21	2.0	-3	-24
	2006	1304	89%	16.3	5.2	0.62	8.1	0.06	0.8	0.24	3.2	0.06	0.8	0.71	9.3	15	195	1.59	20.8	0.60	7.8	0.25	3.3	-8	-104
Piotta	2005	714	97%	11.8	5.3	0.29	2.0	0.02	0.1	0.16	1.1	0.06	0.4	0.53	3.8	8	59	0.99	7.1	0.41	2.9	0.23	1.7	-3	-23
	2006	1176	81%	10.3	5.2	0.31	3.7	0.03	0.4	0.21	2.4	0.05	0.6	0.33	3.8	5	62	0.86	10.2	0.35	4.1	0.31	3.6	2	18
Robiei	2005	1476	83%	12.0	5.2	0.35	5.1	0.02	0.4	0.06	0.8	0.05	0.8	0.74	11.0	7	102	1.37	20.2	0.56	8.2	0.08	1.2	0	-3
	2006	2146	82%	9.4	5.1	0.25	5.4	0.03	0.6	0.07	1.6	0.05	1.1	0.35	7.5	3	60	0.85	18.3	0.33	7.1	0.09	2.0	4	94
Sonogno	2005	1033	50%	10.9	5.2	0.37	3.8	0.02	0.2	0.13	1.4	0.05	0.5	0.36	3.7	7	74	0.94	9.7	0.33	3.4	0.16	1.6	-1	-9
	2006	1858	97%	11.3	5.1	0.42	7.8	0.09	1.6	0.23	4.3	0.12	2.2	0.30	5.6	10	187	0.99	18.3	0.33	6.0	0.18	3.4	-3	-48
Stabio	2005	935	96%	19.6	5.2	0.51	4.8	0.06	0.5	0.22	2.1	0.10	0.9	1.05	9.8	16	152	1.74	16.3	0.78	7.3	0.31	2.9	-10	-92
	2006	1184	90%	17.1	5.2	0.48	5.6	0.06	0.8	0.30	3.5	0.09	1.0	0.87	10.2	12	141	1.60	18.9	0.67	7.9	0.34	4.0	-6	-70

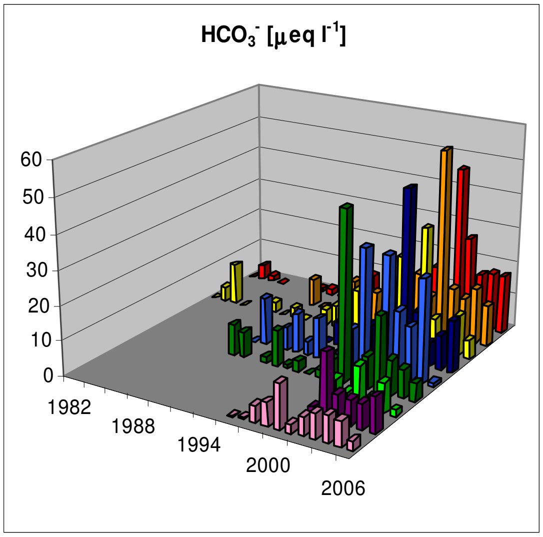
Figure 2.3 Temporal variations of annual mean rain water concentrations and deposition rates

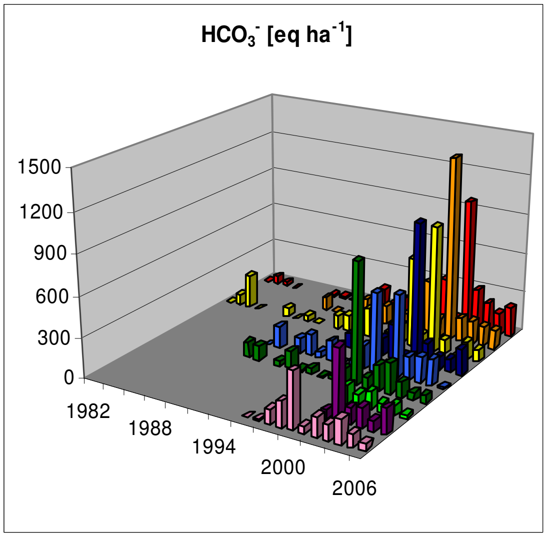
Base cations correspond to non sea salt base cations (calcium, magnesium and potassium)

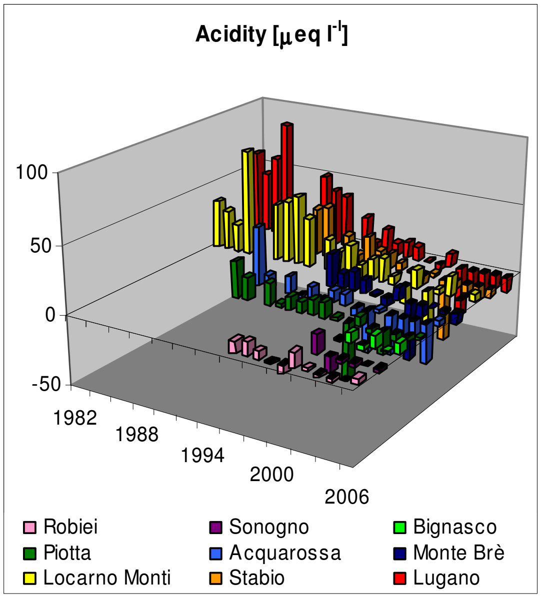



Base cations [μeq l^{-1}]


Base cations [eq ha^{-1}]


HCO_3^- [μeq l^{-1}]


HCO_3^- [eq ha^{-1}]


Acidity [μeq l^{-1}]

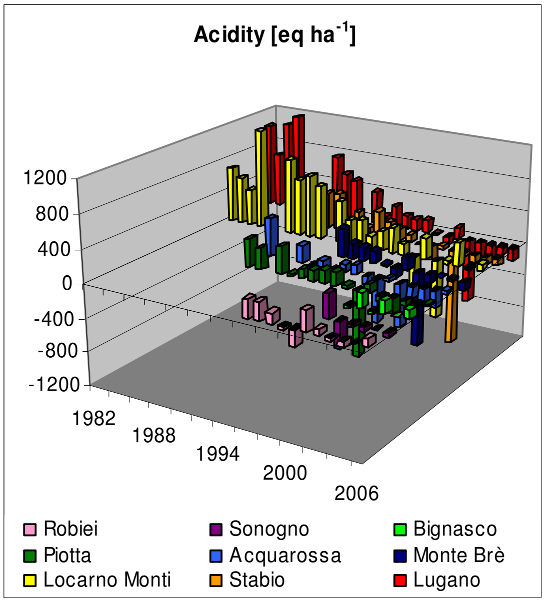
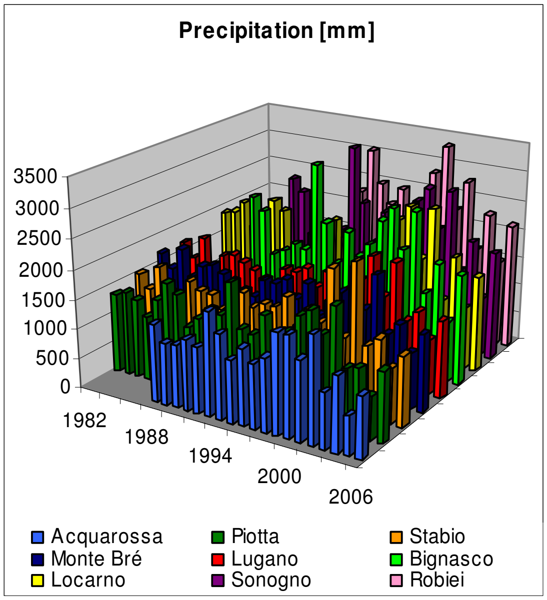

Acidity [eq ha^{-1}]

Figure 2.4 Yearly precipitations

Data from MeteoSwiss



2.4.2 Alpine lake

For lake yearly average concentrations of 2005 and 2006 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 9.7 and 25.5 μS cm^{-1}, alkalinity between -9 and 86 μeq l^{-1}, pH between 5.2 and 7.2, sulphate between 0.88 and 4.80 mg l^{-1}, nitrate between 0.13 and 0.89 mg N l^{-1}, dissolved organic carbon between 0.13 and 1.33 mg C l-$^{-1}$, reactive dissolved silica between 0.79 and 3.79 mg SiO2 l^{-1} and total dissolved aluminium between 2.6 and 84.9 μg l^{-1}. Ortho-phosphate concentrations were on average smaller than 9 μg P l^{-1} and ammonia and nitrite were neglectable small compared to nitrate.

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 2005 and 2006 it can be observed that 2 lakes have alkalinities below 0 μeq l^{-1} and are therefore acid (Lago di Tomè and Lago del Starlaresc da Sgiof) 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 were therefore also characterized by high concentrations of dissolved aluminium (43-85 μg l^{-1}). In general concentrations of non sea salt base cations also correlated 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 did 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) are rich in geogenic sulphate. Differences in nitrate concentrations among lakes should be more related to differences in nitrogen retention capacity of the catchment and in case by the presence of cattle during summer.

It is worth to mention, that already during 2005 but especially in 2006 for some lakes nitrate concentrations were occasionally consistently above and alkalinity and pH below the normally observed mean values. This phenomena has been observed for Laghetto Leit in July 2006, for Laghetto Inferiore, Laghetto Leit, Lago Barone and Lago di Tomè in October 2006 and for Laghetto Superiore and Laghetto d'Antabia in November 2006. The reason is not yet clear. The influence of rain events preceding the sampling day should be analysed. It is possible, that the recent dry and warm years (2003-2005) increased mineralization of nitrogen leading to an accumulation of nitrate in soils of the lakes watersheds. As a consequence, great amounts of nitrate could have been washed out during recent wetter periods increasing nitrate concentrations and decreasing lake alkalinities temporarily.

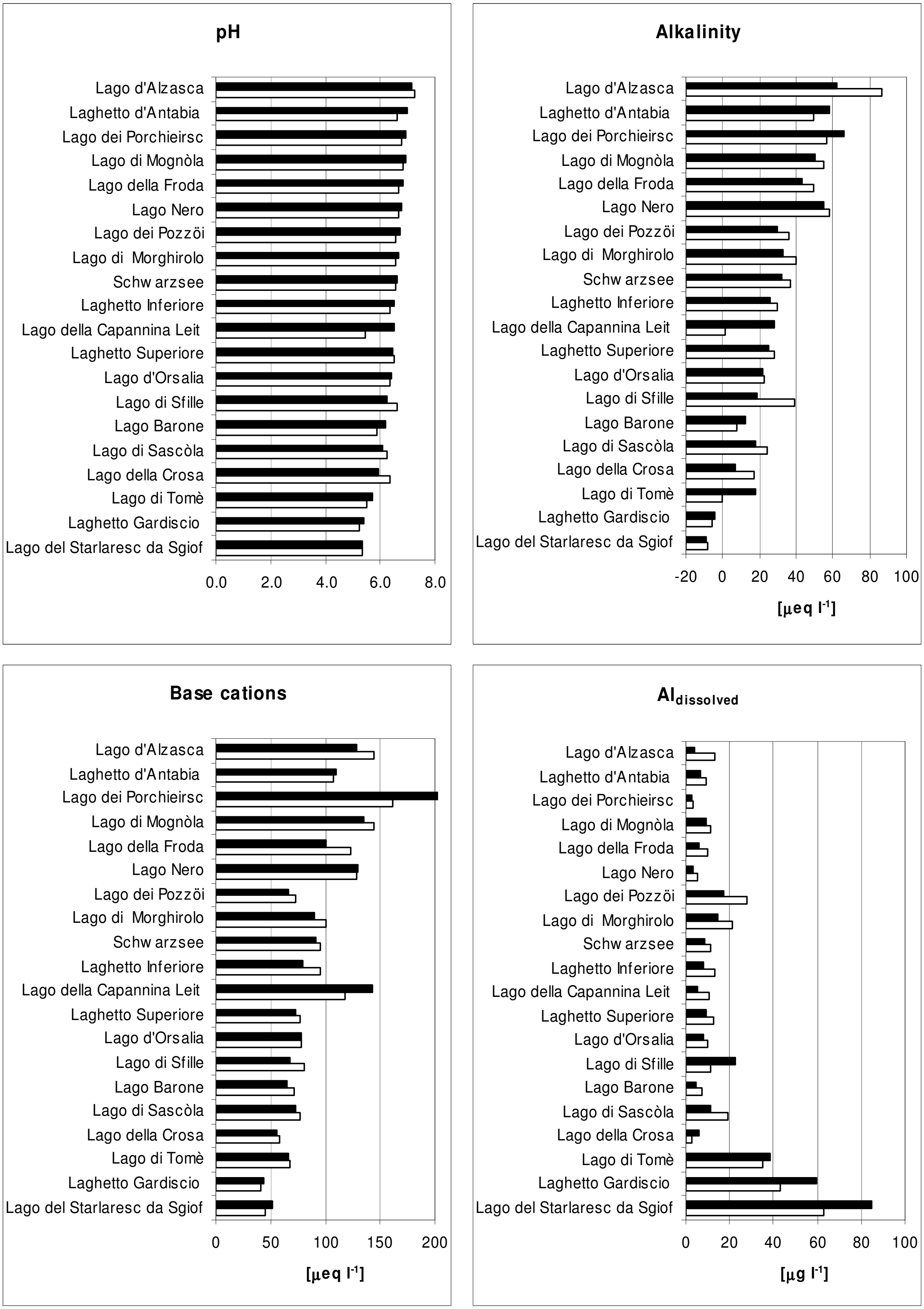
Table 2.3 Average lake surface water concentrations during 2005 and 2006

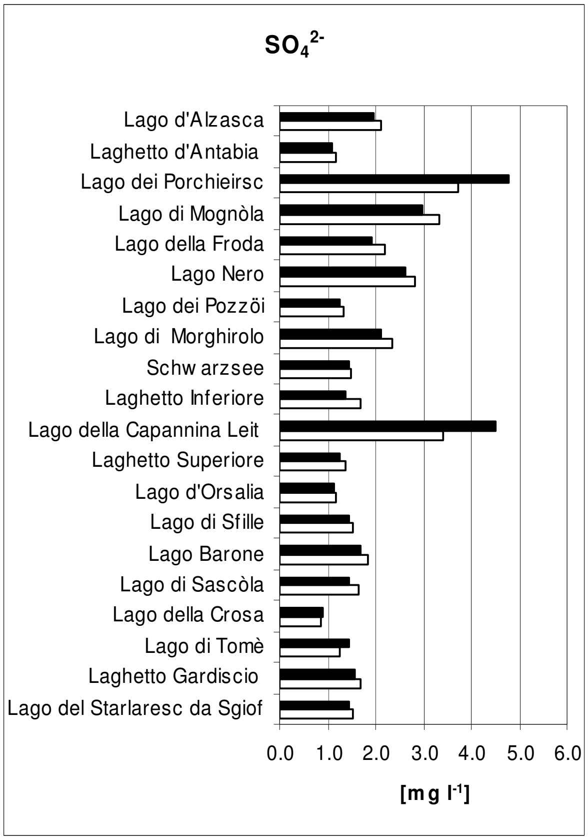
Average values with some values below the quantification limit were preceded with <

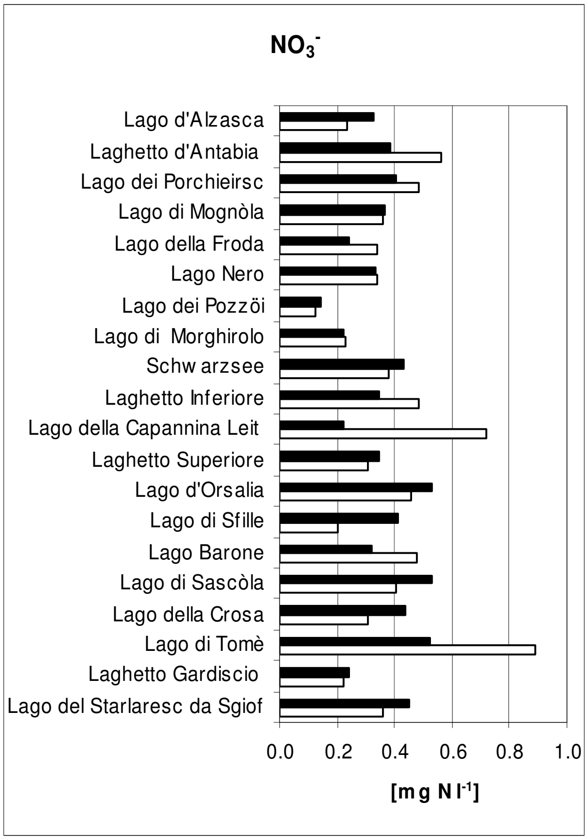
Lake name	Year	Conductivity 25°C. (µS cm^{-1})	pH	Alkalinity (µeq l^{-1})	Ca^{2+} (mg l^{-1})	Mg^{2+} (mg l^{-1})	Na^{+} (mg l^{-1})	K^{+} (mg l^{-1})	NH_4^{+} (mg N l^{-1})	SO_4^{2-} (mg l^{-1})	NO_3^{-} (mg N l^{-1})	Cl^{-} (mg l^{-1})	NO_2^{-} (µg N l^{-1})	o-PO_4 (µg P l^{-1})	Ptot (µg P l^{-1})	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	2005	11.8	5.3	-9	0.75	0.10	0.33	0.19	0.038	1.45	0.45	0.17	2.1	<3.0	<3.4	0.65	1.61	84.9	123.3	2.5	3.1	6.8	7.9
	2006	11.6	5.4	-8	0.62	0.10	0.33	0.21	0.030	1.51	0.36	0.16	<1.6	<2.1	4.6	0.89	1.90	62.8	77.9	<0.3	<0.4	5.7	6.5
Lago di Tomè	2005	11.6	5.7	18	1.09	0.09	0.35	0.18	0.013	1.43	0.52	0.16	3.6	<2.7	<2.2	0.23	2.01	38.7	46.5	1.1	2.0	3.8	4.7
	2006	12.4	5.5	0	1.09	0.09	0.56	0.23	0.005	1.26	0.89	0.12	<1.0	<2.0	3.0	0.35	2.66	35.3	45.3	0.7	1.8	4.7	4.9
Lago dei Porchieirsc	2005	25.5	7.0	66	3.54	0.20	0.58	0.52	0.007	4.80	0.41	0.25	2.9	<2.0	<2.2	0.29	3.22	2.6	5.0	0.7	2.2	1.9	2.3
	2006	22.1	6.8	57	2.74	0.16	0.47	0.45	0.005	3.73	0.48	0.15	2.5	<2.0	5.6	0.25	3.79	3.5	8.6	0.5	0.6	2.1	2.0
Lago Barone	2005	10.8	6.2	13	1.08	0.07	0.27	0.20	0.018	1.69	0.32	0.13	3.1	<3.0	<2.0	0.31	1.35	4.6	8.9	<0.8	<0.8	1.5	1.8
	2006	11.8	5.9	8	1.18	0.08	0.34	0.22	0.016	1.83	0.48	0.16	2.3	2.8	4.4	0.38	1.67	7.1	10.2	1.2	0.8	1.5	3.7
Laghetto Gardiscio	2005	10.5	5.4	-5	0.56	0.10	0.26	0.31	0.035	1.59	0.24	0.21	1.3	<3.0	<2.0	0.14	0.87	59.4	75.4	1.1	1.4	3.5	3.1
	2006	9.7	5.2	-6	0.53	0.10	0.19	0.25	0.015	1.68	0.22	0.08	1.4	<2.0	3.6	0.13	1.14	42.9	42.7	0.6	0.7	2.5	2.8
Lago Leit	2005	18.6	6.5	28	2.05	0.34	0.42	0.50	0.017	4.50	0.22	0.11	2.7		3.6	0.44	2.00	5.2	21.3	1.1	1.3	2.0	2.3
	2006	20.7	5.5	1	1.66	0.28	0.41	0.47	0.011	3.41	0.72	0.11	1.9	<2.8	6.9	0.42	2.06	10.4	18.1	<0.6	<0.7	0.7	2.2
Lago di Morghirolo	2005	13.3	6.7	33	1.32	0.17	0.34	0.44	0.011	2.10	0.22	0.11	2.4	<3.0	<3.2	0.33	0.79	14.3	53.7	0.6	1.1	0.9	1.7
	2006	17.9	6.6	40	1.47	0.19	0.36	0.47	0.012	2.36	0.23	0.06	<1.7	<2.1	8.3	0.25	1.43	21.4	148.1	1.2	1.5	2.1	3.2
Lago di Mognòla	2005	19.4	6.9	50	2.02	0.26	0.60	0.53	0.006	3.00	0.36	0.13	3.1	<3.0	<2.7	0.28	2.71	9.2	18.3	0.8	0.9	1.6	1.7
	2006	19.9	6.9	55	2.17	0.28	0.59	0.53	<0.004	3.33	0.36	0.11	1.9	<2.0	5.0	0.26	3.07	11.4	15.9	0.9	1.5	1.7	2.7
Laghetto Inferiore	2005	11.5	6.5	26	1.22	0.10	0.31	0.38	0.010	1.39	0.35	0.11	3.1	<3.0	<2.7	0.28	1.36	7.7	16.1	<0.7	<0.6	<0.8	2.3
	2006	13.2	6.3	30	1.47	0.12	0.38	0.45	0.006	1.69	0.48	0.10	1.8	<2.3	4.9	0.32	1.80	13.2	14.6	0.5	0.4		2.2
Laghetto Superiore	2005	10.8	6.5	25	1.14	0.09	0.28	0.33	<0.009	1.27	0.35	0.08	2.5	<2.7	<2.3	0.28	1.27	9.6	27.0	<1.4	<1.5	4.1	5.8
	2006	10.8	6.5	28	1.19	0.11	0.31	0.33	0.008	1.37	0.31	0.13	1.9	<2.0	6.9	0.37	1.45	12.9	15.4	0.4	0.5	2.8	2.4
Lago Nero	2005	17.7	6.8	55	2.09	0.16	0.38	0.47	<0.010	2.64	0.33	0.10	2.3	<3.0	<2.5	0.28	1.06	3.2	5.1	<0.9	<1.0	1.4	1.2
	2006	18.2	6.7	58	2.04	0.16	0.42	0.52	0.046	2.81	0.34	0.09	1.5	<2.0	5.1	0.39	0.53	5.2	5.8	0.7	0.6	2.1	1.9

Lake name	Year	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})	NO_2^{-} (µg N l^{-1})	o-PO_4 (µg P l^{-1})	P_{tot} (µg P 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 Bianco	2005																						
	2006	90.8	7.6	478	14.76	0.97	0.45	0.95	<0.003	15.03	0.26	0.12	<1.0	<2.0	4.6	0.27	2.08	10.2	14.2	0.6	1.4	0.7	1.5
Lago della Forda	2005	13.6	6.9	43	1.74	0.09	0.27	0.25	<0.007	1.90	0.24	0.08	2.1	<3.0	<4.0	0.26	1.37	5.7	12.6	<1.0	<0.7	1.1	1.1
	2006	14.7	6.7	50	2.14	0.11	0.34	0.28	<0.005	2.19	0.34	0.09	<1.4	<2.2	4.8	0.39	1.60	10.0	11.4	<0.3	<0.4	0.8	1.2
Lago d’Antabia	2005	14.5	7.0	58	1.94	0.09	0.35	0.25	0.009	1.11	0.38	0.11	3.5	<3.0	<2.2	0.21	2.32	6.3	12.1	<1.0	<0.6	1.1	1.1
	2006	15.3	6.6	50	1.81	0.09	0.44	0.34	0.005	1.16	0.56	0.11	2.9	<2.5	5.3	0.35	2.43	9.3	10.8	<0.5	<0.7	0.4	1.2
Lago della Crosa	2005	9.8	6.0	7	0.91	0.07	0.27	0.18	0.007	0.91	0.44	0.10	3.1	<3.0	<2.2	0.23	1.52	5.7	8.3	<1.0		<1.2	1.2
	2006	8.9	6.3	17	0.93	0.09	0.26	0.18	0.012	0.88	0.31	0.12	3.2	2.7	4.3	0.27	1.16	2.6	5.4	<0.2		0.7	1.4
Lago d'Orsalìa	2005	12.2	6.4	22	1.29	0.08	0.37	0.24	0.014	1.12	0.53	0.18	4.0	<3.0	<3.1	0.28	1.22	8.2	23.9	<0.7	<1.1	1.5	1.8
	2006	11.3	6.3	23	1.33	0.09	0.29	0.17	0.006	1.17	0.46	0.11	2.9	<2.0	4.3	0.23	1.66	10.0	13.1	0.5	0.8		1.7
Schwarzsee	2005	13.3	6.6	32	1.52	0.10	0.36	0.29	<0.009	1.46	0.43	0.15	2.5	<3.0	<2.2	0.27	1.87	8.5	18.7	<0.7	<0.8	1.1	1.3
	2006	13.0	6.6	37	1.59	0.11	0.34	0.26	<0.003	1.49	0.38	0.10	<2.0	<2.6	3.9	0.25	2.00	11.2	13.9	0.3	0.4		1.4
Laghi dei Pozzöi	2005	10.0	6.7	30	1.05	0.11	0.35	0.19	<0.011	1.25	0.15	0.11	1.9	<3.0	<2.2	0.64	1.93	17.0	31.8	<0.6	<0.7	0.8	1.3
	2006	10.2	6.6	36	1.17	0.12	0.38	0.20	<0.005	1.35	0.13	0.14	<1.1	<2.0	4.6		2.06	28.1	34.3	0.4	0.5	1.2	1.4
Lago di Sfille	2005	11.4	6.2	19	1.11	0.10	0.37	0.14	0.008	1.46	0.41	0.14	2.5	<3.0	<2.5		1.88	22.2	39.1		0.8	1.4	2.8
	2006	11.6	6.6	39	1.33	0.13	0.43	0.16	0.010	1.51	0.20	0.12	<1.9	<2.0	4.2	0.53	1.97	11.6	14.7	<0.4	<0.5	1.7	1.5
Lago di Sascòla	2005	12.3	6.1	18	1.03	0.16	0.34	0.36	0.014	1.47	0.53	0.12	4.4	<3.0	<2.2	0.51	1.50	11.0	25.9	0.9	2.5	2.9	4.5
	2006	12.2	6.3	24	1.16	0.14	0.41	0.30	0.011	1.63	0.41	0.12	2.7	<2.2	5.3	0.57	2.17	19.4	21.6	0.4	0.6	2.3	2.3
Lago d'Alzasca	2005	17.7	7.1	62	1.97	0.21	0.53	0.51	0.009	1.94	0.33	0.19	3.7	<3.0	<2.2	0.74	2.43	3.8	15.3	<0.6	<0.8	1.2	1.7
	2006	18.3	7.2	86	2.22	0.23	0.55	0.54	<0.006	2.13	0.23	0.25	2.4	3.2	6.1	1.33	2.60	13.4	16.3	<0.3	<0.5	1.0	1.4

Figure 2.5 Annual average concentrations of the main chemical parameters in 20 Alpine lakes during 2005 (black bar) and 2006 (white bar)
Base cations correspond to non sea salt base cations (calcium, magnesium and potassium)



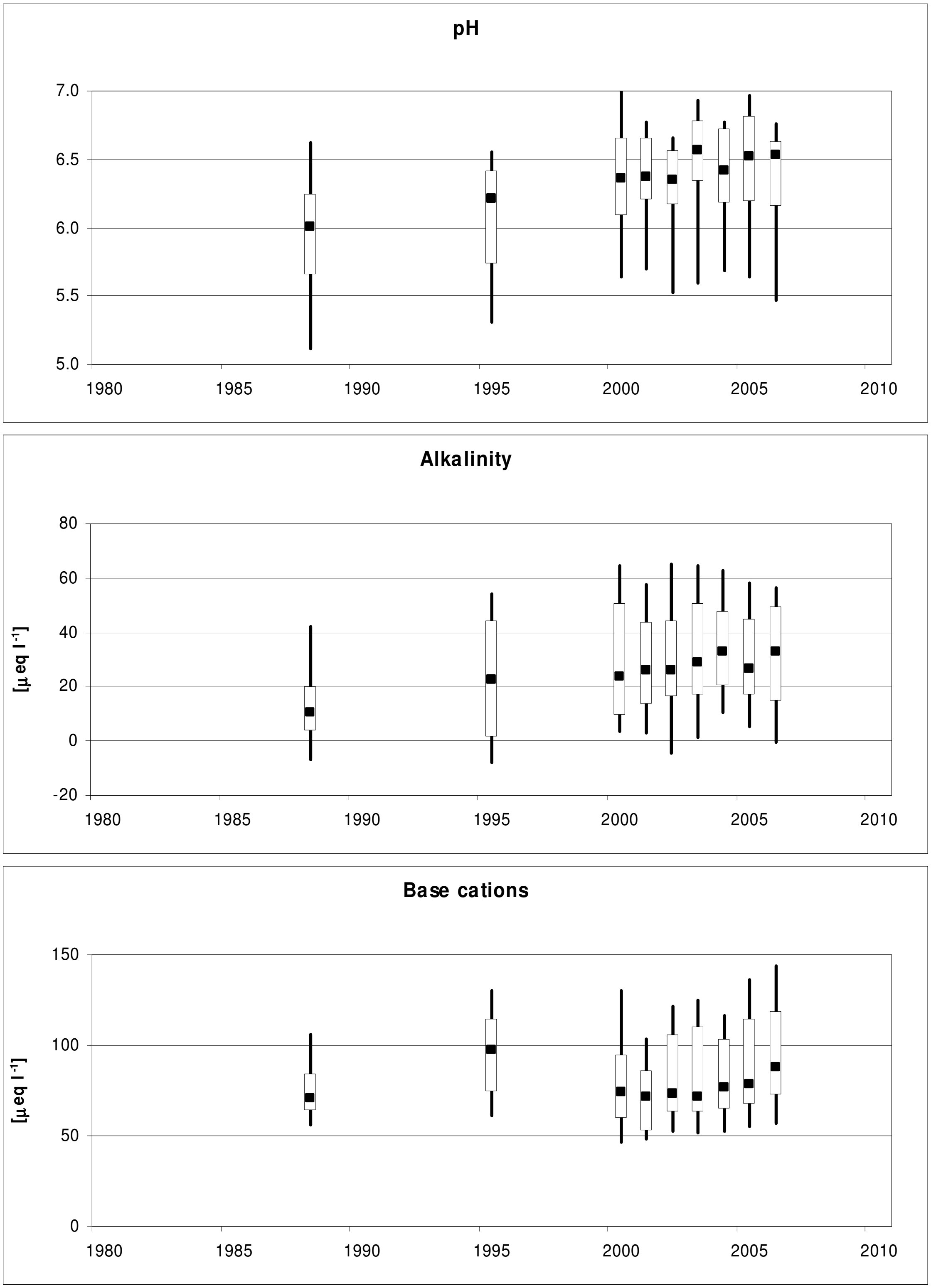


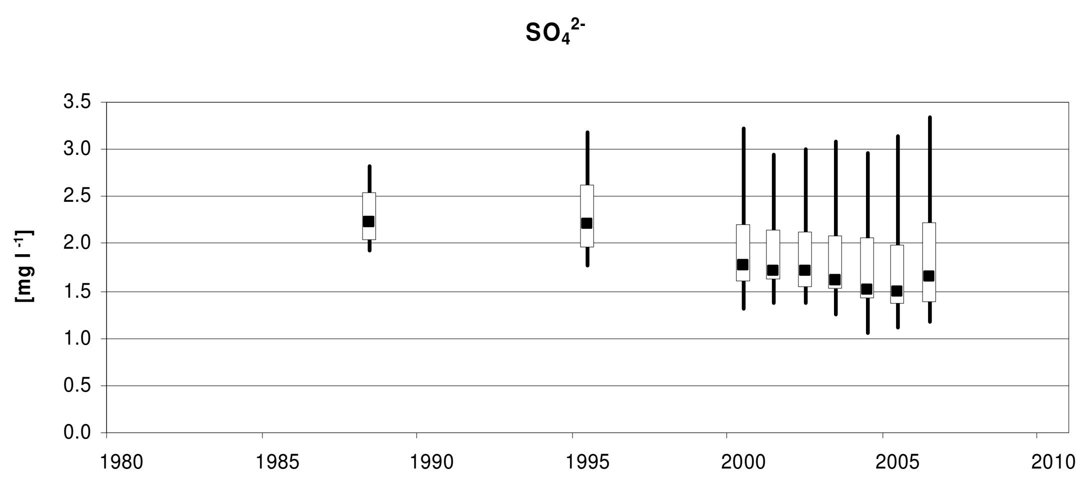


In order to show temporal variations of lake quality, annual median values of pH, alkalinity and concentrations of non sea salt base cations, sulphate and nitrate of all lakes with their 10th, 25th, 75th and 90th percentile values are represented in Fig. 2.6. In order to detect variations with time only years, where all 20 alpine lakes have been monitored were chosen. As already discussed in Steingruber and Colombo (2006), after 1980's lake pH and alkalinity increased, while sulphate decreased, mainly as a consequence of the reduction of the sulphur content in heating oils and the partial substitution of sulphur rich carbon with other fossil fuels. Base cations and nitrate concentrations seem to slightly increase after 2000. It is not yet clear if the increase in nitrate concentrations has to be seen as a sort of short time effect as consequence of recent meteorology or instead the beginning of a long term tendency reflecting climate warming (increased mineralization) and/or nitrogen saturation of soils.

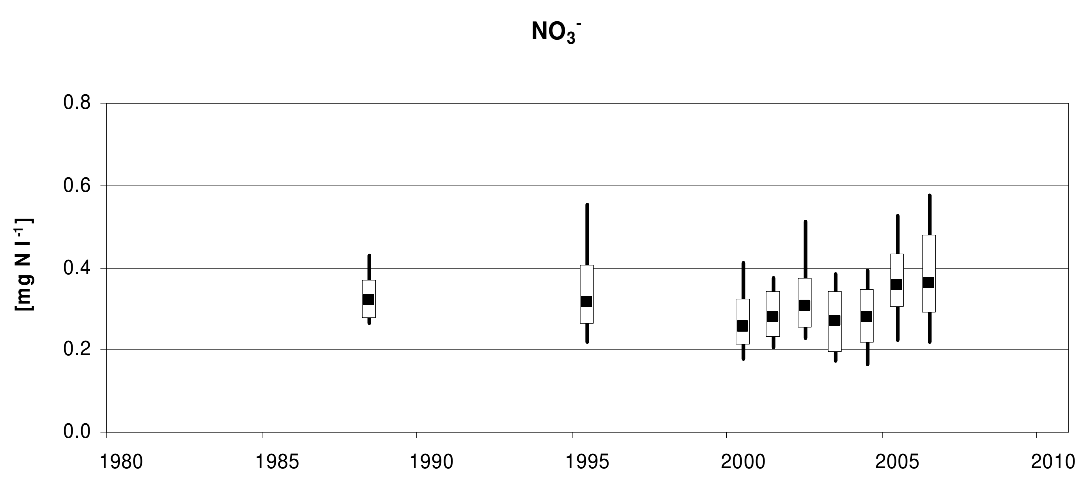
Figure 2.6 Temporal variations of annual median values and their 10th, 25th, 75th, 90th percentiles of parameters measured in 20 Alpine lakes from 1988 to 2006

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





SO_4^{2-}
[mg l -1]
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1980
1985
1990
1995
2000
2005
2010



NO_3^-
[mg N l -1]
0.8
0.6
0.4
0.2
0.0
1980
1985
1990
1995
2000
2005
2010

2.4.3 Alpine rivers

Annual mean concentrations of the parameters measured in rivers Maggia, Vedeggio and Verzasca during 2005 and 2006 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 2005 and 2006.
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	2005	7.5	69.8	313	9.01	0.76	1.92	1.72	<0.011	10.59	0.55	1.36	0.47	5.27	8.8	12.4	<1.9	<1.6	<1.9	<2.6
	2006	7.5	68.9	303	8.83	0.76	1.81	1.53	<0.005	10.04	0.64	1.48	0.53	5.25	10.0	12.6	<0.5	<0.6	<1.0	<1.3
Vedeggio	2005	7.1	49.7	147	5.23	1.06	1.79	0.66	<0.010	6.82	1.12	1.00	0.55	7.21	10.1	20.4	<2.0	<1.9	<2.4	2.7
	2006	7.1	50.9	162	5.43	1.06	1.65	0.64	<0.005	6.69	1.27	1.08	0.61	7.21	9.9	18.6	<0.7	<1.1	1.6	2.2
Verzasca	2005	6.8	27.0	61	3.10	0.25	0.78	0.63	<0.007	3.96	0.76	0.18	0.27	3.08	8.4	10.2	<1.8	<1.8	<3.5	<3.5
	2006	6.9	27.8	65	3.21	0.26	0.80	0.63	<0.004	3.99	0.90	0.24	0.37	4.43	6.5	7.7	<0.4	<0.6	<0.7	1.1

Average alkalinities in 2005 and 2006 were 313/303 μeq l^{-1} in river Maggia, 147/162 μeq l^{-1} in river Vedeggio and 61/65 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} (Fig. 3.4). Average pH's during 2005 and 2006 were 7.5 in river Maggia, 7.1 in river Vedeggio and 6.8/6.9 in river Verzasca. Their minimum pH's (Fig. 3.4) were not much lower (Maggia: 7.2/7.4, Vedeggio: 7.0/7.0, Verzasca: 6.7/6.8). As a consequence of the relatively high pH's, dissolved aluminium concentrations were on average low (≤ 15 μg l^{-1}). However, higher aluminium concentrations up to 30.4, 22.1, 20.6 μeq l^{-1} in river Maggia, Vedeggio and Verzasca, respectively occurred occasionally, often contemporaneously to pH minima.

Fig. 2.7 shows the variations of the concentrations of sulphate, nitrate, base cations, aluminium, alkalinity and pH during 2005 and 2006. 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 highest values were measured in winter 2005 and 2006 and in summer 2006. Lowest values occurred during spring 2005 and 2006 and in fall 2006. For nitrate and aluminium concentrations the temporal trend was inverted.

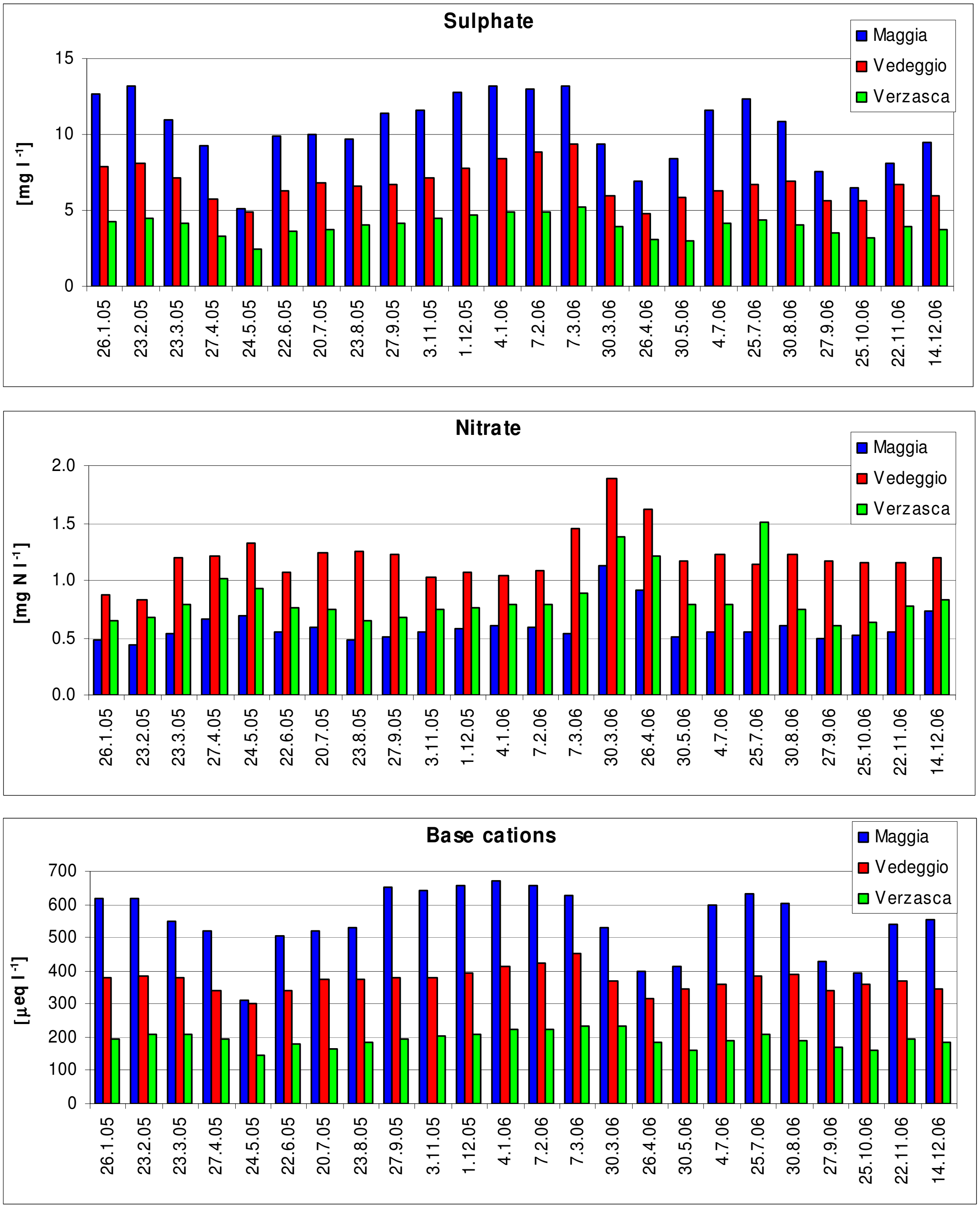
Comparing the seasonality of concentrations during 2005 and 2006 with the temporal variations of the river discharge (Fig. 2.8, for river Maggia without the influence of hydropower production), it can be observed that discharge maxima overlap with concentrations minima of sulphate, base cations, alkalinity 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.

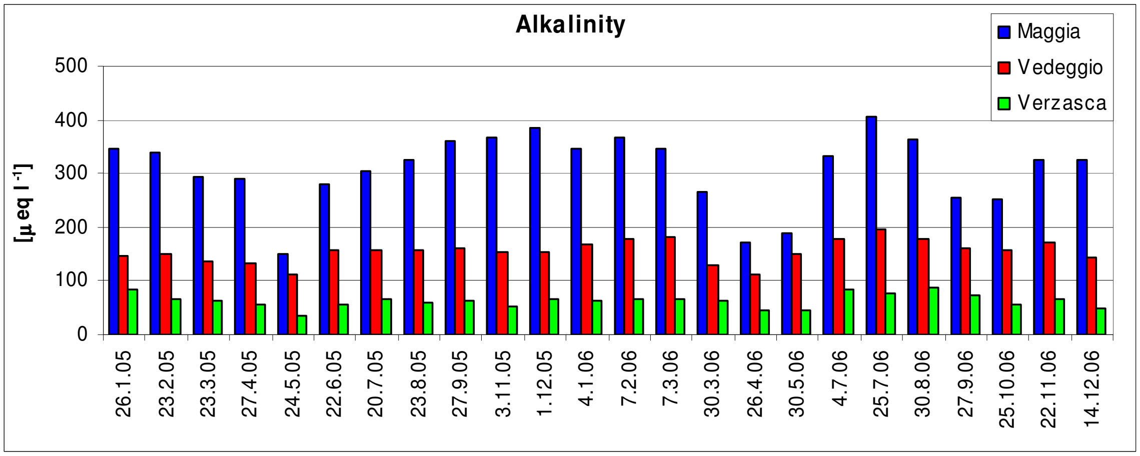
In order to detect time trends, annual mean concentrations of sulphate, nitrate, base cations, dissolved aluminium, alkalinity and pH from 2000 to 2006 are presented graphically in Fig. 2.9. For sulphate, base cations, alkalinity, pH and dissolved aluminium a slight positive trend seem to exist. However, these increasing concentrations may be related to decreased yearly average discharges (Fig. 2.10). In other words, as a consequence of the recently dry period, the average dilution of sulphate and base cations could have been diminished increasing their average concentrations. It follows that alkalinity would have increased not only because of a decreased dilution but also as a consequence of decreased consumption and pH increased as a direct consequence of decreased acidic deposition. Increasing pH and decreasing precipitation would suggest decreased dissolved aluminium concentrations. However, the opposite seems to occur. The reason is not clear. A concentration effect, as a consequence of lower water table may be hypothesized. For nitrate no trend seem to exist.

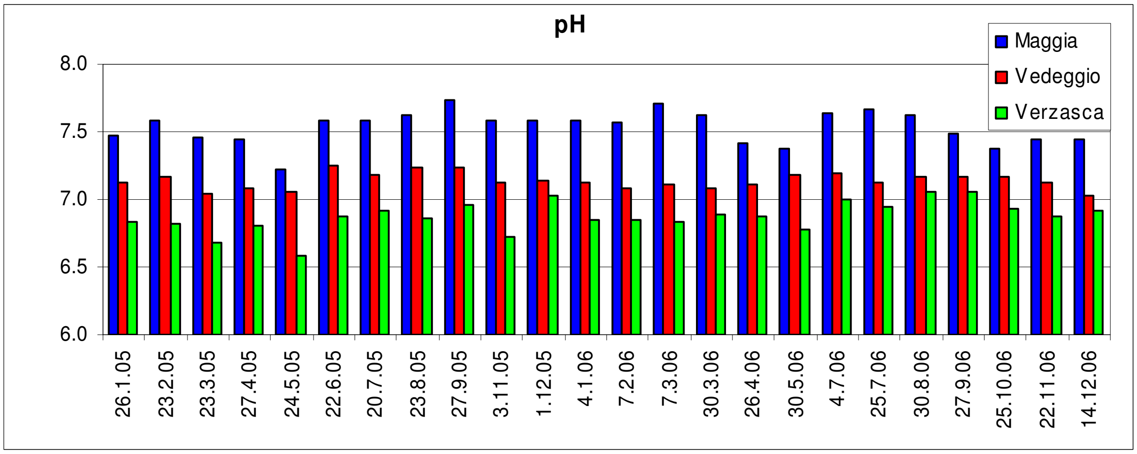
It can be concluded, that hydrology highly influences river water quality. As a consequence, seasonal variations and long term trends in concentrations should not be discussed separately from hydrology.

Figure 2.7 Concentrations of the main chemical parameters in river water during 2005 and 2006

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




Alkalinity
Maggia
Vedeggio
Verzasca
500
400
300
200
100
0
[µeq l-1]
26.1.05
23.2.05
23.3.05
27.4.05
24.5.05
22.6.05
20.7.05
23.8.05
27.9.05
3.11.05
1.12.05
4.1.06
7.2.06
7.3.06
30.3.06
26.4.06
30.5.06
4.7.06
25.7.06
30.8.06
27.9.06
25.10.06
22.11.06
14.12.06


pH
Maggia
Vedeggio
Verzasca
8.0
7.5
7.0
6.5
6.0
26.1.05
23.2.05
23.3.05
27.4.05
24.5.05
22.6.05
20.7.05
23.8.05
27.9.05
3.11.05
1.12.05
4.1.06
7.2.06
7.3.06
30.3.06
26.4.06
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4.7.06
25.7.06
30.8.06
27.9.06
25.10.06
22.11.06
14.12.06

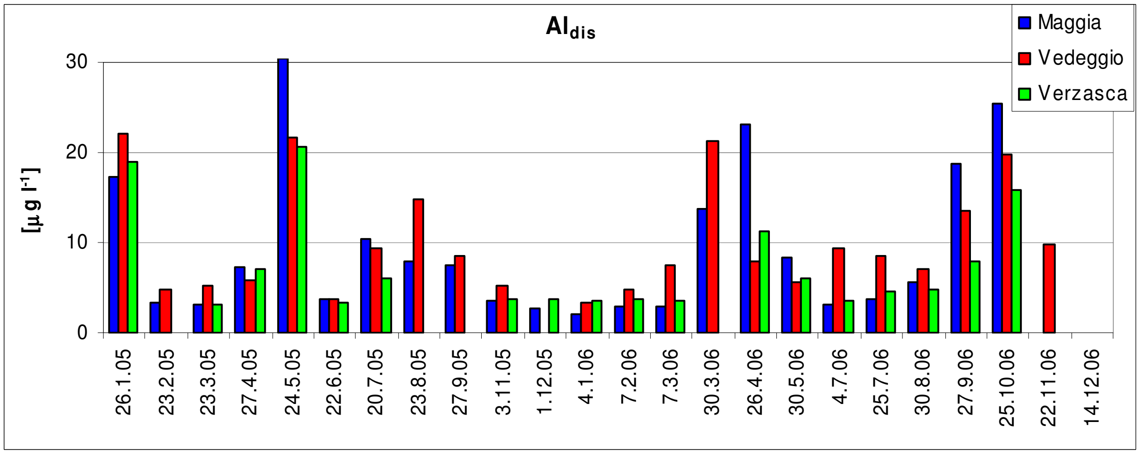

Al dis
Maggia
Vedeggio
Verzasca
30
20
10
0
[µg l-1]
26.1.05
23.2.05
23.3.05
27.4.05
24.5.05
22.6.05
20.7.05
23.8.05
27.9.05
3.11.05
1.12.05
4.1.06
7.2.06
7.3.06
30.3.06
26.4.06
30.5.06
4.7.06
25.7.06
30.8.06
27.9.06
25.10.06
22.11.06
14.12.06

Figure 2.8 Daily average discharge during sampling days in 2005 and 2006

Discharge of river Vedeggio at Isone is measured by Istituto Scienze della Terra (2006). 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 (IST, 2000-2006).

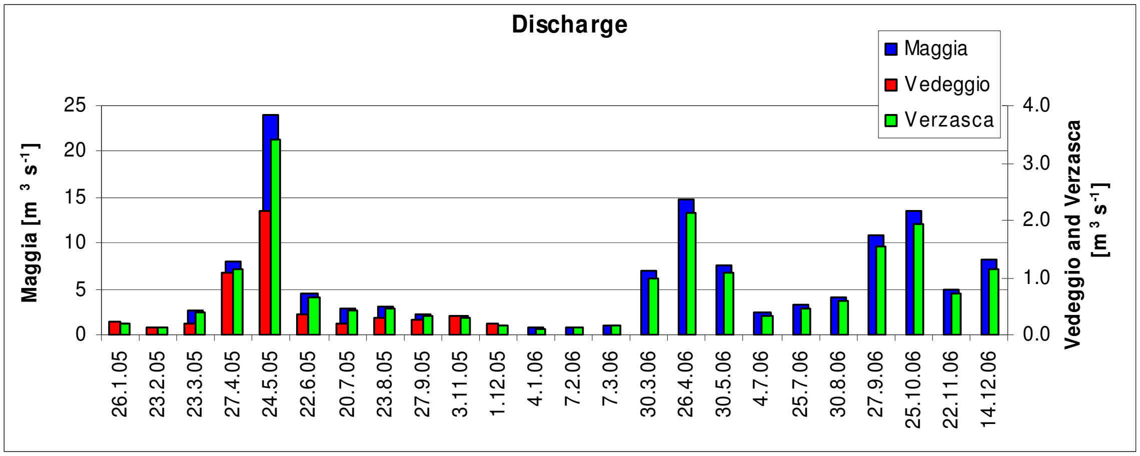


Figure 2.9 Annual mean concentrations of the main chemical parameters in river water from 2000 to 2006

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

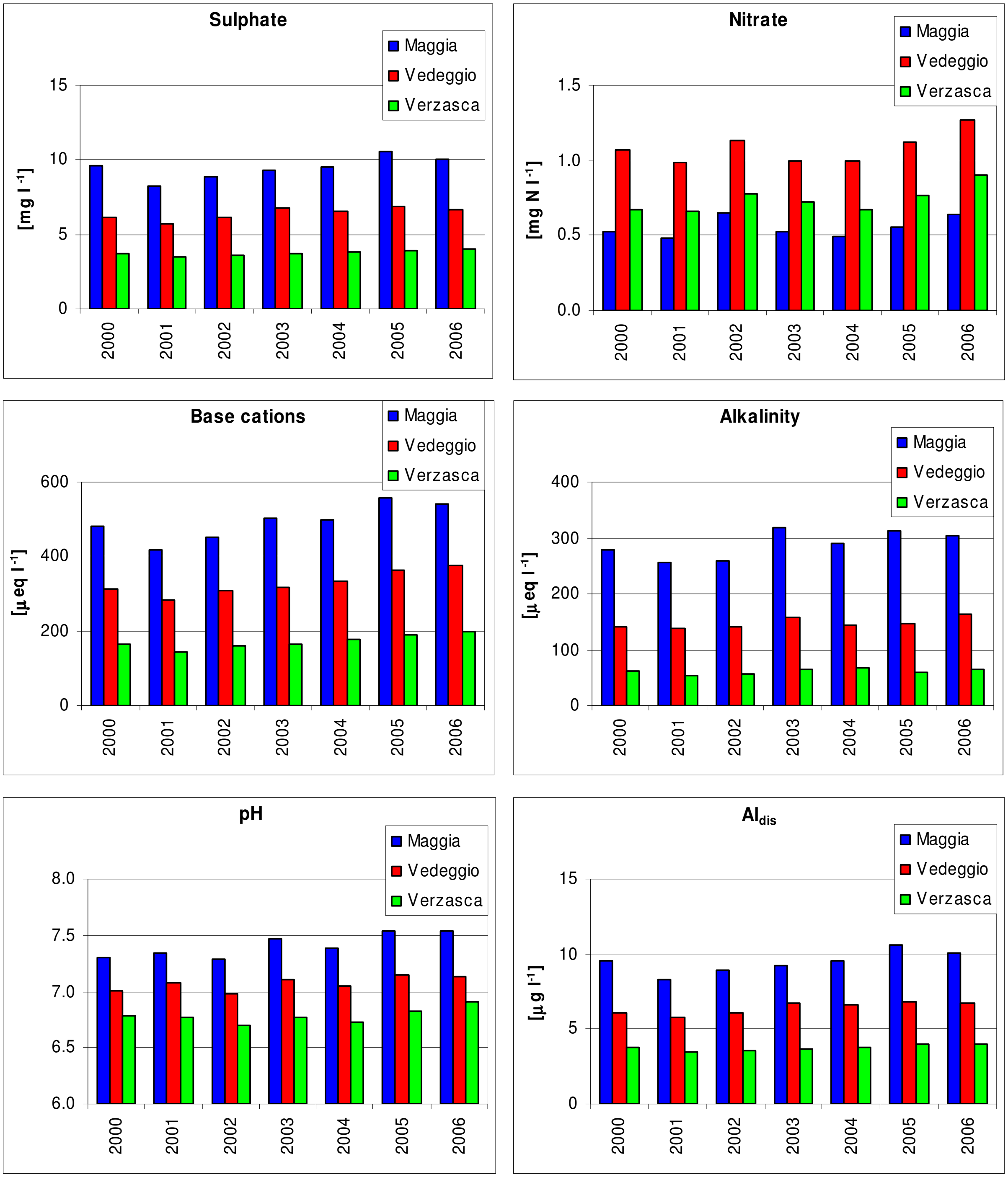
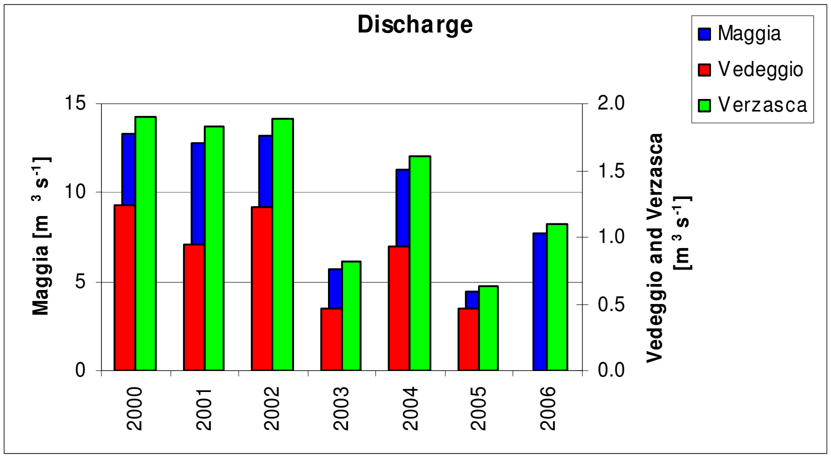


Figure 2.10 Yearly mean discharge of river Maggia, Vedeggio and Verzasca from 2000 to 2006

Discharge of river Vedeggio at Isone was measured by Istituto Scienze della Terra (IST, 2000-2006). 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 (2000-2006).



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 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: 70%) followed by *Oligochaeta* (average: 12%) and *Others* (average: 11%). In the emissaries other orders like *Plecoptera* are also important. The species diversity (=E.B.I. taxa number) was generally 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 mainly due to differences in water acidity. Average pH during 2005-2006 was 7.6, 6.5, 6.4, 5.6, 5.3 in Lago Bianco, Laghetto Superiore, Laghetto

Inferiore, Lago di Tomè and Lago del Starlaresc da Sgiof, respectively. The E.B.I. taxa number was highest in Laghetto Inferiore, followed by Laghetto Superiore, Lago di Tomè and Lago del Starlaresc da Sgiof both in the emissary and in the littoral. Similarly, behaved the EPT indexes. Interestingly, although having the highest pH, the littoral of Lago Bianco was characterized by low E.B.I. taxa number and the outlet by average values compared to other lakes. Differences in the relative abundances of the main macroinvertebrate groups were irrelevant in samples from the littoral but significant in samples from the outlets. In Laghetto Inferiore and Laghetto Superiore most taxas belonged to the order *Diptera* (average: 43%) and *Oligochaeta* (average: 38%) and *Plecoptera* (average: 11%). A similar population was observed in Lago Bianco: *Diptera* (average: 39%), *Oligochaeta* (average: 45%). However, the abundance of Plecopetera was slightly smaller (average: 7%) and of *Ephemeroptera* slightly higher (average: 4%). In Lago di Tomè *Diptera* dominated the macroinvertebrate population (average: 70%) followed by *Plecoptera* (average: 24%), while Oligochaeta were almost absent. The dominance of *Diptera* was also observed in Lago del Starlaresc da Sgiof (average: 91%). In all lakes *Diptera* was mainly represented by *Chirononmidae* and in some occasions by *Simulidae* (some occasions in Laghetto Inferiore and Superiore). 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 and Laghetto Superiore. A still low but higher abundance of *Ephemeroptera* was found in Lago Bianco (4%), mainly due to the presence of *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 2005 and 2006

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
	2005	2006	2005	2006	2005	2006	2005	2006	2006	2005	2006	2005	2006	2005	2006	2005	2006	2006
no. of samples	3	2	3	2	2	2	2	2	2	3	2	3	2	2	2	2	2	2
no. organisms	5223	3228	8700	4491	1581	1527	1489	2353	4898	8338	6086	6631	5742	2160	3066	2730	6293	6195
no. taxa E.B.I.	18	10	14	9	12	10	9	6	8	18	17	17	15	13	15	13	11	15
EPT index	6	3	4	3	5	5	1	1	1	10	9	8	8	5	6	3	4	7
Ephemeroptera	0%	0%	0%	0%	0%	0%	0%	0%	0%	1%	1%	1%	0%	0%	0%	0%	0%	4%
Plecoptera	2%	4%	4%	3%	1%	1%	0%	0%	0%	12%	13%	11%	10%	13%	35%	1%	1%	7%
Trichoptera	0%	1%	1%	3%	5%	7%	0%	0%	0%	3%	1%	1%	1%	2%	2%	0%	0%	1%
Diptera	74%	76%	70%	55%	71%	64%	73%	88%	78%	45%	43%	47%	38%	83%	57%	86%	95%	39%
Coleoptera	1%	1%	1%	1%	0%	2%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
Oligochaeta	17%	12%	11%	8%	15%	16%	16%	5%	10%	30%	35%	38%	50%	0%	0%	3%	1%	45%
Others	5%	6%	14%	30%	8%	10%	11%	7%	12%	8%	7%	1%	1%	1%	5%	9%	2%	4%

Tab. 3.2 presents the number of taxa for the five “Braukmann and Biss” indexes from 2002 to 2006, 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 taxa with “Braukmann and Biss indexes” ≥ 2, while in other lakes and in the littoral 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 could 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 because of aluminium dissolution start to occur below pH 6 (Petri-Heil, 1986). 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 2006

The gray colored areas indicate the absence of samples

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

Table 3.3 Macroinvertebrate species with lowest "Braukmann and Biss index" in 5 Alpine lakes from 2000 to 2006

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

River	Taxa	Index	2000	2001	2002	2003	2004	2005	2006
Laghetto Inferiore	Ecdyonurus sp.	2					x	x	x
	Ecdyonurus helveticus-Gr.	2				x	x	x	x
	Rhitrogena semicolorata-Gr.	2				x			
	Isoperla rivuloruum	2							x
	Perlodes sp.	2					x		
	Perlodes intricatus	2					x	x	
	Protonemoura nimborum	2	x					x	x
	Philopotamus lucidificatus	2				x		x	x
Laghetto Superiore	Baetis alpinus	2				x	x		x
	Ecdyonurus sp.	2				x	x	x	x
	Ecdyonurus gr. helveticus	2				x		x	
	Ecdyonurus parahelveticus	2					x		
	Rhitrogena gr. semicolorata	2					x		
	Isoperla rivulorum	2				x	x		
	Perlodes sp.	2					x		
	Perlodes intricatus	2					x	x	
	Perlodes microcephalus	2				x			
	Protonemoura nimborum	2						x	x
Lago Tomè	Perla grandis	1	▨	x					
	Protonemura nimbrorum	2	▨					x	
	Protonemura meyeri	4	▨	x					
	Odontocerum albicorne	4	▨						x
	Potamophylax cingulatus	4	▨					x	x
	Ryacophila (Ryacophila) sp.	4	▨			x	x	x	x
	Ryacophila sensu stricto-Gr.	4	▨					x	x
	Sialis sp.	4	▨		x	x			
	Sialis fuliginosa	4	▨				x	x	x
Lago del Starlaresc da Sgiof	Allogamus uncatus		▨					x	x
	Oligotricha striata	4	▨	x	x	x	(x)	x	x
	Sialis sp.	4	▨				(x)	(x)	(x)
Lago Bianco	Alainites muticus	2	▨	▨	▨	▨	▨	▨	x
	Baetis alpinus	2	▨	▨	▨	▨	▨	▨	x
	Ecdyonurus sp.	2	▨	▨	▨	▨	▨	▨	x
	Protonemura nimborum	2	▨	▨	▨	▨	▨	▨	x
	Perlodes sp.	2	▨	▨	▨	▨	▨	▨	x
	Perlodes intricatus	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 (minimum pH 2005-2006: 6.9 and 7.1, respectively).

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 2005 and 2006 are shown in Tab. 3.4. The number of E.B.I. taxa and the EPT index were highest in river Vedeggio and Maggia, followed by river Verzasca. In river Vedeggio and Maggia *Diptera* was the dominant order (average: 35%), followed by *Plecoptera* (average: 21%) and *Ephemeroptera* (average: 20%) in river Vedeggio and by *Ephemeroptera* (average: 27%) and *Plecoptera* (average: 16%) in river Maggia. Differently, the most abundant order in river Verzasca was *Ephemeroptera* (average: 41%) followed by *Coleoptera* (average: 20%), *Diptera* (average: 20%) and *Plecoptera* (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 2005 and 2006.

	Maggia		**Vedeggio**		**Verzasca**	
	2005	**2006**	**2005**	**2006**	**2005**	**2006**
no. of samples	4	4	4	4	4	4
no. organisms	9857	11904	7243	11672	12901	15019
no. taxa E.B.I.	40	36	40	39	28	30
EPT index	17	16	20	19	12	14
Ephemeroptera	31%	23%	16%	23%	45%	36%
Plecoptera	16%	15%	24%	17%	14%	16%
Trichoptera	3%	7%	15%	10%	2%	2%
Diptera	35%	36%	36%	31%	19%	20%
Coleoptera	9%	13%	6%	14%	16%	24%
Oligochaeta	2%	1%	1%	1%	1%	0%
Others	4%	4%	3%	3%	4%	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 2006

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

Table 3.6 Macroinvtebrate species with lowest "Braukmann and Biss index" in 3 Alpine rivers from 2000 to 2006

River	Taxa	Index	2000	2001	2002	2003	2004	2005	2006
Maggia	Ephemerella ignita	1	x	x		x	x	x	x
	Habroleptoides confusa	1	x	x			x	x	x
	Perla sp.	1	x		x	x	x	x	x
	Perla grandis	1	x	x	x	x	x	x	x
Vedeggio	Ephemerella ignita	1	x					x	
	Habroleptoides confusa	1	x					x	
	Perla sp.	1	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
	Perla grandis	1	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
Maggia	1	0%	0%	0%	0%	40%	0%	0%
	2	100%	100%	100%	100%	60%	100%	100%
Vedeggio	1	0%	0%	50%	0%	0%	0%	0%
	2	100%	100%	50%	100%	100%	100%	75%
Verzasca	1	0%	0%	0%	0%	0%	0%	0%
	2	100%	100%	100%	100%	100%	100%	100%

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

4.1 Introduction

Persistent organic pollutants (POP's) are chemical substances that persist in the environment, bioaccumulate through the food web and can have negative effects to human health and the environment. POP's can be transported for long distances through the atmosphere from warm (low latitudes, low altitudes) to cold regions (high latitudes, high altitudes). In order to verify the presence of a concentrations gradient with altitude, in 2005 POP's in fish muscle from 4 Alpine lakes with different altitude were analysed. In addition, metals concentrations were also measured.

4.2 Methods

Fish were angled in fall 2005 in 4 Alpine lakes laying at different altitudes: Lago di Tomè (1692), Laghetto Inferiore (2074) , Laghetto Superiore (2128), Lago di Valsabbia (2396 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, in Lago di Tomè only brook trouts (*Salvelinus fontinalis*) and in Lago di Valsabbia 5 different species were fished (*Salvelinus fontinalis* ,*Oncorhynchus mykiss, Salmo trutta fario, Salvelinus alpinus, Salvelinus namaycush*). Fish number and average fish weight, length, conditioning index, age and lipid content are shown in Tab. 6.1.

Table 4.1 Fish number and average weight, length, conditioning index (C.I.) and age.
n.d. stays for not determine.

	Altitude (m a.s.l.)	Species	Fish number	Weight (g)	Length (cm)	C.I.	Age (month)
Lago di Tomè	1692	*Salvelinus fontinalis*	12	85.7	19.6	1.05	n.d.
Laghetto Inferiore	2074	*Oncorhynchus mykiss*	21	87.7	20.4	1.02	39
Laghetto Superiore	2128	*Oncorhynchus mykiss*	23	84.7	20.3	1.01	40
Lago di Valsabbia	2396	*Salvelinus fontinalis*	6	70.0	18.3	1.05	n.d.
		Oncorhynchus mykiss	4	25.3	13.6	1.00	n.d.
		Salmo trutta fario	3	44.7	17.2	0.87	n.d.
		Salvelinus alpinus	3	68.7	22.1	0.63	n.d.
		Salvelinus namaycush	2	72.0	21.5	0.73	n.d.

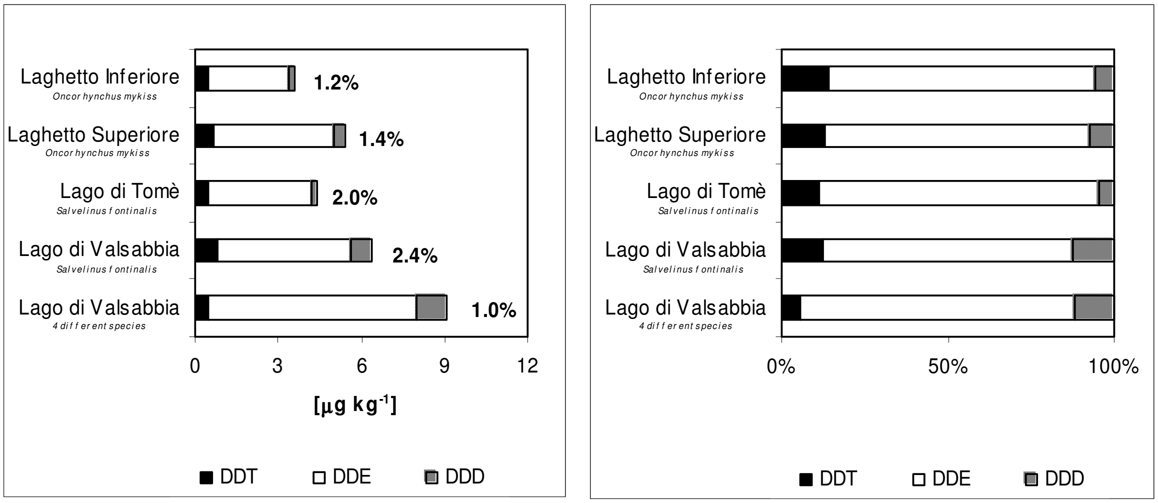
As suggested by their geographic vicinity, the fish populations in Laghetto Inferiore and Laghetto Superiore are very similar: same species and similar average weight, length, CI and age. Comparing the population data of *Oncorhynchus mykiss* in Laghetto Superiore and Laghetto Inferiore with those of Lago di Valsabbia, it results that in the latter fish were smaller and lighter. However, the CI above 1 indicates a good physical condition in all 3 lakes. Similar average weight, length and C.I. (> 1) can also be observed between fish population of

Salvelinus fontinalis in Lago di Tomè and Lago di Valsabbia. Critical average coefficient indexes were only observed in Lago di Valsabbia for *Salmo trutta fario*, *Salvelinus alpinus* and *Salvelinus namaycush*. However, it should also be added that for these species the number of cached fish was small (2-3) and therefore not very representative.

4.3.2 DDT's in fish muscle

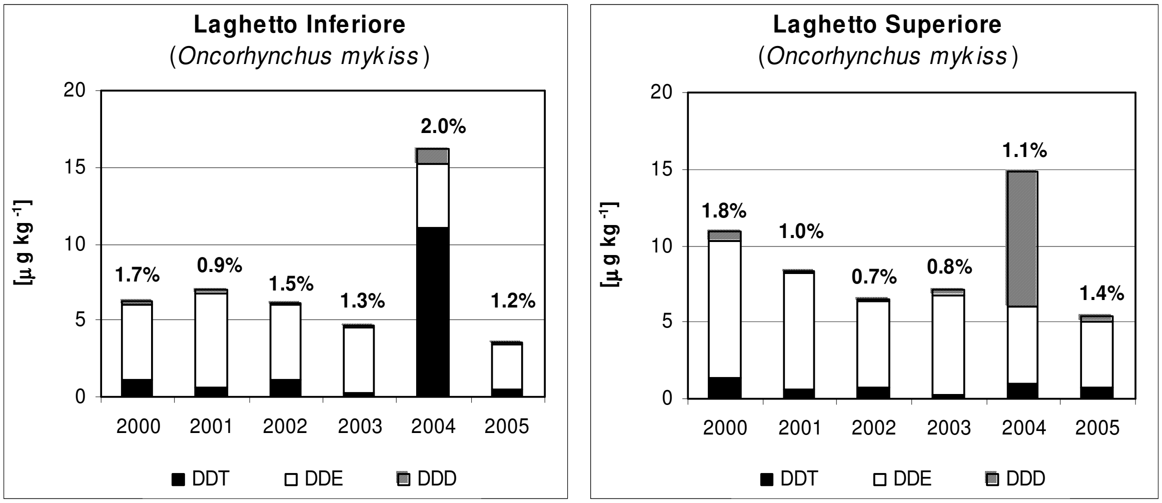
Results from DDT measurements in fish muscle of 2005 are shown in Fig . 4.1. Total DDT concentrations varied between 3 and 9 μg kg^{-1} and in all lakes DDE was the main component. DDE is a metabolite of DDT. Values are therefore below the Swiss edibility limit for total DDT (1 mg kg^{-1}). Unfortunately, it was not possible to obtain samples of the same fish species for all lakes, so that direct comparison among all lakes becomes difficult. However, comparing lakes with same fish species as Laghetto Inferiore with Laghetto Superiore and Lago di Tomè with Lago di Valsabbia, it results that no significant difference between lakes can be observed. In particular, there is no evidence for an altitude dependent concentration of DDT.

Figure 4.1 Absolute (μg^{-1} kg wet weight) and relative (%) concentrations of DDT's in fish muscle measured in 2005
The percentage value refers to the lipid content.



Compared to results from former years (Fig. 4.2), concentrations of DDT in fish muscle from Laghetto Inferiore and Laghetto Superiore from 2005 are the smallest ever measured. Omitting data from 2004, that are exceptionally high, DDT concentrations seem to decrease with time, probably reflecting the cessation of the DDT production activity in 1996 of a factory situated along the shore of Lago Maggiore. In fact, a general decreasing trend of DDT in fish from Lago Maggiore, interrupted by single years of increased concentrations due to resuspension of sediments containing DDT as a consequence of flooding events, has been described (Cipais, 2001-2005). Very difficult to explain are instead the high concentrations of 2004. Even more strange is the difference between relative concentrations of DDT's in fish from Laghetto Inferiore with respect to Laghetto Superiore during 2004. Different causes can be hypothesised. A particular meteorological event may for example have been responsible for an atmospheric deposition rich in DDT originating from countries were it is still used (e.g. Africa). The very hot and dry summer of 2003 may also have been responsible for the observed phenomena. In fact, it may have caused an increased evaporation of DDT from the Lago Maggiore area, where DDT concentrations are a factor 3-4 higher, or/and an accumulation of DDT in the watersheds of Alpine lakes during 2003, which could have be discharged into the lakes during precipitation events in 2004.

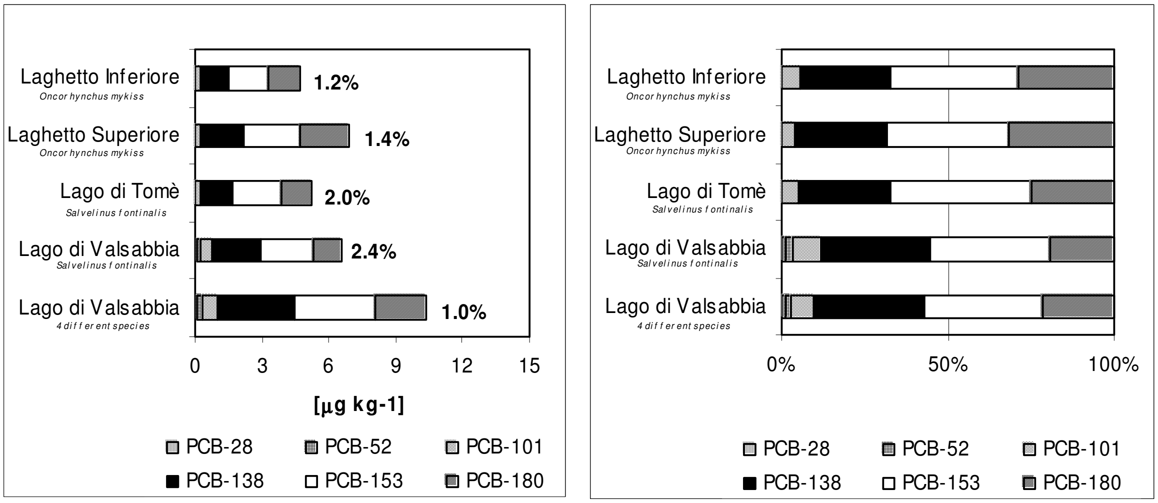
Figure 4.2 Concentrations of DDT's in fish muscle of Laghetto Inferiore and Laghetto Superiore between 2000 and 2005
The percentage value refers to the lipid content.



4.3.3 PCB's in fish muscle

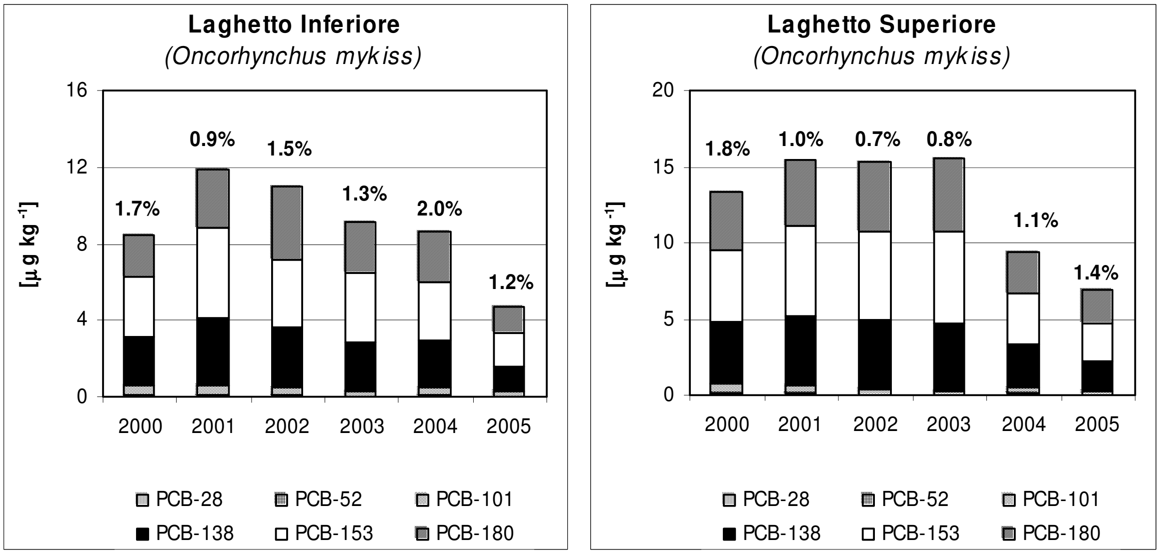
Similarly to what observed for DDT, PCB concentrations measured in fish muscle in 2005 did not vary significantly between lakes (Fig. 4.3). Total PCB concentrations ranged between 5 and 10 µg kg^{-1} and the 3 heavier isotopes PCB-138, PCB-153, PCB-181 were the main cogeners. The Swiss edibility limit of PCB in fish (1 mg kg^{-1}) was therefore not exceeded.

Figure 4.3 Absolute (µg^{-1} kg wet weight) and relative (%) concentrations of PCB's in fish muscle measured in 2005
The percentage value refers to the lipid content.



Looking at the time series of PCB concentrations in Laghetto Inferiore and Laghetto Superiore (Fig. 4.4), a reduction of total PCB after 2001 in Laghetto Inferiore and after 2003 in Laghetto Superiore can be observed. The trend may reflect a global decrease in PCB emissions.

Figure 4.4 Concentrations of PCB's in fish muscle of Laghetto Inferiore and Laghetto Superiore between 2000 and 2005
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, Laghetto Superiore, Lago di Tomè and Lago di Valsabbia measured in 2005 was lower than 1 µg kg^{-1} (edibility limit: 100 µg kg^{-1}) and no temporal trend could be observed in Laghetto Inferiore and Laghetto Superiore after 2000.

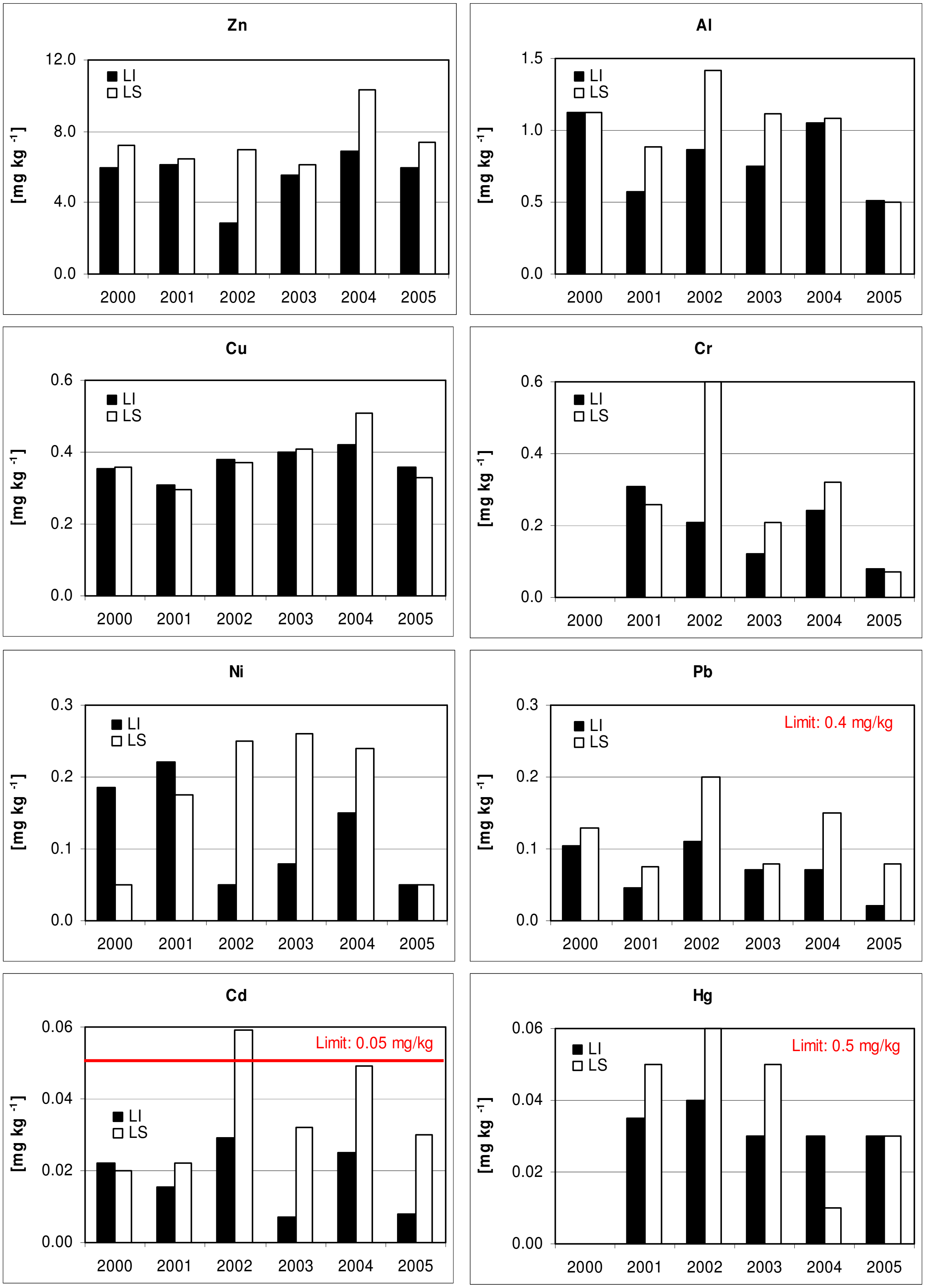
4.3.5 Metals in fish muscle

Metals concentrations in fish muscle sampled in 2005 did also not differ greatly between lakes (Tab. 4.2). Variations in metal concentrations through time after 2000 in Laghetto Inferiore and Laghetto Superiore are shown in Figure 4.5. So far no general trend can be observed. In addition, during some years and for some parameters significant differences between the 2 lakes existed, whereas concentrations in fish from Laghetto Superiore were mostly higher with respect to Laghetto Inferiore. The average pH of the 2 lakes is similar (Laghetto Inferiore: 6.5, Laghetto Superiore: 6.4) and can therefore not explain the difference in metal concentrations. Instead, since the watershed of Laghetto Superiore (125 ha) is included in the watershed of Laghetto Inferiore (182 ha) it is possible that Laghetto Superiore acts as a sink for metals and other chemical parameters (also POP's) with respect to Laghetto Inferiore. 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 metals that reached the bottom of Laghetto Inferiore remain there. 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) the Swiss edibility limit for fish are also indicated in Fig. 4.5. Pb and Hg concentrations were always below the limit, while Cd concentrations exceeded the limit in Laghetto Superiore during 2002.

Table 4.2 Metal concentrations in fish muscle (mg^{-1} kg wet weight) measured in 2005

	Laghetto Inferiore (*Oncorhynchus mykiss*)	**Laghetto Superiore** (*Oncorhynchus mykiss*)	**Lago di Tomè** (*Salvelinus fontinalis*)	**Lago di Valsabbia** (*Salvelinus fontinalis*)	**Lago di Valsabbia** (*4 different species*)
Zn	5.93	7.37	5.30	6.08	5.67
Al	0.51	0.50	0.50	0.39	0.48
Cu	0.36	0.33	0.36	0.40	0.28
Cr	0.08	0.07	0.06	0.30	0.22
Ni	<0.05	<0.05	<0.05	<0.05	<0.05
Pb	<0.02	0.08	0.08	<0.02	<0.02
Cd	0.01	0.03	0.02	0.00	0.01
Hg	0.03	0.03	0.04	0.04	0.06

Figure 4.5 Metal concentrations in fish muscle (mg^{-1} kg wet weight) measured in 2005



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