Repubblica e Cantone Ticino
Dipartimento del territorio

Acidifying Deposition in Southern Switzerland

Monitoring, maps and trends 1988-2013

Ufficio dell'aria, del clima e delle energie rinnovabili
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Content

Abstract

Sulphur and nitrogen oxides from combustion processes and ammonia from agriculture can be transported over long distances, transformed and then loaded on natural ecosystems causing acidification and eutrophication of sensitive ecosystems. Because of its proximity to the emission rich Po Plain and its generally abundant precipitations, Southern Switzerland is particularly exposed to deposition of anthropogenic pollutants.

Total sulphur, nitrogen and acid deposition maps for the Canton of Ticino for the 5 time periods 1988-1992, 1993-1997, 1998-2002, 2003-2007, 2008-2012 were calculated by adding up wet with dry deposition maps. Wet deposition maps were obtained by multiplying precipitation maps with rainwater concentration maps, calculated with multiple linear regression equations describing rainwater concentrations as a function of latitude, longitude and altitude. Dry deposition maps were delivered by Meteotest.

The results show that during the last 25 years average total sulphur deposition decreased on average by a factor 3 from 111 to 38 meq m^{-2} y^{-1}. Average total deposition of nitrogen decreased much less (from 152 meq m^{-2} y^{-1} to 126 meq m^{-2} y^{-1}) and the amount of yearly precipitation is still an important influencing factor, so that during particularly rainy periods deposition can increase again to levels similar to those observed at the beginning of the monitoring period. As a consequence of reduced sulphur and nitrogen deposition, the average present load of acidity also decreased significantly (from 218 to 118 m^{-2} y^{-1}).

The analysis also showed that most deposition of acidifying compounds occurs through wet deposition (67-79%). As a consequence of reduced deposition of sulphur, during the last 25 years the relative importance of sulphur compounds in determining total deposition of acidifying compounds has decreased from 42% to 32%, while that of nitrogen compounds has increased from 58% to 68%, with oxidized and reduced nitrogen contributing about 50% each to the total.

Summary

Sulphur and nitrogen oxides from combustion processes and ammonia from agriculture can be transported over long distances, transformed and then loaded on natural ecosystems causing acidification and eutrophication of sensitive ecosystems. Because of its proximity to the emission rich Po Plain and its generally abundant precipitations, Southern Switzerland is particularly exposed to deposition of anthropogenic pollutants.

It is for this reason that rainwater quality has been studied in Southern Switzerland since the beginning of the eighties, first only at Locarno Monti and Lugano later also at other sampling stations. Nowadays weekly precipitation is collected at 9 sampling sites distributed over the whole area of the Canton of Ticino. A trend analysis on concentrations of chemical parameters in rainwater sampled at 9 stations in Canton Ticino during the last 25 years showed that sulphate concentrations decreased significantly at all sites, reflecting the decrease of SO_2 emissions since 1980 due to reduction of the sulphur content in liquid fuels and the partial substitution of sulphur rich coal with other fossil fuels. Because of reduced emissions of NO_x, mainly determined by the equipment of cars with catalytic converters and stationary combustion sources with $DeNO_x$-systems, nitrate concentrations also decreased at most sites. The same was observed for base cations, while concentrations of ammonium decreased significantly only at 3 sites. As a consequence of decreased sulphate concentrations, rainwater acidity has also decreased and pH values increased. From the end of the eighties to the beginning of this millennium annual average rainwater pH values at Locarno Monti and Lugano increased from 4.4 to 5.2/5.4 and after 2000 at most sites yearly average acidity started to be negative. Nevertheless during particular years concentrations could deviate from these general trends. In general, because of dilution, during wet years concentrations were lower and during dry years higher than the average. In addition, years with frequent alkaline rain events, often occurring during particular rainy years, were characterized by very high positive base cations and negative acidity peaks. Special environmental events like the volcanic eruption at Eyafjellajokull (Iceland) in 2010 could also influence massively mean annual rainwater concentrations (sulphate peak).

It has also been observed that most chemical parameters in rainwater correlated significantly with one or more of the geographic parameters latitude, longitude and altitude. Sulphate, nitrate and ammonium concentrations correlated negatively with latitude and altitude, reflecting the transportation of these pollutants from the urban area of Milan (SO_2, NO_x) and from the agricultural areas situated in the Po Plain (NH_3) towards north. Differently, base cations, especially calcium and magnesium, generally correlated better with longitude, probably because of precipitation that tends to decrease from west to east and creating a sort of dilution gradient with lower base cations concentrations at the western and higher at the eastern sampling sites. Rainwater acidity correlated negatively with latitude at the beginning of the monitored period (1988-1992), but has been more and more influenced by longitude during the successive time periods, suggesting that during the first period acidity was mainly determined by emissions of SO_2, NO_x and NH_3, whereas afterwards base cations were more important.

The geographic distribution of chemical parameters in rainwater suggested the possibility to develop a multiple regression model with the variables latitude, longitude, altitude

capable of describing the geographic distribution of the concentrations of single chemical parameters in rainwater. Multiple linear regression analysis were performed for different parameters and 5 time periods 1988-1992, 1993-1997, 1998-2002, 2003-2007, 2008-2012. The regression parameters were then used to map concentrations of the main chemical parameters over Southern Switzerland with a resolution of 1km x 1km.

Wet deposition maps for Southern Switzerland were finally derived by multiplying concentration maps of the chemical parameters in rainwater with the precipitation maps. Observations made for concentrations of chemical parameters in rainwater are not substantially different from those for wet deposition. In general, time trends with decreasing deposition of sulphate could be observed. The decrease in nitrogen deposition was not evident as it was for rainwater concentrations because of the influence of precipitation volume. During rain rich years deposition of anthropogenic pollutants were in general higher than the average. Even greater is the effect for base cations, since rain rich years seem to increase the probability of alkaline rain events to occur.

In addition to wet deposition also dry deposition of gases and aerosols contribute to total acidifying deposition. Maps of dry deposition were delivered by Meteotest. The sum of wet and dry deposition was used to derive maps of total sulphur and nitrogen deposition and total acidity and potential acidity loads.

Total deposition of sulphur, nitrogen and acidity decrease along a south to north and altitude gradient in all studied time periods. During the last 25 years total sulphur deposition decreased on average by a factor 3 from 111 to 38 meq m^{-2} y^{-1}. Consequently, deposition of the present load of acidity decreased from 218 to 118 m^{-2} y^{-1}. Total deposition of nitrogen decreased much less and the amount of yearly precipitation was still an important influencing factor, so that during particularly rainy periods deposition could increase again to levels similar to those observed at the beginning of the monitoring period.

The analysis also showed that most deposition of acidifying compounds occurred through wet deposition (67-79%). As a consequence of reduced deposition of sulphur, during the last 25 years the relative importance of sulphur compounds in determining total deposition of acidifying compounds has decreased from 42% to 32%, while that of nitrogen compounds has increased from 58% to 68%, with oxidized and reduced nitrogen contributing about 50% each to the total.

Introduction

"Acid rain" is a broad term used to describe the deposition pathway of acidifying compounds from the atmosphere to the surface of the earth. Acidifying deposition has two components: wet and dry. Wet deposition refers to acidifying rain, fog, and snow, while dry deposition refers to acidifying gases and particles. The primary causes of acidifying deposition are the emissions of sulphur dioxide (SO_2) and nitrogen oxides (NO_x) from combustion of fossil fuels. In the atmosphere these gases can be oxidized to sulphuric and respectively nitric acid causing acid precipitation. Besides the mechanism described above, due to the activities of agriculture, also the emissions of ammonia (NH_3) contribute to acidifying precipitation. Although ammonia itself reacts as a base in the atmosphere (resulting in the formation of ammonium, NH_4^+), during the assimilation by plants the temporary bound proton is released again to the environment. In addition, in soils and waters ammonium can be oxidized by microorganisms to nitrate (nitrification), releasing two protons. In this way, ammonia emissions can contribute to the acidification of soils and waters.

Acidifying deposition affects the environment in several ways. Acidification of surface waters gradually leads to severe changes in biological communities. Effects range from reductions in diversity without changes in total biomass to elimination of all organisms (Dillon et al. 1984). Damages to forests include weakening of the root system, nutrient imbalances and defoliation. Building materials and works of art can also be destroyed by acid deposition. Also health problems, especially respiratory and cardiovascular diseases, have been found to be associated with increased concentrations of particulate matter (i.e. aerosols) and ozone, both formed by precursors such as sulphur oxides, nitrogen oxides, volatile organic compounds and ammonia.

Acidifying deposition first began with the industrial revolution, when large amounts of fossil fuels were burnt to produce steam power needed to drive machinery. The term "acid rain" was coined in the 19th century by the scientist Robert Smith, working at the time in Manchester (Smith 1852). In those times acid rain was confined to industrial towns and cities. However, the situation gradually worsened and widespread environmental damage on a global scale was observed by scientists in the second half of the 20th century.

In the sixties the link between sulphur emissions in continental Europe and acidification of Scandinavian lakes had been demonstrated (Odén 1968). Between 1972 and 1977 several studies confirmed the hypothesis that air pollutants can travel several thousands of kilometers before deposition and damage occur, evidencing that cooperation on an international level was necessary to solve problems such as acidification. As a consequence in 1979 34 Governments, including Switzerland, and the European Community (EC) signed the Convention on Long-range Transboundary Air Pollution (CLRTAP). The Convention entered into force in 1983. Today it has 51 Parties and has been extended by eight specific protocols. Four of these protocols control acidifying pollutants.

The Helsinki Protocol of 1985 aimed at reducing sulphur emissions by at least 30%. The goal of the 1988''s Sofia Protocol was the freezing of the emissions of NO_x. The 1994's Oslo Protocol required further reduction of sulphur emissions and the Gothenburg Protocol

of 1999 set national emission ceilings for sulphur, NO_x, VOC's and ammonia for 2010. As a consequence, a substantial reduction in the emissions of sulphur and nitrogen oxides (Schulz et al. 2013) has been achieved over the last 20-25 years leading to an improved quality of atmospheric deposition.

Fig. A shows the emissions of sulphur and nitrogen oxides and ammonia in Switzerland from 1900 to 2030 (Künzler 2005; Heldstab et al. 2014). The sulphur and nitrogen oxides emissions started to increase steeply after the second world war. Sulphur oxides reached their maximum between 1965 and 1980, while nitrogen oxides peaked around 1985. Afterwards, both sulphur and nitrogen oxides decreased continuously until present (2014). For ammonia only a small decrease could be observed. The reduction of sulphur dioxide emissions has mainly been caused by a reduction of the sulphur content in liquid fuels and the partial substitution of sulphur rich coal with other fossil fuels. The decrease of the nitrogen oxides emissions after 1985 has been mainly determined by the equipment of cars with catalytic converters and stationary combustion sources with $DeNO_x$-systems. However, because of its particular topography and meteorology the air quality in southern Switzerland is not only influenced by local emissions but also by transboundary air pollution originating from the Po Plain and particularly from the heavily polluted urban area of Milan. In fact, wet deposition in southern Switzerland is mainly determined by warm, humid air masses originating from the Mediterranean Sea, passing over the Po Plain and colliding with the Alps. Furthermore, high altitude soils and freshwaters of southern Switzerland are particularly sensitive to acidification because of the dominance of base-poor rocks with low buffering capacity. As a consequence, acidifying deposition in southern Switzerland has become particularly relevant.

Acidifying deposition in southern Switzerland has already been assessed by Barbieri and Pozzi (2001) and by Steingruber and Colombo (2010) for the following time periods: 1988-1992, 1993-1997, 1998-2002, 2003-2007. This report is an update of Steingruber and Colombo (2010) that includes the most recent 5-years time period 2008-2012. In particular, the aims of this report are:

- to describe rainwater quality at different sampling stations in southern Switzerland from 1988 to 2013;
- to calculate temporal trends for the main chemical parameters present in rainwater involved in the process of acidification;
- to perform a principal component and factor analysis including Swiss and close-by Italian sites in order to highlight changes in similarities and differences among chemical and geographic parameters and sampling stations through five different periods (1988-1992, 1993-1997, 1998-2002, 2003-2007, 2008-2012);
- to map wet deposition of the main chemical parameters for southern Switzerland for the last 5 five-years periods with the aid of multiple regression analysis between concentrations of parameters relevant for acidification and geographic parameters;
- to map total deposition by adding up wet and dry deposition, the latter being modeled by Meteotest.

The here calculated rainwater concentration models for southern Switzerland were then integrated in the Swiss deposition maps developed under request of the Swiss Federal Office for the Environment (FOEN, in prep.).

1. Precipitations in Southern Switzerland

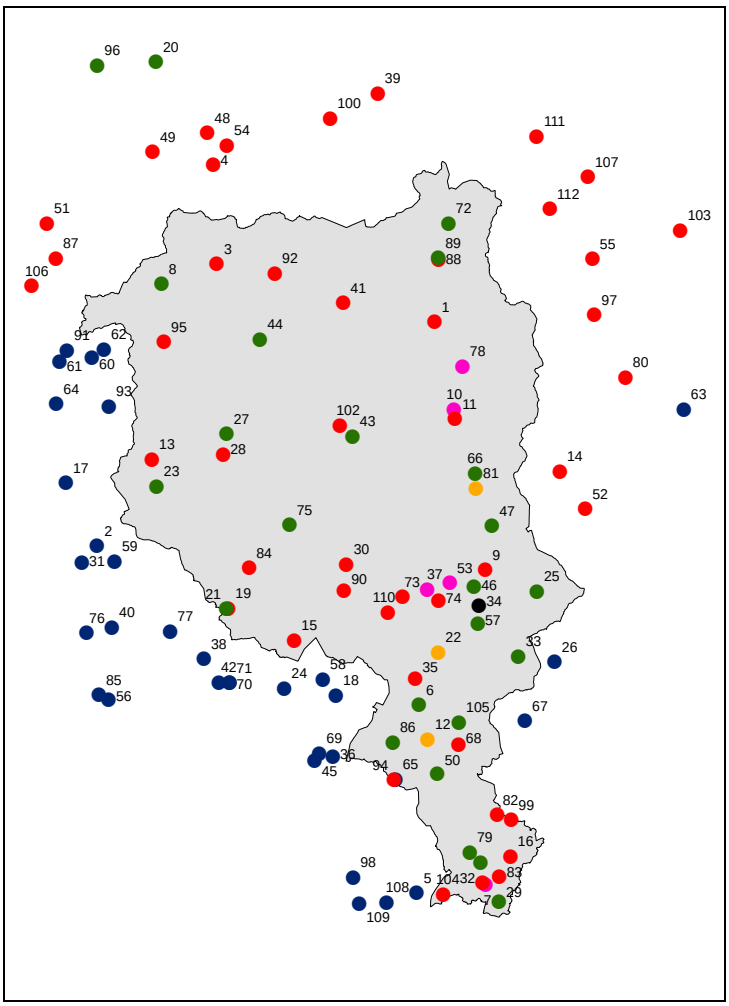
1.1 Introduction

Precipitation volumes influence very much rainwater quality and the amount of wet deposition of air pollutants. For this reason the geographic distribution of precipitation during the last five 5-years time periods has been mapped.

1.2 Sampling sites

Yearly precipitation from totally 111 pluviometric stations were used to estimate the amount of precipitation over southern Switzerland. Swiss data originated from different precipitation monitoring networks: the Federal Office of Meteorology and Climatology (MeteoSwiss), the Swiss Centre for Agricultural Research (Agrometeo), the Canton of Ticino with data from Ufficio dei corsi d'acqua (UCA) and from Ufficio del monitoraggio ambientale (OASI). At one station the amount of precipitation was measured by the Federal Institute for Forest, Snow and Landscape Research (WSL). Italian data were provided by the Institute of Ecosystem Study (ISE-CNR), the Regional Agencies for the Protection of the Environment of Piedmont and Lombardy (ARPA Piemonte and ARPA Lombardia), the national agency for electric energy (ENEL), the hydroelectric power agencies (Idroelettriche Riunite S.p.A.) and the Centro Geofisico Prealpino. The geographic distribution of the precipitation sampling sites is shown in Fig. 1.1. Longitudes, latitudes, altitudes and source of the data are reported in Tab. A1 of the Appendix.

Figure 1.1: Precipitation sampling sites. Swiss sites: red (MeteoSwiss), green (UCA), pink (Agrometeo), orange (OASI), black (WSL); Italian sites: blue.



1.3 Mapping method

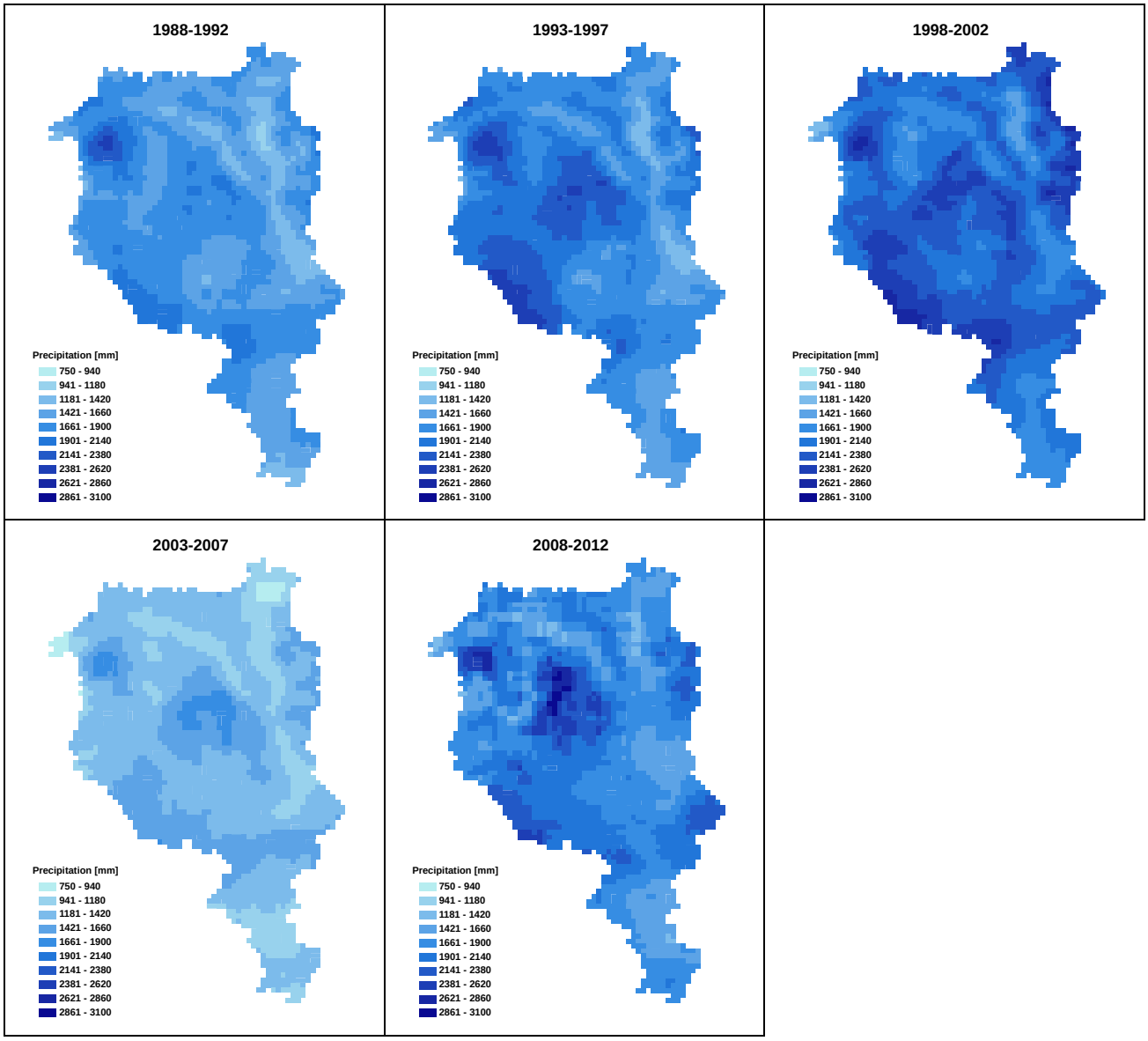
Existing national precipitation maps were refined for the study area with the following procedure: for each of the 111 sampling stations listed in Tab. A1 of the Appendix the average precipitation volumes over the five periods of 1988-1992, 1993-1997, 1998-2002, 2003-2007 and 2008-2012 were calculated and divided by values extracted from national precipitation maps (resolution: 1km x 1km). For the period of 1988-1999 the precipitation maps were supplied by Meteotest based on a dataset of FOWG (2000), whereas for the period 2000-2007, they were calculated by the company Meteotest using the same method based on monitoring data of MeteoSwiss. For the period 2008-2012 the maps were prepared based on gridded data of MeteoSwiss.

The resulting factors were interpolated by the inverse distance weighting method in ArcGIS® (registered trademark of Esri Inc., Redlands, USA) using the following parameters: distance exponent = 2, number of points = 3, maximal search distance = 11 km, resolution = 1 km x 1km. The resulting factor maps were then multiplied back by the national precipitation maps from the Swiss hydrological atlas.

1.4 Precipitation maps

The calculated precipitation maps are shown in Fig. 1.2. Mean annual precipitation was 1675 mm in 1988-1992, 1880 mm in 1993-1997, 2132 mm in 1998-2002, 1320 mm in 2003-2007 and 1890 mm in 2008-2012. Interestingly, 1998-2002 was one of the wettest and 2003-2007 one of the driest 5-year period ever measured. It can also be observed that the wettest region is situated in the western part of the study area. This region includes the Centovalli's, the Onsernone's and the lower Maggia's valley. The reasons for this distribution are air masses rich in humidity moving predominantly from southwest toward the southern Alps and the particular orography of the area causing a steep raise of the air masses to higher altitudes. Other rain rich regions are located in the northwestern part (higher Maggia valley), in the north-central part (higher Verzasca valley) and in the centre of the Canton of Ticino (mount Tamaro-Gradiccioli). Precipitation is lowest in the eastern part of the Canton due to less frequent exposure to humid currents. For a more detailed description of the climate in the studied area one may refer to Spinedi and Isotta (2004) and MeteoSvizzera (2012).

Figure 1.2: Precipitation maps: 1988-1992, 1993-1997, 1998-2002, 2003-2007, 2008-2012



2. Rainwater quality

2.1 Sampling sites

Sampling of wet deposition was carried out at weekly intervals. Between 1982 and 1985 rainwater was collected at Locarno Monti and Lugano with bulk samplers. Since 1988, wet-only samplers have been used. Sampling of wet deposition started at Acquarossa, Piotta and Stabio in 1990, at Monte Bré in 1995, at Robiei in 1996, at Bignasco and Sonogno in 2001. Sampling sites were chosen along a south-north axis and at various altitudes (200-1900 m a.s.l.). In order to better describe the dependency on geography, results from the closed-by Italian sampling sites have been also considered in the statistical analysis (data have been provided by the Institute of Ecosystem Study in Pallanza, Italy). In addition, to facilitate the modeling of rainwater concentrations at very high altitudes results from the analysis of snow sampled at the Basodino glacier (2650-3100 m) were also considered. Snow cores representing the snow fallen between October and May were samples almost every spring since 1993. The geographic distribution of the sampling sites and their geographic coordinates are shown in Fig. 2.1 and Tab. 2.1, respectively.

Figure 2.1: Study area with wet deposition sampling points. Swiss: red, Italian: blue.

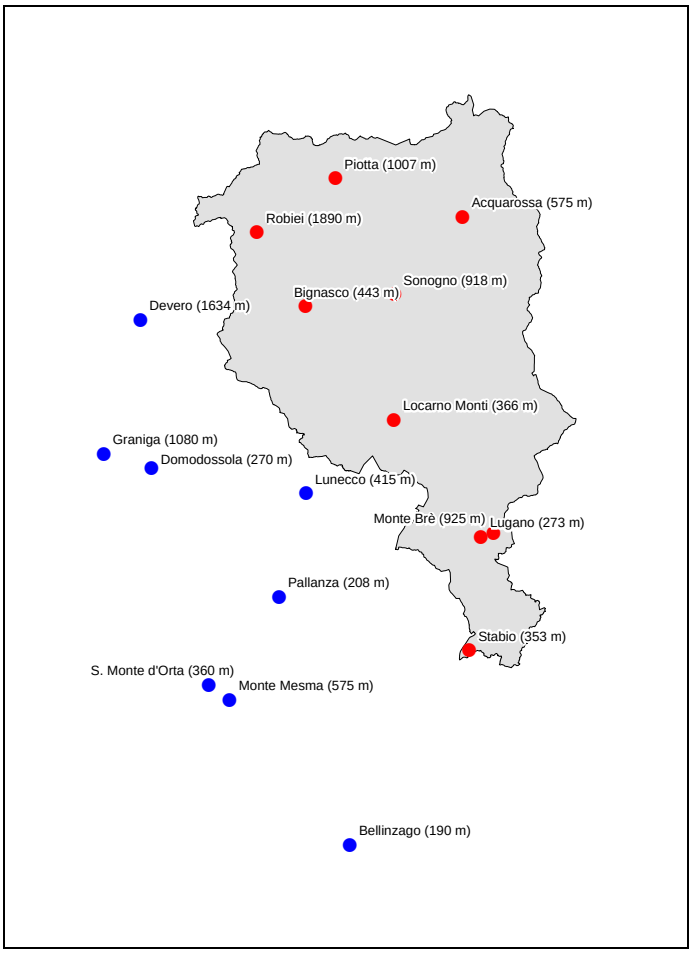


Table 2.1: Swiss (CH) and Italian (I) wet deposition sampling sites and their geographic (WGS84) and Swiss (CH1903 LV03) coordinates, altitudes and sampling years

Sampling site	WGS84		CH1903 LV03 (m)		Altitude (m a.s.l.)	Sampling years
	North	East	North	East		
Acquarossa (CH)	46°27'41''	8°56'12''	146440	714998	575	1990-1991, 1993-2013
Bignasco (CH)	46°00'32''	8°59'17''	132257	690205	443	2001-2013
Locarno Monti (CH)	46°10'27''	8°47'17''	114350	704160	367	1982-1985, 1988-1991, 1993-2013
Lugano (CH)	46°00'24''	8°57'18''	95870	717880	273	1982-1985, 1989-1991, 1993-2013
Monte Brè (CH)	46°00'32''	8°59'17''	96470	719900	925	1995-2013
Piotta (CH)	46°31'07''	8°40'35''	152500	694930	1007	1990-1991, 1993-2013
Robiei (CH)	46°26'43''	8°30'51''	143984	682540	1890	1996-2013
Sonogno (CH)	46°21'05''	8°47'14''	134150	704250	918	2001-2012
Stabio (CH)	45°51'36''	8°55'52''	77970	716040	353	1990-1991, 1993-2013
Bellinzago (I)	45°34'27"	8°41'31"	47245	697217	190	1989-2012
Devero (I)	46°19'19"	8°16'29"	130156	664132	1634	1996-2012
Domodossola (I)	46°06'42"	8°17'41"	106767	665875	270	1986-2012
Graniga (I)	46°07'52"	8°11'59"	108936	658342	1080	1994-2012
Lunecco (I)	46°04'28"	8°36'39"	102774	690264	415	1989-2012
Monte Mesma (I)	45°46'43"	8°26'38"	70166	678202	575	2003-2012
Pallanza (I)	45°55'42"	8°34'48"	86386	686003	208	1985-2012
S. Monte d'Orta (I)	45°48'13"	8°24'41"	72547	674929	360	1990-1999
Basodino glacier (CH)	46°25'04''	8°28'34"	141000-141500	679500-680000	2650-3100	1993-2003, 2006-2013

2.2 Analytics

Rain samples were analyzed for pH, alkalinity, conductivity and the main cations and anions. Parameters, analytical methods and quantification limits are shown in Tab. 2.2.

Table 2.2: Measured parameters, analytical methods, accuracy and quantification limits

Parameter	Filtration	Conservation	Methods	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 chromatography	0.010 mg l^{-1}
Mg^{2+}	CA filter	PP bottle, 4°C	ion chromatography	0.005 mg l^{-1}
Na^{+}	CA filter	PP bottle, 4°C	ion chromatography	0.005 mg l^{-1}
K^{+}	CA filter	PP bottle, 4°C	ion chromatography	0.010 mg l^{-1}
NH^{4+}	CA filter	PP bottle, 4°C	spectrophotometry	3 mg N l^{-1}
SO_4^{2-}	CA filter	PP bottle, 4°C	ion chromatography	0.005 mg l^{-1}
NO_3^{-}	CA filter	PP bottle, 4°C	ion chromatography	0.010 mg N l^{-1}
Cl^{-}	CA filter	PP bottle, 4°C	ion chromatography	0.010 mg l^{-1}

The quality of the data was assured by regular participation to national and international intercalibration tests. In addition, data were accepted only if the calculation of the ionic balance and the comparison between the measured and the calculated conductivity corresponded to the quality requests included in the programme manual of ICP Waters (ICP waters Programme Centre, 2010).

2.3 Concentrations of chemical parameters in rainwater

Fig. 2.2 shows the yearly average concentrations of the main chemical parameters measured in precipitation sampled at the 9 Swiss sampling sites Acquarossa, Bignasco,

Monte Brè, Locarno Monti, Lugano, Piotta, Robiei and Sonogno between 1988 and 2013. The corresponding data are tabulated in Tab. A2 of the Appendix. Yearly mean concentrations were calculated by weighting weekly concentrations with the sampled precipitation volume:

$$C(X)_a = \frac{\sum_w P_w \cdot C(X)_w}{P_a}$$ where

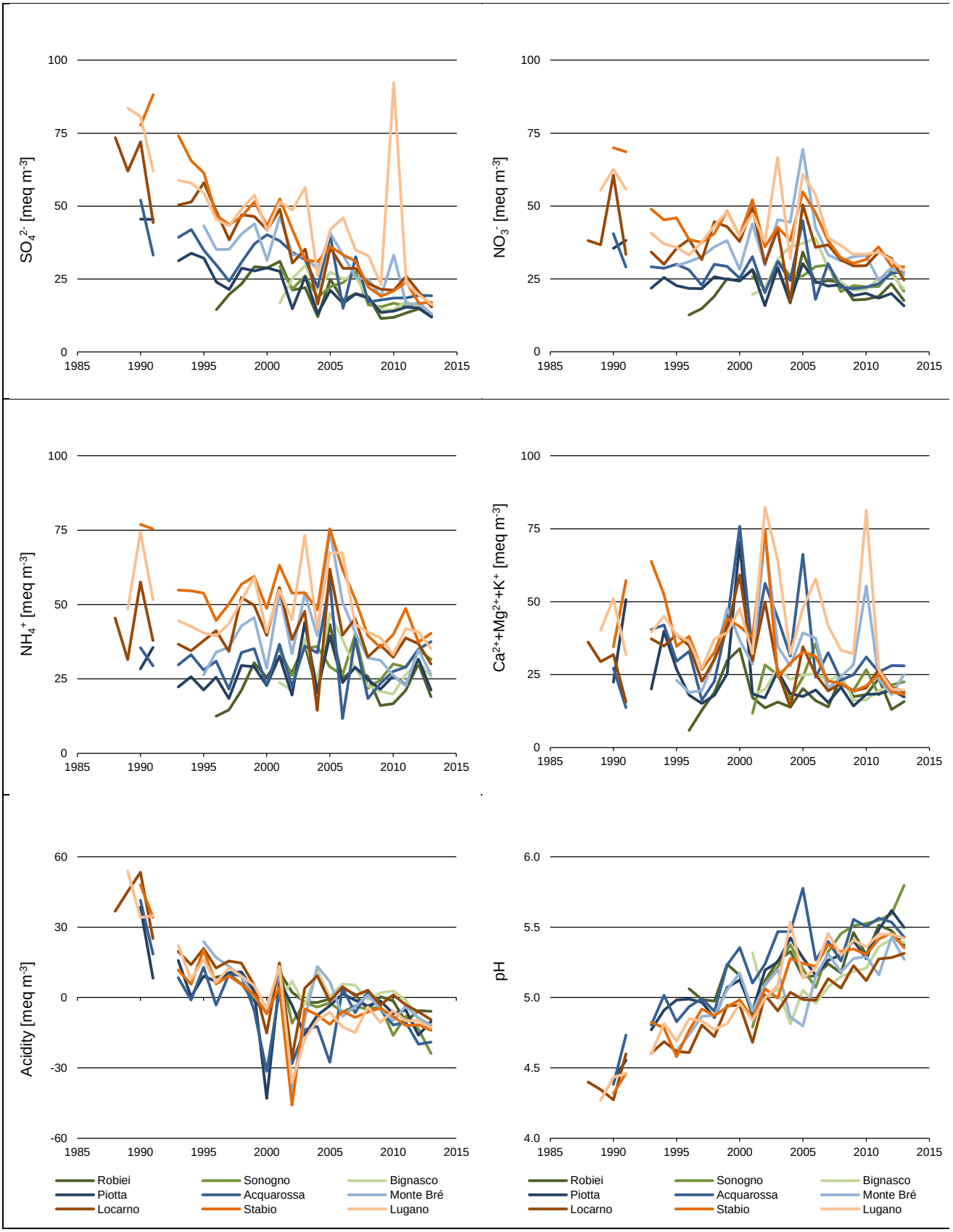
P_w = weekly precipitation volume (measured with the wet-only sampler)

$C(X)_w$= weekly concentration of compound X

P_a = annual precipitation volume calculated as sum of P_w

In addition to the temporal trends that are analyzed and discussed in chapter 2.4, it can be observed that concentrations can vary very much from one year to the other. Because of dilution, during wet years concentrations of sulphate, nitrate and ammonium tend to be lower and during dry years higher than average. It also can happen that single particularly intense rain events with alkaline characteristics can heavily influence yearly mean base cation concentrations and acidity. Exceptionally high base cations and low acidity peaks can be observed at sampling stations Acquarossa, Locarno Monti and Piotta in 2000 (alkaline event in October) and at Monte Bré, Locarno Monti, Lugano and Stabio in 2002 (alkaline event in November). Both events have lead to floods in the region. When and why such events appear is still not clear. It is possible that rain rich years increase the chance of the occurrence of alkaline rain events. The sulphate and base cations peaks at Lugano in 2010 was the consequence of the volcanic eruption at Eyafjellajokull (Iceland) in April 2010.

Figure 2.2: Mean annual concentrations in wet deposition at the sampling sites. Base cations are defined as the sum of calcium, magnesium and potassium.



2.4 Trends in rainwater quality

2.4.1 Statistical methods

Trend analyses were performed on the key variables involved in acidification: sulphate, nitrate, ammonium, base cations (calcium, magnesium and potassium), H^+ and acidity. For each site and each parameter the mean monthly concentrations weighted with the precipitation volume were calculated and temporal trends were tested with the seasonal Mann-Kendall test (Hirsch et al. 1982) with a correction among blocks (Hisch and Slack, 1984). The two sided tests for the null hypothesis that no trend is present were rejected for p-values below 0.05. Estimates for temporal variations in rainwater quality were quantified with the seasonal Kendall slope estimator (Gilbert, 1987). All trend analysis were calculated with the CRAN package "rkt 1.3" (Marchetto, 2014).

2.4.2 Results from trend analysis

Results from the trend analyses are shown in Tab. 2.3. As a consequence of reduced SO_2 emissions the concentrations of sulphate decreased significantly at all sampling sites. The decrease in emissions of NO_x caused a decrease in nitrate concentrations at most sites, while concentrations of ammonium decreased significantly only at Locarno Monti, Piotta and Stabio. Concentrations of base cations also decreased at most sites. Concentrations of acidity, that can be calculated as the difference between acid anions and base cations and ammonia, decreased significantly at all sites. In general, concentrations of acidity decreased from values around 30-40 meq m^{-3} to values around -15 meq m^{-3}. The described decrease of acidity caused an increase of pH from average values around 4.3 in the 1990's to values ranging between 5.3 and 5.6 today.

Table 2.3: Results from trend analyses (significant trends in red). p corresponds to the probability level obtained with the Mann-Kendall test and the trend (meq m^{-3} yr^{-1}) to the Sen's slope.

Station		Acquarossa	Bignasco	Locarno Monti	Lugano	Monte Brè	Piotta	Robiei	Sonogno	Stabio
Period		1990-2013	2001-2013	1988-2013	1989-2013	1995-2013	1990-2013	1996-2013	2001-2013	1990-2013
SO_4^{2-}	p	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.000
	trend	-1.14	-1.02	-1.49	-2.04	-1.42	-0.97	-0.74	-0.79	-2.44
NO_3^-	p	0.012	0.024	0.002	0.039	0.107	0.000	0.314	0.043	0.000
	trend	-0.41	-0.70	-0.77	-0.62	-0.42	-0.56	-0.13	-0.43	-0.98
NH_4^+	p	0.305	0.192	0.013	0.297	0.191	0.048	0.189	0.666	0.010
	trend	-0.14	-0.40	-0.54	-0.27	-0.31	-0.19	-0.14	-0.13	-0.65
Base cations	p	0.545	0.018	0.000	0.067	0.459	0.000	0.125	0.804	0.000
	trend	-0.139	-0.31	-0.55	-0.46	-0.18	-0.68	-0.27	-0.07	-1.03
H^+	p	0.000	0.006	0.000	0.000	0.000	0.000	0.003	0.002	0.000
	trend	-0.60	-0.63	-1.49	-1.04	-0.73	-0.64	-0.36	-0.43	-0.82
Acidity	p	0.000	0.013	0.000	0.000	0.000	0.000	0.006	0.005	0.000
	trend	-1.67	-1.04	-2.25	-2.21	-1.65	-1.10	-0.63	-1.57	-1.88

2.5 Principal component analysis (PCA)

2.5.1 Principles of PCA

Smith (2002) defined the principle component analysis (PCA) as "a way of identifying patterns in data, and expressing the data in such a way as to highlight their similarities and differences. Since patterns in data can be hard to find in data of high dimension, where the luxury of graphical representation is not available, PCA is a powerful tool for analyzing data." This technique consists in the opportunity of compressing these patterns by reducing the number of dimensions, without much loss of information.

A detailed description of the different calculation steps necessary for a PCA can be found within specific tutorials (Smith 2002; Wuensch 2005). However, the main outputs are presented here. The first output matrix of a PCA is the correlation matrix. For each variable a correlation with all other variables is calculated. From this matrix the principal components are extracted by calculating the eigenvalues and eigenvectors of the matrix. For *n* variables and *n* eigenvalues, *n* components are obtained. Eigenvalues "contain" the variance of the correlation matrix. Each eigenvalue represents the amount of variance that has been captured by a single component. Each component is a linear combination of *n* variables. The first component accounts for the largest possible amount of variance. The second component, formed from the variance remaining after extraction of that associated with the first component, accounts for the second largest amount of variance, etc. For further data analyses only components with the largest variance fraction are considered.

Another interesting PCA output matrix is the loadings matrix, or component matrix. Loadings are correlations between variables and the chosen components. For 2 components the loadings of the variables can be plotted on an x,y graph. Variables being best described by the 2 components are placed along a circle of radius 1 centered on the axes origin. Loading plots display how variables are correlated to each other: the closer 2 variables are, the better their correlation is; the closer the variables are to the circle with radius 1, the better they are described by the 2 principal components shown by the axis. In order to get the axes crossing the main variable clusters we rotated here the two principal component solution (method: varimax).

Very useful is also the extraction of factor scores for each sampling site (method: regression). Factor scores are defined by a weighted sum of the raw variables. Factor score plots show how sampling sites are correlated to each other with respect to their variables.

PCA was performed for average concentrations of the main chemical parameters over the following 5-years time periods: 1988-1992, 1993-1997, 1998-2002, 2003-2007, 2008-2012. For the analysis the statistic software SPSS was used (SPSS Inc., 2008).

In order to get better results, not only data from Switzerland but as well from Italy were used (provided by the Institute of Ecosystem Study in Pallanza). Sampling stations are described in Tab. 2.1 (17 sampling stations). In addition to chemical parameters also the mean annual precipitation over the 5-years periods and geographic parameters such as longitude, latitude and altitude of the sampling stations were considered in the analysis. In

order to prevent underestimation of yearly deposition because of occasionally missing weekly data, for Swiss sites precipitation volumes from MeteoSwiss were mostly used. In particular, for our sampling sites, data from the following pluviometric stations of MeteoSwiss have been chosen: Acquarossa → Acquarossa/Comprovasco, Bignasco → Cevio (until 2004), Locarno Monti → Orselina, Lugano → Lugano, Monte Brè → Lugano, Piotta → Piotta, Robiei → Robiei, Sonogno → Sonogno, Stabio → Stabio. After 2005 pluviometric data for Bignasco originated from a sampling station of the Canton of Ticino situated in Cavergno. Data used for the analysis are reported in Tab. A3 of the Appendix (black figures only).

2.5.2 Results from PCA

The loading plot is an efficient method to represent the relationships existing amongst the single variables. Loading plots for the 5 studied time periods are shown in Fig. 2.3 (left figures). The x and y axes represent the correlation with the first, respectively with the second component. The percentage values shown in the axes legends refer to the percentage amount of the variance captured by the component. The closer the sum of the percentage values of the two principal components is to 100%, the better the principal components are able to describe the set of variables.

Fig. 2.3 shows that in every time period two principal components were able to capture most of the variance of the correlation matrix (1988-1992: 82%, 1993-1997: 85%, 1998-2002: 77%, 2003-2007: 78%, 2008-2012: 71%). It also appears that most variables were very well described by the combination of the 2 principal components (close to a circle with radius 1).

In particular, the geographic parameters latitude and altitude were always situated close to each other and are described very well by component 1. This indicates that a positive relationship exists between these parameters. In fact, since the study area is situated on the southern slope of the Alps, altitude normally increases with latitude. Variables displaying a negative correlation with latitude and altitude are close to the x axe but with opposite site with respect to latitude and altitude. Variables that always correlate negatively with latitude and altitude are nitrate, ammonium, sulphate and conductivity.

The negative correlation with latitude is related to the fact that precipitation in southern Switzerland is mainly determined by warm, humid air masses originating from the Mediterranean Sea, passing over the Po Plain and colliding with the Alps. As a consequence, concentrations of sulphate, nitrate and ammonium are related to the distance from northern Italy, because of important NO_x and SO_2 emissions in the urban area of Milan and NH_3 emissions from the agricultural areas situated in the Po Plain. The decrease of concentrations with altitude reflects both the pollutants gradient from south towards north and the decrease of anthropogenic pollutants with altitude.

Base cation concentrations, especially calcium and magnesium generally correlated better with longitude. Base cation concentrations increaseed with increasing longitude from west to east. This observation is not easy to explain but we think that it has to do with the fact that in Ticino precipitation is mainly caused by wet air masses moving from south-west to north-east (Spinedi and Isotta, 2004) and because of the orography of the territory that cause in general higher precipitation volumina in the west with respect to the east, so that

base cations get somehow enriched at the more eastern situated sampling sites. The same conclusion might be drawn from the slight negative correlation of longitude with precipitation that appeared in the PCA analysis.

Interestingly, rainwater acidity, defined as the difference of concentrations between acid anions (especially sulphate and nitrate) and base cations (especially calcium) and ammonium, correlated positively with sulphate, nitrate and ammonium in the first time period (1988-1992), but has been more and more influenced by calcium and magnesium during the successive time periods. This probably means that over the years, because of the reduction of SO_x and NO_x emissions, base cations became more important in determining differences in rainwater acidity over the territory than acid anions.

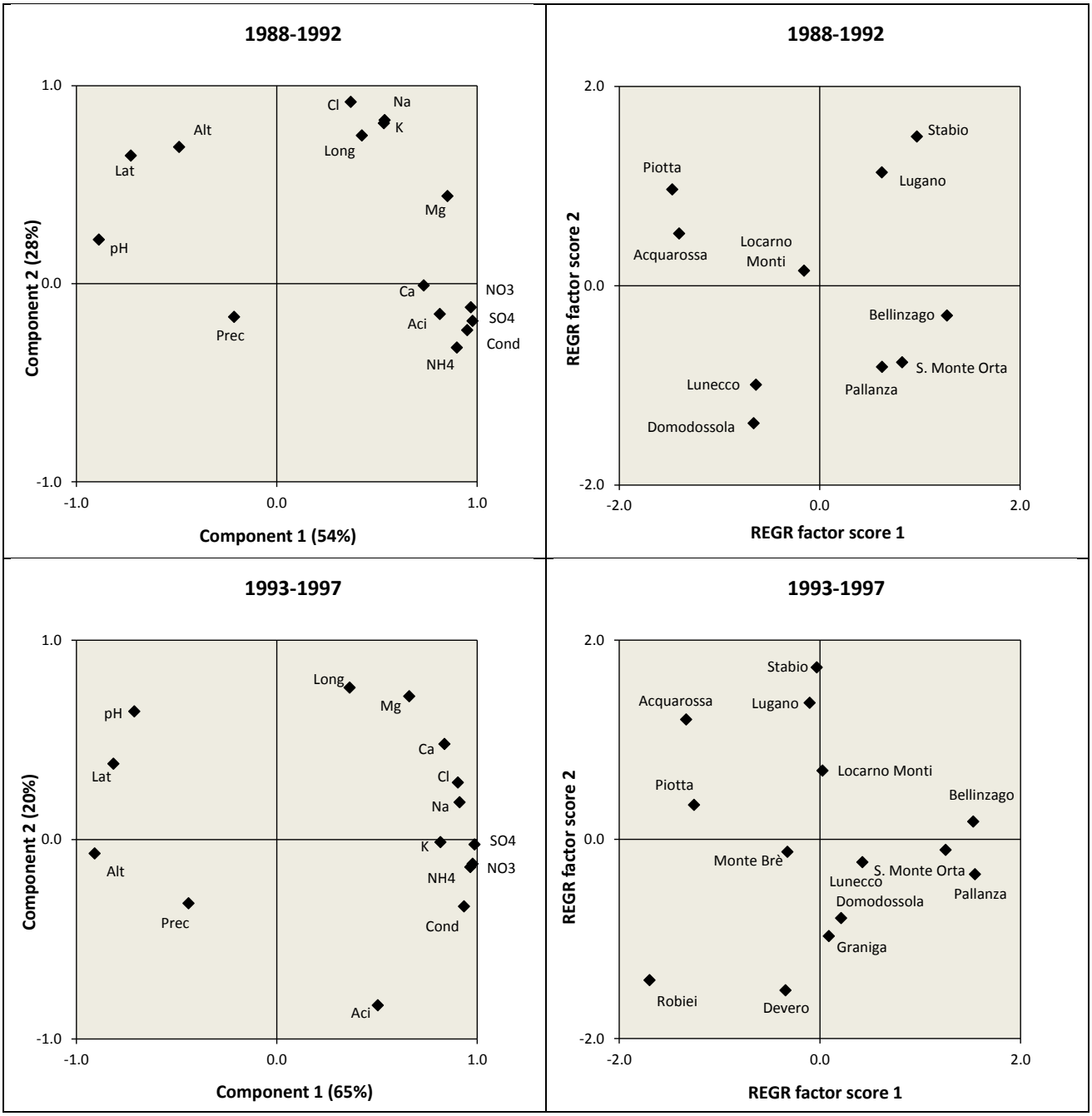
During the first three time periods the y axis was mainly represented by longitude while afterwards pH became more important.

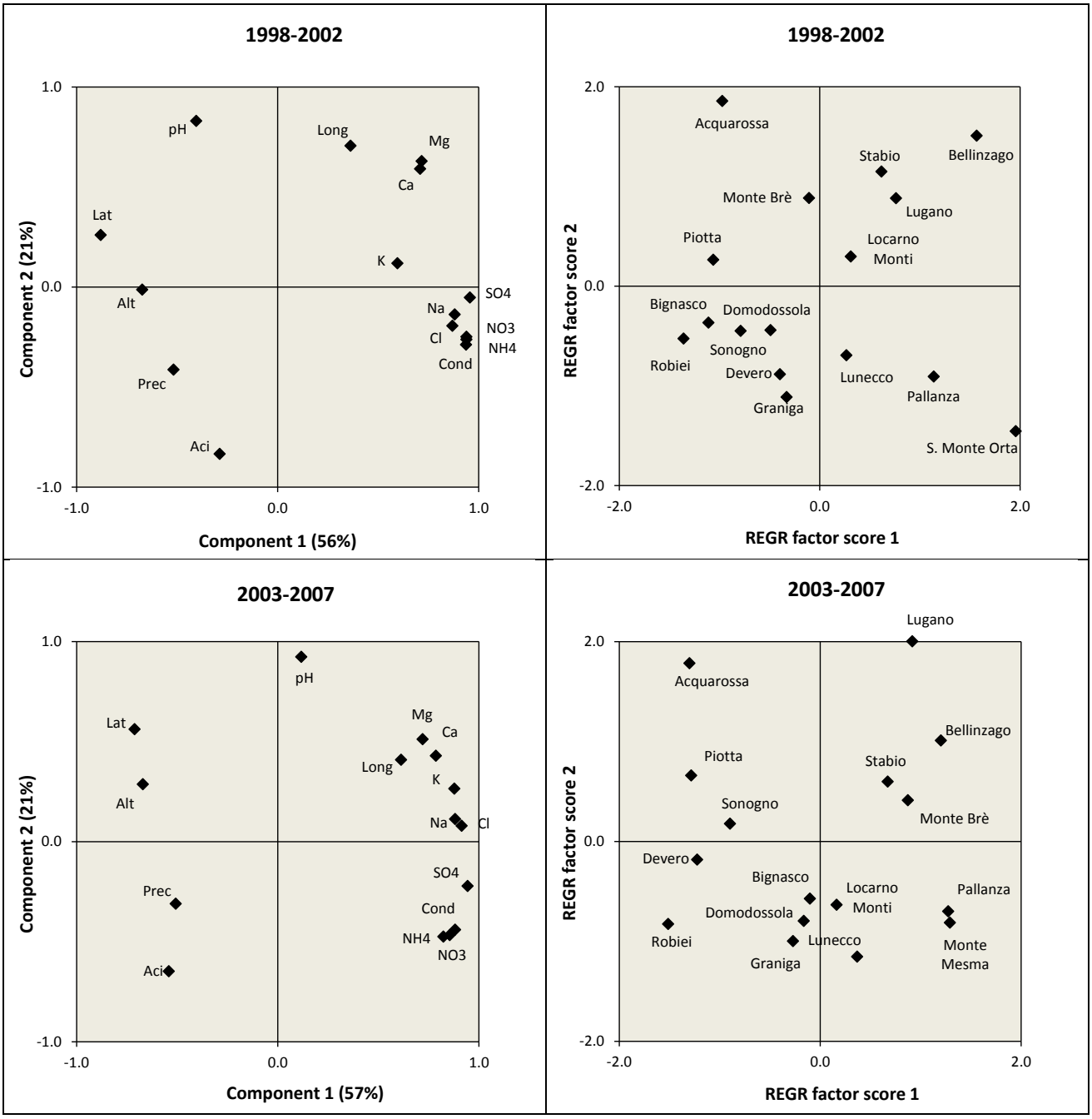
From the observations made previously it follows that increasing x-values reflect an increase of sulphate, nitrate and ammonium concentrations and a decrease of latitudes and altitudes. Conversely, increasing y-values follow an increase of longitude and of both calcium and magnesium during the first 3 time periods (1988-1992, 1993-1997, 1998-2002) and of pH afterwards.

Factor score plots that show how sampling sites are correlated to each other with respect to their variables are also shown in Fig. 2.3 (right side). In order to simplify the interpretation of the factor score plots, stations were grouped according to the information obtained from the loading plots. The graphs were divided into two parts with the simplified characteristics “acid” and “non acid” and into two further parts defined as “high anthropogenic pollutants” and “low anthropogenic pollutants”. Sampling stations could therefore be divided into 4 groups: (a) low acidity and low concentrations of sulphate, nitrate, ammonium, (b) low acidity and high concentrations of sulphate, nitrate, ammonium, (c) high acidity and low concentrations of sulphate, nitrate, ammonium, (d) high acidity and high concentrations of sulphate, nitrate, ammonium. It is important to note that these definitions are qualitative and as such enable a comparison of different sampling stations over a determined period of time, but do not allow considering concentration changes over time. These informations were used to represent sampling sites with different color on a geographic map (Fig. 2.4).

In the 1988-1992 map sampling sites were divided in two categories: “acid and polluted” and “less acid and less polluted” . The first category is situated in the southern and the second in the northern part of the monitored area. After 1993 the situation became more complicated. Nitrogen and sulphur rich sites (red points) are again concentrated in the southern part of the map, while less polluted sites (green points) are situated in the northern part. However, places with “acid rain” (plain points) are shifted toward the western part of the area and less acid sites (empty points) prevail in the eastern part. The figures therefore show what has been mentioned before. They reflect the south to north gradient of nitrogen and sulphur emissions, that also determines during the first time periods the distribution of rain acidity. From 1998-2002 the geographic distribution of acidity is better described by concentrations of base cations that is probably influenced by the amount of yearly precipitation.

Figure 2.3: PCA loading plots (left side) and factor score plots (right side)




1998-2002
1.0
0.0
-1.0
-1.0
0.0
1.0
Component 2 (21%)
Component 1 (56%)
pH
Long
Mg
Ca
Lat
K
SO4
Alt
Na
NO3
Cl
NH4
Cond
Prec
Aci
1998-2002
2.0
0.0
-2.0
-2.0
0.0
2.0
REGR factor score 2
REGR factor score 1
Acquarossa
Stabio
Bellinzago
Monte Brè
Lugano
Piotta
Locarno
Monti
Bignasco
Domodossola
Sonogno
Robiei
Devero
Lunecco
Pallanza
Graniga
S. Monte Orta
2003-2007
1.0
0.0
-1.0
-1.0
0.0
1.0
Component 2 (21%)
Component 1 (57%)
pH
Lat
Mg
Ca
Long
K
Alt
Na
Cl
SO4
Prec
Cond
NH4
NO3
Aci
2003-2007
Lugano
2.0
0.0
-2.0
-2.0
0.0
2.0
REGR factor score 2
REGR factor score 1
Acquarossa
Bellinzago
Piotta
Stabio
Sonogno
Monte Brè
Devero
Bignasco
Locarno
Pallanza
Monti
Domodossola
Robiei
Lunecco
Monte
Mesma
Graniga

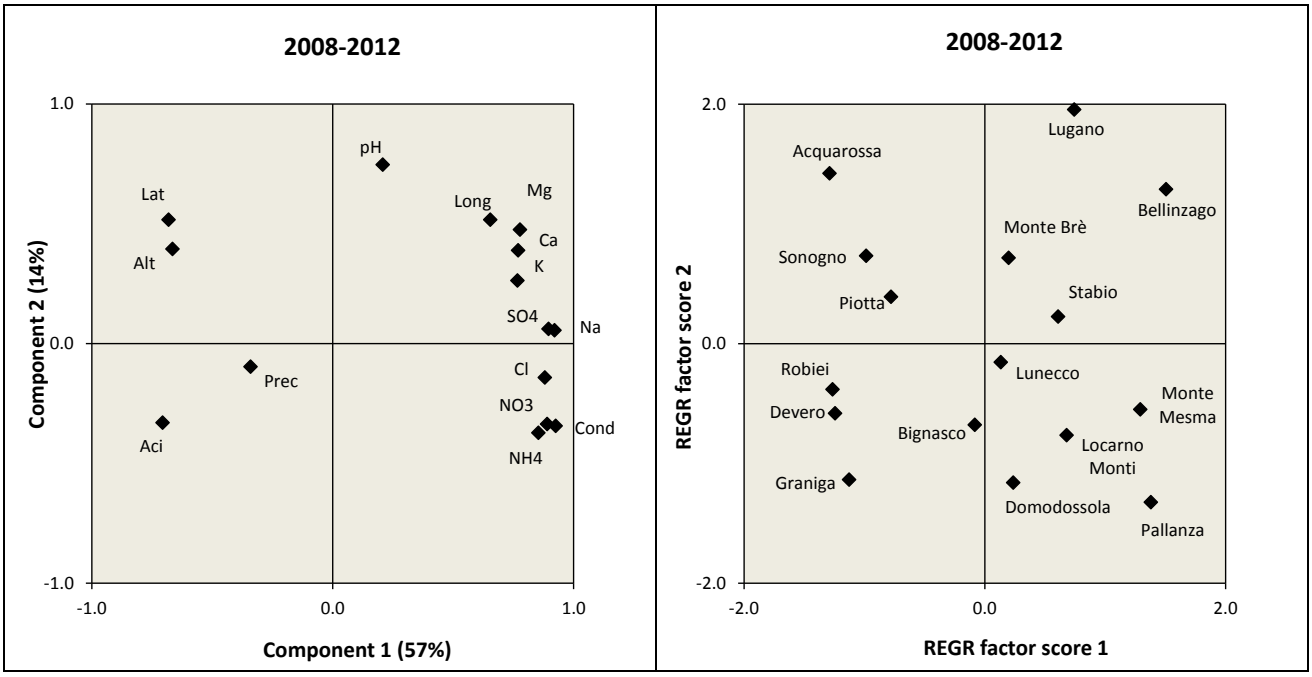
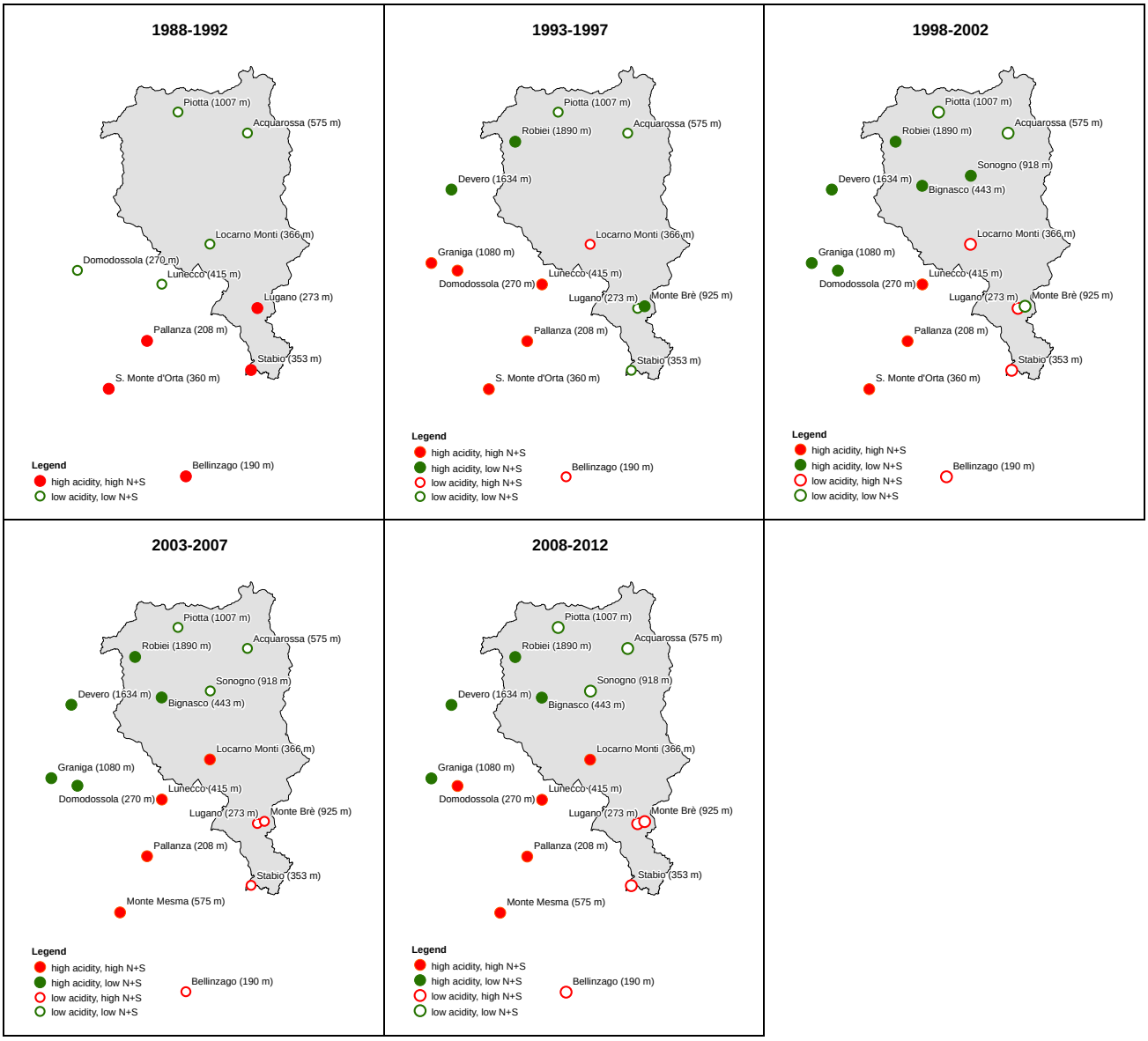

2008-2012
1.0
0.0
-1.0
-1.0
0.0
1.0
Component 2 (14%)
Component 1 (57%)
pH
Lat
Long
Mg
Ca
Alt
K
SO4
Na
Cl
Prec
NO3
Cond
Aci
NH4
2008-2012
2.0
0.0
-2.0
-2.0
0.0
2.0
REGR factor score 2
REGR factor score 1
Lugano
Acquarossa
Bellinzago
Monte Brè
Sonogno
Stabio
Piotta
Robiei
Lunecco
Monte
Mesma
Devero
Bignasco
Locarno
Monti
Graniga
Domodossola
Pallanza

Figure 2.4: Sampling sites with their PCA quadrant characteristics



2.6 Multiple regression analysis

The geographic distribution of chemical parameters in rainwater discussed in the PCA analysis suggests the possibility of developing a multiple regression model with the variables latitude, longitude and altitude. With this model the geographic distribution of the concentrations of single chemical parameters in rainwater can be described. Multiple linear regression analyses were performed for sulphate, nitrate, ammonium and base cations for the periods of 1988-1992, 1993-1997, 1998-2002 and 2003-2007, 2008-2012. Parameters for the following multiple linear regressions were derived:

$C = m_{long}$*longitude + m_{lat}*latitude + m_{alt}*altitude + C_0

where:

C = mean concentration weighted with the amount of precipitation over the studied time period
C_0 = intercept

m_{lat}, m_{long}, m_{alt} = linear regression coefficients (=slopes)

Longitude, latitude and altitude are given in m (Swiss projection CH1903 LV03).

For the first 2 periods (1988-1992 and 1993-1997) rainwater concentrations from missing sampling sites (Bignasco, Monte Brè, Robiei, Sonogno, Devero, Graniga, Basodino) were estimated by multiplying values from successive periods by a parameter's specific factor (average value of sites monitored in the present period divided by average value of sites monitored in the successive period). Average mean concentrations for the different parameters and time periods are reported in Tab. A3 of the Appendix.

The linear regression coefficients for sulphate, nitrate, ammonium, base cations and the values describing the statistic significance of the regression model are reported in Tab. A4 of the Appendix.

3. Wet deposition

3.1 Geographic interpolation

The multiple parameter regression model described in the previous chapter permitted the calculation of concentrations maps. The area under investigation was divided into 1km x 1km cells. For every cell centre a concentration of the chemical parameter for the corresponding longitude, latitude and altitude was calculated.

Wet deposition maps of sulphate, nitrate, ammonium and base cations were obtained by multiplying concentration maps with precipitation maps.

3.2 Maps

Wet deposition maps of sulphate, nitrate, ammonium and base cations are shown in Fig. 3.1-3.4 . In general the geographic distribution is similar to that described for rainwater

concentrations with sulphate, nitrate and ammonium decreasing along a south to north and an altitude gradient. Base cations show the same gradient as anthropogenic pollutants during the first time period (1988-1992) and correlate afterwards more and more also with longitude.

Wet deposition values also changed with time. Especially for sulphate a significant decrease in deposition values can be observed. A decrease in deposition of nitrate and ammonium is more difficult to observe because of the influence of precipitation volume. The slight decrease in concentrations tend still to be compensated by an increase in wet deposition amounts when precipitation volume is high. Particularly rain rich (1998-2002) and rain poor (2003-2007) years had visible consequences on deposition. As an example deposition of nitrate and ammonium were slightly higher during 1998-2002 compared to the immediately previous and successive time periods, while lowest values were reached during the dry years between 2003 and 2007. Wet deposition of base cations tends to be constant over time but can increase significantly when alkaline rain events are frequent as it happened during the wet years between 1998 and 2002.

Figure 3.1: Wet deposition of sulphate

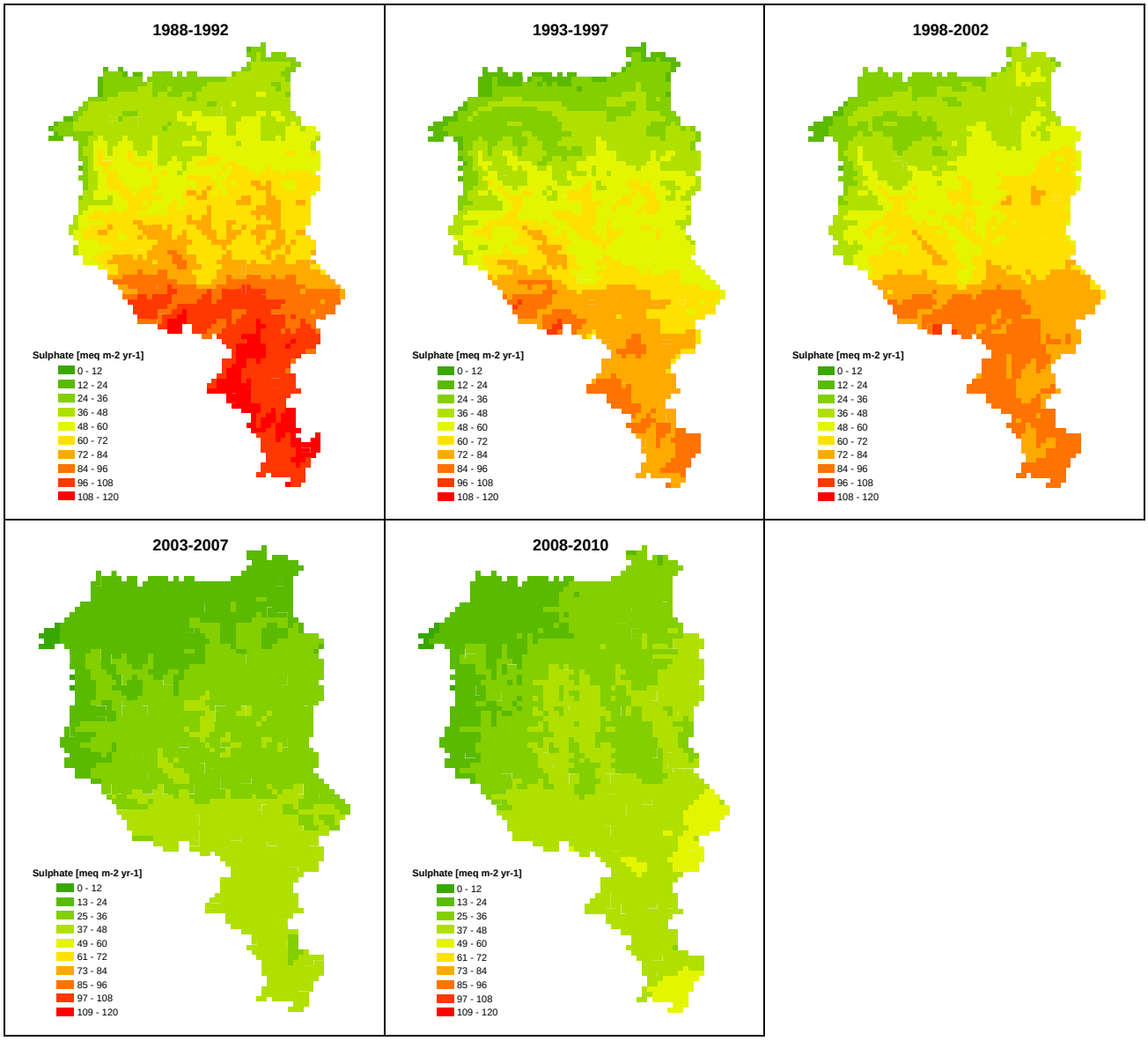


Figure 3.2: Wet deposition of nitrate

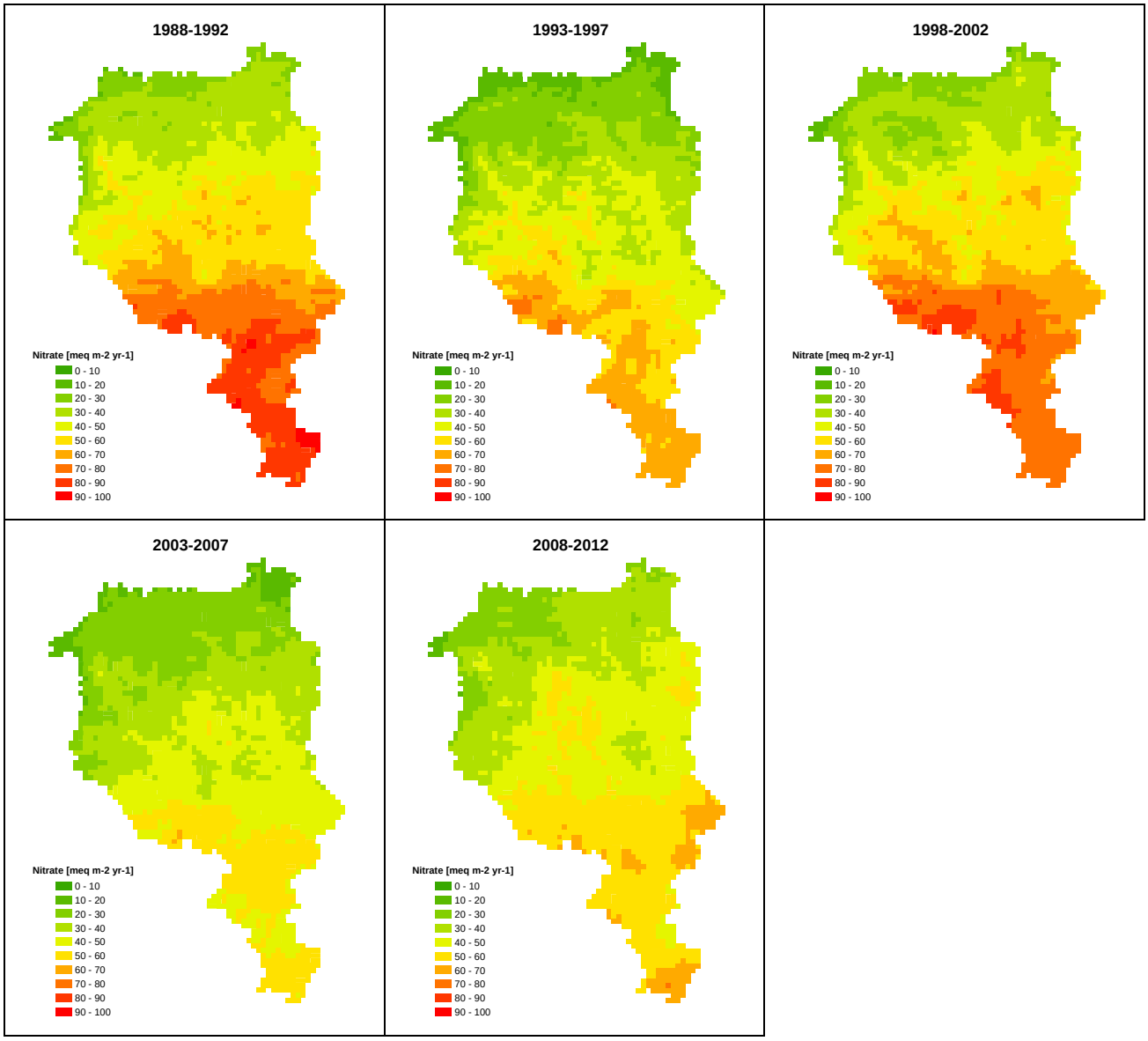


Figure 3.3: Wet deposition of ammonium

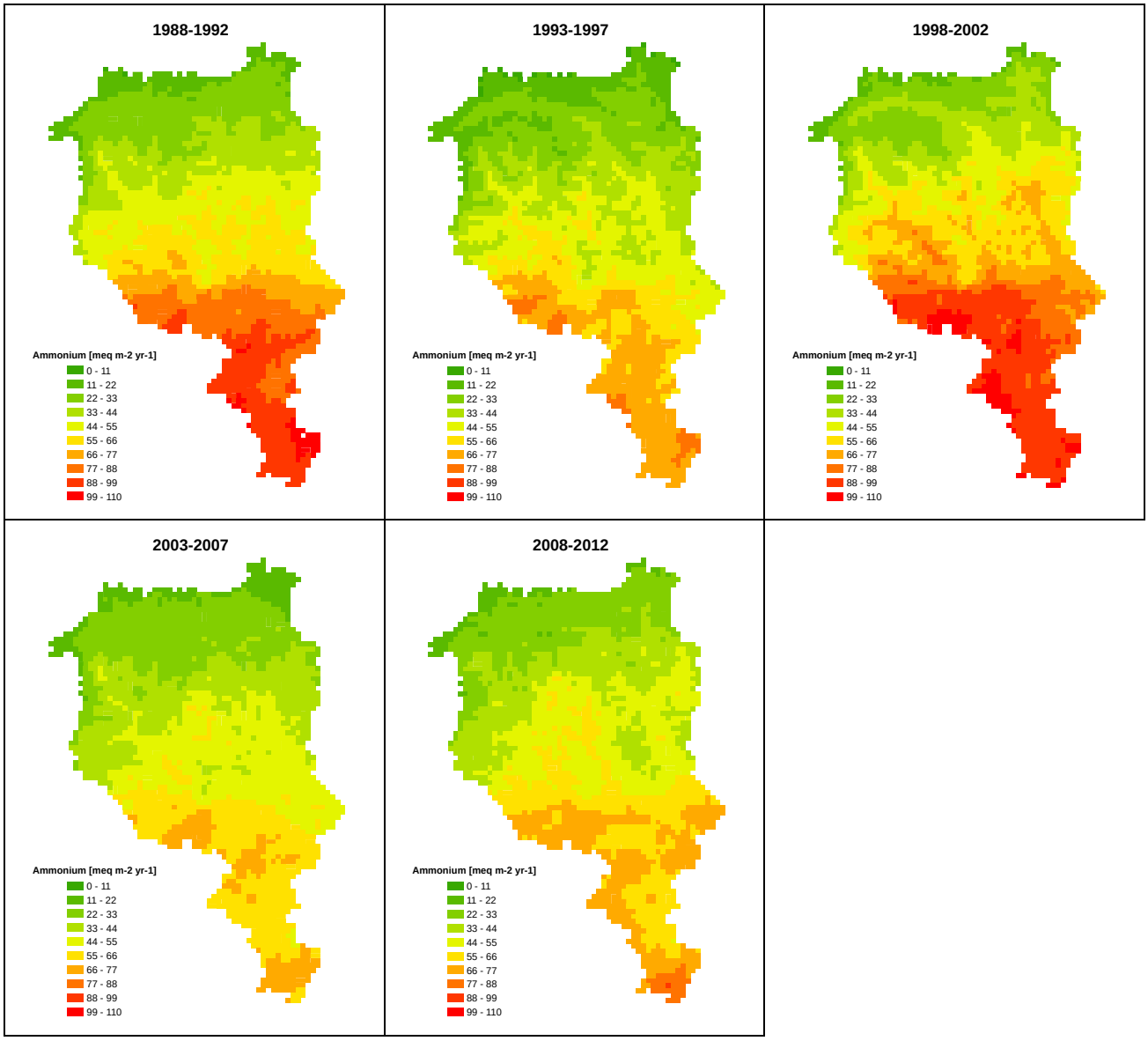
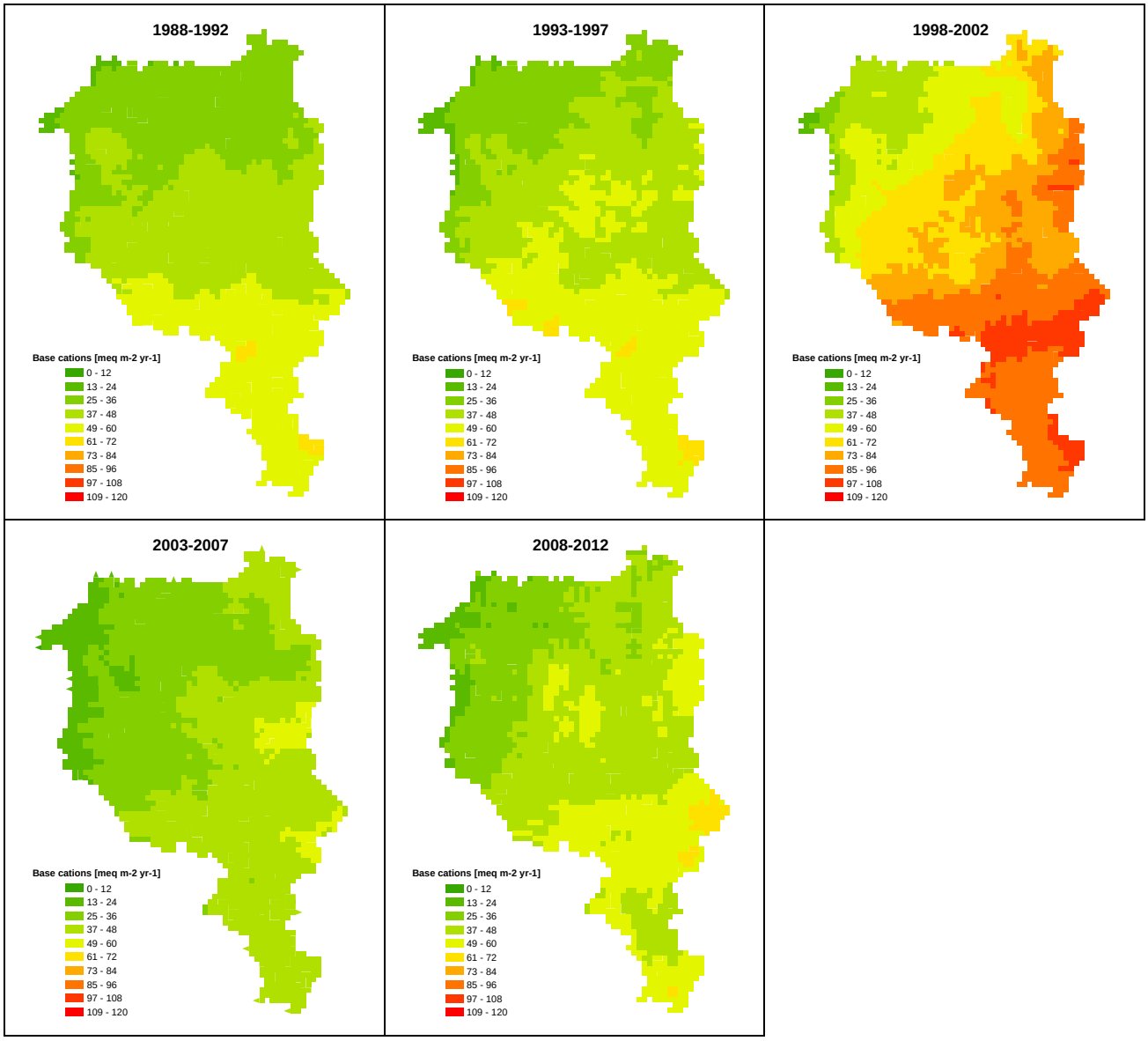


Figure 3.4: Wet deposition of base cations (Ca^{2+}+Mg^{2+}+K^{+})



4. Dry deposition

4.1 Mapping methods

Besides wet deposition, dry deposition of gases and aerosols also contribute to total deposition. For quantifying total acidifying deposition, dry deposition of the gaseous compounds NH_3, NO_2, SO_2 , HNO_3 and of the NH_4^+- and NO_3^--containing aerosols has to be known. Dry deposition of sulphate is not considered since its values are negligible compared with those due to wet deposition (Hertz and Bucher, 1990). SO_2 and NO_x are emitted from combustion of fossil fuels, HNO_3 is formed by photochemical oxidation of NO_2, while NH_3 is mainly emitted from livestock breeding and from use of mineral fertilizers.

Unlike wet deposition, dry deposition cannot be measured directly. Therefore, dry deposition maps were calculated by Meteotest using straightforward inferential deposition models as summarised by Roth et al. 2013. For the year 2000 the method is described in EKL (2005) and Thimonier et al. (2005). For 2010, the same approaches were used with updated input data FOEN (in prep.). Dry deposition of gases and aerosols was calculated by multiplying air concentrations with land-use or altitude specific deposition velocities. The concentration fields of the gaseous pollutants NH_3 and NO_2 were calculated using emission maps and statistical dispersion models (FOEN 2011; Thöni et al., 2004). For SO_2, concentrations over Switzerland were mapped by geo-statistical interpolation of data from 52 sampling stations with continuous measurements. Concentrations of the gaseous HNO_3 were derived from existing maps of air humidity, temperature, ozone concentrations and NO_2 concentrations applying an empirical relationship developed by ICP materials (ICP Materials Programme Centre, 2005). The content of particulate NO_3^- and NH_4^+ in fine dust PM10 was assumed to be constant over time. Thus concentrations of particulate NO_3^- and NH_4^+ in 1990, 2005 and 2010 were calculated by multiplying concentrations of PM10 in 1990, 2005 and 2010 with the fraction of NO_3^- and NH_4^+ in PM10 in 2000. Concentrations in 1995 correspond to the mean of the concentrations in 1990 and 2000.

Deposition velocities were taken from literature. For NH_4^+ and NO_3^- they are assumed to depend on altitude (Thimonier et al., 2005), while for the gaseous compounds NH_3 and NO_2 they depend on the land-use type (forests, agricultural land, aquatic systems, settlements, rocks). Dry deposition maps of the years 1990, 1995 and 2005 were derived from deposition of the year 2000.

In particular, dry deposition of NH_3 in 1990 was calculated by multiplying dry deposition of 2000 with emissions of 1990 and divided by emissions of 2000. Dry deposition of 1995 was obtained by averaging dry deposition of 1990 and 2000. Due to the fact that no decrease in the concentrations of gaseous NH_3 can be observed since 2000, dry deposition of 2005 was set equal to that of 2000.

Dry deposition of NO_2 in 1990, 1995 and 2005 was calculated as described above for ammonia.

Dry deposition of SO_2 in 1990, 1995 and 2005 was calculated by multiplying deposition of 2000 with average concentrations measured in Ticino in 1990, 1995 and 2005,

respectively, and by dividing it with the average concentrations monitored in Ticino in 2000.

Dry deposition of HNO_3 was assumed to be constant for all 5 studied time periods.

Since there is almost no measurement for dry depositions of non-marine base cations, values modelled by EMEP for the year 2000 were used for the calculations. Wet and dry deposition values of calcium, magnesium and potassium of the 3 main 50km x 50km grid falling in Canton Ticino (EMEP i,j: 70, 38; 71, 37; 71, 38) were used to calculate their ratio. Afterwards, wet deposition maps of base cations were divided by the average wet to dry deposition ratio (=14) to create dry deposition maps of base cations.

4.2 Maps

It can be assumed that the dry deposition map of the year in the middle of each period is representative for the whole period, e.g. 1990 for the period 1988-1992. Dry depositions of gases and aerosols of the five 5-years time periods are therefore mapped in Fig. 4.1-4.6. For all parameters and time periods a decrease of deposition with altitude can be observed. As a result from the reduction of SO_2 emissions, also dry deposition of SO_2 decreased during the last 25 years. Dry deposition of NO_2 also slightly decreased between the first two time periods. Almost no change with time occurred for dry deposition of NH_3 and HNO_3. Dry deposition of NH_4^+ and NO_3^- in aerosols seems to decrease a little after 1988-1992 due to a decrease in PM10 concentrations.

Figure 4.1: Deposition of sulphur dioxide

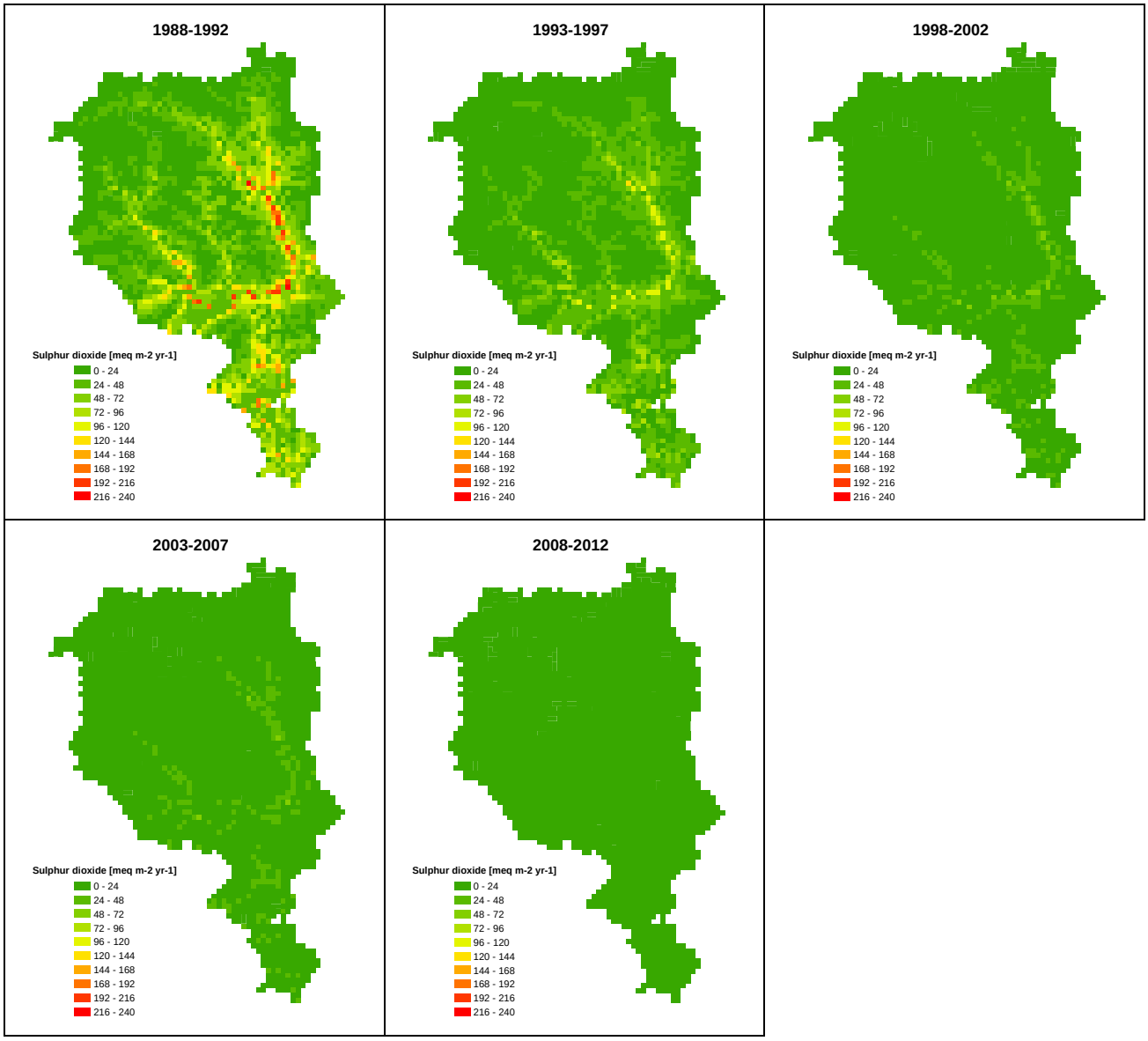


Figure 4.2: Deposition of nitrogen dioxide

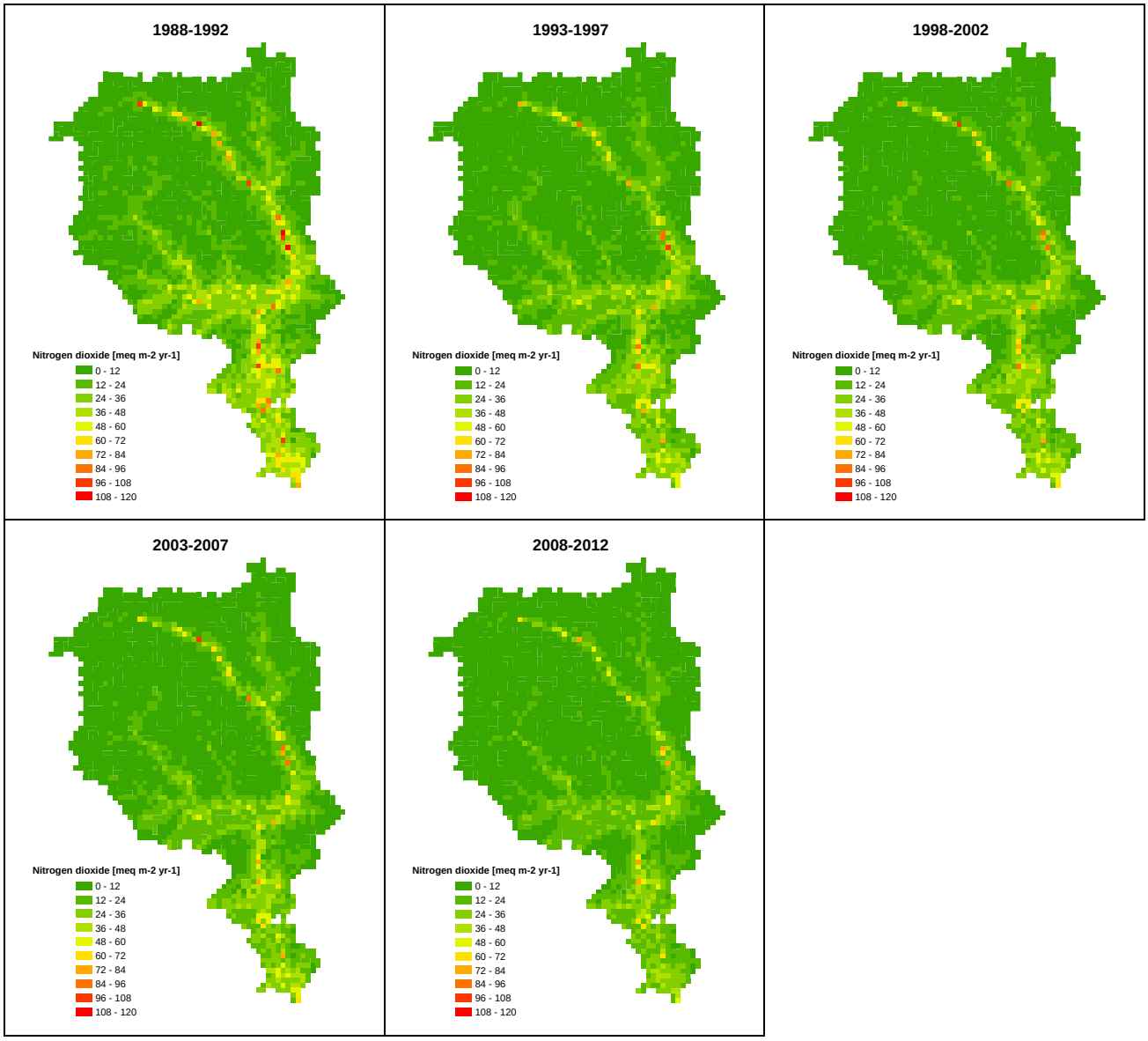


Figure 4.3: Deposition of gaseous nitric acid

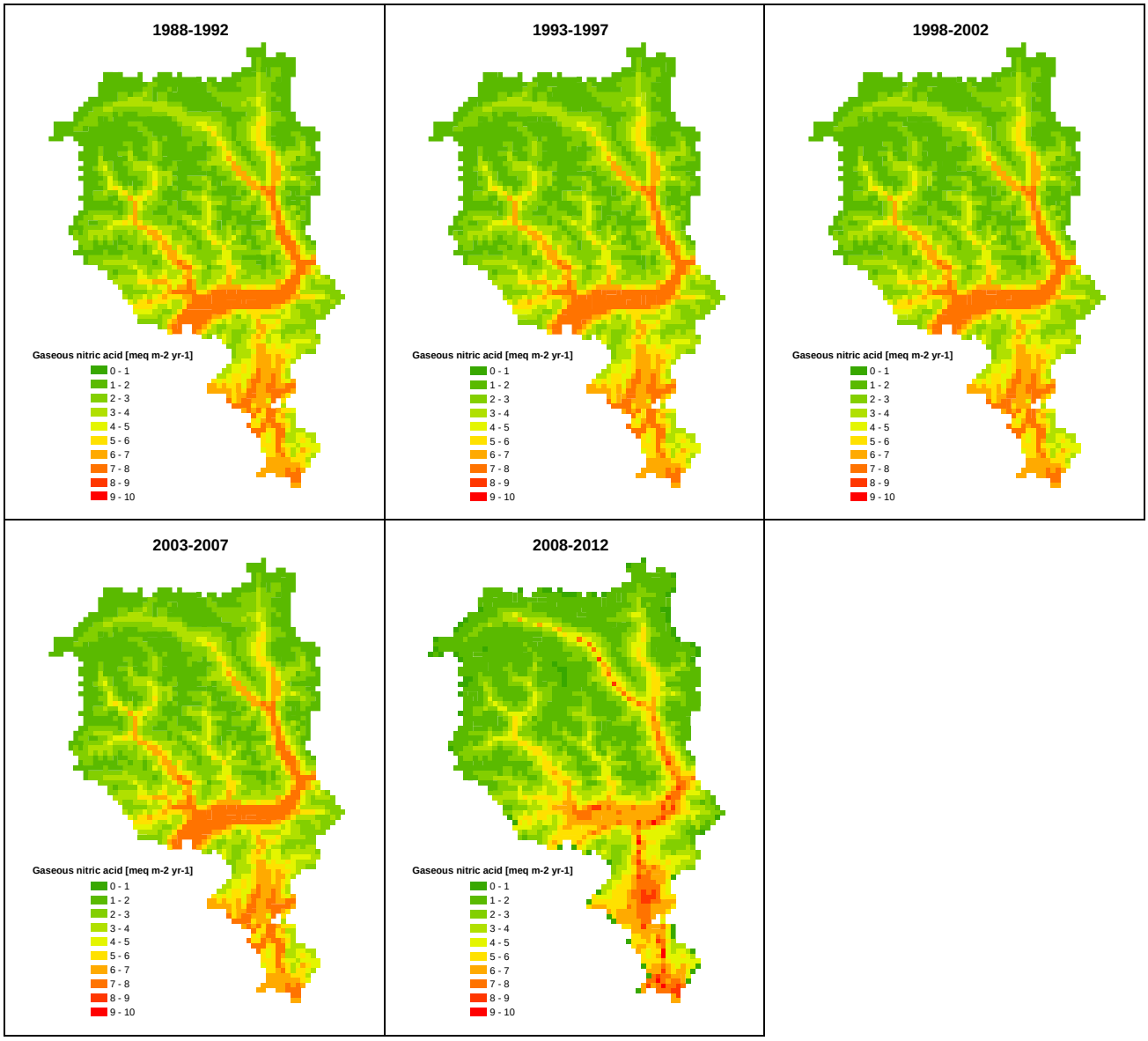


Figure 4.4: Deposition of ammonia

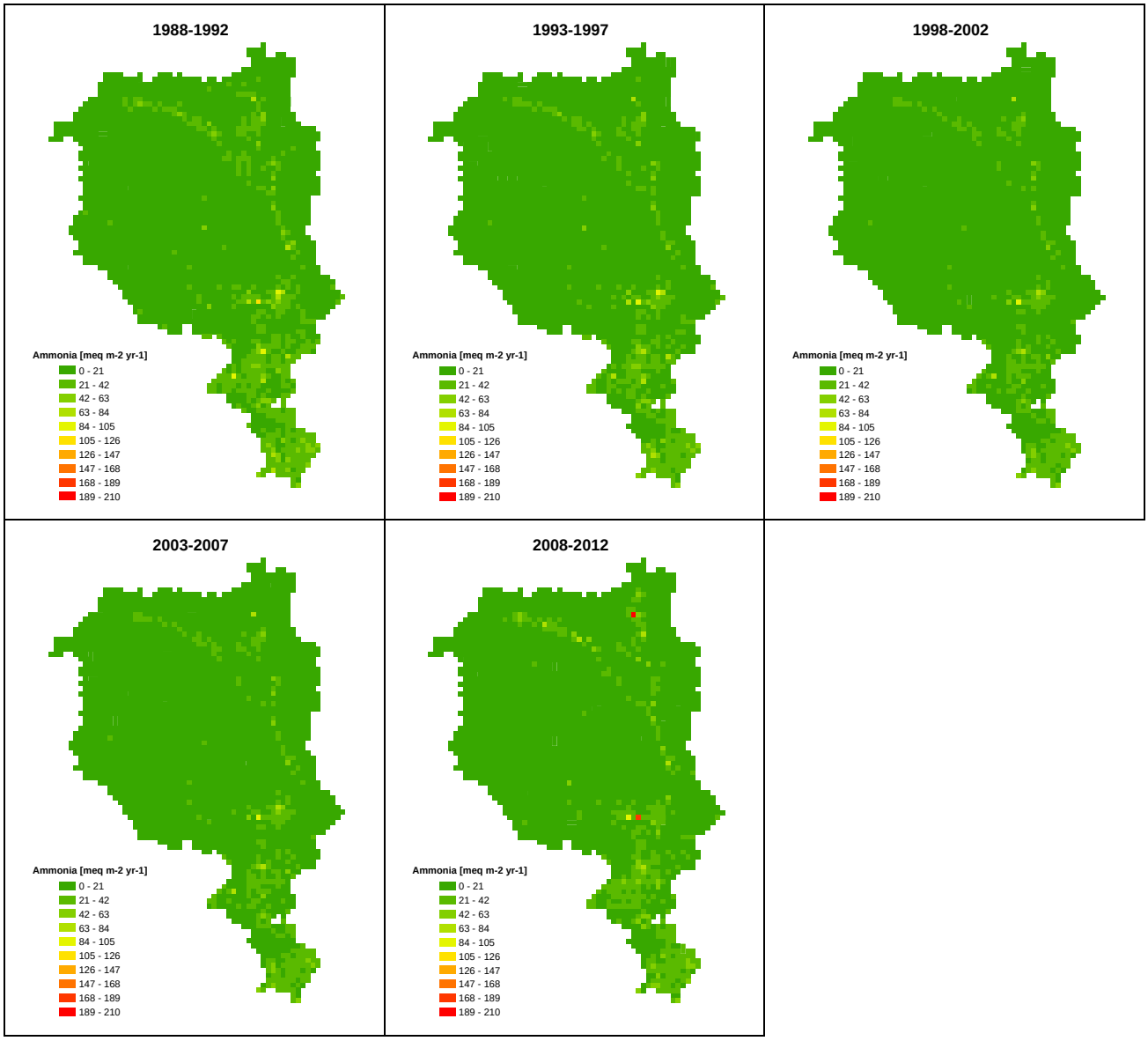


Figure 4.5: Deposition of nitrate in aerosol

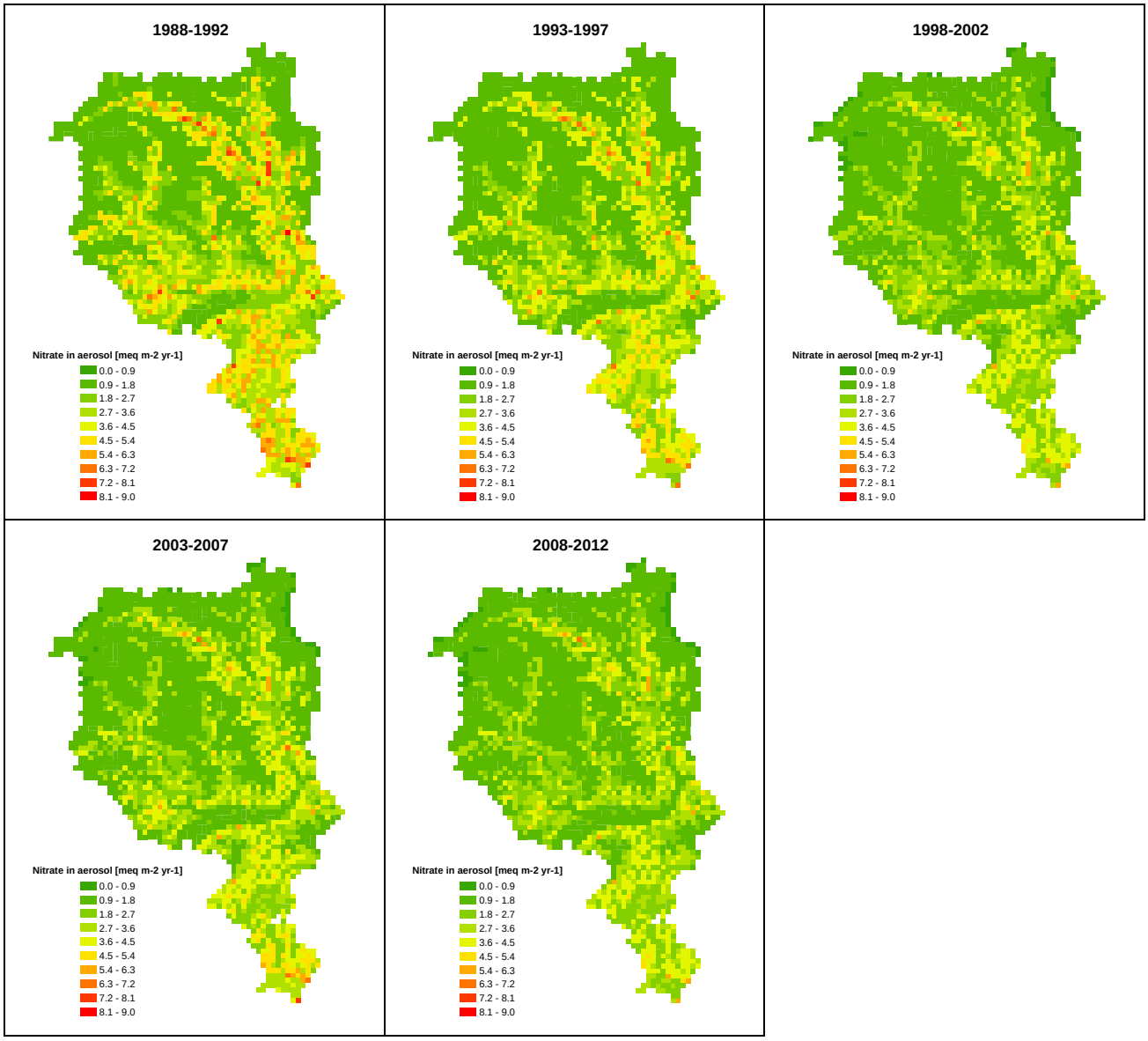
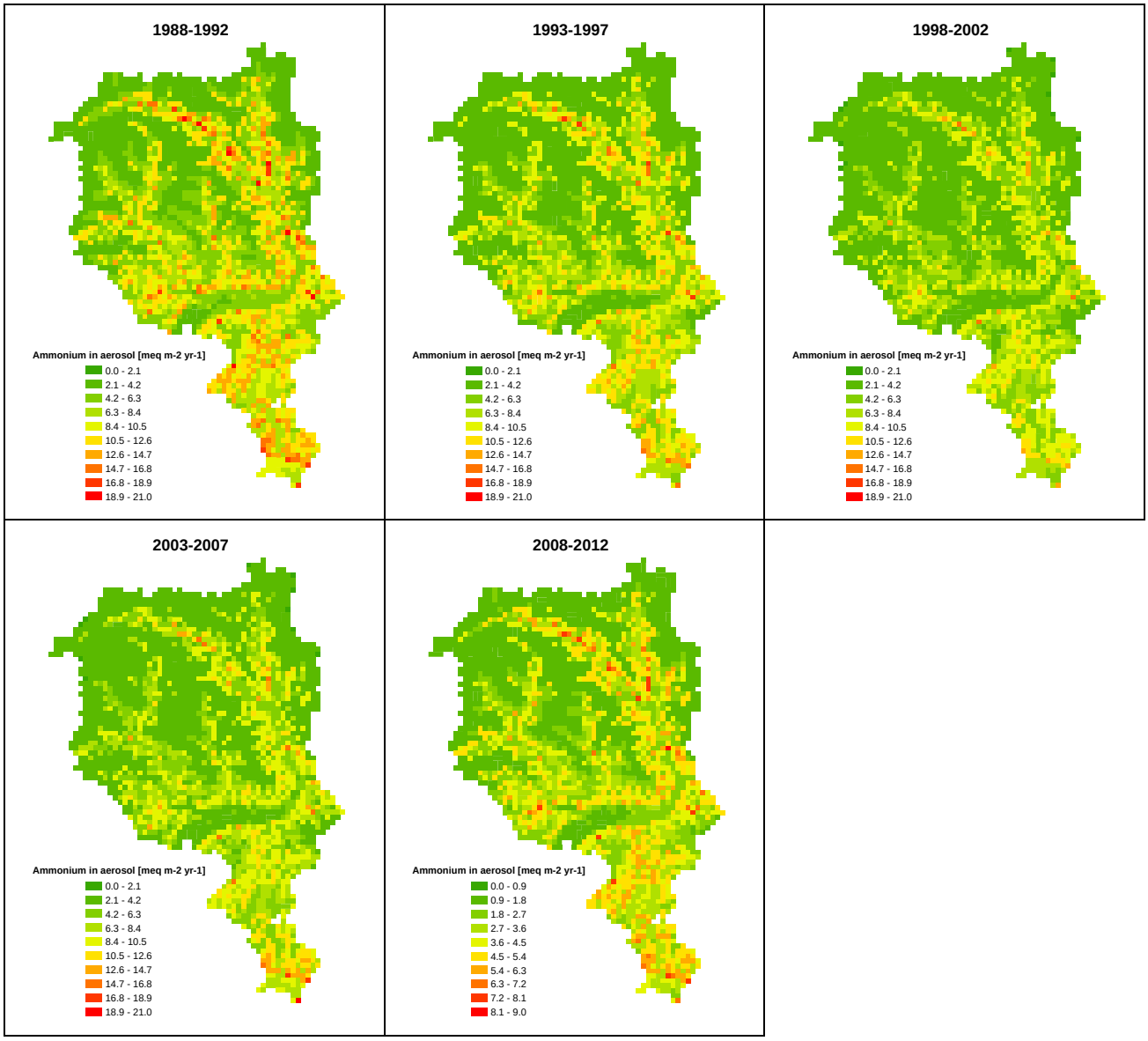


Figure 4.6: Deposition of ammonium in aerosol



5. Total deposition

5.1 Mapping methods

Fig. 5.1-5.5 illustrate the maps for total deposition of sulphur, nitrogen, oxidized nitrogen, reduced nitrogen and the present load of acidity. The latter is also known as potential acidity since ammonia is considered as a potential acid.

These maps were produced by adding up the maps of wet and dry depositions discussed in the previous chapters. Thus, the total deposition maps were calculated as follows:

Total sulphur deposition:
wet deposition (SO_4^{2-}) + dry deposition (SO_2)

Total nitrogen deposition:
wet deposition (NO_3^- + NH_4^+) + dry deposition (NH_3 + NH_4^+ + NO_2 + NO_3^- + HNO_3)

Total oxidized nitrogen deposition:
wet deposition (NO_3^-) + dry deposition (NO_2 + NO_3^- + HNO_3)

Total reduced nitrogen deposition:
wet deposition (NH_4^+) + dry deposition (NH_3 + NH_4^+)

Present load of acidity:
Total nitrogen deposition + Total sulphur deposition - wet deposition (Ca^{2+} + Mg^{2+} + K^+) - dry deposition (Ca^{2+} + Mg^{2+} + K^+)

5.2 Maps

For all total deposition maps (sulphur, nitrogen, acidity) a decreasing south to north and altitude gradient can be observed (Fig. 5.1-5.6). As observed for wet deposition of sulphate, total deposition of sulphur also decreased consistently during the monitored period of time. Average total deposition decreased from 111 to 38 meq m^{-2} yr^{-1}. Average total deposition of nitrogen decreased much less since 1988. Moreover, during particularly wet periods as it happened in the period 1998-2002, deposition of nitrogen can increase again to levels similar to those observed at the beginning of the monitoring period. In fact, average total deposition of nitrogen during the five periods were 152, 125, 148, 117 and 126 meq m^{-2} yr^{-1}. Oxidized and reduced nitrogen contributed with about 50% each to the total. As a consequence of the reduction of sulphur deposition, deposition of the rpesent load of acidity also decreased significantly. Average present load of acidity decreased from 218 to 118 meq m^{-2} yr^{-1}.

Tab. 5.1 represents the relative contribution of wet and dry sulphur and nitrogen deposition to total acidifying load. Wet deposition contributes most to total deposition of acidifying compounds (between 67% and 79%), depending on the amount of yearly precipitation. Dry deposition, especially that of aerosols, is therefore less important. The contribution of sulphur compounds to total deposition of acidifying compounds decreased from 42% in the period 1988-1993 to 23% in the period 2008-2012. This is explained by the reduction of sulphur emissions over time. Accordingly, nitrogen compounds became more important in

determining acidifying deposition. In fact, the percentage of reduced and oxidized nitrogen compounds increased from 28% to 39% and from 30% to 38%, respectively.

Figure 5.1: Total deposition of sulphur

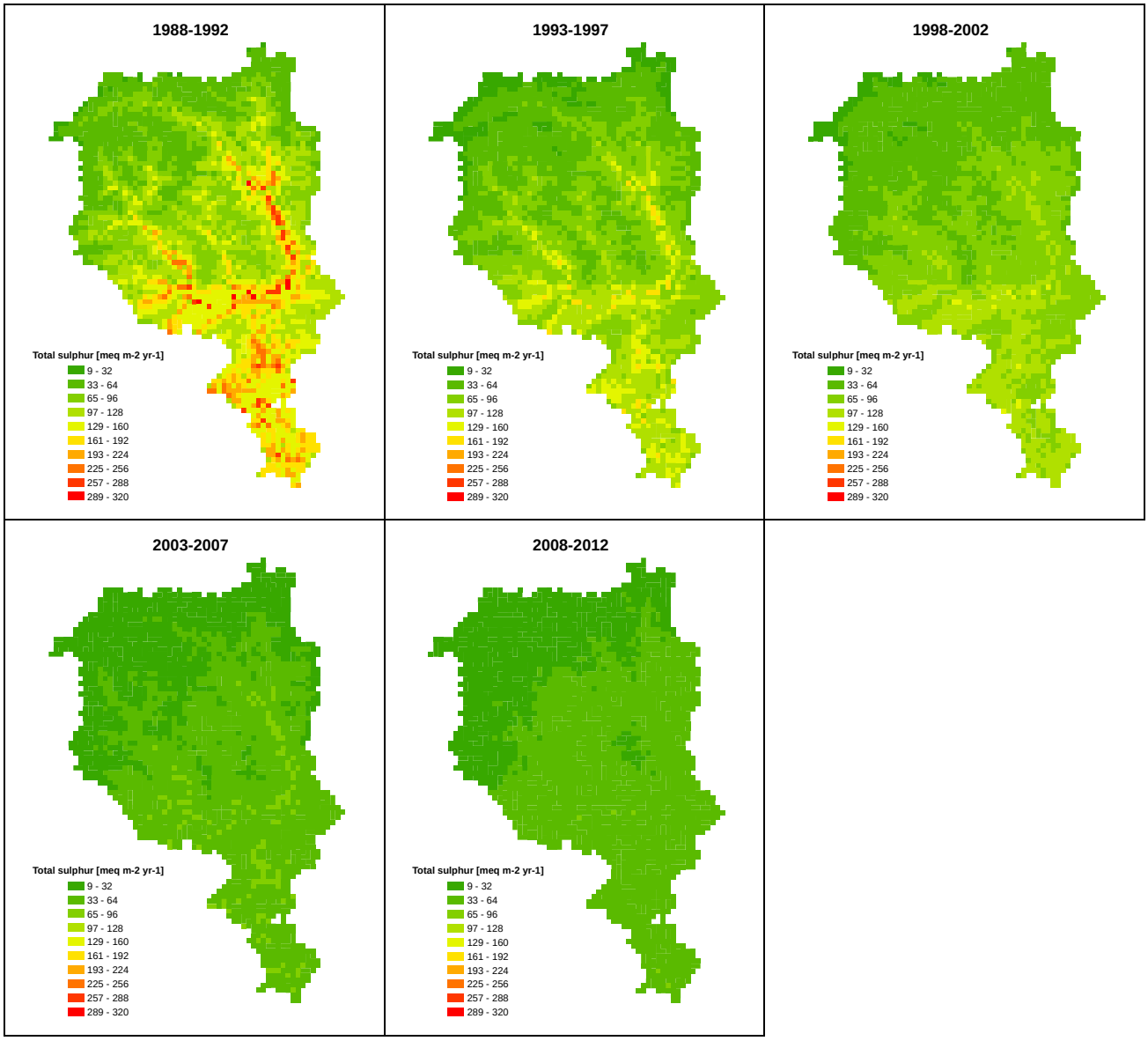


Figure 5.2: Total deposition of nitrogen

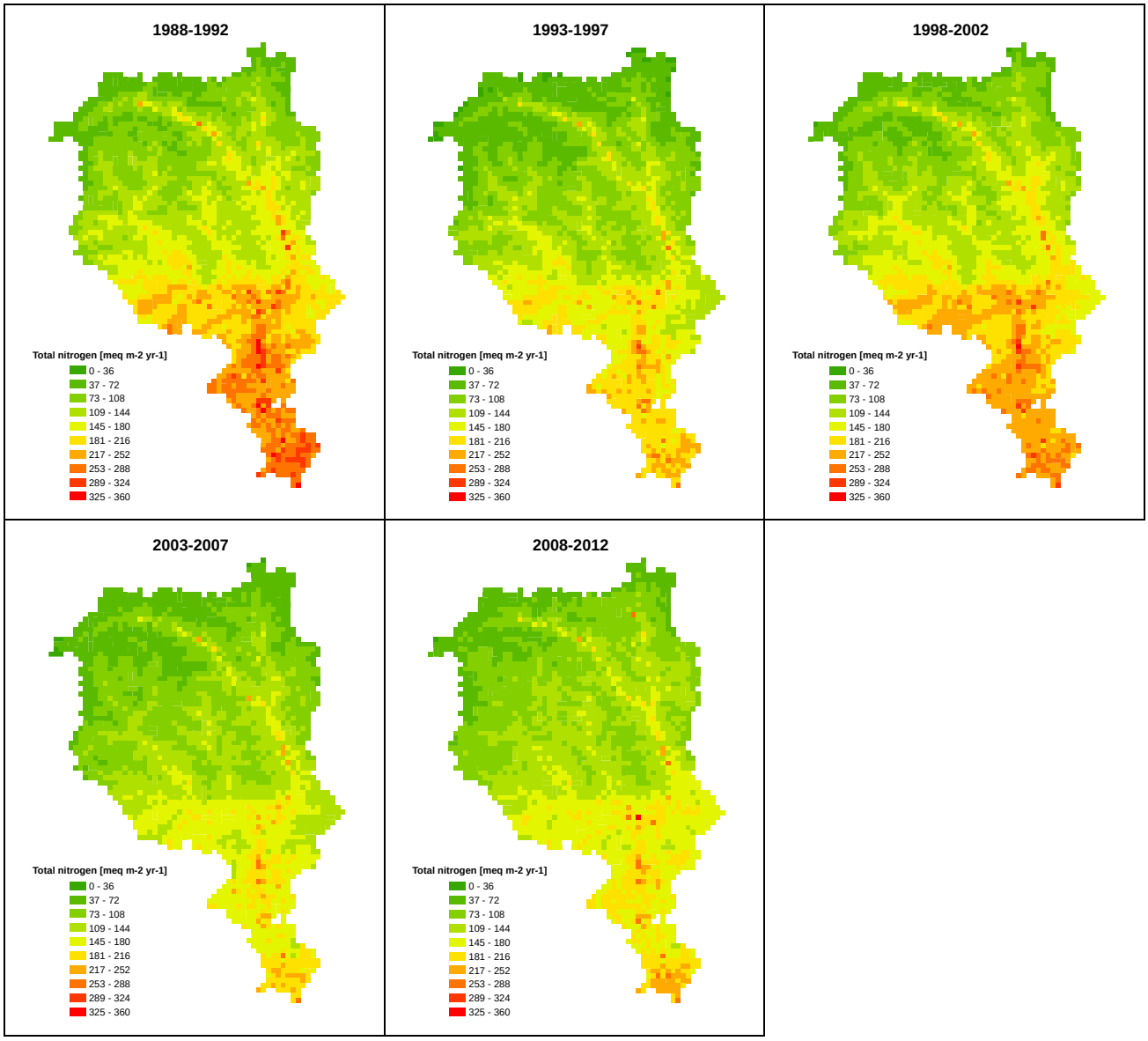


Figure 5.3: Total deposition of oxidized nitrogen

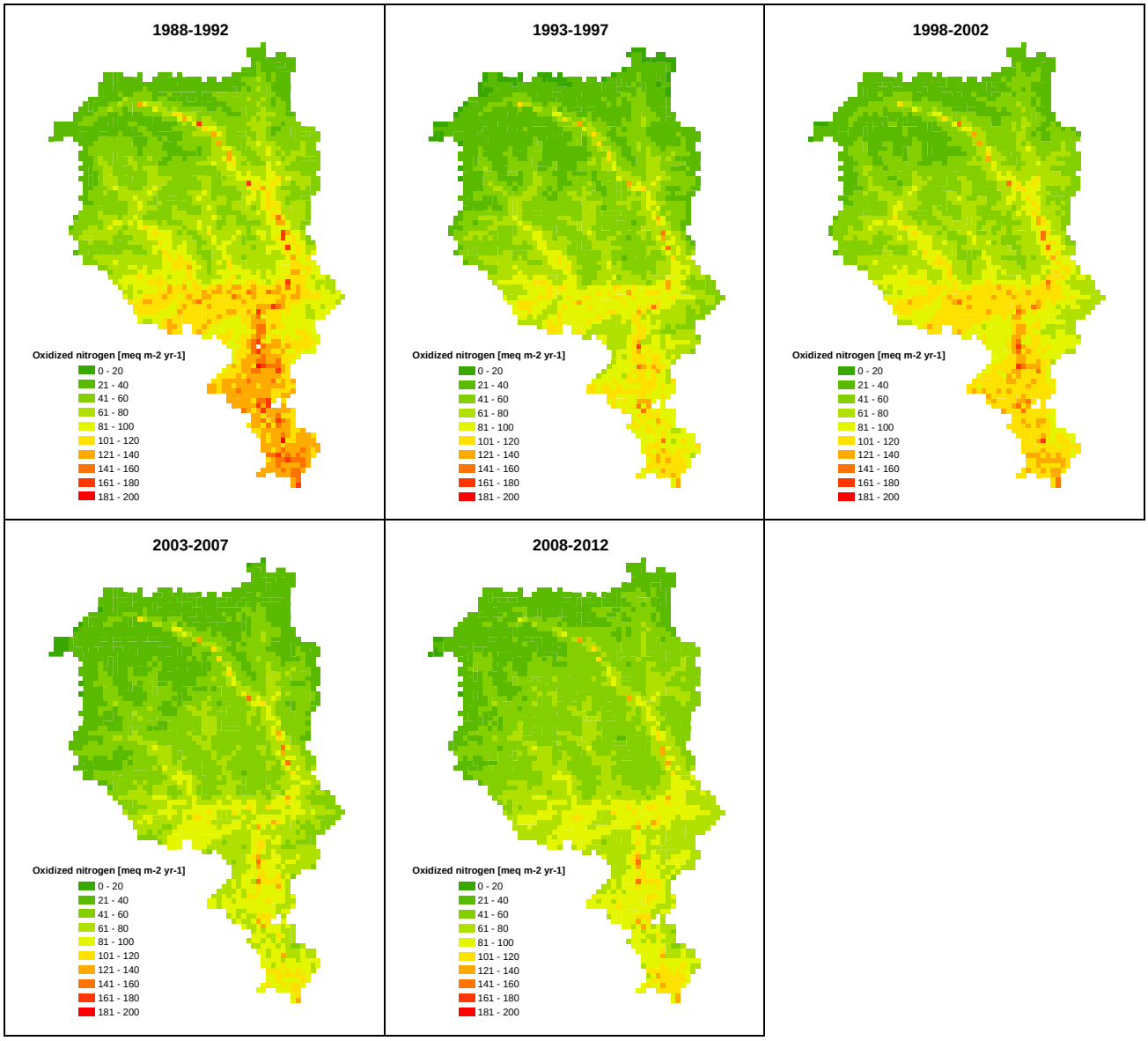


Figure 5.4: Total deposition of reduced nitrogen

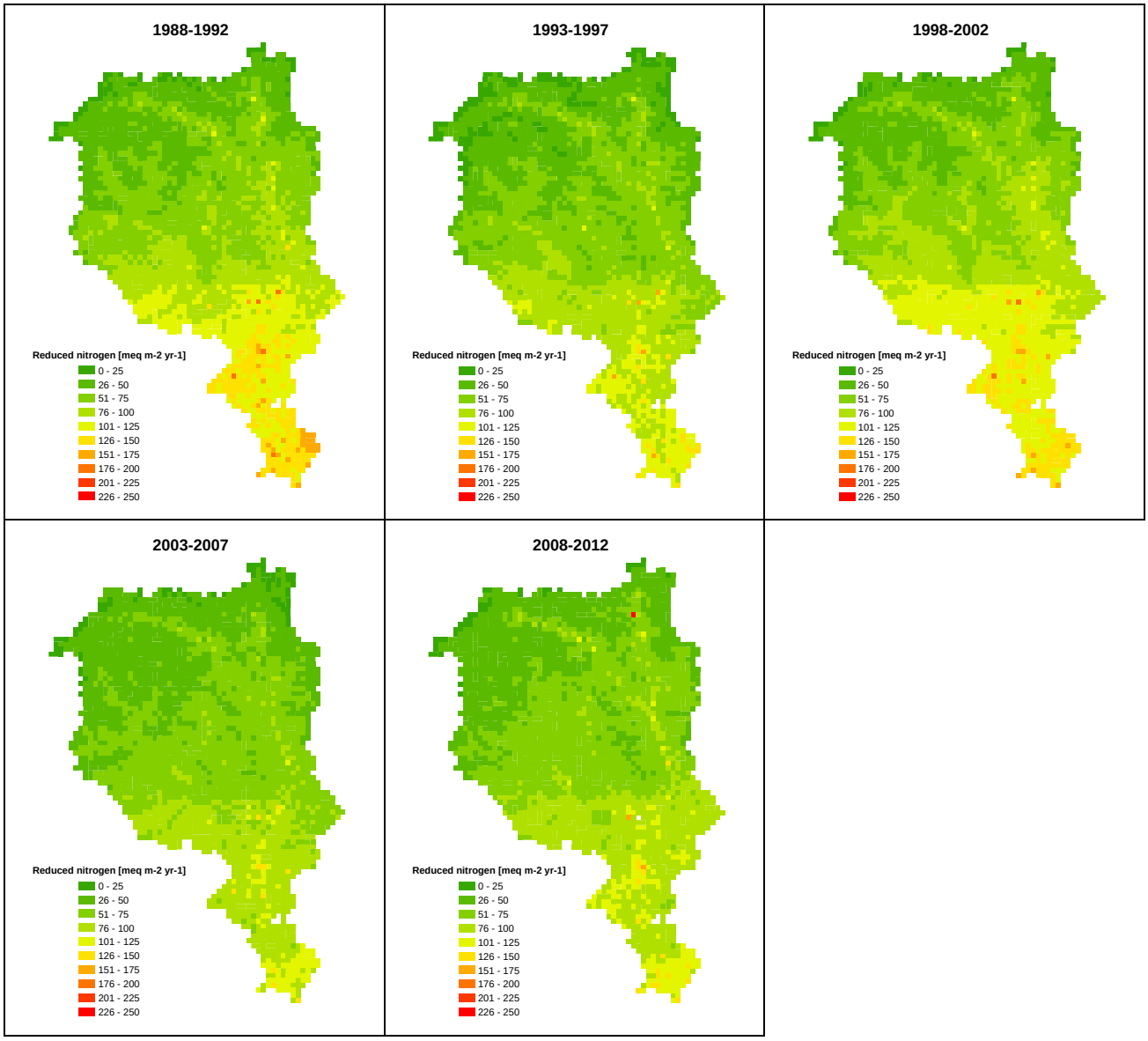


Figure 5.5: Deposition of potential acidity

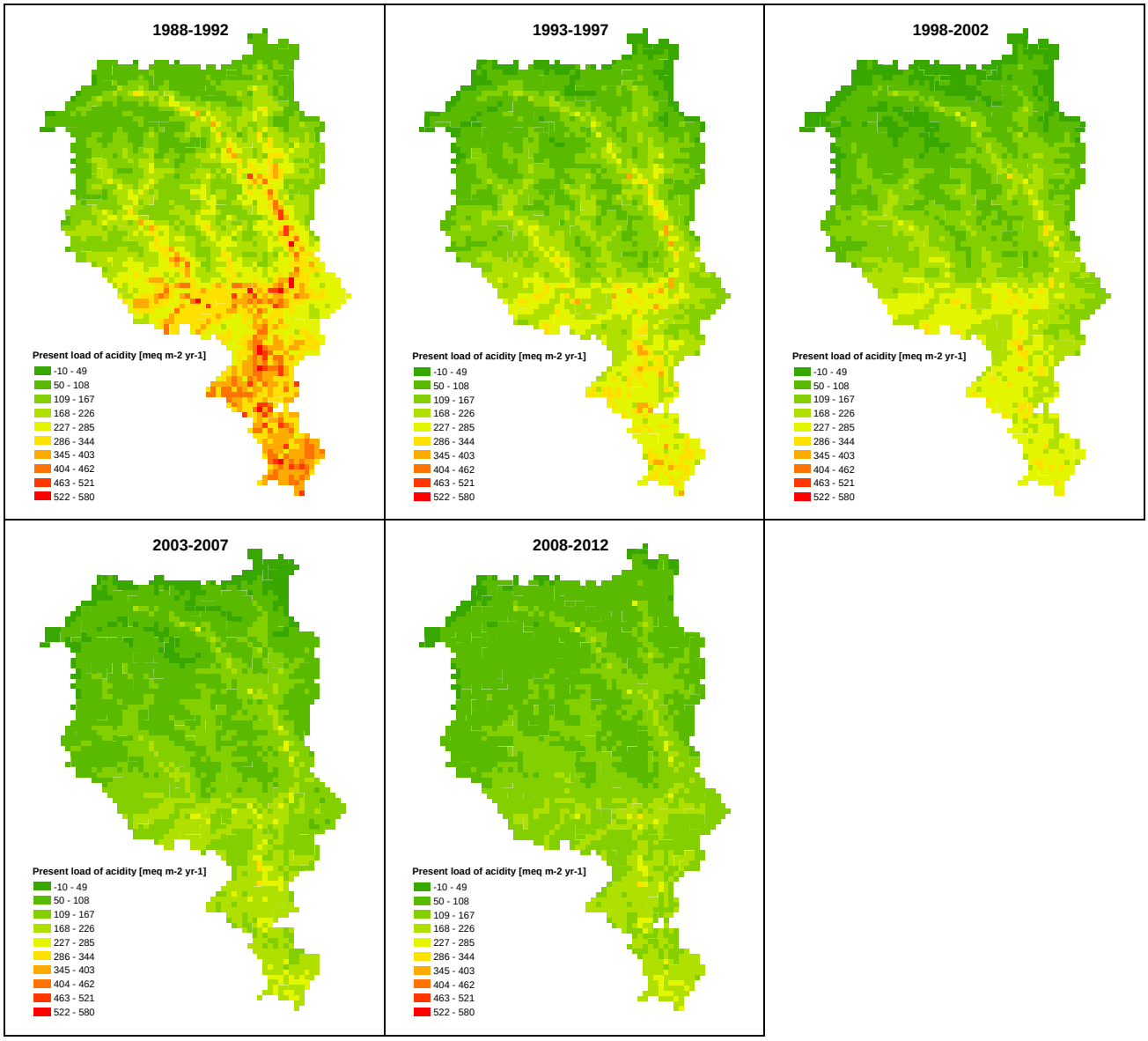


Table 5.1: Relative contribution of wet and dry nitrogen and sulphur deposition to total acidifying load

Period	Oxidized sulphur		Oxidized nitrogen		Reduced nitrogen	
	wet	dry	wet	dry	wet	dry
1988-1992	26%	15%	21%	9%	21%	8%
1993-1997	27%	11%	21%	10%	22%	9%
1998-2002	27%	5%	24%	9%	28%	7%
2003-2007	19%	6%	24%	13%	28%	10%
2008-2012	21%	2%	27%	11%	29%	10%

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Appendix

Table A1: Swiss (CH) and Italian (I) precipitation sampling sites and their Swiss coordinates (CH1903 LV03), altitudes, data source and period used for the calculation of depositions

N°	Sampling site	Longitude (m)	Latitude (m)	Altitude (m a.s.l.)	Date source	Period
1	Acquarossa/Comprovasco (CH)	714998	146440	575	MeteoSwiss	1988-2012
2	Agrasina (I)	674587	119675	1370	Idroelettriche Riunite S.p.A.	1988-2012
3	Airolo (CH)	688910	153400	1139	MeteoSwiss	1988-2012
4	Andermatt (CH)	688500	165340	1442	MeteoSwiss	1988-2012
5	Arcisate (I)	712824	78131	383	ARPA Lombardia	2008-2012
6	Arosio (CH)	713130	100610	860	UCA	1988-2012
7	Balerna (CH)	721080	79110	330	Agrometeo	2008-2012
8	Bedretto (CH)	682303	151023	1397	UCA	2008-2012
9	Bellinzona (CH)	721060	116800	225	MeteoSwiss	2008-2012
10	Biasca (CH)	717320	136000	310	Agrometeo	2008-2012
11	Biasca (CH)	717470	134870	291	MeteoSwiss	1988-2012
12	Bioggio (CH)	714170	96525	285	OASI	2008-2012
13	Bosco Gurin (CH)	681160	130025	1505	MeteoSwiss	1988-2012
14	Braggio (CH)	729975	128600	1315	MeteoSwiss	1988-2012
15	Brissago (CH)	698200	108390	280	MeteoSwiss	1988-2012
16	Bruzella (CH)	724090	82490	620	MeteoSwiss	1988-2007
17	Cadarese (I)	670854	127200	725	ISE-CNR	1988-1992
18	Cadero Veddasca (I)	703188	101753	570		1988-1997
19	Camedo (CH)	690296	112207	590	MeteoSwiss	1988-2012
20	Camedo diga (CH)	690940	112220	520	UCA	1988-2007
21	Camedo paese (CH)	690050	112110	570	UCA	2008-2012
22	Camignolo (CH)	715430	106905	435	OASI	2008-2012
23	Campo Vallemaggia (CH)	681711	126785	1303	UCA	2003-2012
24	Cannobio (I)	696999	102584	201	ARPA Piemonte	1988-1997
25	Carena (CH)	727230	114230	942	UCA	2008-2012
26	Cavargna (I)	729353	105751	1100	ARPA Lombardia	2008-2012
27	Cavergno (CH)	690081	133073	455	UCA	2008-2012
28	Cevio (CH)	689688	130565	417	MeteoSwiss	1988-2012
29	Chiasso (CH)	722690	77090	240	UCA	1988-2012
30	Cimetta (CH)	704433	117452	1661	MeteoSwiss	1988-2012
31	Cipata (I)	672770	117664	937	Idroelettriche Riunite S.p.A.	1988-1992
32	Coldrerio (CH)	720725	79400	345	MeteoSwiss	1988-2012
33	Colla (CH)	725030	106400	1140	UCA	2008-2012
34	Copera (CH)	720318	112564	665	WSL	1988-1992
35	Crana-Torricella (CH)	712660	103750	1002	MeteoSwiss	1988-2012
36	Creva (I)	702821	94488	233		1988-1997
37	Cugnasco (CH)	714100	114470	212	Agrometeo	2008-2012
38	Cursolo O. (I)	687359	106129	940	ARPA Piemonte	1993-2007
39	Disentis/Sedrun (CH)	708189	173789	1197	MeteoSwiss	1988-2012
40	Druogno (I)	676379	109921	831	ARPA Piemonte	1988-2007
41	Faido (CH)	704060	148750	760	MeteoSwiss	1988-2012
42	Falmenta (I)	689153	103324	662	ISE-CNR	1988-1992
43	Frasco (CH)	705180	132790	890	UCA	1988-2007
44	Fusio (CH)	694090	144380	1300	UCA	1988-1992
45	Germignaga (I)	700623	93901	203	ISE-CNR	1988-2007
46	Giubiasco (CH)	719712	114774	215	UCA	1988-2012

N°	Sampling site	Longitude (m)	Latitude (m)	Altitude (m a.s.l.)	Date source	Period
47	Gnosca (CH)	721880	122072	247	UCA	1988-2012
45	Germignaga (I)	700623	93901	203	ISE-CNR	1988-2007
46	Giubiasco (CH)	719712	114774	215	UCA	1988-2012
47	Gnosca (CH)	721880	122072	247	UCA	1988-2012
48	Göschenen (CH)	687775	169085	1099	MeteoSwiss	1988-2012
49	Göscheneralp (CH)	681250	166790	1745	MeteoSwiss	1988-2012
50	Grancia (CH) (CH)	715328	92408	310	UCA	2008-2012
51	Grimsel Hospiz (CH)	668583	158215	1980	MeteoSwiss	1988-2012
52	Grono (CH)	733015	124080	324	MeteoSwiss	1988-2012
53	Gudo (CH)	716820	115230	310	Agrometeo	2008-2012
54	Gütsch ob Andermatt (CH)	690140	167590	2287	MeteoSwiss	1988-2012
55	Hinterrhein (CH)	733900	153980	1611	MeteoSwiss	1988-2012
56	In la Piana (I)	675991	101220	960	ISE-CNR	1993-1997
57	Isone (CH)	720176	110336	792	UCA	1988-2012
58	Lago Delio (I)	701638	103711	835		1988-1992
59	Lago Larecchio (I)	676705	117781	1860	Idroelettriche Riunite S.p.A.	1988-1992, 1998-2007
60	Lago Morasco (I)	673976	142207	1820	ENEL	1988-2012
61	Lago Sabbione (I)	670084	141680	2462	ENEL	1988-2012
62	Lago Toggia (I)	675395	143193	2160	ENEL	1988-2012
63	Lago Truzzo (I)	744807	136010	2064	ARPA Lombardia	2008-2012
64	Lago Vannino (I)	669705	136641	2153	ENEL	1988-2007
65	Lavena Ponte Tresa (I)	710314	91714	274	ARPA Lombardia	1988-2012
66	Lodrino (CH)	719843	128306	258	UCA	1988-2012
67	Loggio Valsolda (I)	725804	98721	380		1988-1992
68	Lugano (CH)	717874	95884	273	MeteoSwiss	1988-2012
69	Luino (I)	701193	94821	205	ARPA Lombardia	2008-2012
70	Lunecco (I)	690425	103234	415	Comunità Montana Valle Cannobina	1988-2007
71	Lunecco (deposizioni) (I)	690264	102774	415	ISE-CNR	1988-2007
72	Luzzone diga (CH)	716665	158232	1612	UCA	1998-2012
73	Magadino/Aeroporto (CH)	711170	113542	197	MeteoSwiss	1988-2007
74	Magadino/Cadenazzo (CH)	715475	113162	203	MeteoSwiss	2008-2012
75	Maggia (CH)	697620	122190	316	UCA	1988-2012
76	Maglietto (I)	673351	109253	657	Idroelettriche Riunite S.p.A.	1988-1992
77	Malesco (I)	683345	109433	700		1988-1992
78	Malvaglia (CH)	718340	141150	375	Agrometeo	2008-2012
79	Mendrisio (CH)	719211	82996	290	UCA	1988-2012
80	Mesocco (CH)	737850	139825	830	MeteoSwiss	1988-2012
81	Moleno (CH)	719940	126559	255	OASI	2008-2012
82	Monte Generoso (CH)	722503	87456	1600	MeteoSwiss	2003-2012
83	Morbio Superiore (CH)	722750	80075	440	MeteoSwiss	1988-2012
84	Mosogno (CH)	692800	117040	760	MeteoSwiss	1988-2012
85	Mottac (I)	674798	101814	1695	ARPA Piemonte	1998-2007
86	Novaggio (CH)	709980	96160	620	UCA	2008-2012
87	Oberwald (CH)	669650	154050	1375	MeteoSwiss	1988-2002
88	Olivone (CH)	715450	153870	906	MeteoSwiss	1988-2012
89	Olivone (CH)	715410	154120	909	UCA	1988-2012
90	Orselina (CH)	704160	114350	367	MeteoSwiss	1988-2012
91	Piano dei Camosci (I)	670991	143013	2450	ARPA Piemonte	1998-2012
92	Piotta (CH)	695888	152261	990	MeteoSwiss	1988-2012
93	Ponte Formazza (I)	676012	136332	1300	ENEL	1988-2012
94	Ponte Tresa (CH)	710110	91630	274	MeteoSwiss	2008-2012
95	Robiei (CH)	682588	144091	1895	MeteoSwiss	1988-2012
96	Sambuco diga (CH)	693720	145550	1471	UCA	1998-2007
97	S. Bernardino (CH)	734112	147296	1639	MeteoSwiss	1988-2012
98	S. Maria del Monte (I)	705240	79963	881	Centro Geofisico Prealpino	1988-1992

N°	Sampling site	Longitude (m)	Latitude (m)	Altitude (m a.s.l.)	Date source	Period
99	Scudellate (CH)	724175	86850	925	MeteoSwiss	1988-2012
100	Sedrun (CH)	702480	170825	1400	MeteoSwiss	1988-2012
101	Somazzo (CH)	720490	81758	527	UCA	1998-2012
102	Sonogno (CH)	703640	134050	925	MeteoSwiss	1988-2012
103	Splügen-Dorf (CH)	744420	157435	1460	MeteoSwiss	1988-2012
104	Stabio (CH)	716034	77964	353	MeteoSwiss	1988-2012
105	Trevano (CH)	717900	98520	342	UCA	2008-2012
106	Ulrichen (CH)	666740	150760	1346	MeteoSwiss	1988-2007
107	Vals (CH)	733340	163820	1278	MeteoSwiss	1988-2012
108	Varese (I)	709409	77093	410	Centro Geofisico Prealpino	1988-1997, 2003-2007
109	Vira Gambarogno (CH)	709400	111680	199	MeteoSwiss	1988-2012
110	Vrin (CH)	727220	168670	1458	MeteoSwiss	1988-2012
111	Zervreila (CH)	728780	160000	1738	MeteoSwiss	1988-2012

Table A2: Mean annual concentrations in wet deposition sampling sites. Prec and Cond correspond to precipitation and conductivity, respectively.

Year	Prec	Analysed Prec	Cond 20°C	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	NO_3^{-}	SO_4^{2+}	Cl^{-}	Acidity
	mm	%	µS cm^{-1}		meq m^{-3}								
Acquarossa													
1990	1056	44	25	4.4	16	6	19	5	36	41	52	30	41
1991	1201	42	15	4.7	7	4	15	2	29	29	33	8	19
1993	1746	79	15	4.8	32	6	8	2	30	29	39	12	8
1994	1432	91	14	5.0	31	12	7	1	33	29	42	8	-2
1995	1044	56	13	4.8	19	8	4	3	28	30	35	4	13
1996	1282	72	13	4.9	26	6	6	1	31	28	30	8	-3
1997	1083	77	10	5.0	11	3	4	1	22	23	24	5	10
1998	1227	80	13	4.9	17	5	6	1	34	30	31	5	9
1999	1688	72	12	5.2	32	9	5	2	35	29	37	5	-5
2000	1684	85	14	5.4	62	12	8	2	23	25	40	7	-31
2001	1344	88	12	5.1	23	9	5	1	37	33	38	4	3
2002	1792	87	12	5.2	42	7	10	7	23	20	34	4	-28
2003	923	77	12	5.5	34	8	6	2	36	31	32	5	-14
2004	1241	64	9	5.5	23	6	7	3	34	24	22	5	-12
2005	661	74	16	5.8	48	14	6	4	58	45	40	5	-28
2006	1018	31	7	5.3	17	6	4	1	12	18	15	4	4
2007	954	85	11	5.4	24	7	6	2	38	30	33	4	-7
2008	1696	55	7	5.3	17	5	4	1	18	22	17	4	2
2009	1355	91	7	5.6	18	6	3	1	23	22	18	4	-5
2010	1388	89	8	5.5	23	7	3	1	28	22	19	3	-12
2011	1048	88	8	5.6	19	5	5	2	29	23	19	5	-11
2012	1507	97	10	5.5	20	3	8	2	35	27	19	7	-20
2013	1393	76	10	5.4	23	4	5	2	38	27	19	5	-19
Bignasco													
2001	2099	4	8	5.3	13	3	4	2	24	20	17	4	-1
2002	2564	69	10	5.0	13	3	8	4	21	22	25	6	7
2003	1087	92	12	5.1	21	3	6	3	39	32	30	5	-3
2004	1663	14	12	4.8	18	2	5	3	24	36	21	5	12
2005	1030	77	13	5.1	20	3	5	2	47	37	27	4	0
2006	1308	52	14	5.0	19	4	10	2	38	39	25	6	6
2007	1148	101	11	5.1	16	4	7	3	28	29	26	6	5
2008	1983	101	9	5.1	20	3	7	2	23	24	18	8	-1
2009	1945	89	8	5.2	11	2	7	3	21	21	14	6	2
2010	1544	93	7	5.2	12	2	5	2	20	21	15	4	3
2011	1302	97	8	5.4	15	3	4	1	26	25	17	4	-1
2012	1684	98	9	5.4	15	4	7	2	31	27	16	7	-9
2013	1737	106	8	5.4	15	2	5	2	26	22	13	5	-11

Year	Prec	Analysed Prec	Cond 20°C	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	NO_3^{-}	SO_4^{2+}	Cl^{-}	Acidity
	mm	%	µS cm^{-1}		meq m^{-3}								
Monte Brè													
1995	1412	42	15	4.6	14	8	6	1	26	30	43	6	24
1996	1721	75	14	4.7	14	4	5	1	34	31	35	5	17
1997	1227	76	14	4.9	14	4	5	1	36	33	35	6	13
1998	1508	84	15	4.9	23	5	9	2	43	36	40	6	9
1999	1699	90	15	5.1	38	7	10	3	46	38	44	10	0
2000	2149	90	12	5.2	29	6	10	2	29	28	31	7	-6
2001	1499	87	17	4.9	21	5	11	2	54	44	46	9	10
2002	2105	98	16	5.1	64	6	8	3	33	30	33	9	-40
2003	1167	88	15	5.2	25	5	10	4	54	45	32	9	-9
2004	1373	19	15	4.9	20	4	12	3	40	45	28	8	13
2005	947	92	24	4.8	29	6	20	5	75	69	41	20	7
2006	1304	89	15	5.2	31	5	11	2	51	43	33	7	-8
2007	1143	94	11	5.3	15	3	8	2	41	33	26	7	-4
2008	2188	89	11	5.2	17	5	9	2	32	31	25	9	1
2009	1680	79	10	5.3	21	5	6	3	31	33	19	7	-5
2010	1854	79	12	5.3	40	9	9	6	26	33	33	8	-10
2011	1179	52	9	5.2	17	4	6	2	23	24	16	6	-4
2012	1412	96	10	5.4	13	4	8	2	35	29	17	8	-9
2013	1713	89	10	5.3	16	4	7	5	26	26	13	8	-12
Locarno Monti													
1988	2127	66	25	4.4	29	5	10	2	45	38	73	11	37
1989	1478	73	25	4.3	20	5	13	4	31	37	62	15	45
1990	1474	62	34	4.3	19	6	21	6	58	61	72	35	53
1991	1782	50	19	4.6	9	4	21	3	38	33	44	14	25
1993	2134	80	19	4.6	29	7	11	2	37	34	50	13	20
1994	1865	81	18	4.7	25	9	8	1	34	30	51	9	14
1995	1406	86	19	4.6	28	9	6	2	38	35	58	9	21
1996	1661	72	20	4.6	26	8	9	1	41	39	48	10	13
1997	1564	90	15	4.8	16	5	7	2	34	32	38	9	16
1998	1752	83	19	4.7	23	5	10	3	52	45	47	8	15
1999	2367	76	17	4.9	33	6	9	2	50	43	46	8	5
2000	2623	83	17	4.9	49	8	11	2	40	38	42	9	-15
2001	1711	86	20	4.7	23	5	9	1	56	49	49	8	15
2002	2646	94	15	5.0	44	4	6	2	38	30	30	6	-26
2003	1107	83	15	4.9	21	3	7	2	48	42	35	6	4
2004	1894	11	8	5.0	11	2	5	1	14	17	16	2	9
2005	1057	88	17	5.0	28	4	8	2	62	50	36	5	-2
2006	1629	72	14	5.0	19	4	11	2	40	36	29	9	5
2007	1501	87	12	5.1	15	3	5	1	45	37	29	5	1
2008	2346	92	11	5.1	17	3	7	1	32	32	24	7	3
2009	2092	94	10	5.2	15	3	5	1	36	29	22	5	-3
2010	2020	86	10	5.1	17	3	5	1	32	30	21	5	1
2011	1578	91	11	5.3	21	4	6	2	39	34	26	5	-3
2012	1863	89	11	5.3	15	4	7	2	37	32	20	7	-6
2013	1947	88	9	5.3	15	3	5	1	30	25	15	5	-9

Year	Prec	Analysed Prec	Cond 20°C	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	NO_3^{-}	SO_4^{2+}	Cl^{-}	Acidity
	mm	%	µS cm^{-1}		meq m^{-3}								
Lugano													
1989	1468	68	32	4.3	27	8	19	5	48	55	84	19	54
1990	1342	57	32	4.4	37	8	19	6	74	63	81	32	34
1991	1288	39	26	4.5	18	7	26	7	52	56	62	14	35
1993	1590	75	20	4.6	30	7	11	3	45	41	59	13	22
1994	1703	82	18	4.8	31	12	11	2	43	37	58	12	8
1995	1412	77	18	4.7	26	10	8	2	40	36	55	8	16
1996	1721	64	16	4.8	27	8	10	1	39	33	45	11	6
1997	1227	97	16	4.8	19	6	8	2	44	38	43	9	13
1998	1508	78	19	4.8	27	6	10	3	51	43	49	9	9
1999	1699	66	20	4.8	31	7	10	2	59	48	54	11	5
2000	2149	86	16	5.0	38	7	11	2	41	40	42	9	-5
2001	1498	66	18	4.8	22	6	13	4	55	47	51	11	13
2002	2099	91	19	5.0	70	7	12	5	45	38	49	11	-36
2003	1181	77	23	5.1	49	9	14	5	73	67	56	12	-18
2004	1373	49	11	5.5	25	5	7	3	42	32	26	6	-10
2005	947	54	19	5.1	36	7	10	5	67	61	42	9	-6
2006	1304	56	19	5.2	42	12	17	4	67	54	46	16	-13
2007	1143	66	14	5.5	29	7	13	6	43	39	35	9	-15
2008	2188	77	12	5.3	24	6	10	2	41	36	33	10	-4
2009	1680	73	11	5.4	25	5	6	2	39	33	23	7	-11
2010	1854	81	18	5.4	39	8	30	34	33	34	92	9	-6
2011	1179	77	11	5.4	19	4	5	4	42	34	23	5	-10
2012	1412	81	11	5.4	14	4	9	2	41	32	20	9	-10
2013	1713	74	10	5.4	15	3	7	2	35	28	16	7	-13
Piotta													
1990	1281	41	22	4.4	15	4	17	4	28	35	46	25	38
1991	1475	30	22	4.6	40	6	22	5	36	38	45	23	8
1993	2005	84	12	4.8	15	3	6	1	22	22	31	9	16
1994	1279	80	13	4.9	30	9	9	1	26	26	34	10	0
1995	1235	78	11	5.0	20	6	9	1	21	23	32	10	9
1996	1597	69	10	5.0	13	5	8	1	26	22	24	8	7
1997	1345	73	10	5.0	11	3	9	1	18	22	21	9	11
1998	1426	69	12	4.9	13	3	8	1	30	26	29	6	11
1999	1722	78	11	5.1	21	4	5	1	29	25	28	5	3
2000	1853	83	14	5.1	63	6	9	1	23	24	29	8	-43
2001	1505	89	12	4.9	14	3	9	1	33	28	28	8	7
2002	2017	94	7	5.2	14	2	4	1	20	16	15	3	-3
2003	1061	87	12	5.3	20	4	9	2	44	29	26	9	-16
2004	1118	73	8	5.4	14	3	13	2	21	17	13	11	-8
2005	644	101	11	5.3	14	2	6	1	39	30	21	6	-4
2006	1176	78	9	5.2	16	3	9	1	24	24	17	8	2
2007	1313	80	9	5.3	12	2	5	1	29	23	20	5	-1
2008	1803	85	9	5.3	16	4	11	1	25	23	18	10	-4
2009	1360	89	7	5.4	11	2	7	1	22	19	14	7	-1
2010	1377	83	9	5.3	13	3	9	3	26	20	14	9	-7
2011	1269	91	7	5.5	14	3	9	2	23	18	15	8	-5
2012	1602	85	8	5.6	15	3	8	2	32	20	15	7	-16
2013	1692	86	7	5.5	14	2	7	1	21	16	12	7	-10

Year	Prec	Analysed Prec	Cond 20°C	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	NO_3^{-}	SO_4^{2+}	Cl^{-}	Acidity
	mm	%	µS cm^{-1}		meq m^{-3}								
Robiei													
1996	2465	24	6	5.1	4	2	0	0	12	13	13	1	9
1997	2202	88	8	5.0	10	2	3	1	15	15	15	3	10
1998	2216	90	10	5.0	15	3	6	1	21	19	19	3	6
1999	2845	68	10	5.2	22	7	6	1	30	25	25	4	-2
2000	3330	86	11	5.2	28	5	6	1	25	24	24	4	-6
2001	2258	92	12	4.9	13	3	5	1	32	28	28	3	11
2002	2782	72	9	5.1	10	2	3	1	27	21	21	2	2
2003	1625	91	9	5.3	12	2	3	1	37	29	29	2	-2
2004	2277	42	6	5.3	11	2	4	1	20	17	17	3	-2
2005	1357	78	12	5.1	17	2	2	1	43	34	34	2	-1
2006	2145	77	8	5.2	13	2	3	1	25	24	24	3	4
2007	1639	96	9	5.2	11	2	3	1	29	24	24	3	1
2008	3188	62	9	5.2	21	3	4	1	26	24	24	4	-5
2009	2094	46	6	5.5	15	2	3	1	16	18	18	5	0
2010	2599	75	6	5.3	11	6	2	1	17	18	18	2	-1
2011	2071	80	7	5.5	21	2	2	1	21	19	19	2	-10
2012	2721	77	8	5.4	10	2	3	1	30	23	23	3	-6
2013	2601	80	7	5.4	13	2	3	1	19	18	12	3	-6
Sonogno													
2001	2099	11	12	4.8	7	3	6	2	35	26	29	6	13
2002	2782	87	11	5.1	17	5	6	6	26	22	22	4	-11
2003	1435	76	11	5.2	20	3	6	2	35	31	26	6	-2
2004	1980	37	9	5.4	12	3	8	2	36	26	19	5	-4
2005	1033	42	11	5.2	21	2	5	1	29	26	22	4	-2
2006	1858	66	12	5.1	22	9	11	4	26	29	24	5	-6
2007	1659	84	10	5.3	15	3	6	3	40	30	28	4	-4
2008	2957	80	8	5.5	16	3	7	2	22	21	16	7	-5
2009	2033	95	8	5.5	14	3	6	2	25	23	15	6	-4
2010	2116	90	9	5.5	19	6	5	2	30	22	17	4	-16
2011	1776	84	8	5.5	13	3	5	2	29	22	16	4	-8
2012	2413	82	10	5.6	15	3	8	3	35	28	17	8	-13
2013	2003	75	8	5.8	16	2	7	4	32	21	13	5	-24

Year	Prec	Analysed Prec	Cond 20°C	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	NO_3^{-}	SO_4^{2+}	Cl^{-}	Acidity
	mm	%	µS cm^{-1}		meq m^{-3}								
Stabio													
1990	1231	35	36	4.3	23	7	24	5	77	70	78	26	48
1991	1181	56	32	4.5	38	10	30	9	75	69	88	23	34
1993	1394	64	22	4.8	47	13	13	4	55	49	74	15	12
1994	1485	91	21	4.8	39	12	13	2	55	45	66	14	6
1995	1487	81	22	4.6	26	8	10	1	54	46	61	10	20
1996	1706	61	18	4.8	29	8	12	2	45	38	47	10	6
1997	1269	87	16	4.9	20	6	8	1	50	37	44	9	9
1998	1566	90	17	4.9	25	7	10	2	57	41	47	11	6
1999	1410	89	19	4.9	35	8	12	2	59	48	52	11	1
2000	2336	88	16	5.0	33	7	11	2	49	40	43	9	-7
2001	1251	97	19	4.9	29	6	11	2	63	52	52	10	4
2002	2438	77	19	5.1	67	6	10	2	54	36	42	11	-46
2003	1206	90	15	5.0	19	4	8	2	54	43	32	7	-5
2004	1364	69	12	5.3	21	4	8	4	48	38	31	6	-7
2005	898	95	17	5.2	26	5	9	3	75	55	36	9	-11
2006	1184	90	15	5.2	24	5	13	2	62	48	33	10	-6
2007	1183	88	13	5.4	15	4	10	4	52	38	31	8	-8
2008	2121	93	11	5.3	15	4	9	3	40	32	22	9	-6
2009	1613	99	10	5.3	14	4	8	2	36	30	19	8	-5
2010	2132	92	10	5.3	16	3	7	2	40	32	21	6	-8
2011	1239	92	12	5.4	20	4	7	2	49	36	24	6	-12
2012	1443	96	10	5.5	14	4	9	2	37	29	17	8	-12
2012	1443	96	10	5.5	14	4	9	2	37	29	17	8	-12
2013	1527	100	11	5.4	13	3	8	2	40	29	17	7	-14

Table A3: Average concentrations in rainwater in the periods of 1988-1992, 1993-1997, 1998-2002, 2003-2007, 2008-2012. Prec and Cond correspond to precipitation and conductivity, respectively. Values in red are estimates.

Period	Prec	Cond 20°C	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	NO_3^{-}	SO_4^{2+}	Cl^{-}	Acidity
	mm	µS cm^{-1}		meq m^{-3}								
Aquarossa												
1988-1992	1143	20	4.5	11	5	17	4	32	34	42	19	29
1993-1997	1317	13	4.9	25	7	6	2	29	28	35	8	5
1998-2002	1547	13	5.2	37	8	7	3	30	27	36	5	-13
2003-2007	959	11	5.4	27	8	6	2	34	28	27	5	-10
2008-2012	1399	8	5.5	19	6	5	1	26	23	18	4	-9
Bignasco												
1988-1992	1552	14	4.6	10	3	9	4	26	26	33	9	22
1993-1997	1917	9	4.9	9	4	5	2	20	20	25	6	11
1998-2002	2144	9	5.1	13	3	6	3	22	21	21	5	3
2003-2007	1247	12	5.0	19	3	7	2	34	35	25	5	5
2008-2012	1697	8	5.2	15	3	6	2	24	24	16	6	-1
Monte Brè												
1988-1992	1451	21	4.5	15	5	9	2	41	41	50	9	33
1993-1997	1530	14	4.7	14	5	5	1	32	31	38	6	16
1998-2002	1791	15	5.0	37	6	9	2	40	34	38	8	-7
2003-2007	1189	15	5.0	24	5	12	3	51	46	32	10	0
2008-2012	1663	11	5.3	22	5	8	3	30	31	23	8	-5
Locarno Monti												
1988-1992	1701	25	4.4	20	5	16	4	43	41	63	18	39
1993-1997	1726	18	4.7	25	7	9	2	37	34	49	10	17
1998-2002	2220	17	4.9	36	6	9	2	46	40	42	8	-4
2003-2007	1438	13	5.0	18	3	7	2	39	34	27	5	4
2008-2012	1980	11	5.2	17	3	6	1	35	31	22	6	-1
Lugano												
1988-1992	1451	30	4.4	28	8	21	6	58	58	76	22	41
1993-1997	1530	18	4.7	27	9	10	2	42	37	52	11	13
1998-2002	1791	18	4.9	40	7	11	4	49	43	48	10	-5
2003-2007	1189	17	5.3	36	8	12	4	58	50	41	11	-12
2008-2012	1663	13	5.4	25	6	13	10	39	34	41	8	-8
Piotta												
1988-1992	1375	22	4.5	28	5	19	5	32	37	46	24	22
1993-1997	1492	11	4.9	17	5	8	1	23	23	29	9	9
1998-2002	1705	11	5.0	26	4	7	1	26	23	25	6	-7
2003-2007	1062	10	5.3	15	3	9	2	30	24	19	8	-5
2008-2012	1482	8	5.4	14	3	9	2	26	20	15	8	-7
Robiei												
1988-1992	2362	10	4.8	7	2	3	1	17	18	23	3	17
1993-1997	2476	7	5.0	7	2	2	0	13	14	17	2	9
1998-2002	2686	10	5.1	18	4	5	1	27	24	27	3	1
2003-2007	1808	9	5.2	12	2	3	1	29	25	19	2	0
2008-2012	2535	7	5.3	15	3	3	1	23	21	14	3	-4
Sonogno												
1988-1992	1820	18	4.5	10	4	8	6	35	29	38	9	30
1993-1997	2245	12	4.7	9	5	5	3	27	22	28	5	15
1998-2002	2446	11	4.9	13	4	6	4	30	23	25	5	0
2003-2007	1593	10	5.2	17	4	7	2	33	29	24	5	-4
2008-2012	2259	8	5.5	16	4	6	2	28	23	16	6	-9

Period	Prec	Cond 20°C	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	NO_3^{-}	SO_4^{2+}	Cl^{-}	Acidity
	mm	µS cm^{-1}		meq m^{-3}								
Stabio												
1988-1992	1381	34	4.4	30	8	27	7	76	69	83	24	41
1993-1997	1468	20	4.8	32	9	11	2	51	43	58	11	10
1998-2002	1800	18	5.0	40	7	11	2	55	42	46	10	-13
2003-2007	1167	14	5.2	21	4	10	3	57	44	32	8	-7
2008-2012	1709	11	5.4	16	4	8	2	40	32	21	7	-8
Bellinzago (Italy)												
1988-1992	955	33	4.4	31	6	12	3	80	62	82	14	34
1993-1997	1135	24	4.5	23	5	10	2	53	46	57	11	26
1998-2002	1155	21	4.9	41	8	14	8	62	46	50	13	-20
2003-2007	849	16	5.2	21	5	11	4	66	43	36	10	-13
2008-2012	1198	14	5.5	19	5	11	7	56	35	27	12	-20
Devero (Italy)												
1988-1992	1488	18	4.5	11	2	6	3	28	28	33	7	34
1993-1997	1723	13	4.7	10	2	4	1	22	22	25	4	18
1998-2002	2070	12	4.9	19	3	11	3	26	24	25	10	0
2003-2007	1180	10	5.2	15	3	5	2	31	25	20	4	-3
2008-2012	1629	7	5.4	10	2	4	2	20	16	13	3	-3
Domodossola (Italy)												
1988-1992	1273	21	4.5	20	4	5	2	31	32	46	6	29
1993-1997	1475	16	4.7	17	3	5	2	28	27	35	5	19
1998-2002	1622	13	4.9	24	3	5	2	31	27	27	4	-4
2003-2007	1045	12	5.1	15	3	4	1	42	33	23	4	0
2008-2012	1489	9	5.2	14	3	5	1	26	22	14	5	-3
Graniga (Italy)												
1988-1992	1599	22	4.4	36	19	3	8	4	37	37	46	32
1993-1997	1763	15	4.7	20	17	3	5	2	30	28	35	16
1998-2002	1950	14	4.8	14	20	3	6	2	32	29	28	1
2003-2007	1309	12	5.0	9	15	3	4	1	42	32	23	-3
2008-2012	1697	6	5.4	8	2	2	1	16	15	9	2	-1
Lunecco (Italy)												
1988-1992	2057	22	4.5	19	4	8	2	45	38	51	9	27
1993-1997	2304	19	4.7	19	4	9	2	39	34	44	9	18
1998-2002	2670	17	4.8	26	4	8	2	43	35	37	7	-2
2003-2007	1493	13	5.0	14	3	5	1	47	37	28	5	4
2008-2012	2352	10	5.4	13	4	7	3	34	27	18	6	-6
Pallanza (Italy)												
1988-1992	1735	30	4.4	23	5	11	2	61	49	69	11	39
1993-1997	1972	25	4.5	21	5	9	2	52	44	57	10	28
1998-2002	2189	20	4.7	27	4	10	3	56	43	44	9	3
2003-2007	1426	16	5.0	16	4	8	2	65	46	34	7	-2
2008-2012	1982	12	5.2	12	3	7	1	44	32	21	7	-3
S. Monte Orta (Italy)												
1993-1997	1391	32	4.6	26	5	10	3	70	57	70	10	36
1998-2002	1725	23	4.7	22	5	10	2	53	44	55	10	22
2003-2007	2846	22	4.7	19	5	13	3	66	51	52	13	16
Monte Mesma (Italy)												
2003-2007	1257	16	5.0	18	4	8	2	59	47	34	7	3
2008-2012	1760	12	5.3	15	4	8	2	48	35	22	8	-8
Basodino (Glacier)												
1988-1992	2362	7	5.1	13	5	4	1	9	10	16	6	4
1993-1997	2476	5	5.4	12	5	3	1	7	7	12	4	0
1998-2002	2686	4	5.5	10	2	3	1	4	7	7	2	-2
2003-2007	1808	5	5.4	7	2	4	1	10	10	7	3	0
2008-2012	2535	5	5.3	5	1	4	1	10	12	6	4	5

Table A4: Results from multiple regression analysis for different time periods. n, r^2, F, p stay for data number, coefficient of determination, F statistic and p-values.

Period	n	r^2	F	p	m_{lat}	m_{long}	m_{alt}	C_0
					meq m^{-4}	meq m^{-4}	meq m^{-4}	meq m^{-3}
Base cations								
1988-1992	17	0.43	5.0	0.016	-1.8E-4	1.2E-4	-2.5E-3	-34.8
1993-1997	17	0.48	5.9	0.009	-1.1E-4	2.0E-4	-3.4E-3	-97.2
1998-2002	17	0.65	10.9	0.001	-1.7E-4	3.6E-4	-3.3E-4	-197.2
2003-2007	17	0.51	6.6	0.006	-2.0E-5	2.7E-4	-3.7E-3	-157.9
2008-2012	17	0.60	9.2	0.002	-4.7E-5	2.7E-4	-2.4E-3	-155.9
Ammonium								
1988-1992	17	0.86	33.2	0.000	-5.1E-4	1.7E-4	-6.0E-3	-15.4
1993-1997	17	0.86	33.9	0.000	-3.1E-4	6.8E-5	-7.1E-3	26.0
1998-2002	17	0.82	24.8	0.000	-3.6E-4	6.9E-5	-7.2E-3	36.6
2003-2007	17	0.89	43.9	0.000	-3.4E-4	5.0E-5	-7.3E-3	52.1
2008-2012	17	0.77	19.3	0.000	-2.6E-4	1.2E-4	-4.6E-3	-22.4
Sulphate								
1988-1992	17	0.84	30.0	0.000	-4.2E-4	2.1E-4	-9.1E-3	-41.8
1993-1997	17	0.86	33.5	0.000	-3.0E-4	1.1E-4	-8.1E-3	3.3
1998-2002	17	0.76	17.9	0.000	-2.3E-4	1.5E-4	-6.0E-3	-37.3
2003-2007	17	0.84	28.9	0.000	-1.3E-4	1.1E-4	-5.3E-3	-32.8
2008-2012	17	0.60	8.9	0.002	-8.7E-5	2.0E-4	-2.7E-3	-109.8
Nitrate								
1988-1992	17	0.79	20.8	0.000	-3.3E-4	1.9E-4	-6.2E-3	-47.8
1993-1997	17	0.88	39.4	0.000	-2.4E-4	4.9E-5	-6.2E-3	27.1
1998-2002	17	0.79	21.0	0.000	-2.4E-4	5.2E-5	-5.9E-3	27.1
2003-2007	17	0.81	24.0	0.000	-2.0E-4	1.0E-4	-6.1E-3	-8.2
2008-2012	17	0.84	28.8	0.000	-1.4E-4	1.6E-4	-2.9E-3	-66.4