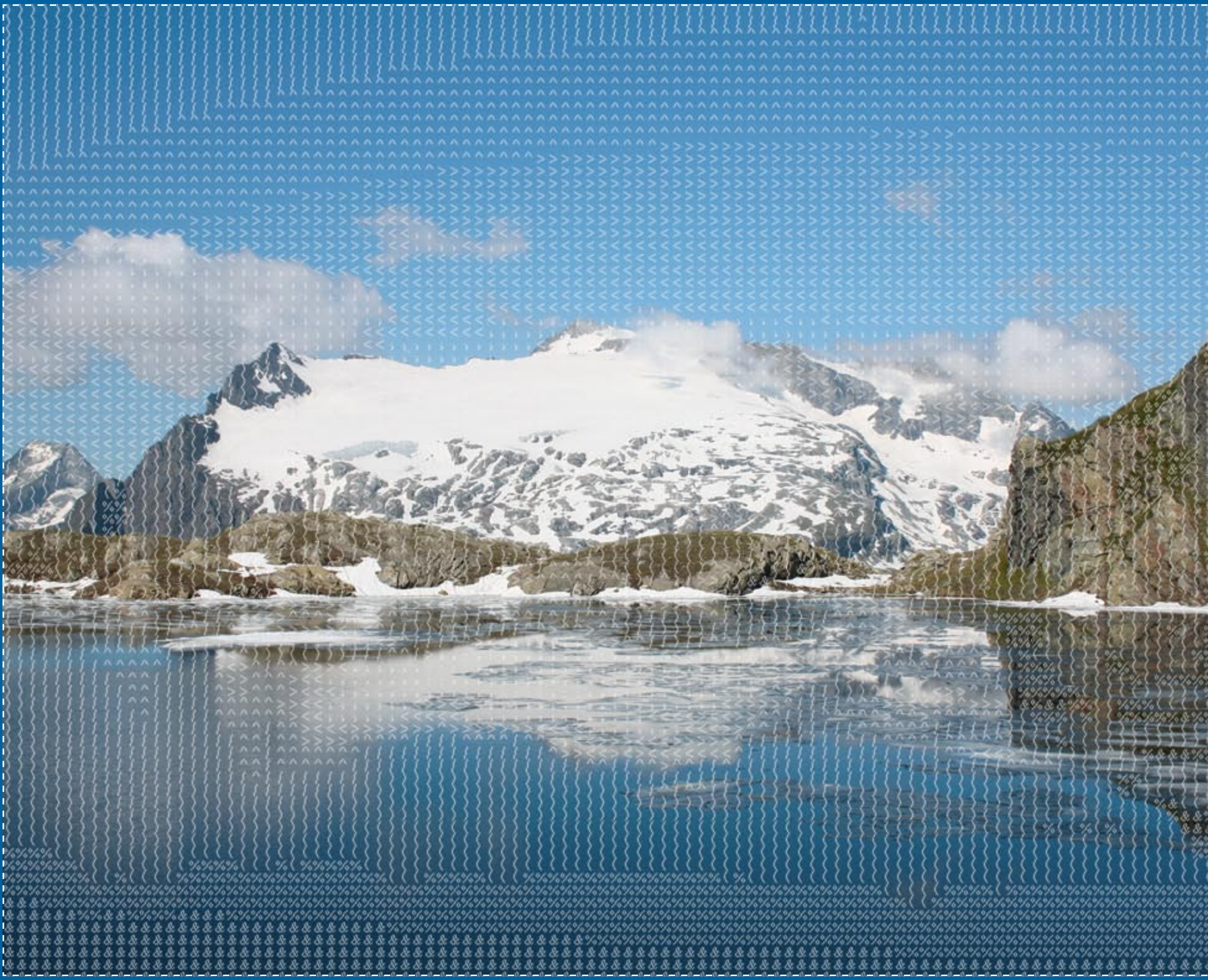
> Acidifying Deposition in Southern Switzerland

Assessment of the trend 1988–2007



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Assessment of the trend 1988–2007

Mit deutscher Zusammenfassung – Con riassunto in italiano

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Authors
Sandra Steingruber and Luca Colombo
Ufficio aria, clima ed energie rinnovabili
Sezione protezione aria, acqua e suolo
Dipartimento del territorio
Via C. Salvioni 2a
6500 Bellinzona
Switzerland

FOEN consultant
Beat Achermann,
Air Pollution Control and Non-Ionizing Radiation Division

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Ursula Nöthiger-Koch, 4813 Uerkheim

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> Abstracts

A trend analysis of rainwater quality over the last 20 years in southern Switzerland shows that sulphate concentrations have decreased, while concentrations of bicarbonate and base cations have increased. Conversely, no significant trend could be observed for ammonium and nitrate concentrations. As a consequence of decreased sulphur emissions and of an increased number of alkaline rain events, acidity has decreased and pH values have thus increased.
Sulphate, nitrate and ammonium concentrations correlate mainly with latitude and altitude reflecting the transport of these pollutants from the urban area of Milan and from rural areas of the Po Plain towards north. On the contrary, base cations and bicarbonate correlate principally with longitude as atmospheric currents causing rainfall are mostly directed from south-west to north-east. A principal component analysis has revealed that acidity was mainly determined by emissions of SO_2, NO_X and NH_3 between 1988–1992, while alkaline rain events have become more significant afterwards.
As a consequence of reduced sulphur deposition the relative importance of sulphur compounds on the total deposition of acidifying compounds has decreased from 42 % to 26 % while that of nitrogen compounds has increased from 58 % to 74 % during the last 20 years.

Keywords:
Precipitation chemistry,
atmospheric deposition,
trend,
acidification,
map

Eine Trendanalyse der Regenwasserqualität während der letzten 20 Jahre im Süden der Schweiz zeigte, dass die Sulphatkonzentrationen abgenommen haben, während die Konzentrationen von Bikarbonat und basischen Kationen zugenommen haben. Im Gegensatz dazu konnte bei den Nitrat- und Ammoniumkonzentrationen kein signifikanter Trend beobachtet werden. Wegen der Abnahme der Schwefelemissionen und der Zunahme von basischen Regenereignissen haben der Säuregehalt abgenommen und die pH-Werte zugenommen.
Sulphat-, Nitrat-, und Ammoniumkonzentrationen korrelieren mit der geographischen Breite und Höhe und widerspiegeln somit den Transport dieser Schadstoffe von der urbanen Gegend von Mailand und der landwirtschaftlich genutzten Flächen der Po Ebene Richtung Norden. Die basischen Kationen und Bikarbonat korrelieren dagegen mit der geographischen Länge, weil atmosphärische Strömungen, die Niederschlag verursachen, meistens von Südwesten Richtung Nordosten gerichtet sind. Eine Hauptkomponentenanalyse hat auch gezeigt, dass der Säuregehalt von 1988–1992 hauptsächlich von den SO_2-, NO_X- and NH_3-Emissionen bestimmt wurde, später aber basische Regenereignisse wichtiger geworden sind.
Als Folge der abnehmenden Schwefeleinträge hat in den letzten 20 Jahren der Schwefelanteil am totalen Eintrag von versauernden Verbindungen von 42 % auf 26 % abgenommen, während derjenige von Stickstoffverbindungen von 58 % auf 74 % zugenommen hat.

Stichwörter:
Niederschlagschemie,
atmosphärischer Eintrag,
Trend,
Versauerung,
Karte

Une analyse de tendance de la qualité de l'eau de pluie en Suisse méridionale, effectuée sur les 20 dernières années, a démontré que les concentrations de sulfate ont diminué, tandis que les concentrations de bicarbonate et de cations alcalins ont augmenté. Pour ce qui est des nitrates et de l'ammonium en revanche, aucune tendance importante ne s'est dessinée. La baisse des émissions de soufre et la hausse des pluies alcalines ont entraîné une réduction de l'acidité et une augmentation du pH.

Les concentrations de sulfate, de nitrate et d'ammonium sont corrélées à la latitude et à l'altitude, reflétant ainsi le transport de ces polluants depuis la région urbaine de Milan et les surfaces agricoles de la plaine du Pô en direction du nord. Les concentrations de cations alcalins et de bicarbonate sont, quant à elles, corrélées à la longitude, car les courants atmosphériques à l'origine de précipitations se déplacent en général du sud-ouest au nord-est. En outre, une analyse en composantes principales a montré que de 1988 à 1992 le taux d'acidité a été caractérisé majoritairement par les émissions de dioxyde de soufre (SO_2), d'oxyde d'azote (NO_X) et d'ammoniac (NH_3), mais que, par la suite, l'influence des pluies alcalines a gagné en importance.

Comme les dépôts de soufre ont progressivement baissé ces 20 dernières années, la part de soufre dans les dépôts de composés acidifiants a diminué de 42 % à 26 %, alors que la part de composés azotés a augmenté de 58 % à 74 %.

Mots-clés:
chimie des précipitations,
dépôt atmosphérique,
tendance,
acidification,
carte

Un'analisi delle tendenze della qualità delle precipitazioni per gli ultimi 20 anni al Sud della Svizzera ha mostrato che le concentrazioni di solfato sono diminuite, mentre quelle di bicarbonato e dei cationi basici sono aumentate. Per contro, nessuna tendenza significativa è stata osservata per le concentrazioni di nitrato e ammonio. A causa della diminuzione delle emissioni di zolfo e dell'aumento del numero di eventi di pioggia alcalini, l'acidità è diminuita e il pH è aumentato.

Le concentrazioni di solfato, nitrato e ammonio correlano soprattutto con la latitudine e l'altitudine riflettendo il trasporto di questi inquinanti dalla zona urbana di Milano e dalle regioni agricole della Pianura Padana verso il nord. I cationi basici e il bicarbonato correlano invece principalmente con la longitudine, perché le correnti atmosferiche che causano precipitazioni sono prevalentemente dirette da sud-ovest a nord-est. Un'analisi delle componenti principali ha anche rivelato che l'acidità era prevalentemente influenzata dalle emissioni di SO_2, NO_X e NH_3 tra il 1988 e il 1992, mentre successivamente sono diventati sempre più importanti gli eventi di precipitazioni alcaline.

A seguito della riduzione delle deposizioni di zolfo, durante gli ultimi 20 anni l'importanza relativa delle componenti di zolfo nella deposizione totale di componenti acidificanti è diminuita dal 42 % al 26 %, mentre è aumentata quella dell'azoto dal 58 % al 74 %.

Parole chiave:
chimica delle precipitazioni,
deposizione atmosferica,
tendenza,
acidificazione,
mappa

> Foreword

Switzerland is a Party to the Convention on Long-range Transboundary Air Pollution covering the region of the United Nations Economic Commission for Europe (UN-ECE). Several protocols developed under the Convention aim at controlling the impact of acidifying and eutrophying air pollutants on sensitive receptors of the environment.

Alpine lakes and parts of rivers at high altitudes in southern Switzerland belong to such sensitive receptors since they are mainly located on crystalline bedrocks with low weathering rates. It is therefore of interest to know the extent of acidifying and eutrophying atmospheric pollution loads on such sensitive ecosystems as well as their change over time.

In the year 2000 Switzerland joined the activities of the International Cooperative Programme on Assessment and Monitoring of Air Pollution on Rivers and Lakes (ICP Waters) operating under the Working Group on Effects of the Convention. But already since 1988 deposition is monitored in southern Switzerland by the Cantone Ticino. Trend analyses of important chemical parameters in rainwater linked with acidification and eutrophication as well as the dry deposition of gases and aerosols over 20 years of monitoring are presented in this report.

We express our warm thanks and appreciation to the Cantone Ticino for carrying out the survey and for participating in the work of ICP Waters.

Martin Schiess
Head of the Air Pollution Control and Non-Ionizing Radiation Division
Federal Office for the Environment FOEN

> Summary

Because of its particular 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. Furthermore, many high altitude soils and freshwaters of southern Switzerland are particularly sensitive to acidification due to the dominance of base-poor rocks with low buffering capacity. As a consequence, acidifying deposition in southern Switzerland becomes particularly relevant.

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 and later also at other sampling stations. Nowadays weekly precipitation is collected at 9 sampling sites distributed over the whole area of Canton Ticino. A trend analysis of the main chemical parameters in rainwater reveals that sulphate concentrations have decreased, reflecting the decrease of SO_2 emissions after 1980. At Locarno Monti and Lugano sulphate concentrations have decreased by around 57–66 % during the last 20 years, while no significant trend could be observed for ammonium and nitrate concentrations. Concentrations of bicarbonate and base cations have increased and were particularly high during the years 1999, 2000, 2002, when precipitation was higher than usual and alkaline rain events were more frequent. As a consequence of decreased sulphate concentrations and increased concentrations of base cations, acidity of rainwater decreased and therefore pH values increased. Since the end of the eighties until the beginning of this millennium the mean annual pH values of rainwater at Locarno Monti and Lugano increased from 4.3 to 5.0/5.3 and after 2000 the mean annual acidity became negative at most sites.

In order to analyze patterns in the data and relations between parameters, a principal component analysis has been performed with average concentrations of the main chemical parameters and with conductivity, precipitation amounts and geographic parameters over the periods of 1988–1992, 1993–1997, 1998–2002 and 2003–2007. The analysis has been extended by considering not only data from Swiss monitoring stations but also from North Italian sampling sites. The analysis has shown that most chemical parameters in rainwater correlate significantly with the geographic parameters latitude, longitude and altitude. Sulphate, nitrate and ammonium concentrations correlate with both latitude and altitude reflecting the transport of these pollutants from the urban area of Milan and from rural areas of the Po Plain towards north. Conversely, mean yearly concentrations of base cations and bicarbonate, which increase with decreasing annual precipitation (smaller dilution of alkaline rain events on an annual base), correlate with longitude because atmospheric currents causing rainfall are mostly directed from south-west to north-east. The principal component analysis also reveals that acidity correlated with latitude during the beginning of the monitored period (1988–1992), but became more and more independent of latitude and dependent of longitude after the interval of 1998–2002. This indicates that acidity was mainly de-

termined by emissions of SO_2, NO_x and NH_3 during the first period, while alkaline rain events became more important afterwards.

The geographic distribution of chemical parameters in rainwater discussed in the principal component analysis suggested the possibility to develop a multiple regression model with the variables latitude, longitude, altitude. This can describe the geographic distribution of the concentrations of single chemical parameters in rainwater. Multiple linear regression analyses have been performed for different parameters in the periods of 1988–1992, 1993–1997, 1998–2002 and 2003–2007. For some parameters and time periods the addition of the mean annual precipitation volume as a regression variable has provided better results. In particular, parameters like base cations, bicarbonate, acidity and pH, whose annual mean concentrations are strongly influenced by sporadic alkaline rain events, are better modeled after 1993 if the amount of precipitation is also considered. The regression parameters have then been used to map concentrations of the main chemical parameters over southern Switzerland with a resolution of 1km x 1km.

Finally, wet deposition maps for southern Switzerland have been derived by multiplying the concentration maps of chemical parameters in rainwater by the precipitation maps. Observations made for the concentrations of chemical parameters in rainwater do not substantially differ from those of wet deposition. In general time trends can be observed, in which sulphate deposition and acidity decrease, whereas the deposition of base cations and of bicarbonate increase. The dependency of the chemical variables on geographic parameters also did not vary over time. However, the particularly rain rich (1998–2002) and rain poor (2003–2007) years had visible consequences on deposition: wet deposition of sulphate, nitrate and ammonium were slightly higher between 1998 and 2002 compared to the immediately previous and subsequent time periods.

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

Since wet deposition mostly contributes to the total deposition of nitrogen (70–77 %) and to the present load of acidity (68–80 %), the temporal trends of wet deposition are found to be similar to those of total deposition. As a consequence of reduced sulphur deposition the relative importance of sulphur compounds within the total deposition of acidifying compounds has decreased from 42 % to 26 % while that of nitrogen compounds has increased from 58 % to 74 % during the last 20 years.

> Zusammenfassung

Wegen der besonderen Meteorologie wird die Luftqualität im Süden der Schweiz nicht nur von lokalen Emissionen beeinflusst, sondern auch von grenzüberschreitender Luftverschmutzung von der Po Ebene, insbesondere vom stark verschmutzten Stadtgebiet Mailand. Zusätzlich sind im Süden der Schweiz viele hochgelegene Böden und Oberflächengewässer säureempfindlich wegen den vorwiegend kalkarmen Gesteinen mit niedriger Pufferkapazität. Es folgt, dass im Süden der Schweiz der Eintrag versauernder Luftschadstoffe besonders relevant ist.

Das ist auch der Grund, weshalb im Süden der Schweiz die Qualität des Regenwassers seit dem Anfang der achtziger Jahre untersucht wird, zu Beginn nur in Locarno Monti und Lugano später auch an anderen Probenahmestellen. Heutzutage wird wöchentlich Niederschlag an 9 über den ganzen Kanton Tessin verteilten Probenahmestellen gesammelt. Eine Trendanalyse der Zeitreihen der wichtigsten chemischen Parameter in Regenwasser ergab, dass die Sulphatkonzentrationen abgenommen haben und somit die Reduktion der SO_2-Emissionen nach 1980 widerspiegeln. In Locarno Monti und Lugano haben in den letzten 20 Jahren die Sulphatkonzentrationen um 57–66 % abgenommen, während für die Nitrat- und Ammoniumkonzentrationen kein signifikanter Trend beobachtet werden konnte. Die Konzentrationen von Bikarbonat und basischen Kationen haben zugenommen, insbesondere in den Jahren 1999, 2000, 2002, als die Niederschlagsmenge höher als üblich war und die basischen Regenereignisse häufiger waren. Als Folge von abnehmenden Sulphatkonzentrationen und zunehmenden Konzentrationen von basischen Kationen haben auch der Säuregehalt und der pH-Wert von Regenwasser zugenommen. Seit Ende der achtziger Jahre bis Anfang dieses Jahrtausends sind die mittleren pH-Werte in Locarno Monti und Lugano von 4,3 auf 5,0/5,3 gestiegen und nach 2000 wurde der Säuregehalt an den meisten Stellen negativ.

Um das Muster der Daten und die Zusammenhänge zwischen den Parametern zu untersuchen, wurde eine Hauptkomponentenanalyse der mittleren Konzentrationen der wichtigsten Parameter, der Leitfähigkeit und der geographischen Parameter über die Zeitperioden 1988–1992, 1993–1997, 1998–2002, 2003–2007 durchgeführt. Die Analyse wurde erweitert, indem nicht nur Daten von schweizerischen Probenahmestellen sondern auch norditalienische berücksichtigt wurden. Die Analyse zeigt, dass die meisten chemischen Parameter in Regenwasser signifikant mit den geographischen Parametern Breite, Länge und Höhe korrelieren. Sulphat-, Nitrat-, und Ammoniumkonzentrationen korrelieren mit Breite und Höhe und widerspiegeln somit den Transport dieser Schadstoffe von der urbanen Gegend von Mailand und der landwirtschaftlich genutzten Flächen der Po Ebene Richtung Norden. Anders die mit abnehmender jährlicher Niederschlagsmenge zunehmenden mittleren Konzentrationen von basischen Kationen und von Bikarbonat (geringere Verdünnung von basischen Regenereignissen im Jahresdurchschnitt). Diese korrelieren mit der geographischen Länge, weil atmosphärische Strömungen, die Niederschlag verursachen, meistens von Südwesten Richtung Nordosten gerichtet sind. Die Hauptkomponentenanalyse hat auch gezeigt, dass der Säuregehalt am Anfang der Untersuchungsperiode (1988–1992) mit der Breite

korreliert hat, aber nach dieser Periode immer unabhängiger von der Breite und abhängiger von der Länge wurde. Dies zeigt, dass der Säuregehalt in der ersten Zeitperiode hauptsächlich von den SO_2-, NO_x- and NH_3-Emissionen bestimmt wurde, später aber basische Regenereignisse wichtiger geworden sind.

Die in der Haupkomponentenanalyse diskutierte Beziehung der chemischen mit den geographischen Parametern suggerierte die Möglichkeit, ein multiples Regressionsmodell mit den Variablen Breite, Länge und Höhe zu entwickeln, das imstande ist, die Abhängigkeit der Konzentrationen einzelner chemischer Parameter von geographischen Parametern zu beschreiben. Eine multiple lineare Regression wurde für verschiedene Parameter und die 4 Zeitperioden 1988–1992, 1993–1997, 1998–2002, 2003–2007 durchgeführt. Für einige Parameter und Zeitperioden hat die zusätzliche Berücksichtigung der mittleren jährlichen Niederschlagsmenge bessere Resultate ergeben. Basische Kationen, Bikarbonat, der Säuregehalt und der pH-Wert, deren jährliche mittlere Konzentration stark von basischen Regenereignisse beeinflusst wird, konnten nach 1993 besser modelliert werden, wenn die Niederschlagsmenge mitberücksichtigt wurde. Die Regressionsparameter wurden dann benutzt, um die Konzentrationen der wichtigsten chemischen Parameter in Regenwasser im Süden der Schweiz mit einer Auflösung von 1km x 1km zu kartieren.

Die Kartierung der Nasseinträge im Süden der Schweiz erfolgte schlussendlich, indem die Konzentrationskarten mit den Niederschlagskarten der gleichen räumlichen Auflösung multipliziert wurden. Beobachtungen, die für die Konzentration von chemischen Parametern in Regenwasser gemacht worden sind, unterscheiden sich nicht wesentlich von denen des Nasseintrags. Im allgemeinen kann man abnehmende Sulphat- und Säureeinträge und zunehmende Einträge von basischen Kationen und Bikarbonat feststellen. Auch die Abhängigkeit von geographischen Parametern blieb dieselbe. Hingegen hatten die besonders nassen (1998–2002) und trockenen (2003–2007) Perioden erkennbare Auswirkungen auf die Einträge: Einträge von Sulphat, Nitrat und Ammonium waren leicht höher während 1998–2002 im Vergleich zu den unmittelbar vorigen oder späteren Zeitperioden.

Zusätzlich zum Nasseintrag trägt auch der Trockeneintrag von Gasen und Aerosolen zum totalen Säureeintrag bei. Trockeneintragskarten wurden von Meteotest bereitgestellt. Die Summe von Nasseintrag und Trockeneintrag wurde benutzt, um den aktuellen Säureeintrag und die totalen Einträge von Schwefel und Stickstoff zu erstellen.

Da der Nasseintrag am meisten zum totalen Eintrag von Stickstoff (70–77 %) und Säure (68–80 %) beiträgt, sind die zeitlichen Entwicklungen der nassen und totalen Einträge ähnlich. Als Folge der abnehmender Schwefeleinträge hat in den letzten 20 Jahren der Schwefelanteil am totalen Eintrag von versauernder Verbindungen von 42 % auf 26 % abgenommen, während derjenige von Stickstoffverbindungen von 58 % auf 74 % zugenommen hat.

> Riassunto

A causa della particolare meteorologia la qualità dell’aria nel Sud della Svizzera non è soltanto influenzata da emissioni locali ma anche da inquinamento transfrontaliero proveniente dalla Pianura Padana in particolare dalla fortemente inquinata zona urbana di Milano. Inoltre, molti suoli e acque superficiali situati ad altitudini elevate al Sud della Svizzera sono particolarmente sensibili all’acidificazione a causa della presenza di rocce poco basiche con bassa capacità tampone. Conseguentemente, la deposizione acida al Sud della Svizzera è un tema particolarmente importante.

È per questo motivo che a partire dagli anni ottanta al Sud della Svizzera è stata studiata la qualità delle precipitazioni, dapprima a Locarno Monti e a Lugano poi anche presso altre stazioni. Attualmente si raccolgono campioni settimanali presso 9 stazioni distribuite in tutto il Canton Ticino. Un’analisi delle tendenze dei principali parametri chimici presenti nelle precipitazioni ha mostrato che le concentrazioni di solfato sono diminuite riflettendo la diminuzione delle emissioni di SO_2 dopo il 1980. A Locarno Monti e a Lugano le concentrazioni di solfato sono diminuite del 57–66 % durante gli ultimi 20 anni, mentre non è stata riscontrata nessuna tendenza significativa per le concentrazioni di nitrato e ammonio. Le concentrazioni di bicarbonato e di cationi basici sono invece aumentate e sono state particolarmente elevate negli anni 1999, 2000, 2002, quando le precipitazioni erano più elevate e più frequenti del solito. A causa della diminuzione delle concentrazioni di solfato e dell’aumento delle concentrazioni di cationi basici, l’acidità delle precipitazioni è diminuita e il pH è aumentato. Dalla fine degli anni ottanta all’inizio di questo millennio il pH medio delle precipitazioni a Locarno Monti e a Lugano è aumentato da 4,3 a 5,0/5,3 e dopo il 2000 presso la maggior parte delle stazioni di monitoraggio l’acidità media annua è diventata negativa.

Per analizzare le relazioni esistenti tra i dati e i parametri è stata effettuata un’analisi delle componenti principali con le concentrazioni medie dei principali parametri chimici, la conducibilità, il volume delle precipitazioni e i parametri geografici per i periodi 1988–1992, 1993–1997, 1998–2002, 2003–2007. L’analisi è stata estesa considerando non soltanto i dati delle stazioni di misura Svizzere, ma anche quelle situate nel Nord dell’Italia. L’analisi ha mostrato che la maggior parte dei parametri presenti nelle precipitazioni correla in modo significativo con i parametri geografici latitudine, longitudine e altitudine. Le concentrazioni di solfato, nitrato e ammonio correlano con la latitudine e l’altitudine riflettendo il trasporto di questi inquinanti dalla zona urbana di Milano e dalle regioni agricole della Pianura Padana verso il nord. Diversamente, le concentrazioni medie annue di cationi basici e bicarbonato, che aumentano con la diminuzione della precipitazione annua (minor diluizione di precipitazioni alcaline sull’arco di un anno), correlano con la longitudine perchè le correnti atmosferiche che causano precipitazioni sono spesso dirette da sud-ovest verso nord-est. L’analisi delle componenti principali ha pure mostrato che l’acidità correlava con la latitudine all’inizio del periodo di monitoraggio (1988–1992), ma è diventata sempre più indipendente dalla latitudine e dipendente dalla longitudine dopo il 1998–2002. Ciò indica

che durante il primo periodo temporale l'acidità era principalmente determinata dalle emissioni di SO_2, NO_x and NH_3, mentre successivamente sono diventati sempre più importanti eventi di precipitazioni alcaline.

La distribuzione dei parametri chimici presenti nelle precipitazioni discussa nell'analisi delle componenti principali ha suggerito la possibilità di sviluppare un modello di regressione multipla con le variabili latitudine, longitudine e altitudine, capace di descrivere la distribuzione geografica delle concentrazioni di singoli parametri chimici nelle precipitazioni. L'analisi di regressione multipla è stata effettuata per diversi parametri e 4 periodi temporali 1988–1992, 1993–1997, 1998–2002, 2003–2007. Per alcuni parametri e periodi temporali l'aggiunta della precipitazione media annua come variabile di regressione ha dato risultati migliori. In particolare, parametri come i cationi basici, il bicarbonato, l'acidità e il pH, la cui concentrazione media annua è fortemente influenzata da sporadici eventi di piogge alcaline, sono modellizzati meglio dopo il 1993, se anche il volume delle precipitazioni viene considerato. I parametri di regressione sono poi stati utilizzati per creare le mappe delle precipitazioni dei principali parametri chimici sopra il Sud della Svizzera con una risoluzione di 1 km x 1 km.

Infine le mappe delle deposizioni umide state create moltiplicando le mappe delle concentrazioni dei parametri chimici presenti nelle precipitazioni con le mappe delle precipitazioni. Le osservazioni fatte per le concentrazioni dei parametri chimici nelle precipitazioni non differiscono molto da quelle fatte per le deposizioni umide. In generale, le tendenze temporali che si possono osservare sono una diminuzione delle deposizioni di solfato e di acidità ed un aumento delle deposizioni di cationi basici e di bicarbonato. Anche la dipendenza delle variabili chimiche dai parametri geografici è la medesima. Tuttavia, anni particolarmente ricchi (1998–2002) o poveri di precipitazioni (2003–2007) influiscono sulle deposizioni: le deposizioni di solfato, nitrato e ammonio erano leggermente più alte durante il periodo 1998–2002 confrontate con i periodi temporali immediatamente precedenti o successivi.

Accanto alle deposizioni umide anche le deposizioni secche di gas e di aerosol contribuiscono alla deposizione acida totale. Le mappe delle deposizioni secche sono state preparate da Meteotest. Sommando le mappe delle deposizioni umide e secche è possibile creare le mappe del carico attuale di acidità e delle deposizioni totali di zolfo e azoto.

Siccome le deposizioni umide rappresentano la parte dominante delle deposizioni di azoto totale (70–77 %) e del carico attuale di acidità (68–80 %), la tendenza temporale delle deposizioni umide e totali è simile. A causa della riduzione delle deposizioni di zolfo, durante gli ultimi 20 anni l'importanza relativa delle componenti di zolfo nella deposizione totale di componenti acidificanti è diminuita da 42 % a 26 %, mentre è aumentata quella dell'azoto da 58 % a 74 %.

> Introduction

Definition of acidifying deposition

“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 intensification 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.

Effects of acidifying deposition

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.

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 or volatile organic compounds.

Convention on Long-range Transboundary Air Pollution

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. 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 in some countries also of nitrogen oxides (Vestreng 2003) has been achieved over the last 20–25 years leading to an improved quality of atmospheric deposition. The decrease in sulphate deposition and therefore also in the deposition of acidity has been observed at many European sites (Schöpp et al. 2003).

Emissions of acidifying compounds in Switzerland

Figure 1.1 shows the emissions of sulphur dioxide, of nitrogen oxides and of ammonia in Switzerland from 1900 to 2010. The sulphur dioxide and nitrogen oxides emissions started to increase steeply after the second world war. Sulphur dioxide reached its maximum between 1965 and 1980, while nitrogen oxides peaked around 1985. Afterwards, both sulphur and nitrogen oxides decreased continuously until 2000. 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 heating oils 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 DeNOx-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.

Aims of the report

Barbieri and Pozzi (2001) and Barbieri et al. (2004) studied acidifying deposition in southern Switzerland during the period of 1993–1998. The objective of this report is to assess acidifying deposition in southern Switzerland as done by Barbieri and Pozzi (2001), but over four different periods (1988–1992, 1993–1997, 1998–2002, 2003–2007), and to discuss changes in deposition over the last 20 years. In particular, the aims of this report are:

Rainwater quality trends

- to describe rainwater quality at different sampling stations in southern Switzerland from 1988 to 2007;
- to calculate temporal trends for the main chemical parameters present in rainwater involved in the process of acidification;

Principal component analysis

- to perform a principal component and factor analysis including Swiss and closed-by Italian sites in order to highlight changes in similarities and differences among chemical and geographic parameters and sampling stations through four different periods (1988–1992, 1993–1997, 1998–2002, 2003–2007);

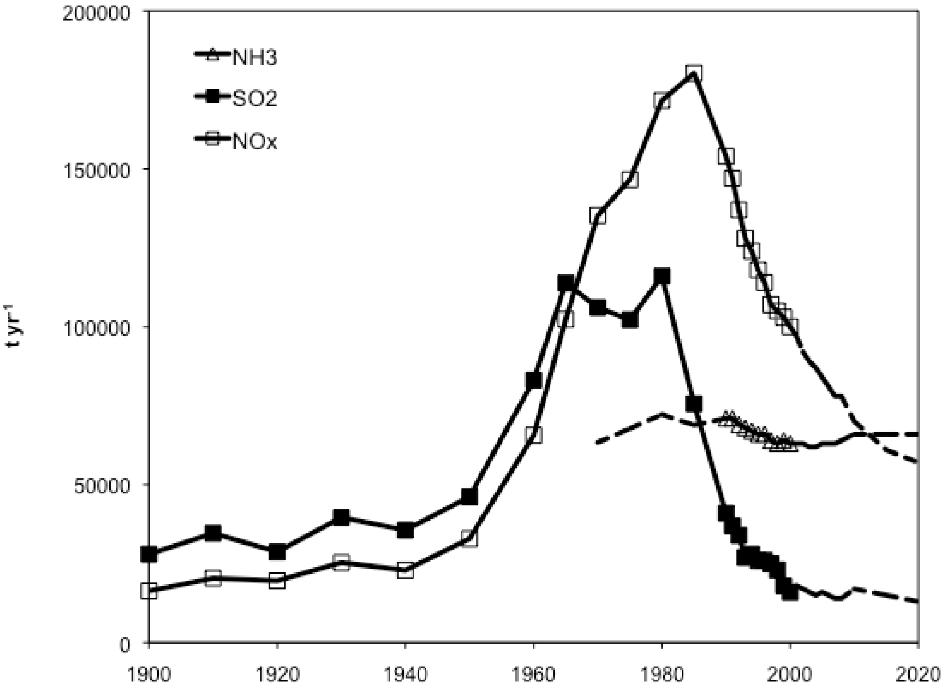
- to map concentrations in precipitation and wet deposition of the main chemical parameters for southern Switzerland for the last 4 five-years periods with the aid of multiple regression analysis between chemical and geographic parameters and precipitation amounts;
- to map the total deposition by adding up wet and dry deposition, the latter being modeled by Meteotest.

Concentrations maps of precipitation through multiple linear regression analysis

Total deposition

Fig. A > Annual sulphur dioxide, nitrogen oxides and ammonia emissions in Switzerland from 1900 to 2010

Dashed lines indicate estimate values.



Source: Künzler, 2005.

1 > Wet deposition

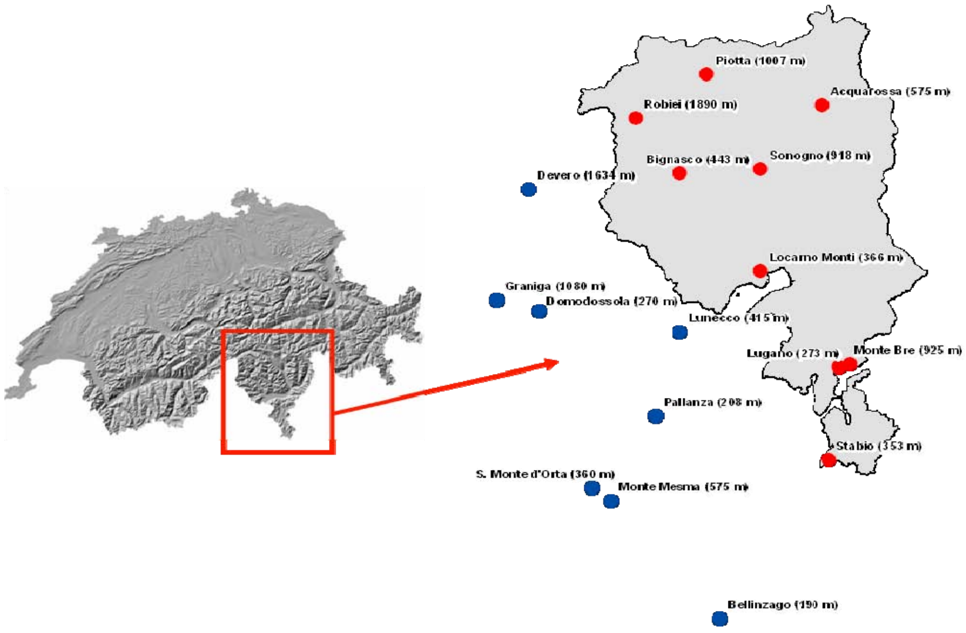
1.1 Sampling sites

Description of rainwater 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 discussion (data have been provided by the Institute of Ecosystem Study in Pallanza, Italy). The geographic distribution of the sampling sites and their geographic coordinates are shown in Figure 1.1 and respectively Table 1.1.

Fig. 1.1 > Study area with wet deposition sampling points

Swiss: red, Italian: blue.



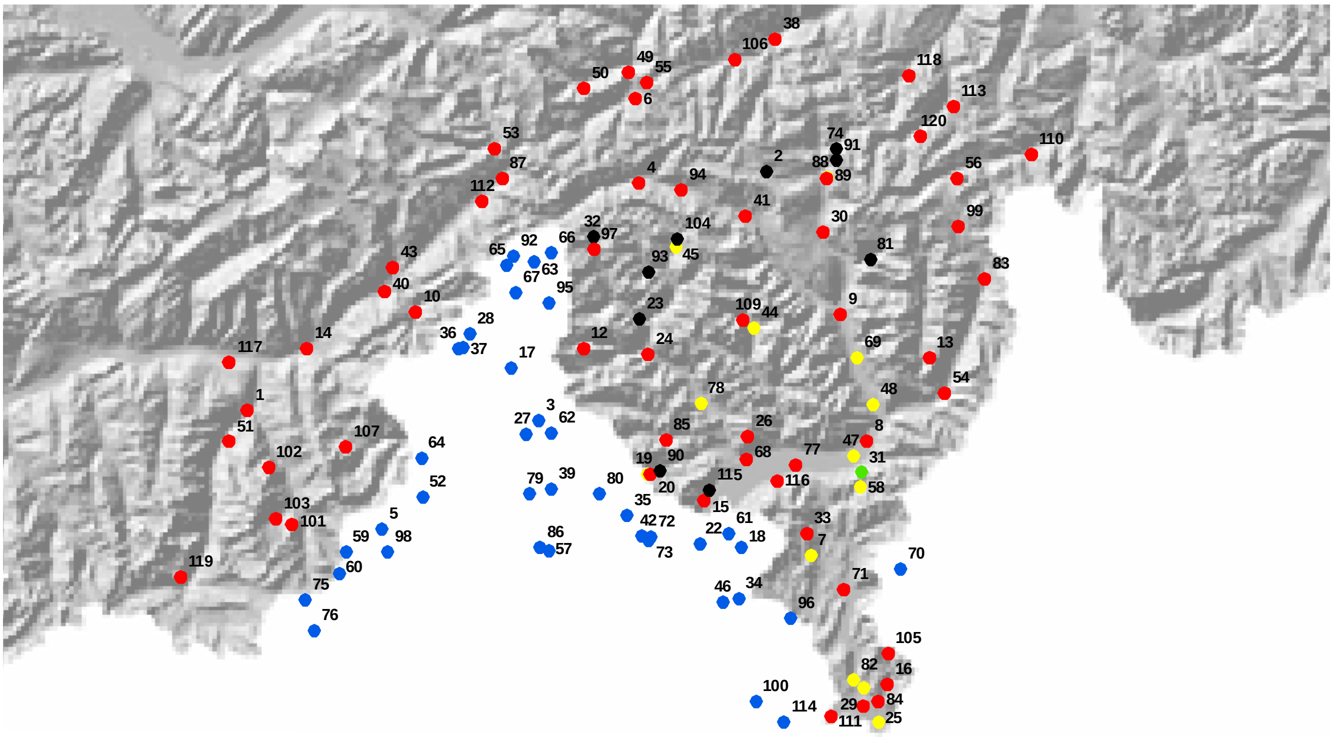
Tab. 1.1 > Swiss (CH) and Italian (I) wet deposition sampling sites and their geographic (WGS84) and Swiss (CH1903) coordinates, altitudes and sampling years

Sampling site	WGS84		CH1903 (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, 1993–2007
Bignasco (CH)	46°00’32’’	8°59’17’’	132257	690205	443	2001–2005
Locarno Monti (CH)	46°10’27’’	8°47’17’’	114350	704160	366	1982–1985, 1988–1991, 1993–2007
Lugano (CH)	46°00’24’’	8°57’18’’	95870	717880	273	1982–1985, 1989–1991, 1993–2007
Monte Brè (CH)	46°00’32’’	8°59’17’’	96470	719900	925	1995–2007
Piotta (CH)	46°31’7’’	8°40’35’’	152500	694930	1007	1990–1991, 1993–2007
Robiei (CH)	46°26’43’’	8°30’51’’	143984	682540	1890	1996–2007
Sonogno (CH)	46°21’05’’	8°47’14’’	134150	704250	918	2001–2007
Stabio (CH)	45°51’36’’	8°55’52’’	77970	716040	353	1990–1991, 1993–2007
Bellinzago (I)	45°34’27”	8°41’31”	47245	697217	190	1989–2007
Devero (I)	46°19’19”	8°16’29”	130156	664132	1634	1996–2007
Domodossola (I)	46°06’42”	8°17’41”	106767	665875	270	1986–2007
Graniga (I)	46°07’52”	8°11’59”	108936	658342	1080	1994–2007
Lunecco (I)	46°04’28”	8°36’39”	102774	690264	415	1989–2007
Monte Mesma (I)	45°46’43”	8°26’38”	70166	678202	575	2003–2007
Pallanza (I)	45°55’42”	8°34’48”	86386	686003	208	1985–2007
S. Monte d’Orta (I)	45°48’13”	8°24’41”	72547	674929	360	1990–1999

Yearly precipitation from 118 precipitation sampling sites were used to estimate the amount of precipitation over southern Switzerland. Swiss data originated from 3 different precipitation monitoring networks: the Federal Office of Meteorology and Climatology (MeteoSwiss), the Institute of Earth Sciences of Canton Ticino (IST) and the hydroelectric power production company “Officine Idroelettriche della Maggia e di Blenio SA” (Ofima/Ofible). 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). The geographic distribution of the precipitation sampling sites and their geographic coordinates are shown in Figure 1.2 and respectively Table 1.2.

Fig. 1.2 > Precipitation sampling sites

Swiss sites: red (MeteoSwiss), yellow (IST), black (Ofima/Ofible), green (WSL); Italian sites: blue (ISE).



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Tab. 1.2 > Swiss (CH) and Italian (I) precipitation sampling sites and their Swiss coordinates (CH1903), altitudes and data source

N°	Sampling site	Longitude (m)	Latitude (m)	Altitude (m a.s.l.)	Data source
1	Ackersand Stalden (CH)	633625	121160	700	MeteoSwiss
2	Acquacalda (CH)	706900	155040	1762	Ofima/Ofible
3	Agrasina (I)	674745	119767	1370	ISE
4	Airolo (CH)	688910	153400	1139	MeteoSwiss
5	Media Alpe Cheggio e Lago Alpe dei Cavalli (I)	652542	104389	1510	ISE
6	Andermatt (CH)	688500	165340	1442	MeteoSwiss
7	Arosio (CH)	713130	100610	860	IST
8	Bellinzona (CH)	721080	116840	225	MeteoSwiss
9	Biasca (CH)	717440	134850	291	MeteoSwiss
10	Binn (CH)	657485	135080	1415	MeteoSwiss
11	Blatten (Loetschen) (CH)	629400	140975	1535	MeteoSwiss
12	Bosco Gurin (CH)	681160	130025	1505	MeteoSwiss
13	Braggio (CH)	729975	128600	1320	MeteoSwiss
14	Brig (CH)	642090	129920	671	MeteoSwiss
15	Brissago (CH)	698200	108390	280	MeteoSwiss

N°	Sampling site	Longitude (m)	Latitude (m)	Altitude (m a.s.l.)	Data source
16	Bruzella (CH)	724090	82490	620	MeteoSwiss
17	Cadarese (I)	670854	127200	725	ISE
18	Cadero Veddasca (I)	703345	101845	570	ISE
19	Camedo (CH)	690050	112220	570	IST
20	Camedo (CH)	690600	112185	550	MeteoSwiss
21	Campo V. Maggia (CH)	681580	126820	1280	IST
22	Cannobio (I)	697590	102307	220	ISE
23	Cavergno Centrale (CH)	688980	134080	535	Ofima/Ofible
24	Cevio (CH)	690300	129200	418	MeteoSwiss
25	Chiasso (CH)	722690	77090	240	IST
26	Cimetta (CH)	704370	117515	1672	MeteoSwiss
27	Cipata (I)	672928	117757	937	ISE
28	Codelago (I)	665032	132105	1885	ISE
29	Coldrerio (CH)	720725	79400	345	MeteoSwiss
30	Comprovasco (CH)	714998	146440	575	MeteoSwiss
31	Copera (CH)	720318	112564	665	WSL
32	Cortino (CH)	682490	145790	2222	Ofima/Ofible
33	Crana-Torricella (CH)	712660	103750	1002	MeteoSwiss
34	Creva (I)	702978	94580	233	ISE
35	Cursolo O. (I)	687167	106379	940	ISE
36	Devero (I)	663437	130029	1640	ISE
37	Devero (I)	664132	130156	1634	ISE
38	Disentis (CH)	708200	173800	1190	MeteoSwiss
39	Druogno (I)	676542	110025	831	ISE
40	Ernen (CH)	653150	138000	1000	MeteoSwiss
41	Faido (CH)	704060	148750	760	MeteoSwiss
42	Falmenta (I)	689311	103417	662	Falmenta (I)
43	Fieschertal (CH)	654200	141350	1095	Fieschertal (CH)
44	Frasco (CH)	705180	132790	890	IST
45	Fusio (CH)	694090	144380	1300	IST
46	Germignaga (I)	700780	93993	203	ISE
47	Giubiasco (CH)	719130	114800	215	IST
48	Gnosca (CH)	721940	121960	247	IST
49	Göschenen (CH)	687580	169080	1100	MeteoSwiss
50	Göschener Alp (CH)	681250	166790	1745	MeteoSwiss
51	Grächen (CH)	631070	116850	1550	MeteoSwiss
52	Graniga (I)	658342	108936	1080	ISE
53	Grimsel (CH)	668580	158210	1980	MeteoSwiss
54	Grono (CH)	732100	123700	382	MeteoSwiss
55	Gütsch ob Andermatt (CH)	690140	167590	2287	MeteoSwiss
56	Hinterrhein (CH)	733900	153980	1611	MeteoSwiss
57	In la Piana (I)	676148	101312	960	ISE
58	Isone (CH)	720180	110320	810	IST
59	Lago Camposecco (I)	647518	101230	2325	ISE

N°	Sampling site	Longitude (m)	Latitude (m)	Altitude (m a.s.l.)	Data source
60	Lago Cingino (I)	646550	98052	2250	ISE
61	Lago Delio (I)	701638	103711	835	ISE
62	Lago Larecchio (I)	676532	118036	1840	ISE
63	Lago Morasco (I)	674133	142300	1820	ISE
64	Lago Paione Superiore (I)	658173	114318	2269	ISE
65	Lago Sabbione (I)	670241	141772	2462	ISE
66	Lago Toggia (I)	676509	143491	2170	ISE
67	Lago Vannino (I)	671502	137905	2175	ISE
68	Locarno Monti (CH)	704160	114350	366	MeteoSwiss
69	Lodrino (CH)	719710	128590	275	IST
70	Loggio Valsolda (I)	725804	98721	380	ISE
71	Lugano (CH)	717880	95870	273	MeteoSwiss
72	Lunecco (I)	690584	103326	415	ISE
73	Lunecco (I)	690264	102774	415	ISE
74	Media Luzzone Diga (CH)	716690	158210	1601	Ofima/Ofible
75	Macugnaga Moos (I)	641807	94400	2820	ISE
76	Macugnaga Fornarelli (I)	643107	90048	1185	ISE
77	Magadino (CH)	711170	113542	197	MeteoSwiss
78	Maggia (CH)	697620	122190	327	IST
79	Maglietto (I)	673509	109346	657	ISE
80	Malesco (I)	683345	109433	700	ISE
81	Malvaglia sotto Diga (CH)	721560	142600	938	Ofima/Ofible
82	Mendrisio (CH)	719210	83000	290	IST
83	Mesocco (CH)	737850	139825	830	MeteoSwiss
84	Morbio Superiore (CH)	722825	80075	480	MeteoSwiss
85	Mosogno (CH)	692800	117040	780	MeteoSwiss
86	Mottac (I)	674937	101849	1695	ISE
87	Oberwald (CH)	669650	154050	1375	MeteoSwiss
88	Olivone (CH)	715410	154120	930	IST
89	Olivone (CH)	715440	154050	905	MeteoSwiss
90	Palagnedra (CH)	691900	112620	498	Ofima/Ofible
91	Passo Muaz (CH)	716840	156680	1701	Ofima/Ofible
92	Piano dei Camosci (I)	671149	143105	2450	ISE
93	Piano di Peccia (CH)	690200	140750	1019	Ofima/Ofible
94	Piotta (CH)	694930	152500	1007	MeteoSwiss
95	Ponte Formazza (I)	676170	136425	1300	ISE
96	Ponte Tresa (I)	710332	91758	274	ISE
97	Robiei (CH)	682600	144075	1898	MeteoSwiss
98	Rovesca (I)	653421	101212	760	ISE
99	S. Bernardino (CH)	734120	147270	1639	MeteoSwiss
100	S. Maria del Monte (I)	705398	80056	881	ISE
101	Saas Almagell (CH)	640030	104990	1680	MeteoSwiss
102	Saas Balen (CH)	636710	113210	1355	MeteoSwiss
103	Saas Fee (CH)	637720	105850	1790	MeteoSwiss

N°	Sampling site	Longitude (m)	Latitude (m)	Altitude (m a.s.l.)	Data source
104	Sambuco (CH)	694300	145540	1521	Ofima/Ofible
105	Scudellate (CH)	724125	86800	904	MeteoSwiss
106	Sedrun (CH)	702480	170825	1450	MeteoSwiss
107	Simplon Dorf (CH)	647570	116110	1495	MeteoSwiss
108	Somazzo (CH)	720600	81930	580	IST
109	Sonogno (CH)	703640	134050	925	MeteoSwiss
110	Splügen-Dorf (CH)	744420	157435	1460	MeteoSwiss
111	Stabio (CH)	716040	77970	353	MeteoSwiss
112	Ulrichen (CH)	666740	150760	1345	MeteoSwiss
113	Vals (CH)	733340	164260	1253	MeteoSwiss
114	Varese (I)	709409	77093	410	ISE
115	Verbano Centrale (CH)	698900	109840	213	Ofima/Ofible
116	Vira Gambarogno (CH)	708450	111220	210	MeteoSwiss
117	Visp (CH)	631150	128020	640	MeteoSwiss
118	Vrin (CH)	727160	168560	1460	MeteoSwiss
119	Zermatt (CH)	624300	97575	1638	MeteoSwiss
120	Zervreila (CH)	728780	160000	1738	MeteoSwiss

1.2 Analytics

1.2.1 Chemical analysis

Rain samples were analyzed for pH, alkalinity, conductivity and the main cations and anions. Parameters, analytical methods and quantification limits are shown in Table Tab. 1.3.

Tab. 1.3 > Measured parameters, analytical methods, accuracy and quantification limits

Parameter	Filtration	Method	Accuracy	Quantification limit
pH	No	potentiometry	0.02	
conductivity	No	Kolrausch bridge (20 °C)	0.5 µS cm^{-1}	
alkalinity	No	potentiometric Gran titration	0.001 meq l^{-1}	
Ca^{2+}	CA filter	ion chromatography		0.010 mg l^{-1}
Mg^{2+}	CA filter	ion chromatography		0.005 mg l^{-1}
Na^{+}	CA filter	ion chromatography		0.005 mg l^{-1}
K^{+}	CA filter	ion chromatography		0.010 mg l^{-1}
NH_4^{+}	CA filter	spectrophotometry		3 µg N l^{-1}
SO_4^{2+}	CA filter	ion chromatography		0.005 mg l^{-1}
NO_3^{-}	CA filter	ion chromatography		0.010 mg N l^{-1}
NO_2^{-}	CA filter	spectrophotometry		1 µg N l^{-1}
Cl^{-}	CA filter	ion chromatography		0.010 mg l^{-1}

1.2.2 Data quality control

The quality of the data was assured by regular participation in 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 Forests (UNECE 2009).

1.3 Concentrations of chemical parameters in wet deposition of southern Switzerland from 1988 to 2007

Fig. 1.3 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 2007. The corresponding data are tabulated in Appendix A1. Yearly mean concentrations were calculated by weighting weekly concentrations with the sampled precipitation volume:

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

$C(X)_a$ = annual mean concentration of compound X
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

Concentrations of sulphate, nitrate and ammonia higher at southern and lower sampling stations because of transboundary air pollution from Po Plain

In general, ion concentrations of anthropogenic origin (sulphate, nitrate, ammonium) are highest at sampling sites with low altitudes and latitudes such as Lugano and Stabio and lowest at sites with high altitude and latitudes such as 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, while the decrease of concentrations with altitude reflects both the pollutants gradient from south towards north and the decrease of anthropogenic pollutants with altitude. Concentrations of bicarbonate increase with the number and intensity of alkaline rain events during the year and decrease with the amount of annual precipitation.

Concentrations of bicarbonate and base cations lower at sampling stations with high annual precipitation because of dilution of alkaline rain events

Therefore high concentrations of bicarbonate are often found at stations with low annual precipitation such as Lugano, Stabio and Acquarossa. Similar results are obtained for the concentration of base cations. With regard to acidity (calculated as the difference between the concentration of H^+ and HCO_3^-), the lowest values are these days measured at Lugano, Stabio and Acquarossa where the concentrations of base cations and bicarbonate are highest. Interestingly, before 2003 Lugano and Stabio were characterized by the highest concentrations of acidity due to the highest concentrations of acidifying pollutants such as sulphate and nitrate. The same scenario is reflected in pH values. Before 2003 Lugano and Stabio were characterized by low pH values, afterwards at these stations, beside Acquarossa, the highest pH values were measured. This indicates that important changes in chemistry must have occurred during the observation period.

Decrease of sulphate concentrations because of SO_2 emissions reduction after 1980

For some parameters temporal trends exist. Sulphate concentrations decreased, reflecting the decrease in sulphur dioxide emissions after 1980. At Locarno Monti and Lugano sulphate concentrations decreased by around 57–66 % between 1988 and 2007. On the contrary, no significant trend can be observed for ammonium and nitrate concentrations. Chloride concentrations also decreased during the monitoring period, even though the reason is not fully clear. In general, literature from sea-close countries describes the years from 1988 to 1992 as a period with particularly intensive storms, with numerous sea-salt episodes leading to increased deposition of chloride (Evans and Monteith 2001). Although southern Switzerland is situated far from the sea it is possible that chloride concentrations in this region's precipitation were also somehow influenced by this phenomenon. Another reason could as well consist in the increasing control of hydrochloric acid emissions from waste incineration plants, coal-fired power plants and from the chemical industry.

Increase of concentration of bicarbonate and base cations because of increase in number of alkaline rain events and decreased capacity of rainwater to "neutralize" bases

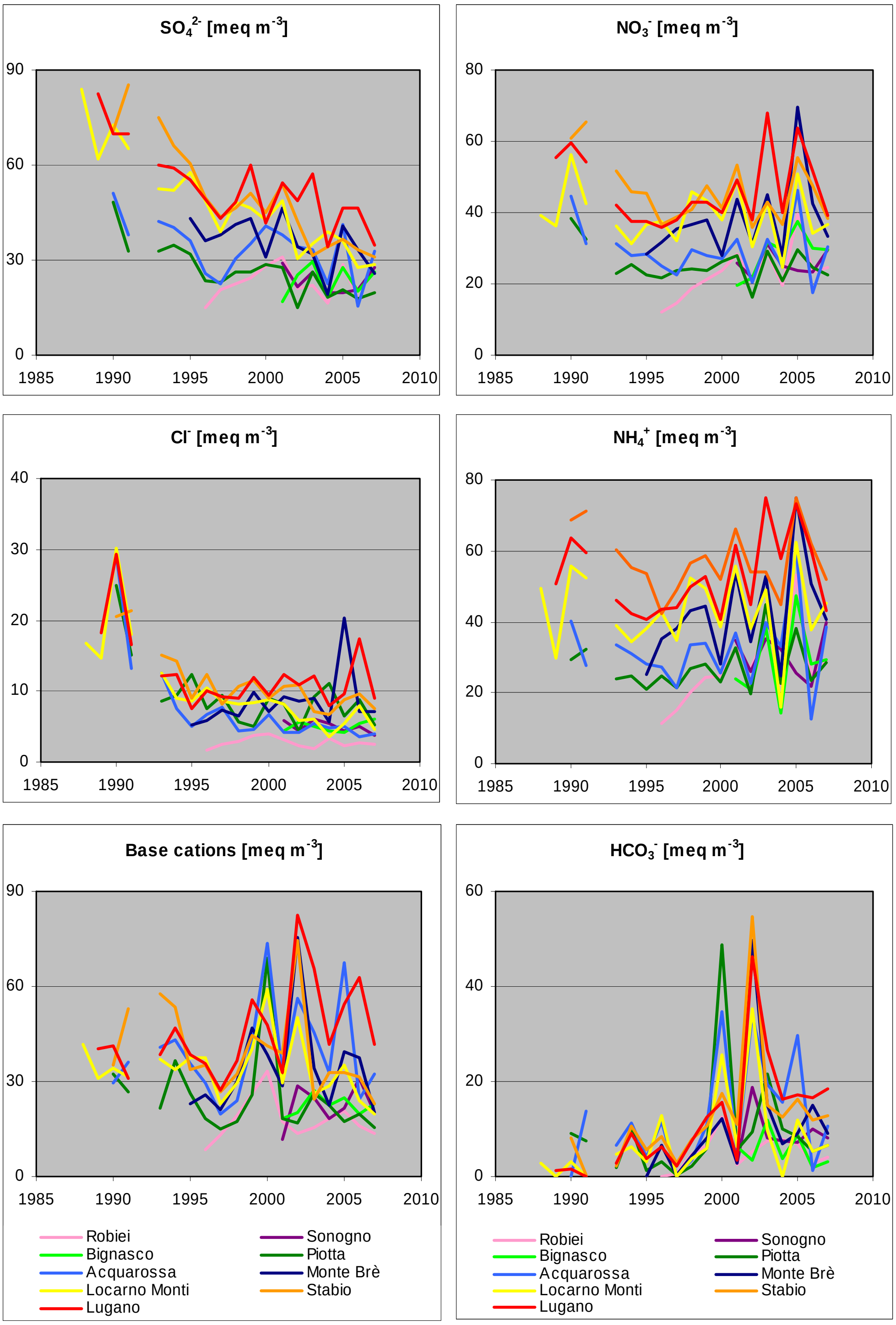
Interestingly, mean annual bicarbonate concentrations increased during the monitoring period and were particularly high during the years 1999, 2000 and 2002, when precipitation was higher than usual. A similar trend can be observed for base cations. This is consistent with the descriptions of Rogora et al. (2004), who observed an increased frequency of alkaline rain events especially during the last decade, many of them caused by the deposition of Saharan dust. It is possible that rain rich years increase the chance of the occurrence of alkaline rain events. In addition, the reduction of sulphate concentrations over the last 2 decades lowered the capacity of rainwater to neutralize alkaline rain events, making them more observable in rainwater chemistry. So far it has not been investigated if climate change may also influence the occurrence of alkaline rain events by increased long distance transport of dust.

Increase of acidity and decrease of pH

To sum up, decreasing sulphur emissions and an increasing number of alkaline rainfall events generated a decrease of acidity and thus an increase of the pH value. Since the end of the eighties until the beginning of this millennium the mean annual pH values of rainwater at Locarno Monti and Lugano increased from 4.3 to 5.0/5.3. After 2000, at most sites the mean yearly acidity turned to negative values.

Fig. 1.3 > Mean annual concentrations in wet deposition at the sampling sites Acquarossa, Bignasco, Locarno Monti, Lugano, Monte Brè, Piotta, Robiei, Sonogno and Stabio

Base cations are defined as the sum of calcium, magnesium and potassium.



1.4 Trends in rainwater quality

1.4.1 Statistical methods

Trend analyses were performed on the key variables involved in acidification: sulphate, nitrate, chloride, bicarbonate, ammonium, base cations (sodium, potassium, magnesium, calcium), H^+ and acidity. For each site and each parameter the mean monthly concentrations weighted with the precipitation volume were calculated and the seasonal Mann-Kendall test was used to detect temporal trends (Hirsch et al. 1982). The two-sided test for the null hypothesis with no present trend was rejected for p-values below 0.05. To quantify temporal trends the Sen's method was used (Sen 1968), but instead of a median slope a mean slope was calculated. The reason for that, especially for parameters related to alkaline rain events (bicarbonate, base cations), is due to the observed trends being not related to a general increase/decrease of concentrations over time during each event, but to an increase/decrease of the number of events with increased/decreased concentrations. A median trend would therefore underestimate the increase/decrease of average concentrations over time.

1.4.2 Results from trend analyses

Results from trend analysis confirm observations made in former paragraph

Results from trend analyses confirm the qualitative observations made in the former chapter (Tab. 1.4). At most sampling sites significant decreasing trends for concentrations of sulphate, chloride, H^+, acidity and increasing trends for bicarbonate can be observed, while no generalized significant trends for nitrate, ammonium and base cations appear. Sulphate trends are insignificant at stations where sulphate concentrations are already small (Acquarossa, Piotta). Trends of chloride concentrations are insignificant at Robiei and Monte Brè, probably because at both sites sampling started after 1994, therefore it does not include the period with high chloride concentrations (1989–1991). With exception of Robiei, trends for bicarbonate, hydrogen ion and acidity are significant at all sites. The absence of a response in Robiei is probably due to both its location (high latitude and altitude) causing small ion concentrations and to its short monitoring period (since 1996). Slopes of hydrogen ion trends ranges from -1.5 to -3.5 meq m^{-3} yr^{-1}, corresponding to pH changes of + 0.06 up to + 0.08 per year or + 0.6 up to + 0.8 per decade. Since acidity can be expressed as the difference between acid anions' and cations' concentrations (Acy = AA–C) and can be approximated as the difference between hydrogen ions' and bicarbonate's concentrations ($Acy = H^+ - HCO_3^-$), the calculated variation in concentrations over time (=trend) can also be expressed by these equations. In fact, acidity trends obtained from the above mentioned equations correspond very well with results from the Sen's statistic (bottom of Tab. 1.4). At sampling sites with a significant acidity trend, the variation of concentrations with time ranges between -1.8 and -4.5 meq m^{-3} yr^{-1}.

Tab. 1.4 > Results from trend analyses (significant trends in red) performed on mean monthly concentrations weighted with the precipitation volume

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	Monte Brè	Locarno Monti	Lugano	Piotta	Robiei	Stabio
Period		1990–2007	1995–2007	1988–2007	1989–2007	1990–2007	1996–2007	1990–2007
Number of data		183	132	203	195	198	138	186
SO_4^{2-}	p	0.168	0.003	0.000	0.000	0.000	0.278	0.000
	trend	-1.18	-2.63	-3.38	-2.78	-1.87	-0.75	-6.33
NO_3^-	p	0.562	0.259	0.168	0.922	0.007	0.052	0.328
	trend	-0.92	-0.04	-0.97	-0.57	-0.96	0.78	-1.32
Cl^-	p	0.002	0.824	0.000	0.018	0.007	0.061	0.006
	trend	-0.89	0.40	-0.89	-0.49	-0.62	-0.10	-0.96
HCO_3^-	p	0.003	0.039	0.001	0.000	0.008	0.479	0.000
	trend	0.97	0.70	0.57	0.99	0.24	0.10	0.69
NH_4^+	p	0.316	0.222	0.704	0.092	0.914	0.101	0.439
	trend	-0.29	-0.42	-0.60	0.49	-0.53	0.85	-1.24
Base cations	p	0.468	0.637	0.006	0.501	0.007	0.402	0.004
	trend	0.03	0.47	-1.61	0.44	-1.39	-0.59	-4.99
H^+	p	0.000	0.001	0.000	0.000	0.000	0.166	0.000
	trend	-2.13	-1.49	-2.92	-3.49	-1.58	-0.27	-1.58
Acidity	p	0.000	0.005	0.000	0.000	0.000	0.160	0.000
	trend	-3.10	-2.19	-3.49	-4.98	-2.53	-0.37	-2.27
Acidity = H^+- HCO_3^-	trend	-3.10	-2.19	-3.49	-4.98	-2.53	-0.37	-2.27
Acidity = AA-C	trend	-3.73	-2.32	-3.03	-4.77	-1.98	-0.33	-2.38

1.5

Principal component analysis (PCA)

1.5.1

Principles of PCA

Smith (2002) defines the principle component analysis (PCA) as "a way of identifying patterns in data, and expressing the data in such a way so to highlight similarities and differences amongst these. Since patterns can be hard to be found in high values data, where the luxury of graphical representation is not available, PCA is a powerful tool for analyzing data. Another main advantage of PCA consists in the opportunity of compressing these patterns by reducing the number of dimensions, without much loss of information."

Description of principal component analysis

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. In this study only 2 components were employed each time. 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.

Very useful is also the extraction of factor scores for each sampling site (one for every chosen component). 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 time periods: 1988–1992, 1993–1997, 1998–2002 and 2003–2007. For the analysis the statistic software SPSS was used.

PCA performed over 4 time periods 1988–1992, 1993–1997, 1998–2002, 2003–2007

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. 1.1 (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. To estimate precipitation volumes at Swiss sites, 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. Data used for the analysis are reported in Appendix A2 (black figures only).

1.5.2 Results from PCA

Tab. 1.5 shows the correlation matrices for 4 different periods reporting the correlation coefficients *r* between couples of variables. *r* can range between -1 and 1. The absolute value indicates the strength and the sign refers to the direction of the correlation. Red numbers refer to statistically significant correlations ($p < 0.05$, F-test). From a closer look at the table it immediately appears that a significant correlation exists between most variables, especially in the periods of 1993–1997, 1998–2002 and 2003–2007. In the first period there are fewer significant correlations, probably due to the smaller amount of data. In fact, between 1988 and 1992 only 4 of the actually 9 Swiss rain sampling stations existed and less than five years were sampled. It is interesting to look at the correlations between the chemical and geographic parameters.

Chemical parameters correlate with geographic parameters latitude, longitude and altitude

Most chemical parameters in rainwater correlate significantly with one or more of the geographic parameters latitude, longitude and altitude. The 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 ammonia emissions from the agricultural areas situated in the Po Plain. As in southern Switzerland altitude correlates with latitude, most chemical parameters that correlate with latitude correlate with altitude, too. Therefore, behind the correlation with altitude does lie again the pollution gradient from the urban area of Milan toward the Alps. However, this might not be the only reason. The decrease of local pollution sources from low altitude to high altitude and the atmospheric stratification process (thermic inversion) also influence chemical concentrations in rainwater. With longitude only base cations and bicarbonate correlate significantly. This positive correlation is probably due to the decrease of precipitation with longitude. Lower mean annual precipitation results in smaller dilution of single alkaline rain events on an annual base. Unfortunately, Tab. 1.5 does not display any correlation between precipitation and longitude. However, by calculating the correlation of annual mean precipitation with the geographic parameters latitude, longitude and altitude for the 4 periods of 1988–1992, 1993–1997, 1998–2002 and 2003–2007, considering data from all 35 precipitation sampling stations situated in Canton Ticino (Tab. 1.2), a significant correlation between precipitation and longitude appears for all the 4 periods (Tab. 1.6).

Tab. 1.5 > PCA correlation matrix for 16 wet deposition sampling stations

Red numbers indicate significant correlations.

	Long.	Lat.	Alt.	Prec.	Cond.	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	HCO_3^{-}	NO_3^{-}	SO_4^{2-}	Cl^{-}	Acidity
1988–1992																
Long.	1.00															
Lat.	0.16	1.00														
Alt.	0.13	0.79	1.00													
Prec.	-0.10	0.14	-0.02	1.00												
Cond.	0.18	-0.85	-0.64	-0.15	1.00											
pH	-0.39	0.43	0.48	-0.08	-0.74	1.00										
Ca^{2+}	0.40	-0.66	-0.40	-0.51	0.85	-0.61	1.00									
Mg^{2+}	0.78	-0.33	-0.33	-0.28	0.63	-0.62	0.75	1.00								
Na^{+}	0.90	0.21	0.30	-0.20	0.21	-0.36	0.43	0.79	1.00							
K^{+}	0.80	0.03	0.13	-0.23	0.32	-0.45	0.49	0.84	0.94	1.00						
NH_4^{+}	0.13	-0.91	-0.60	-0.18	0.96	-0.55	0.82	0.54	0.13	0.22	1.00					
HCO_3^{-}	-0.03	0.41	0.75	-0.38	-0.42	0.69	-0.12	-0.31	0.09	-0.10	-0.26	1.00				
NO_3^{-}	0.32	-0.81	-0.51	-0.26	0.95	-0.62	0.87	0.72	0.37	0.48	0.96	-0.26	1.00			
SO_4^{2-}	0.27	-0.83	-0.68	-0.09	0.97	-0.81	0.85	0.68	0.24	0.36	0.91	-0.54	0.91	1.00		
Cl^{-}	0.90	0.36	0.40	-0.22	0.08	-0.37	0.37	0.67	0.94	0.82	-0.02	0.14	0.20	0.14	1.00	
Acidity	0.23	-0.55	-0.70	0.16	0.77	-0.95	0.53	0.58	0.18	0.31	0.59	-0.83	0.62	0.83	0.14	1.00
1993–1997																
Long.	1.00															
Lat.	-0.10	1.00														
Alt.	-0.34	0.65	1.00													
Prec.	-0.34	0.28	0.44	1.00												
Cond.	0.12	-0.88	-0.82	-0.26	1.00											
pH	0.08	0.88	0.65	0.25	-0.91	1.00										
Ca^{2+}	0.63	-0.49	-0.82	-0.52	0.61	-0.40	1.00									
Mg^{2+}	0.81	-0.28	-0.62	-0.47	0.38	-0.17	0.92	1.00								
Na^{+}	0.51	-0.62	-0.81	-0.38	0.77	-0.54	0.88	0.79	1.00							
K^{+}	0.05	-0.54	-0.82	-0.21	0.66	-0.54	0.72	0.45	0.60	1.00						
NH_4^{+}	0.29	-0.88	-0.81	-0.30	0.96	-0.80	0.76	0.57	0.88	0.68	1.00					
HCO_3^{-}	0.52	-0.29	-0.72	-0.53	0.44	-0.23	0.91	0.79	0.72	0.72	0.58	1.00				
NO_3^{-}	0.31	-0.88	-0.84	-0.36	0.97	-0.83	0.76	0.57	0.87	0.67	0.99	0.58	1.00			
SO_4^{2-}	0.39	-0.83	-0.86	-0.33	0.92	-0.78	0.83	0.68	0.90	0.72	0.98	0.63	0.98	1.00		
Cl^{-}	0.53	-0.57	-0.81	-0.41	0.79	-0.53	0.88	0.78	0.98	0.59	0.85	0.72	0.85	0.88	1.00	
Acidity	-0.31	-0.76	-0.48	-0.04	0.82	-0.92	0.10	-0.14	0.34	0.37	0.66	-0.09	0.68	0.59	0.33	1.00

	Long.	Lat.	Alt.	Prec.	Cond.	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	HCO_3^{-}	NO_3^{-}	SO_4^{2-}	Cl^{-}	Acidity
1998–2002																
Long.	1.00															
Lat.	-0.06	1.00														
Alt.	-0.31	0.60	1.00													
Prec.	-0.16	0.40	0.40	1.00												
Cond.	0.14	-0.89	-0.64	-0.32	1.00											
pH	-0.40	-0.55	0.33	-0.14	-0.65	1.00										
Ca^{2+}	0.67	-0.48	-0.47	-0.55	0.55	0.09	1.00									
Mg^{2+}	0.76	-0.41	-0.41	-0.54	0.51	0.24	0.87	1.00								
Na^{+}	0.22	-0.75	-0.39	-0.43	0.81	-0.41	0.53	0.56	1.00							
K^{+}	0.16	-0.56	-0.39	-0.49	0.43	-0.13	0.29	0.47	0.59	1.00						
NH_4^{+}	0.22	-0.90	-0.63	-0.30	0.98	-0.58	0.53	0.54	0.82	0.45	1.00					
HCO_3^{-}	0.44	-0.54	-0.46	-0.60	0.84	0.00	0.83	0.70	0.44	0.52	0.46	1.00				
NO_3^{-}	0.23	-0.88	-0.63	-0.31	0.98	-0.59	0.57	0.55	0.82	0.39	0.99	0.44	1.00			
SO_4^{2-}	0.40	-0.81	-0.63	-0.37	0.95	-0.42	0.71	0.72	0.83	0.43	0.95	0.52	0.97	1.00		
Cl^{-}	0.20	-0.76	-0.43	-0.41	0.81	-0.45	0.48	0.50	0.99	0.57	0.82	0.39	0.82	0.81	1.00	
Acidity	-0.55	0.16	0.20	0.54	-0.05	-0.44	-0.73	-0.65	-0.16	-0.39	-0.06	-0.88	-0.03	-0.18	-0.09	1.00
2003–2007																
Long.	1.00															
Lat.	-0.07	1.00														
Alt.	-0.35	0.57	1.00													
Prec.	-0.14	0.29	0.42	1.00												
Cond.	0.30	-0.85	-0.69	-0.29	1.00											
pH	0.40	0.25	0.20	-0.35	-0.14	1.00										
Ca^{2+}	0.67	-0.19	-0.37	-0.40	0.56	0.55	1.00									
Mg^{2+}	0.58	-0.16	-0.41	-0.44	0.51	0.63	0.94	1.00								
Na^{+}	0.74	-0.46	-0.50	-0.34	0.66	0.13	0.66	0.51	1.00							
K^{+}	0.67	-0.32	-0.43	-0.26	0.52	0.17	0.69	0.54	0.89	1.00						
NH_4^{+}	0.19	-0.92	-0.62	-0.26	0.94	-0.10	0.38	0.39	0.52	0.34	1.00					
HCO_3^{-}	0.35	-0.47	-0.35	-0.61	0.58	0.56	0.69	0.73	0.54	0.49	0.61	1.00				
NO_3^{-}	0.52	-0.84	-0.66	-0.19	0.98	-0.16	0.53	0.46	0.65	0.49	0.93	0.49	1.00			
SO_4^{2-}	0.61	-0.72	-0.70	-0.24	0.94	0.00	0.69	0.65	0.74	0.69	0.85	0.59	0.92	1.00		
Cl^{-}	0.48	-0.58	-0.48	-0.48	0.75	0.25	0.67	0.56	0.90	0.70	0.68	0.72	0.73	0.74	1.00	
Acidity	-0.41	0.21	0.13	0.57	-0.32	-0.80	-0.69	-0.74	-0.44	-0.41	-0.36	-0.94	-0.24	-0.38	-0.60	1.00

Tab. 1.6 > Correlation matrix for the amount of mean annual precipitation and the geographic parameters latitude, longitude and altitude for 35 Swiss rainwater measuring stations

Red numbers indicate significant correlations.

	Long.	Lat.	Alt.
Prec. 1988–1992	-0.53	-0.07	0.23
Prec. 1993–1997	-0.53	-0.06	0.11
Prec. 1998–2002	-0.47	-0.12	0.01
Prec. 2003–2007	-0.39	0.13	0.21

The loading plot is a clearer method to represent the relationships existing amongst the single variables. Loading plots for the 4 studied time periods are shown in Fig. 1.4. The x and y axes represent the correlation with the first, respectively with the second component. The percentage values shown in the 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. Furthermore, as already mentioned before, the closer to 1 the distance of a single variable to the graph centre is, the better the variable is described by the two principal components.

Figure 1.4 shows that in every time periods two principal components are able to capture most of the variance of the correlation matrix (1988–1992: 79 %, 1993–1997: 84 %, 1998–2002: 76 %, 2003–2005: 75 %). It also appears that most variables are described very well by the combination of the 2 principal components.

Sulphate, nitrate and ammonium correlate negatively with latitude and altitude because of transport of these pollutants from the Po Plain

In particular, the geographic parameters latitude and altitude are always situated close to each other and are described very well by PC1. 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 lie close to the PC1 axe but with opposite site with respect to latitude and altitude. Variables which always correlate negatively with latitude and altitude are the nitrate, ammonium and sulphate ions and conductivity. As already mentioned the negative correlation between these chemical parameters and latitude is caused by huge emissions of NO_x and SO_2 in the urban area of Milan and of ammonia from the agricultural areas situated on the Po Plain.

Calcium and magnesium correlate positively with longitude because of negative south-west toward north-east gradient of precipitation that dilutes alkaline rain events

Longitude is better described by the second principal component (PC2). As already indicated by the correlation matrices (Tab. 1.5) the proximity of calcium and magnesium to longitude during most time periods suggests a positive correlation between the variables. Interestingly, although the correlation matrices do not indicate a correlation between longitude and precipitation, on the loading plot the two variables always stay on the opposite side with respect to the graph centre suggesting a negative correlation between the two.

Rainwater acidity, defined as the difference between acid anions and cations concentrations as well as by the difference between hydrogen ions and bicarbonate concentrations, lays close to sulphate, nitrate and ammonium in the first time period (1988–1992), but moves continuously toward the y axis in the following time periods until becoming independent of latitude/altitude and dependent on longitude/precipitation. The concentrations of bicarbonate show a similar behavior. This can have two causes. First, the reduction of sulphate concentrations over the last 2 decades probably decreased the ability of rainwater to neutralize alkaline rain events making them more observable in rainwater chemistry. Secondly, during the last decade the occurrence of alkaline rain events seems to have increased (Rogora et al. 2004).

Acidity correlated negatively with latitude/altitude in 1988–1992 and negatively with longitude in 1998–2002 and 2003–2007

Very useful is also the extraction of factor scores for each sampling site (one for every chosen component). 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.

In order to identify the relations between different sampling stations it is useful to look at the factor score plots shown in Fig. 1.5. From the observations made previously one may conclude that an increase of the x-values reflects an increase of sulphate, nitrate and ammonium concentrations and a decrease of latitudes and altitudes. Conversely, the increase of the y-values follows an increase of longitude and of both calcium and magnesium concentrations. Also, an increase of the y-values after the period 1993–1997 correlates with an increase of bicarbonate and a decrease of acidity. One may notice that for every considered time period most of the sampling sites are located within the same quadrant defined by the x,y-axes.

In order to simplify the interpretation of the factor score plots, these were combined together with the information obtained from the loading plots mentioned above. The graphs were divided into two parts with the simplified characteristics “acid” and “non acid” and into two further parts defined as “high nutrient” and “low nutrient concentrations”. Sampling stations could therefore be divided into 4 groups: (a) low acidity and low concentrations of SO_4^{2-}, NO_3^-, NH_4^+, (b) low acidity and high concentrations of SO_4^{2-}, NO_3^-, NH_4^+, (c) high acidity and low concentrations of SO_4^{2-}, NO_3^-, NH_4^+, (d) high acidity and high concentrations of SO_4^{2-}, NO_3^-, NH_4^+. It is important to note that these definitions are qualitative and as such enabling a comparison of different sampling stations over a determined period of time, but not allowing to consider concentration changes over time. Additional information can be gained if the sampling sites with the so obtained simplified chemical information are presented on a geographic map (Fig. 1.6).

It appears that in the period of 1988–1992 sampling sites can be divided into the 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 becomes 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, which also determine until 1993 the geographic distribution of rain acidity. After 1993 the geographic distribution of acidity is better described by the amount of mean annual precipitation being higher in the west as atmospheric currents causing rainfall are mostly directed from south-west to north-east (Spinedi and Isotta 2004). In fact, over a period of one year precipitation dilutes the chemistry of alkaline rain events. Alkaline rain events became more frequent after 1993 and were neutralized to a lesser extent by acids arising from sulphur emissions.

Fig. 1.4 > PCA loading plots

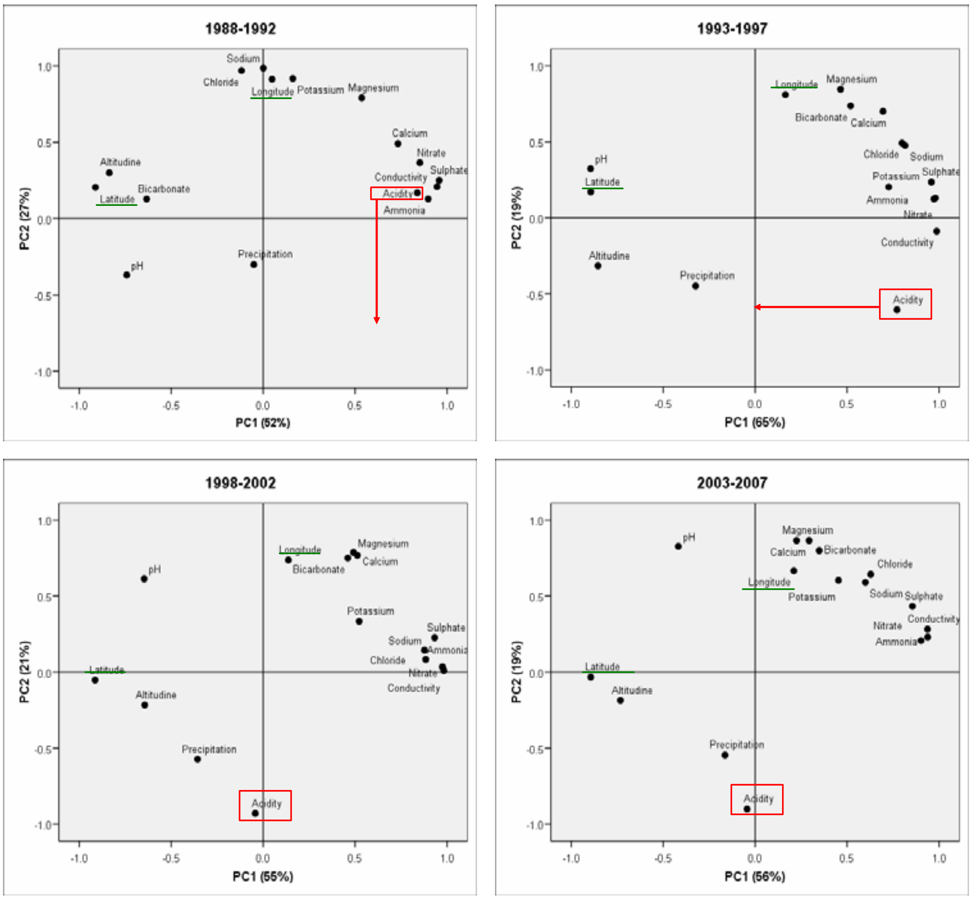


Fig. 1.5 > PCA factor score plots

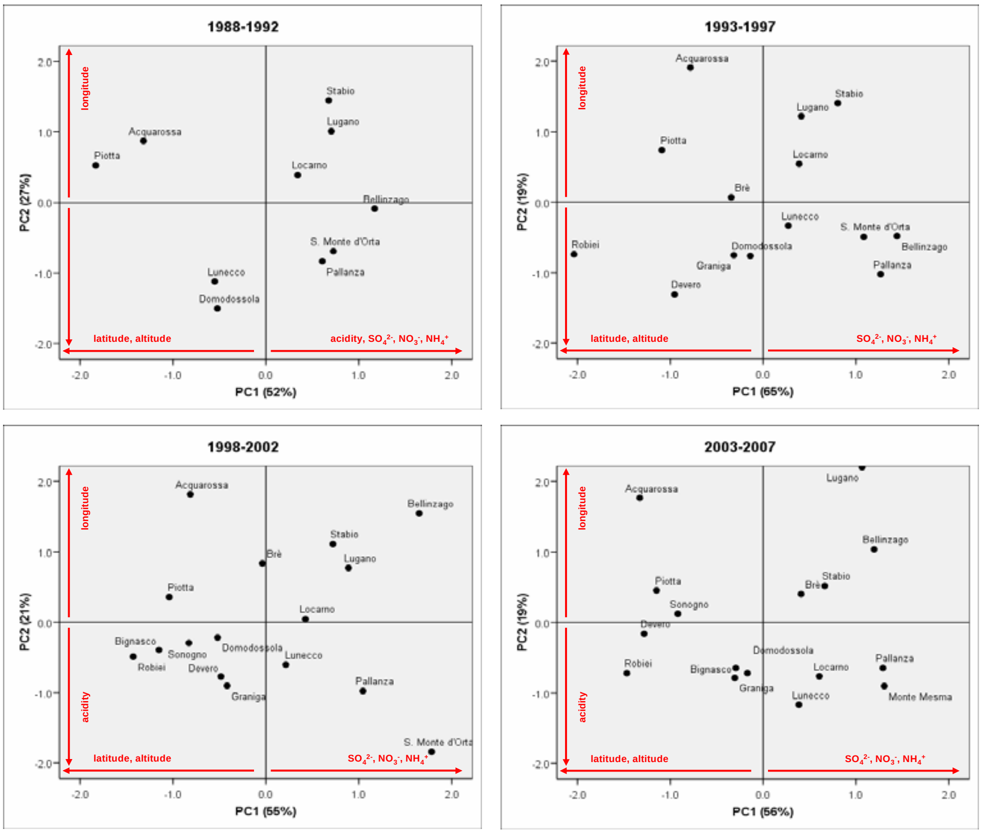
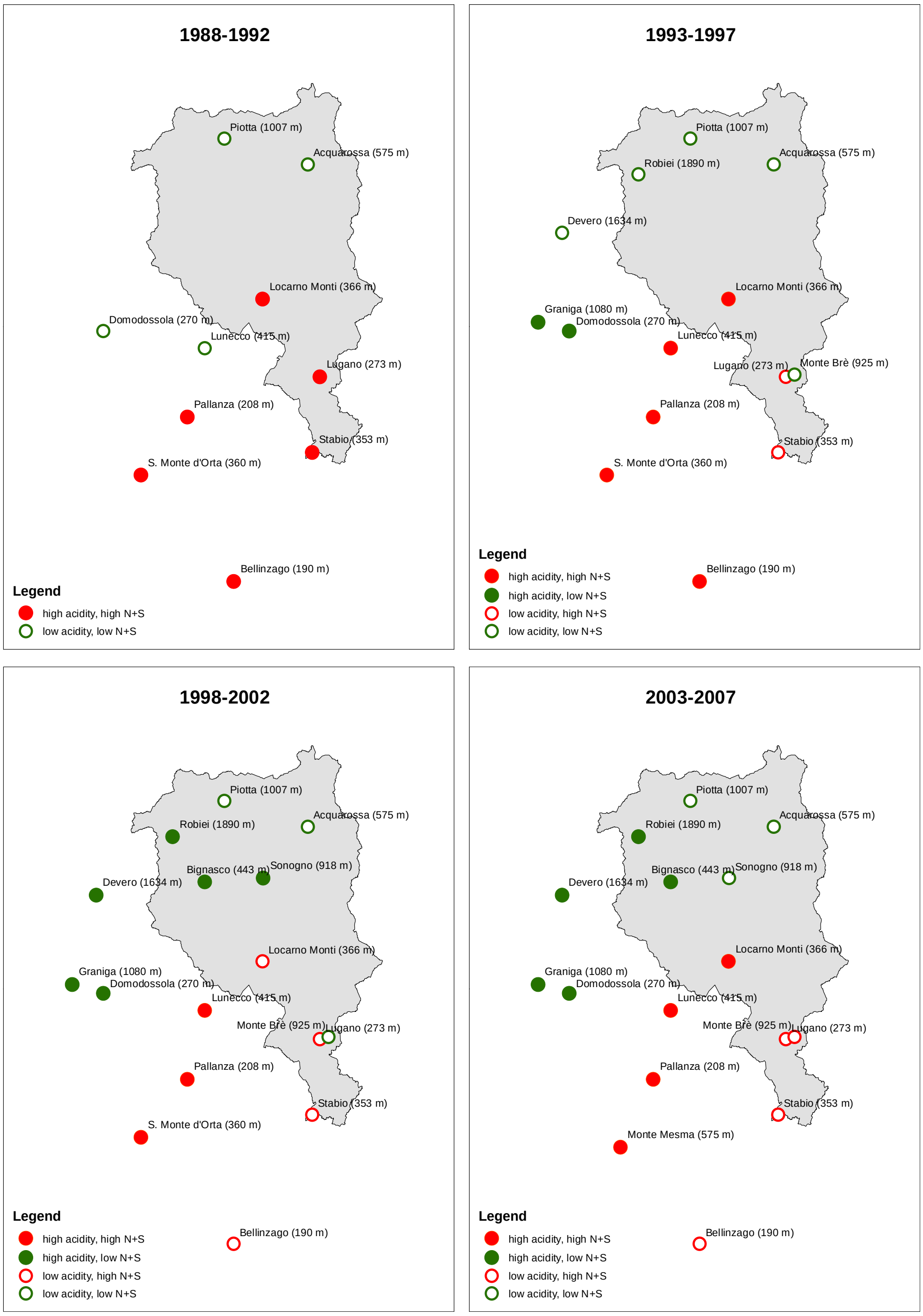


Fig. 1.6 > Sampling sites with their PCA quadrant characteristics



1.6 Multiple regression analysis

Calculation of multiple linear regression parameters for regional modelling of concentrations in precipitation for 4 time periods 1988–1992, 1993–1997, 1998–2002, 2003–2007

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 different parameters for the periods of 1988–1992, 1993–1997, 1998–2002 and 2003–2007. For some parameters and time periods the addition of the mean annual volume of precipitation as a regression variable gave better results. In particular, parameters and time periods whose mean annual concentrations are strongly influenced by sporadic alkaline rain events such as base cations, bicarbonate, acidity and pH after 1993 are better modeled if the amount of precipitation is also considered. Two different multiple linear regression equations were therefore produced:

$$C = m_{long}*\text{longitude} + m_{lat}*\text{latitude} + m_{alt}*\text{altitude} + C_0$$
$$C = m_{long}*\text{longitude} + m_{lat}*\text{latitude} + m_{alt}*\text{altitude} + m_{prec}*\text{precipitation} + C_0$$

where:

C = mean concentration weighted with the amount of precipitation
over the studied time period
C_0 = intercept
m_{lat}, m_{long}, m_{alt}, m_{prec} = linear regression coefficients (= slopes)

To facilitate the modeling of values at very high altitudes results from the analysis of snow samples from the glacier Basodino (2700–2900 m) were also considered. In addition, 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). For chloride and base cations, including sodium, the multiple regression analysis was carried out without considering any data from Piotta, because its winter values are strongly influenced by salt spray (data not shown). Average mean concentrations for the different parameters and time periods are reported in Appendix A2.

The linear regression coefficients for base cations (BC), with and without sodium, for ammonium, sulphate, nitrate, chloride, bicarbonate, acidity and pH, and the values describing the statistic significance of the regression model are reported in Tab. 1.7.

On this basis it is possible to calculate concentration and deposition maps for different parameters and time periods. However, it is firstly necessary to interpolate average precipitation volumes monitored at single sampling sites over the whole study area. The procedure is explained in chapter 1.7.

Tab. 1.7 > Results from multiple linear 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_{long}	m_{lat}	m_{alt}	m_{prec}	C_0
					meq m^{-4}	meq m^{-4}	meq m^{-4}	meq m^{-3} mm^{-1}	meq m^{-3}
Base cations (without Na^+)									
1988–1992	17	0.68	9.1	0.002	1.7E-4	-1.4E-5	-3.5E-3		-68.2
1993–1997	17	0.72	7.7	0.003	1.7E-4	-6.5E-5	-4.4E-3	-7.7E-3	-70.0
1998–2002	17	0.83	14.8	0.000	3.7E-4	-1.4E-4	-4.1E-4	-1.2E-2	-181.0
2003–2007	17	0.57	5.6	0.011	3.0E-4	-2.3E-5	-3.0E-3		-177.0
Base cations (with Na^+)									
1988–1992	16	0.69	9.0	0.002	3.5E-4	-2.0E-4	-5.2E-3		-180.6
1993–1997	16	0.70	9.2	0.002	2.5E-4	-1.6–4	-4.9E-3		-117.6
1998–2002	16	0.85	15.3	0.000	3.9E-4	-2.0E-4	-4.1E-4	-1.4E-2	-179.1
2003–2007	16	0.67	8.2	0.003	4.0E-4	-5.6E-5	-3.6E-5		-236.8
Ammonium									
1988–1992	17	0.90	38.5	0.000	1.6E-4	-4.9E-4	-7.1E-3		-7.3
1993–1997	17	0.89	34.8	0.000	7.7E-5	-3.1E-4	-7.7E-3		20.1
1998–2002	17	0.86	27.8	0.000	7.3E-5	-3.7E-4	-7.2E-3		34.5
2003–2007	17	0.88	30.6	0.000	4.8E-5	-3.5E-4	-6.6E-3		53.7
Sulphate									
1988–1992	17	0.88	31.4	0.000	2.1E-4	-4.1E-4	-1.1E-2		-40.1
1993–1997	17	0.89	33.9	0.000	1.2E-4	-2.9E-4	-8.7E-3		-5.7
1998–2002	17	0.82	19.7	0.000	1.6E-4	-2.4E-4	-6.0E-3		-42.4
2003–2007	17	0.83	21.4	0.000	1.3E-4	-1.2E--4	-5.4E-3		-43.1
Nitrate									
1988–1992	17	0.85	25.2	0.000	1.7E-4	-3.1E-4	-7.2E-3		-39.4
1993–1997	17	0.90	40.1	0.000	5.7E-5	-2.3E-4	-6.6E-3		21.6
1998–2002	17	0.84	22.6	0.000	5.3E-5	-2.4E-4	-5.9E-3		26.6
2003–2007	17	0.84	23.4	0.000	9.0E-5	-1.9E-4	-6.2E-3		-1.3
Chloride									
1988–1992	16	0.63	6.7	0.007	1.8E-4	-2.8E-6	-2.8E-3		-110.1
1993–1997	16	0.79	15.2	0.000	5.2E-5	-4.9E-5	-1.4E-3		-22.3
1998–2002	16	0.71	9.7	0.002	2.3E-5	-9.0E-5	-3.7E-4		1.2
2003–2007	16	0.84	20.4	0.000	7.0E-5	-6.5E-5	2.9E-4		-35.4
Bicarbonate									
1988–1992									
1993–1997	17	0.51	3.2	0.054	3.3E-5	1.2E-6	-1.0E-3	-1.7E-3	-15.9
1998–2002	17	0.63	5.2	0.012	1.2E-4	-8.2E-5	1.4E-4	-7.1E-3	-46.3
2003–2007	17	0.61	4.7	0.017	8.3E-5	-6.3E-5	2.3E-3	-1.0E-2	-28.7

Period	n	r^2	F	p	m_{long}	m_{lat}	m_{alt}	m_{prec}	C_0
					meq m^{-4}	meq m^{-4}	meq m^{-4}	meq m^{-3} mm^{-1}	meq m^{-3}
Acidity									
1988–1992	17	0.77	6.3	0.007	8.7E-6	-9.7E-5	-8.0E-3		40.7
1993–1997	17	0.75	13.0	0.000	-1.3E-4	-1.2E-4	-4.2E-3		123.4
1998–2002	17	0.53	3.4	0.044	-2.2E-4	1.8E-5	-4.0E-3	1.0E-2	132.2
2003–2007	17	0.53	3.3	0.047	-1.4E-4	5.4E-5	-5.4E-3	1.4E-2	75.5
Ph									
1988–1992	17	0.68	9.2	0.002	3.0E-7	5.5E-7	2.2E-4		4.1
1993–1997	17	0.79	16.0	0.000	2.4E-6	2.2E-6	2.2E-4		2.7
1998–2002	17	0.72	11.1	0.001	3.9E-6	1.5E-6	1.8E-4		2.0
2003–2007	17	0.69	6.5	0.005	3.9E-6	6.5E-7	2.2E-4	-2.3E-4	2.5

1.7 Precipitation maps

1.7.1 Geographic interpolation

Calculation of precipitation maps

For each of the 120 sampling stations listed in Tab. 1.2 the average precipitation volumes over the 4 different periods of 1988–1992, 1993–1997, 1998–2002 and 2003–2007 were calculated and divided by values extracted from national precipitation maps (resolution: 1000 m x 1000 m). For the period of 1988–1999 the values were supplied by FOWG (2000), whereas for the period 2000–2007 they were calculated by Meteotest using the same method.

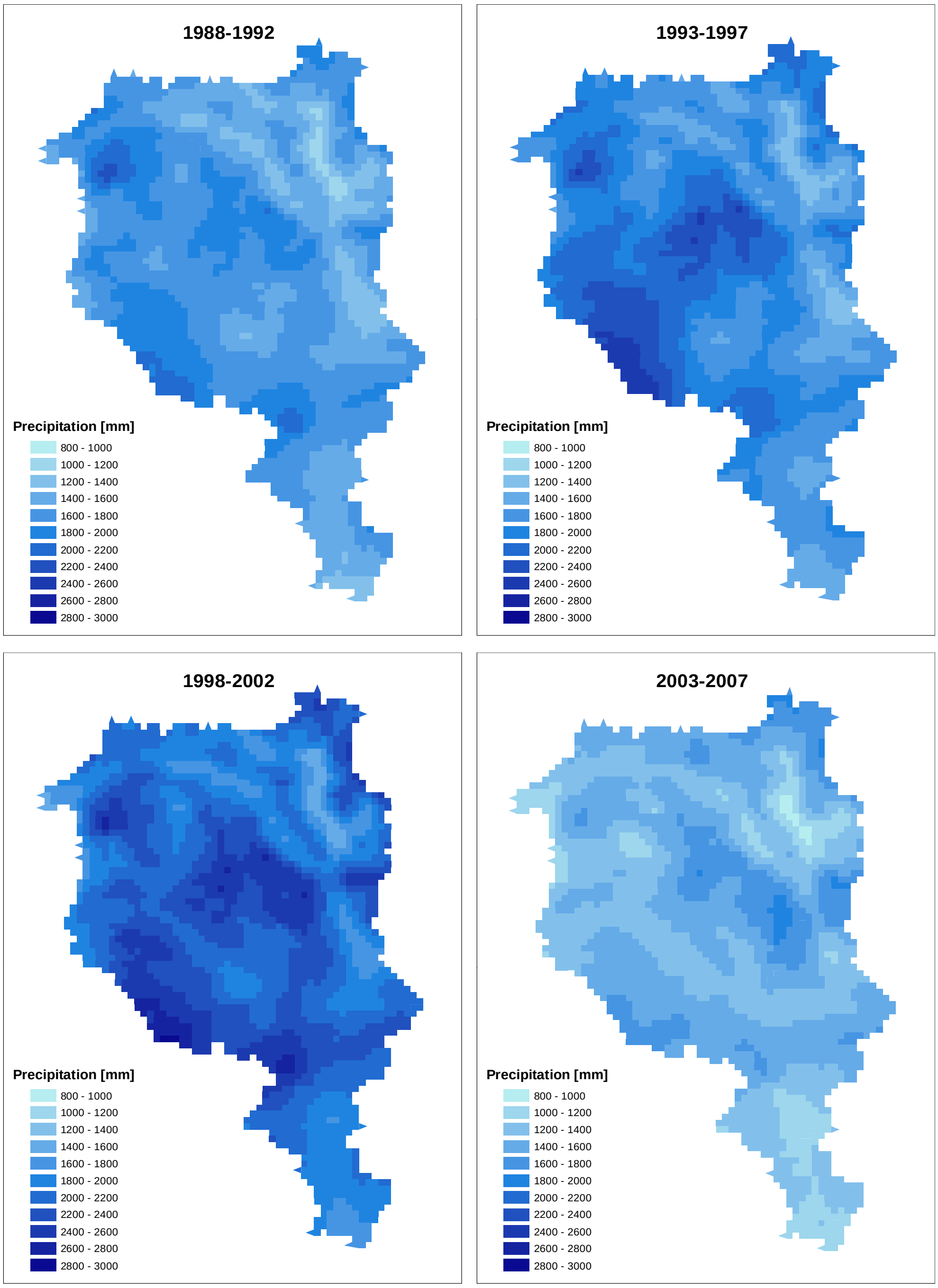
The resulting factors were interpolated by the inverse distance weighting method in ArcGIS® (registered trademark of ESRI Inc., Redlands, USA) using the following parameters: distance exponent = 2, number of points = 3, maximal search distance = 11 km, resolution = 1000 m x 1000 m. The resulting factor maps were then multiplied back by the precipitation maps from the Swiss hydrological atlas.

1.7.2 Maps

1998–2002 very wet and 2003–2007 very dry

The calculated precipitation maps are shown in Fig. 1.7. The mean annual precipitation amount was 1670 mm in 1988–1992, 1860 mm in 1993–1997, 2127 mm in 1998–2002 and 1415 mm in 2003–2007. 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 map. 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 north-western part (higher Maggia valley), in the north-central part (higher Verzasca valley) and in the centre of Canton Ticino (mount Tamaro-Gradiccioli). The lowest precipitation occur in the eastern part 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).

Fig. 1.7 > Precipitation maps: 1988–1992, 1993–1997, 1998–2002, 2003–2007



1.8 Rainwater quality maps

1.8.1 Geographic interpolation

Calculation of rainwater concentration maps

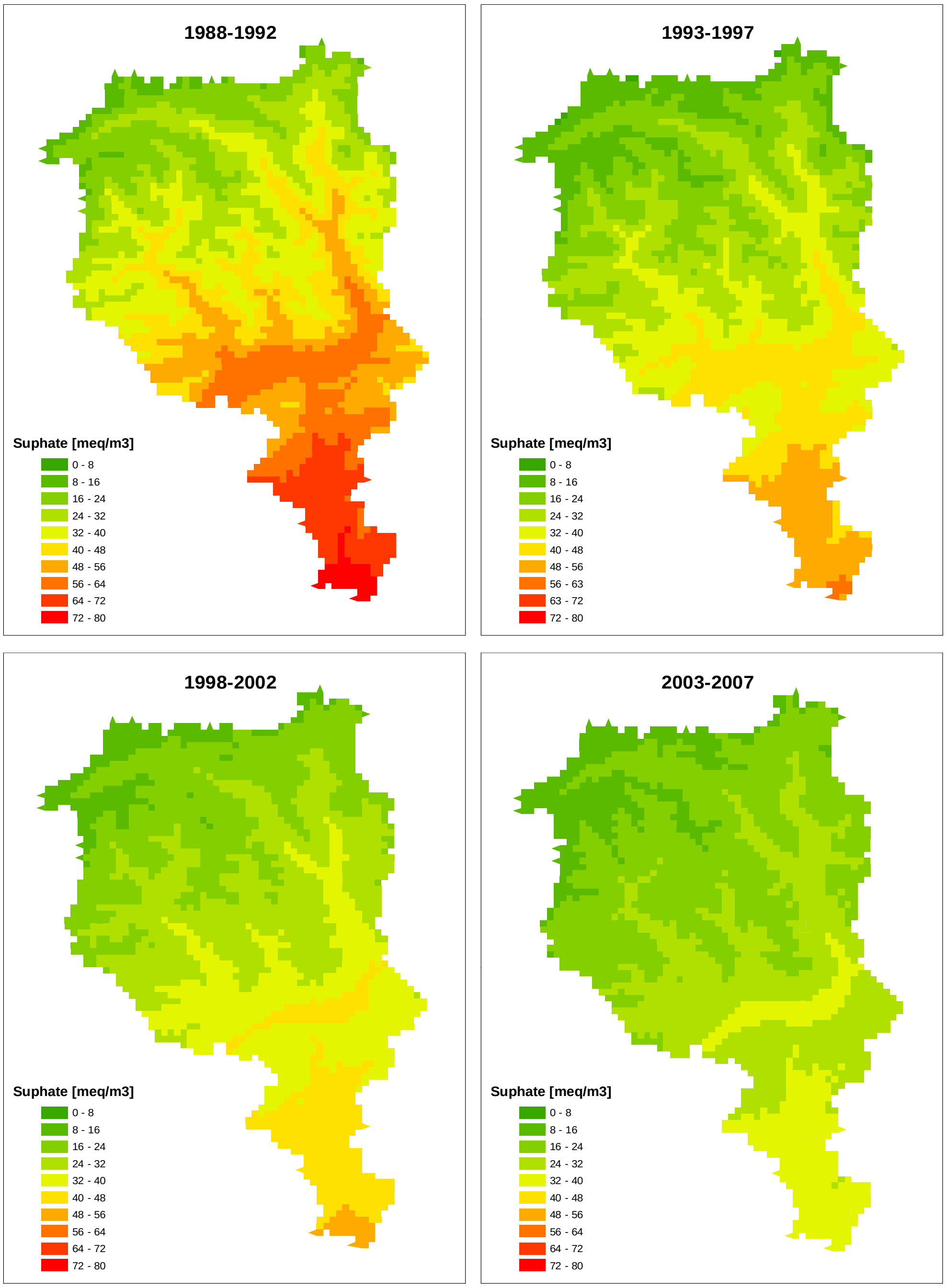
Concentration maps of chemical parameters were obtained by applying the multiple parameter regression models described in chapter 1.6 and Tab. 1.7 and using the data from 17 sampling stations (Tab. 1.1). The area under investigation was divided into 1000 m x 1000 m cells. For every cell centre a concentration of the chemical parameter for the corresponding longitude, latitude and altitude was calculated (see Fig. 1.8). Since for bicarbonate no reliable multiple parameter regression model was found for the period of 1988–1992, no map could be produced.

1.8.2 Maps

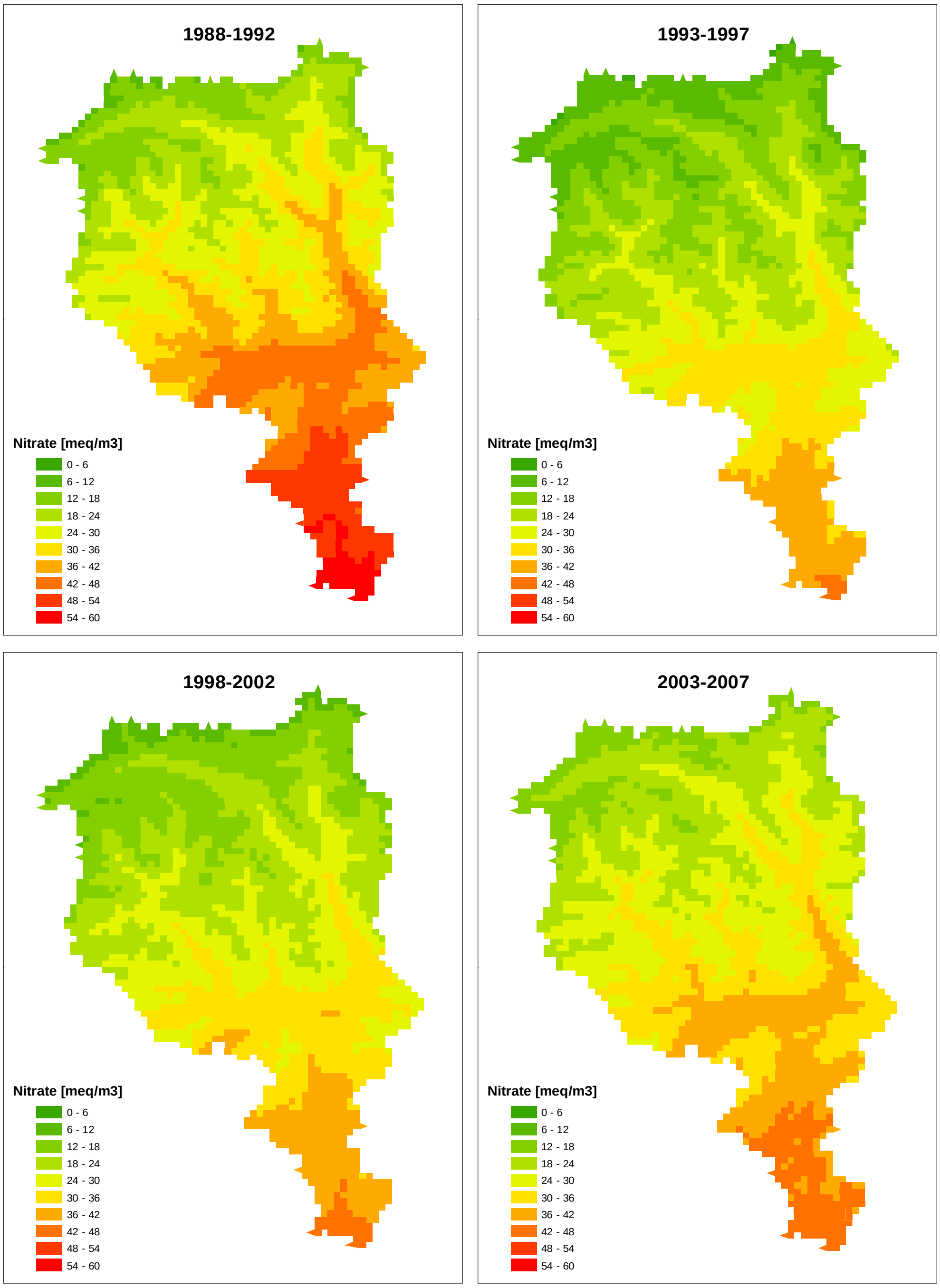
Concentration maps enable a prompt detection of geographic and temporal trends. The modeled maps confirm the results obtained from the PCA analysis: decreasing sulphate, nitrate and ammonium concentrations from south to north during all time periods and decreasing concentrations for base cations and acidity from south to north in the first time period 1988–1992 changing together with bicarbonate to increasing concentrations from west to east in the following time periods. For most parameters and time periods also decreasing concentrations from low to high altitudes appear. The results of the trend analysis, namely decreasing concentrations for sulphate and acidity and increasing concentrations for base cations, bicarbonate and pH, are also confirmed. The particularly high concentrations of base cations and bicarbonate and the low acidity during the period of 1998–2002 are probably related to the particularly high amount of precipitation during these years. In fact, rain rich years may increase the occurrence of alkaline rain events. A reduction of nitrate and ammonium concentrations over the first 2 periods (1988–1997) also seems to have occurred, although the trend analysis gave no significant result. Explanations for the geographic distribution of concentrations over time have already been mentioned in the previous chapters.

Fig. 1.8 > Concentrations in wet deposition: 1988–1992, 1993–1997, 1998–2002, 2003–2007

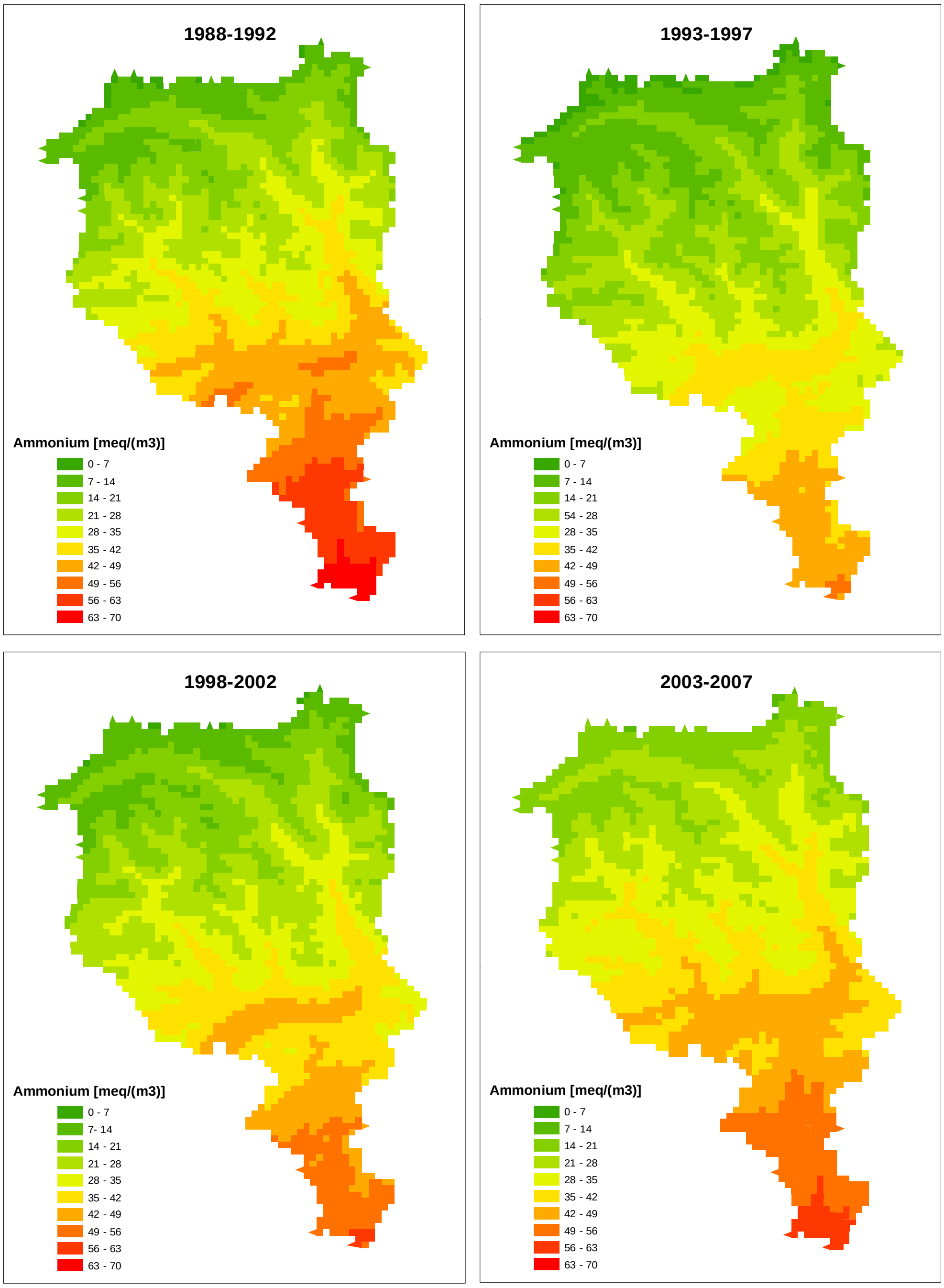
a) Sulphate concentrations



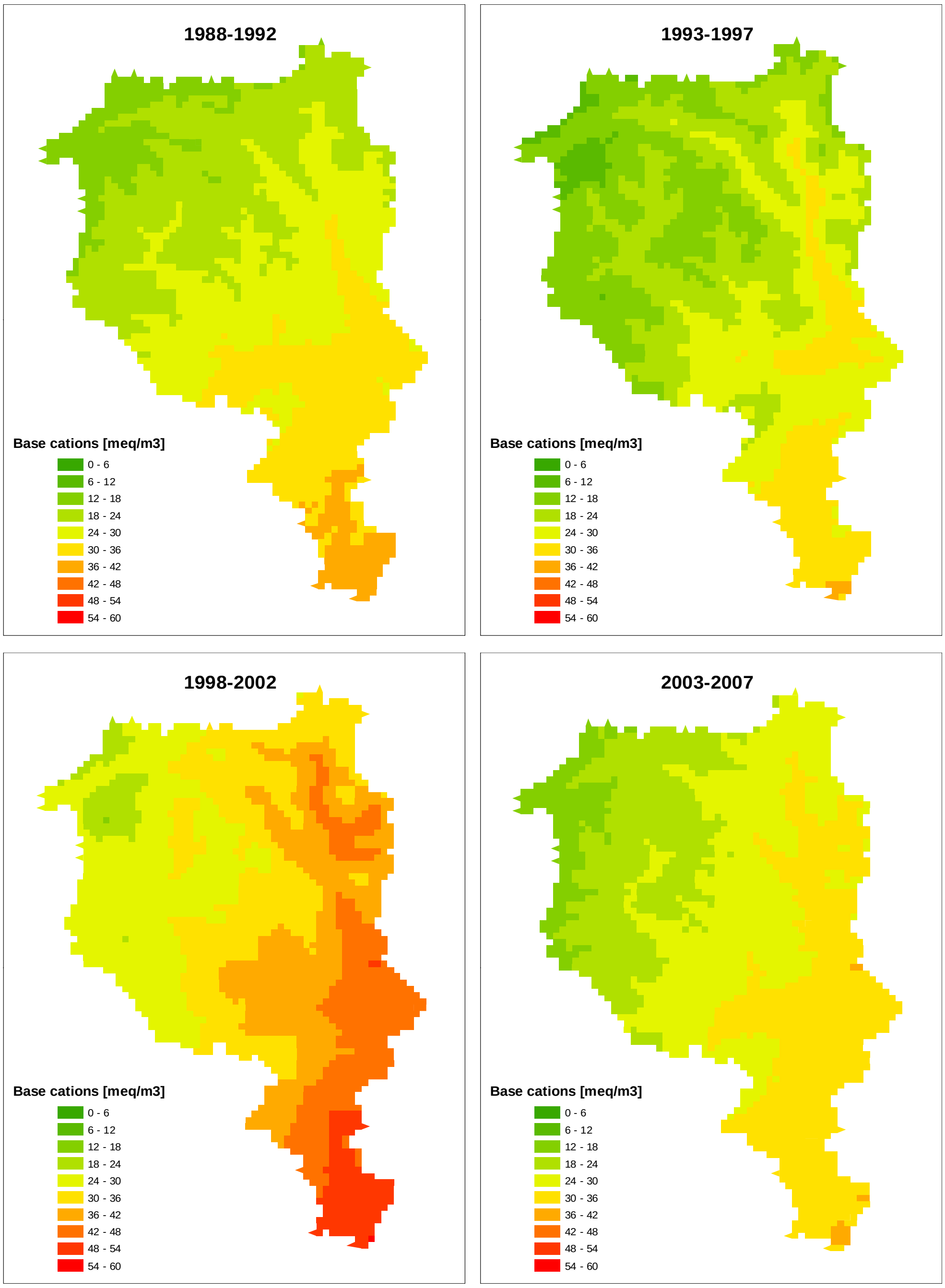
b) Nitrate concentrations



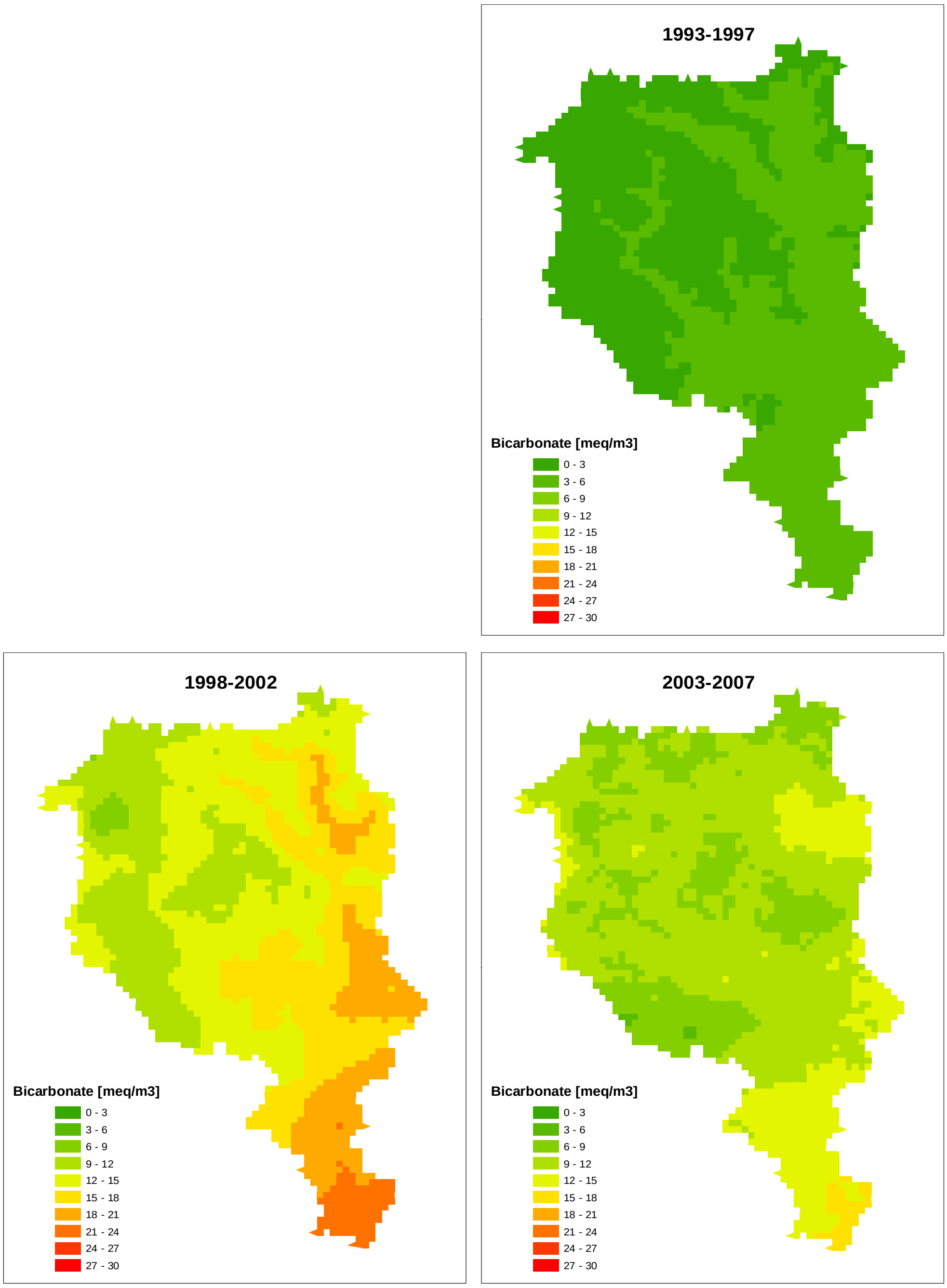
c) Ammonium concentrations



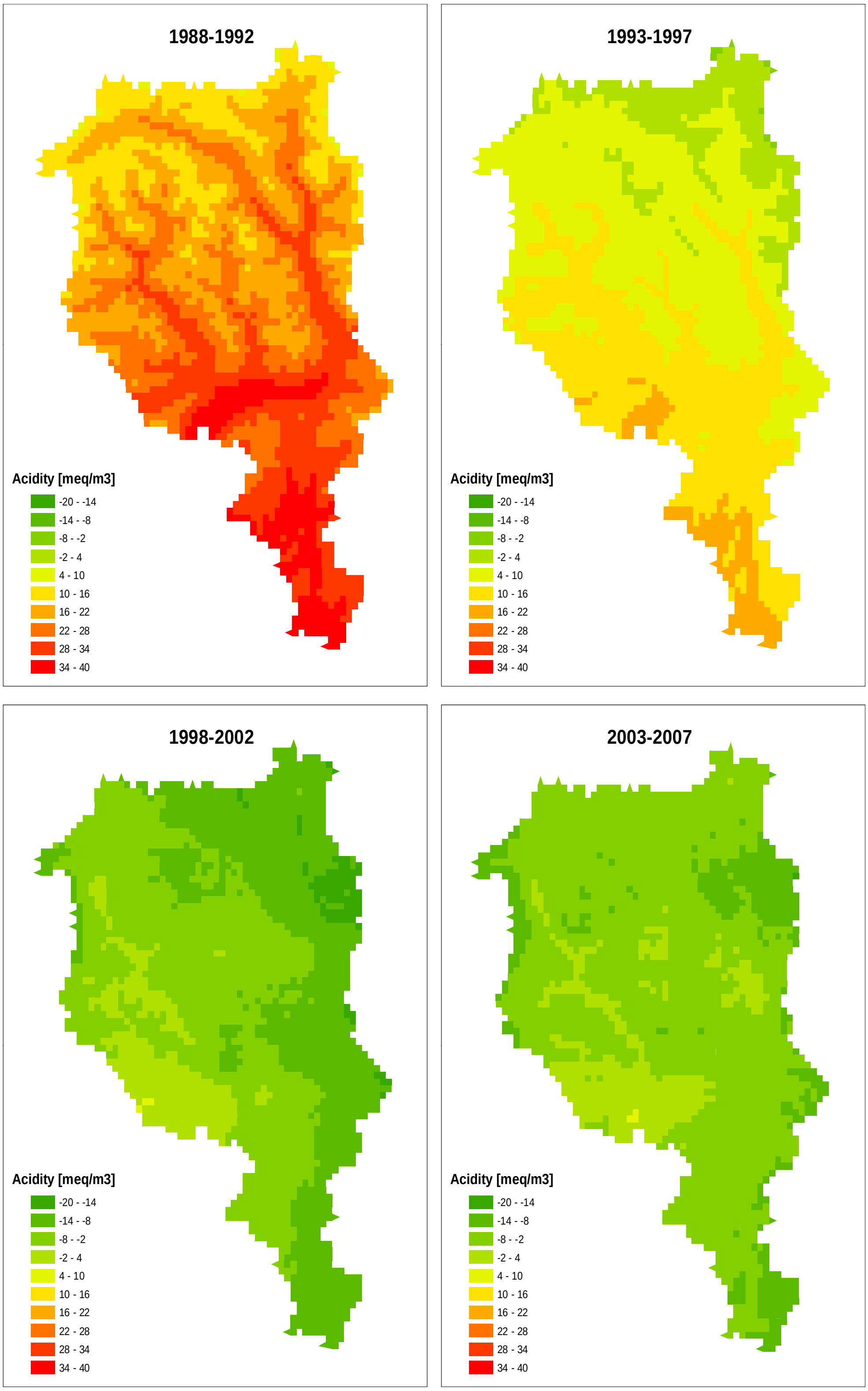
d) Base cations concentrations



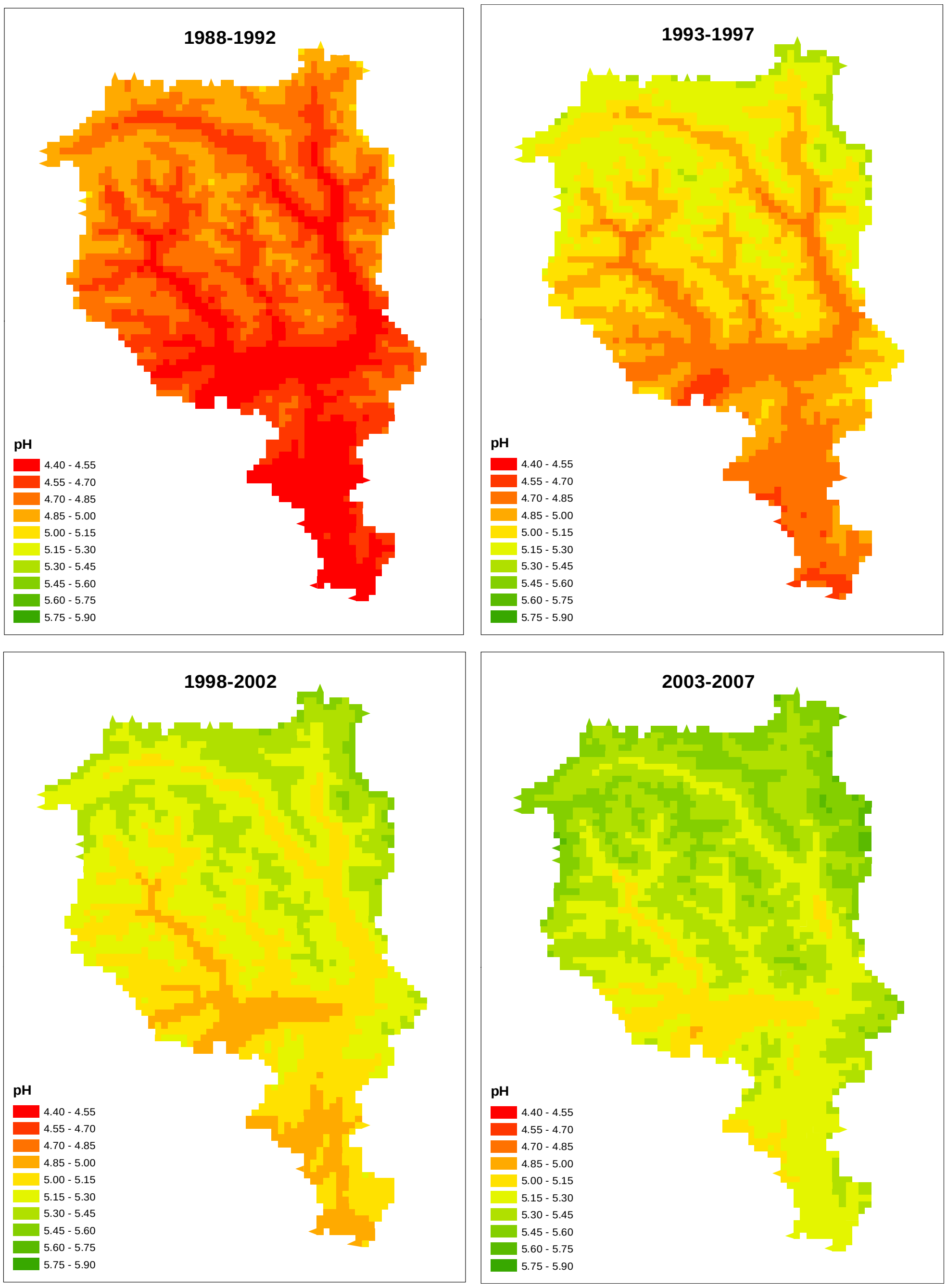
e) Bicarbonate concentrations



f) Concentrations of acidity



g) pH values


1988-1992
pH
4.40 - 4.55
4.55 - 4.70
4.70 - 4.85
4.85 - 5.00
5.00 - 5.15
5.15 - 5.30
5.30 - 5.45
5.45 - 5.60
5.60 - 5.75
5.75 - 5.90
1993-1997
pH
4.40 - 4.55
4.55 - 4.70
4.70 - 4.85
4.85 - 5.00
5.00 - 5.15
5.15 - 5.30
5.30 - 5.45
5.45 - 5.60
5.60 - 5.75
5.75 - 5.90
1998-2002
pH
4.40 - 4.55
4.55 - 4.70
4.70 - 4.85
4.85 - 5.00
5.00 - 5.15
5.15 - 5.30
5.30 - 5.45
5.45 - 5.60
5.60 - 5.75
5.75 - 5.90
2003-2007
pH
4.40 - 4.55
4.55 - 4.70
4.70 - 4.85
4.85 - 5.00
5.00 - 5.15
5.15 - 5.30
5.30 - 5.45
5.45 - 5.60
5.60 - 5.75
5.75 - 5.90

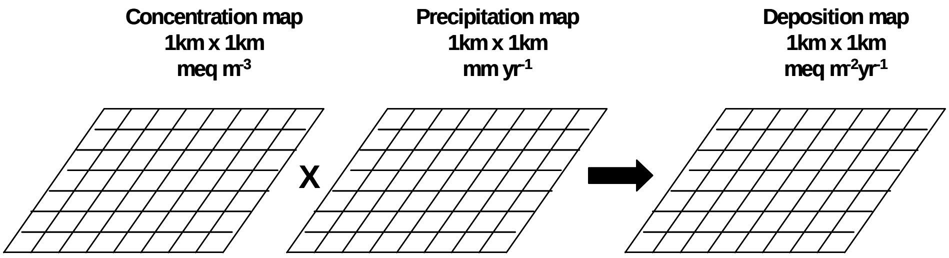
1.9 Wet deposition maps

1.9.1 Geographic interpolation

Wet deposition maps were obtained by multiplying precipitation maps by concentration maps (see. Fig. 1.10)

Calculation of wet deposition maps

Fig. 1.9 > Method for the calculation of deposition maps

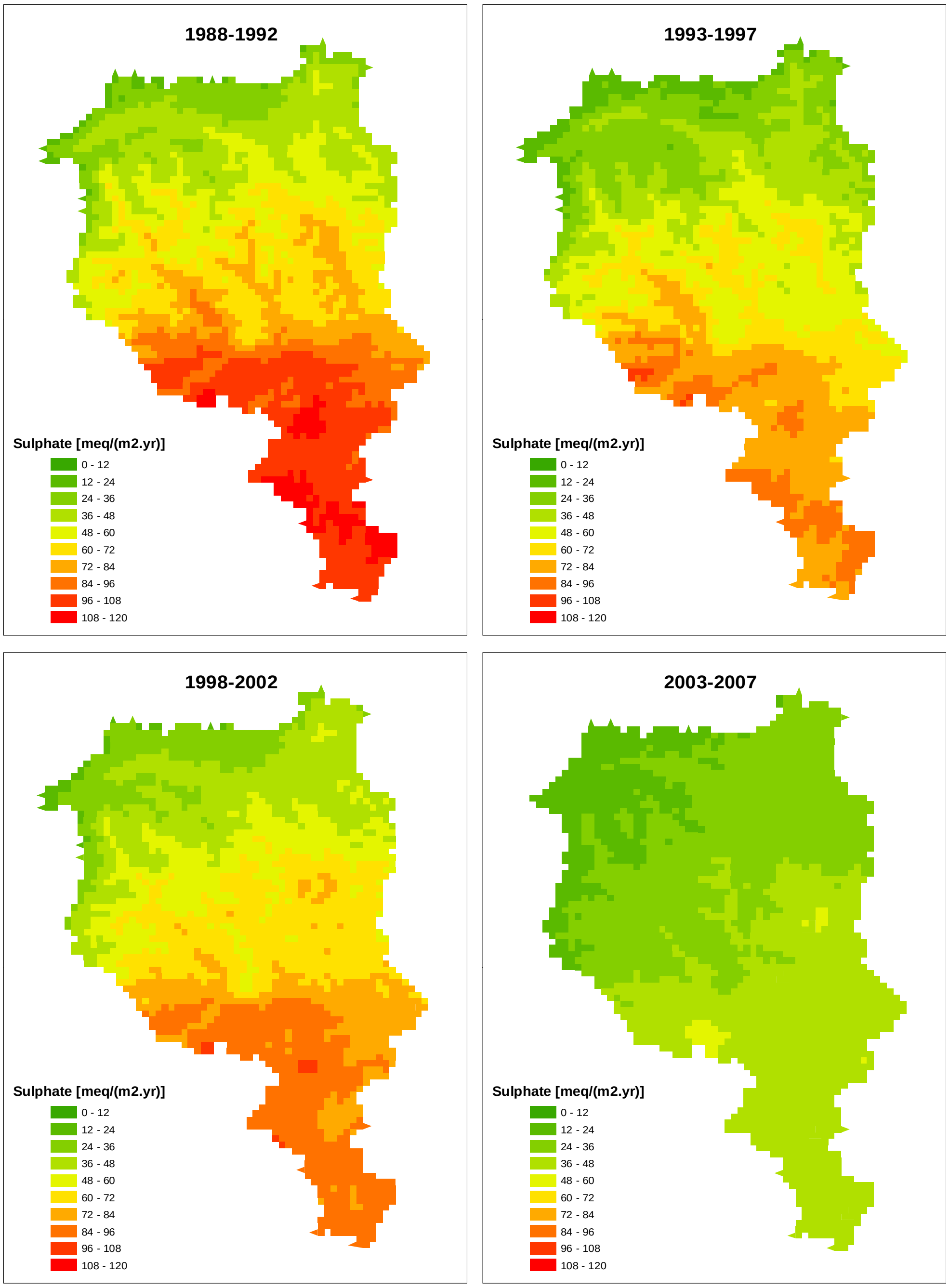


1.9.2 Maps

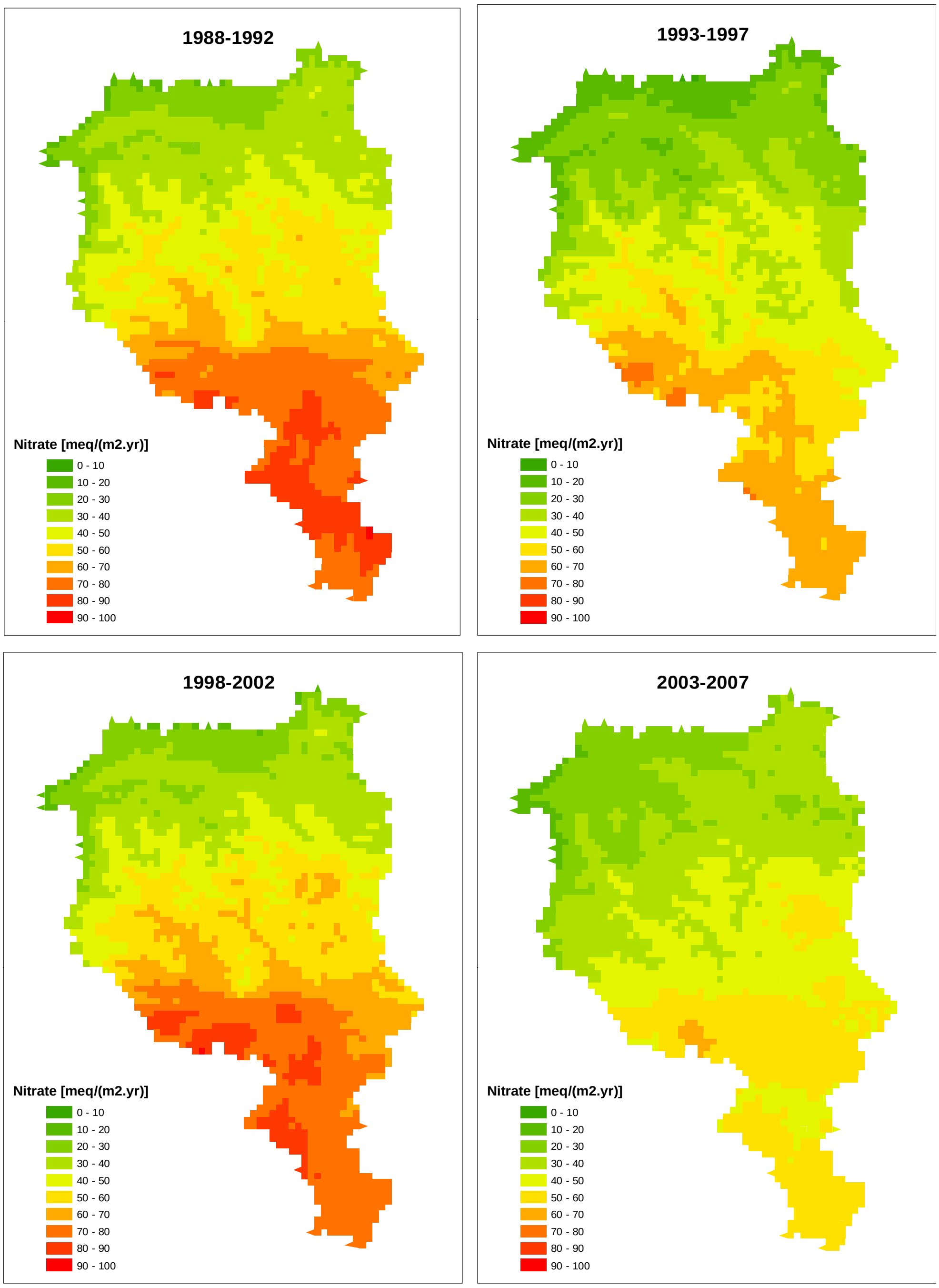
Deposition maps do not substantially differ from concentrations maps. For the deposition of sulphate, nitrate and ammonium a gradient with decreasing south to north concentrations can be observed in every time period. A similar trend is found for base cations and acidity in the first time period but their depositions together with those of bicarbonate change to a gradient with increasing depositions from west to east in the successive time periods. Depositions decreasing with altitude can also be observed for most parameters and time periods. In general, time trends with decreasing depositions of sulphate and acidity and increasing depositions of base cations and bicarbonate can also be observed. However, the particularly rain rich (1998–2002) and rain poor (2003–2007) years had clear consequences on deposition. The deposition of sulphate and nitrate were slightly higher during the period of 1998–2002 compared to the immediately previous and successive time periods. Depositions of ammonium were even higher over the period of 1998–2002 than at the beginning of the monitoring period. As already mentioned for concentration maps, rain rich years probably also increase the occurrence of alkaline rain events. This leads to particularly high depositions of base cations and of bicarbonate and particularly low acidity deposition over the period of 1998–2002.

Fig. 1.10 > **Wet deposition: 1988–1992, 1993–1997, 1998–2002, 2003–2007**

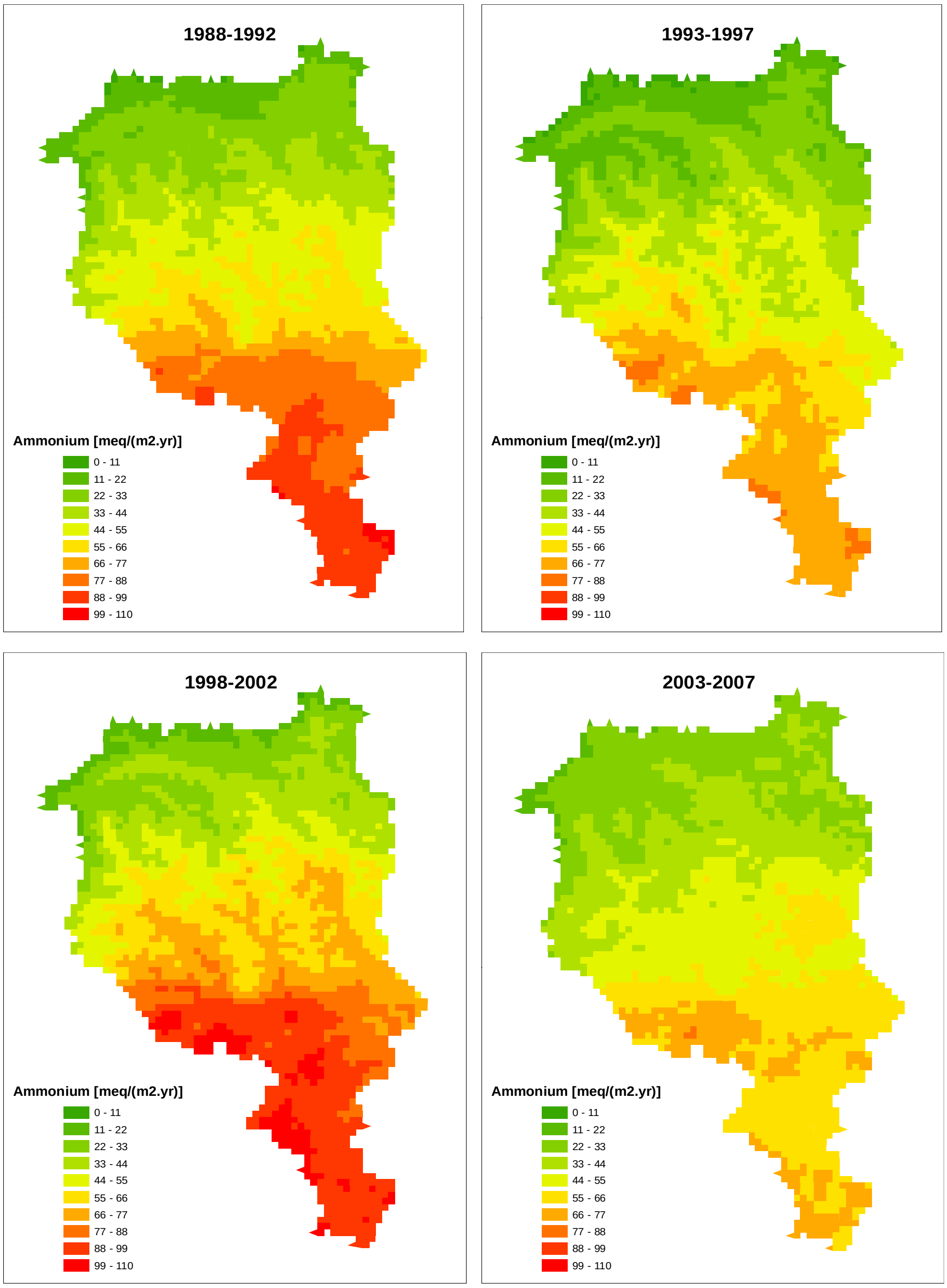
a) Sulphate deposition



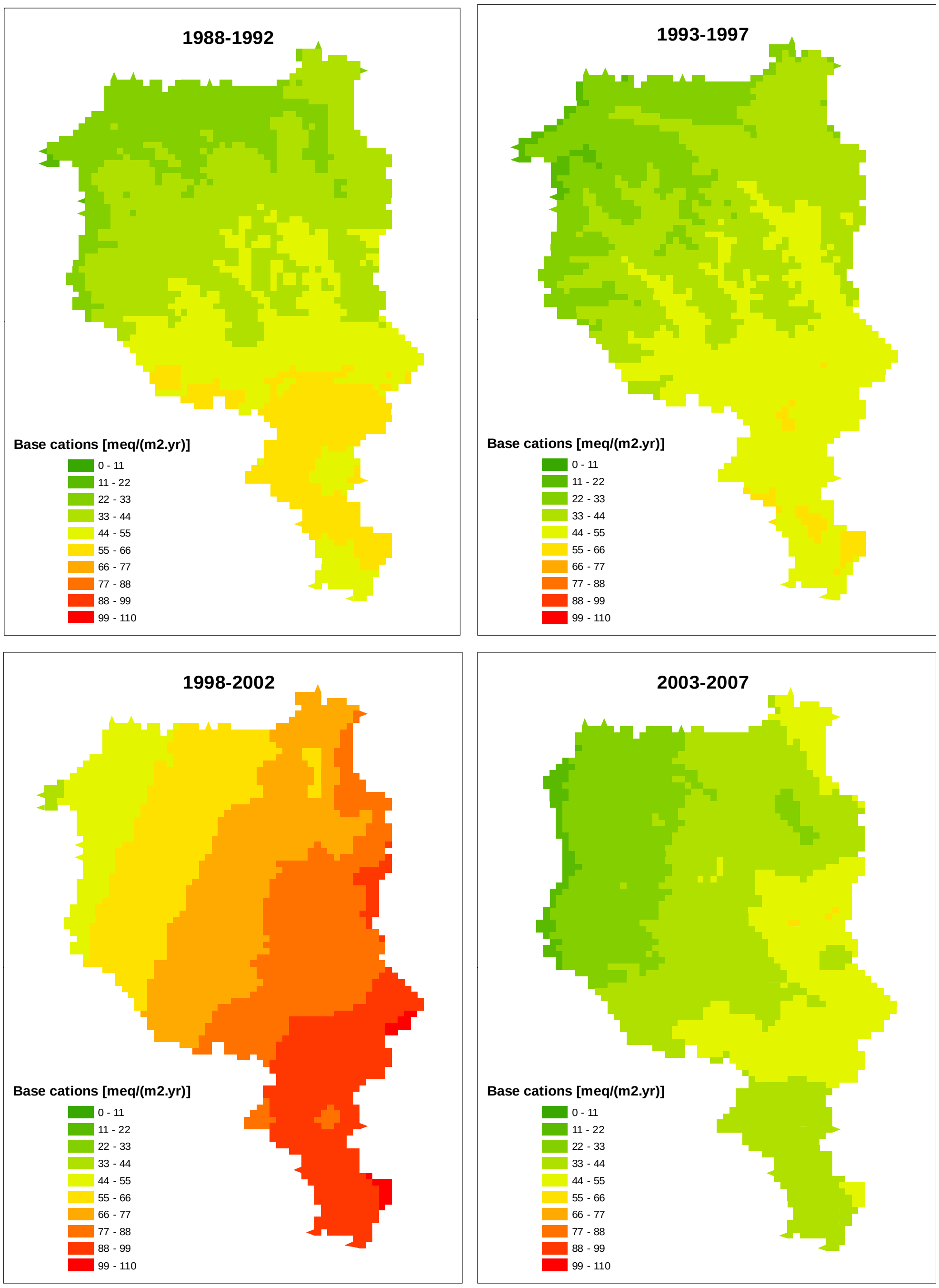
b) Nitrate deposition



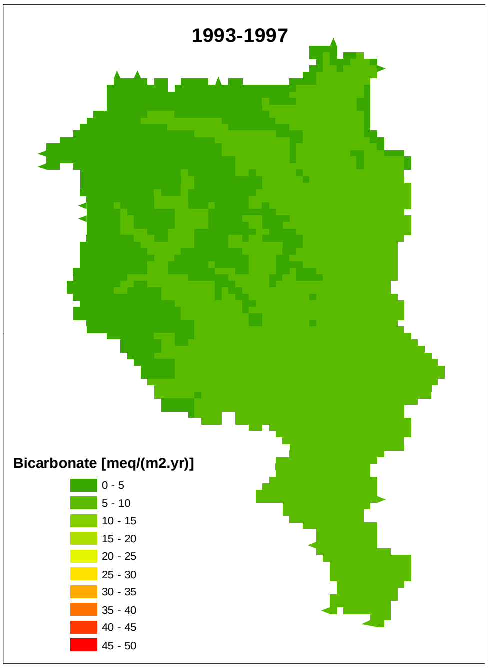
c) Ammonium deposition

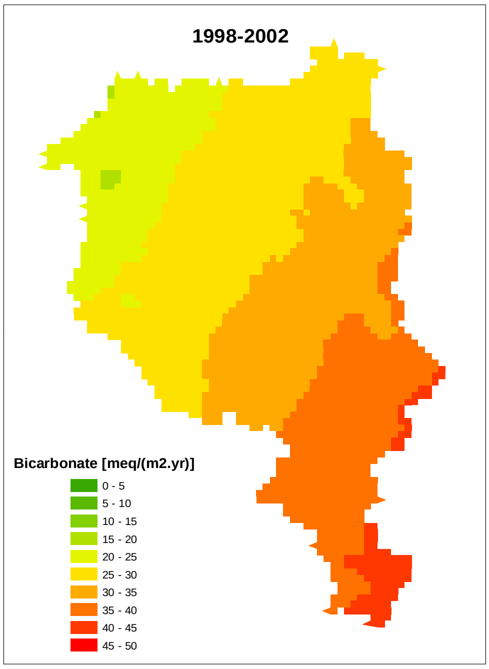


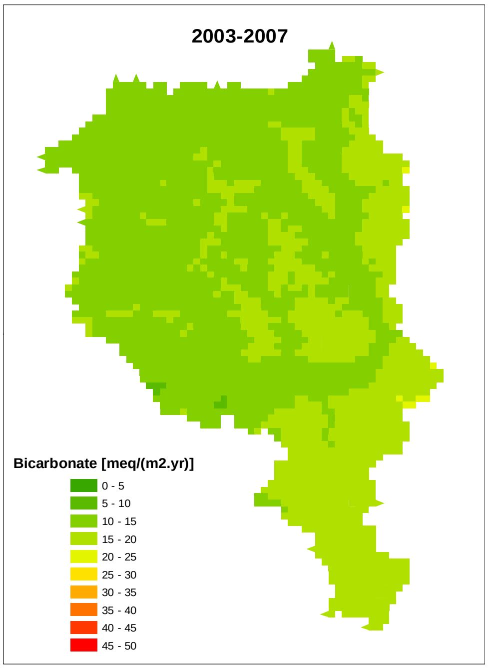
d) Base cations deposition



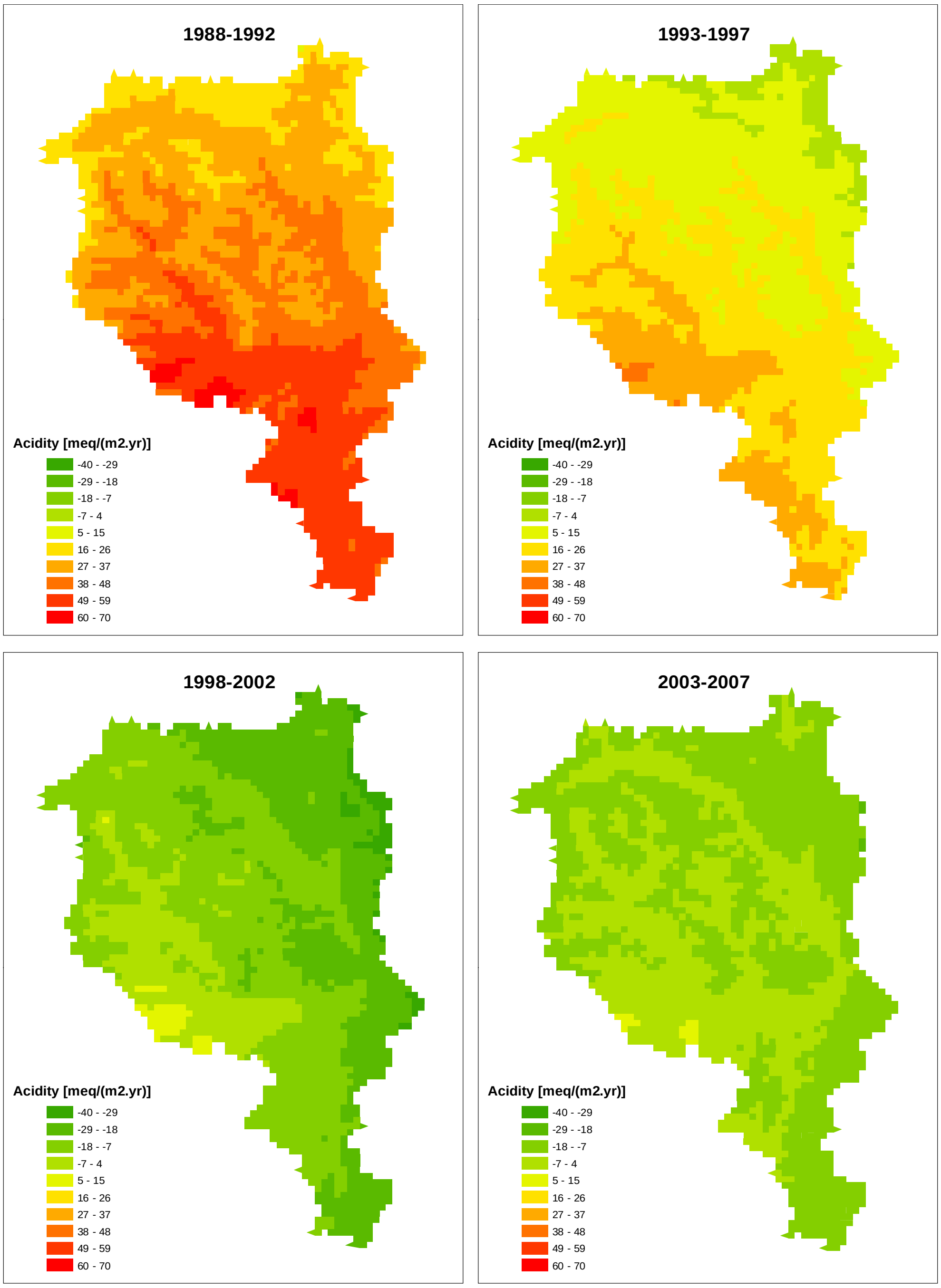
e) Bicarbonate deposition







f) Deposition of acidity



2 > Dry deposition of gases and aerosols

2.1 Mapping methods

Calculation of dry deposition maps

Besides wet deposition also the dry deposition of gases and aerosols contribute to the whole amount of deposition. In order to quantify the total acidifying deposition the dry deposition of the gaseous compounds NH_3, NO_2, SO_2, HNO_3 and that of the NH_4^+- and NO_3-containing aerosols have to be known. The dry deposition of the sulphate ion is not taken into account since its values are negligible if compared to those due to wet deposition (Hertz and Bucher 1990). SO_2 and NO_2 are emitted from the combustion of fossil fuels, HNO_3 is produced by the photochemical oxidation of NO_2, while NH_3 is mainly emitted from intensive livestock breeding and from the widespread use of mineral fertilizers. Differently from wet deposition dry deposition cannot be measured directly. For a site-specific determination of dry deposition the concentrations of gases and aerosols in the air as well as important meteorological parameters including their gradients over the soil have to be measured. Dry deposition maps were calculated by Meteotest. For the year 2000 dry depositions were calculated as described in EKL (2005) and Thimonier et al. (2005). Dry depositions of gases and aerosols were calculated by multiplying air concentrations by land use or altitude specific deposition rates. The concentration fields of the gaseous pollutants NH_3 and NO_2 were calculated from emission inventories, which statistical dispersion models were applied to (Heldstab et al. 2004; Thöni *et al.*). Concentrations of SO_2 over the whole Swiss territory were mapped by means of geo-statistical interpolation of data from 52 sampling stations measuring continuously. Concentrations of the gaseous HNO_3 and of particulate NO_3^- and NH_4^+ were derived from a few point measurements and stratified according to altitude. Deposition rates were taken from the literature. These are assumed to depend on altitude in the case of NO_3^- and NH_4^+ (Rihm 1994), whereas they depend on the land use type (forests, agricultural land, aquatic systems, settlements, rocks) in the case of the gaseous compounds NH_3 and NO_2. The dry deposition maps for the years 1990, 1995 and 2005 were derived from the deposition values of the year 2000.

- The dry deposition of NO_2 in the years 1990, 1995 and 2005 was calculated as described previously for ammonia.
- The dry deposition of SO_2 in the years 1990, 1995 and 2005 was calculated by multiplying the deposition value of 2000 by the average concentrationsmeasured in Ticino in 1990, 1995, respectively 2005 and dividing it by the average concentrations monitored in Ticino in 2000.
- The dry deposition of HNO_3 was assumed to be constant over the studied four periods of time.

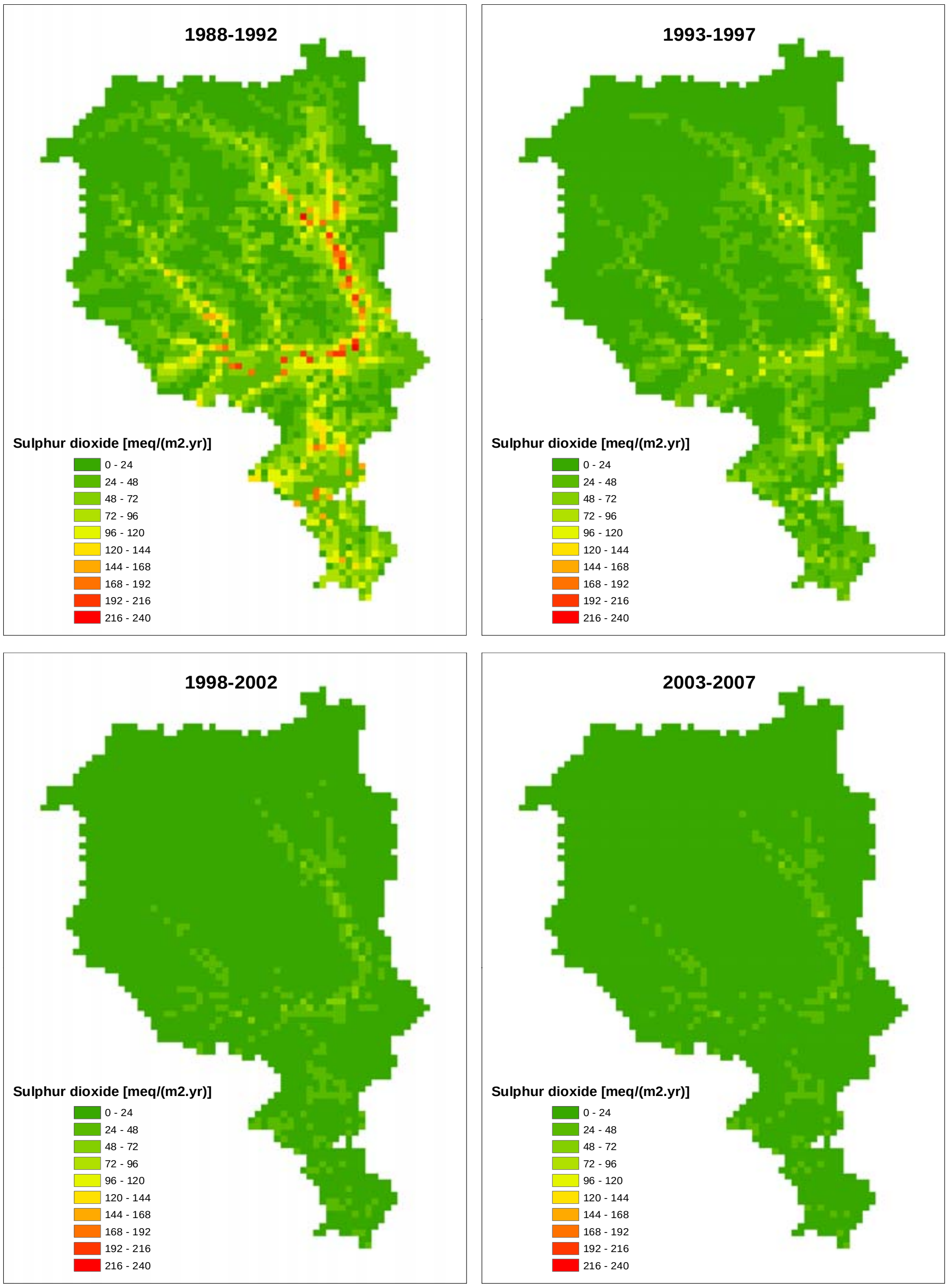
The content of particulate NO_3^- and NH_4^+ in fine dust PM10 was also assumed to be constant over time. Thus their concentrations in 1990 and in 2005 were calculated by multiplying concentrations of PM10 in 1990 and in 2005 by the fraction of NO_3^- and NH_4^+ in PM10 in the year 2000. Concentrations in 1995 correspond to the average of the concentrations in 1990 and 2000.

2.2 Maps

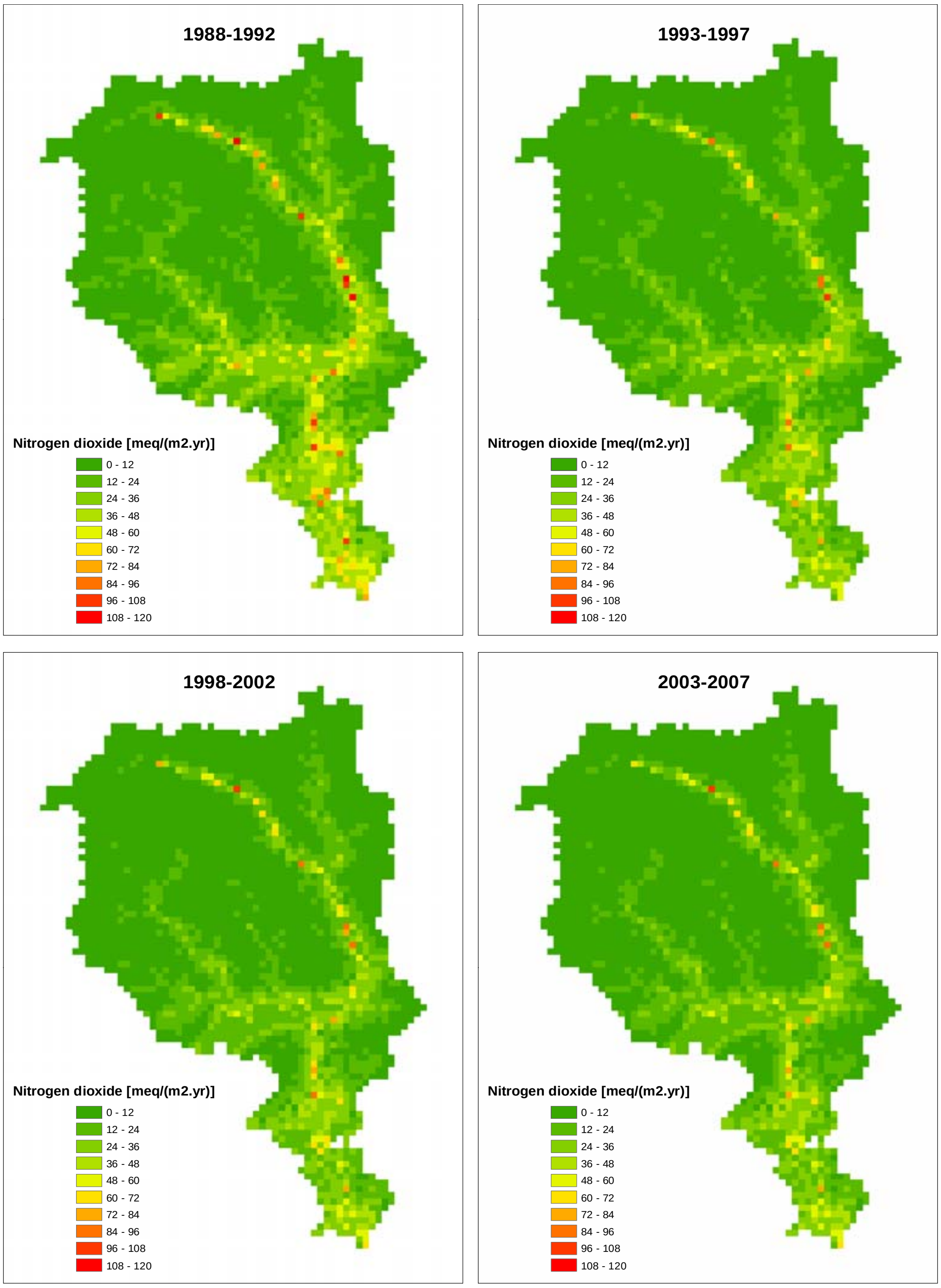
Dry depositions of gases and aerosols are mapped in Fig. 2.1 and respectively in Fig. 2.2 For every parameter and period of time a decrease of deposition with altitude can be observed. As a consequence of the reduction of SO_2 emissions the dry deposition of SO_2 have also decreased over the last 20 years. The dry deposition of NO_2 decreased slightly between the period of 1988–1992 and the period of 1993–1997 but remained generally constant afterwards. Almost no change over time was observed in the case of the dry deposition of NH_3 and HNO_3. The dry deposition of NO_3^- and NH_4^+ in aerosols seems to slightly decrease after the period 1988–1993 due to a decrease in PM10 concentrations.

Fig. 2.1 > **Dry deposition of gases: 1988–1992, 1993–1997, 1998–2002, 2003–2007**

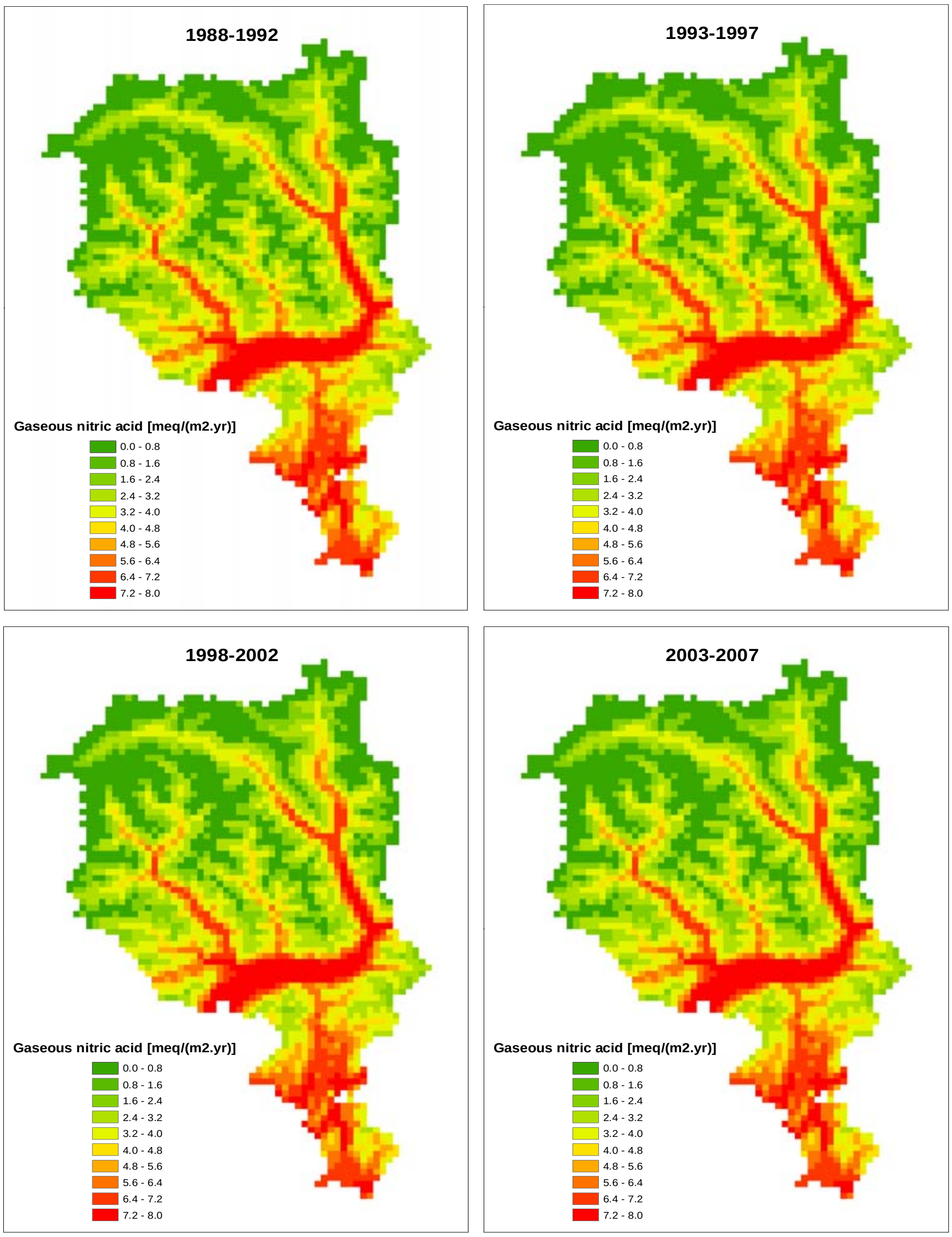
a) Sulphur dioxide deposition



b) Nitrogen dioxide deposition



c) Deposition of gaseous nitric acid



d) Deposition of ammonia

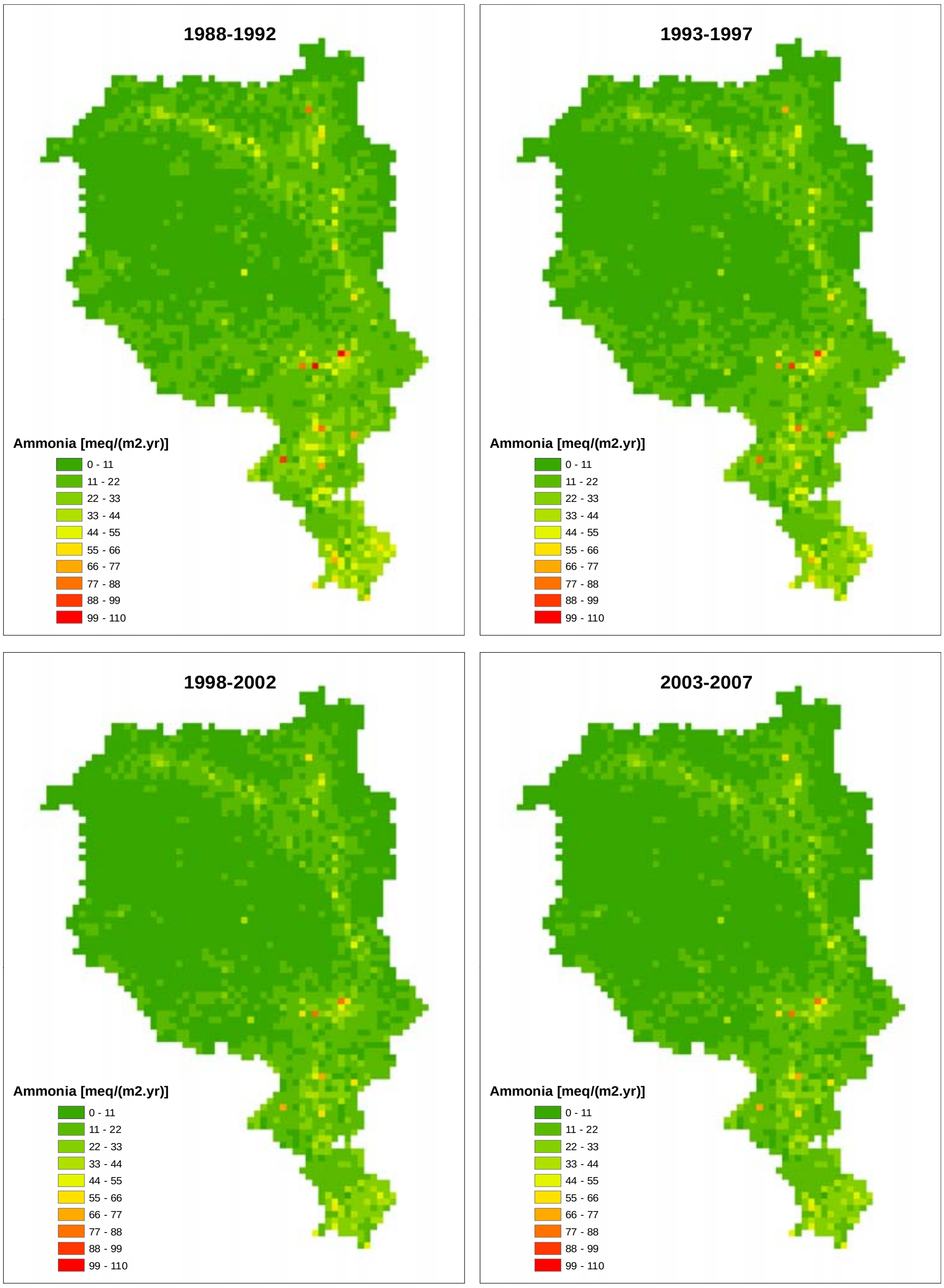
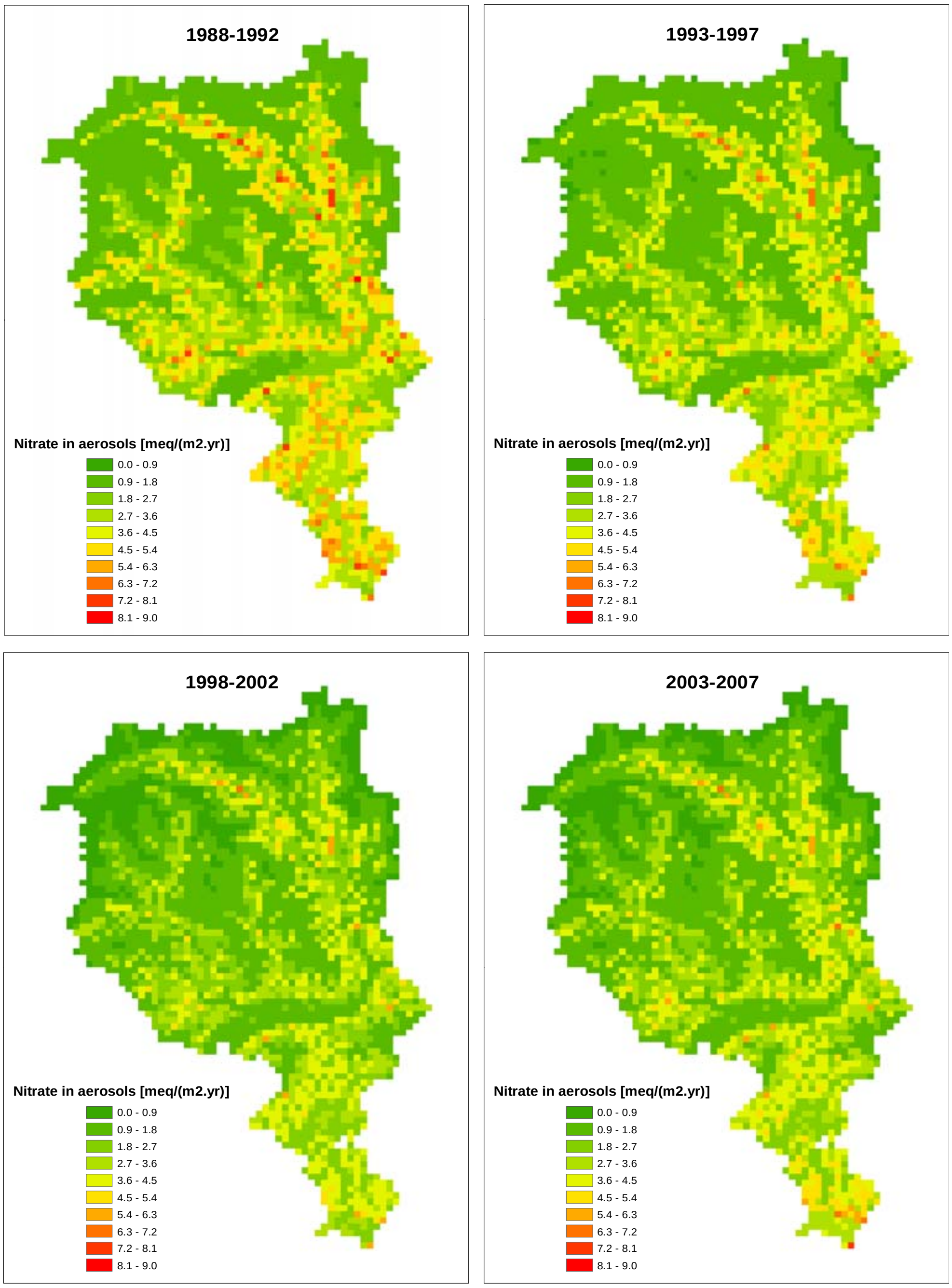


Fig. 2.2 > **Dry deposition of aerosols: 1988–1992, 1993–1997, 1998–2002, 2003–2007**

a) Deposition of nitrate in aerosols



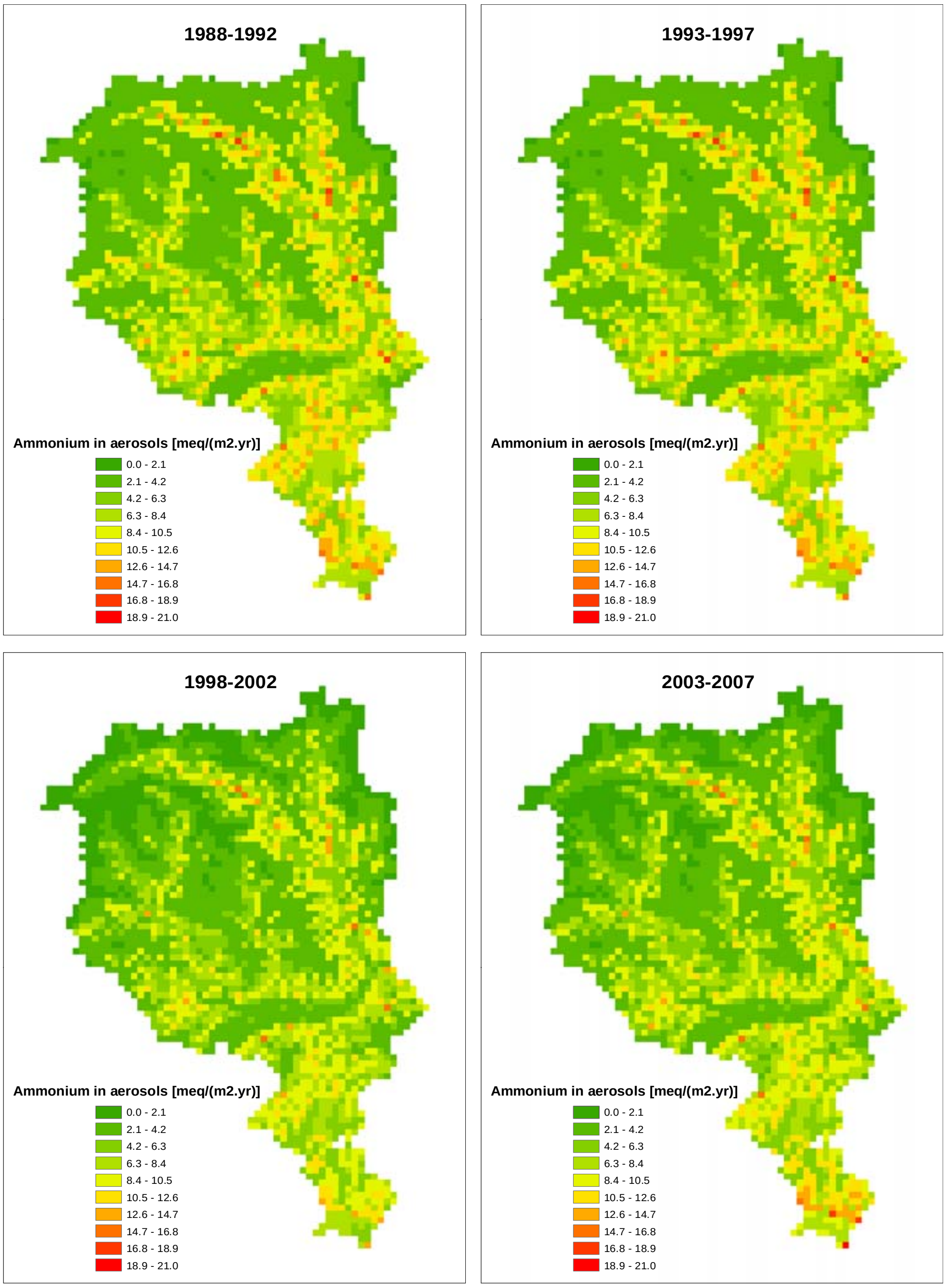
1988-1992

1993-1997

1998-2002

2003-2007

b) Deposition of ammonium in aerosols



3 > Total deposition

3.1 Mapping methods

Calculation of total deposition of sulphur, nitrogen and acidity

Fig. 3.1 illustrates the maps for the total deposition of sulphur, nitrogen, oxidized nitrogen, reduced nitrogen and the present load of acidity. These maps were produced by adding up the maps of wet and dry depositions shown in the previous chapters:

> *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:*
> wet deposition (N + S) + dry deposition (N + S)
> – wet deposition ($Ca^{2+} + Mg^{2+} + K^+$) – dry deposition ($Ca^{2+} + Mg^{2+} + K^+$)

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 all time periods (www.emep.int/basecations). In particular, values of the 50 x 50 km grid were used with the Swiss coordinates 699334, 142654 as centre: dry deposition of non-marine base cations corresponding to 54 meq/(m².yr).

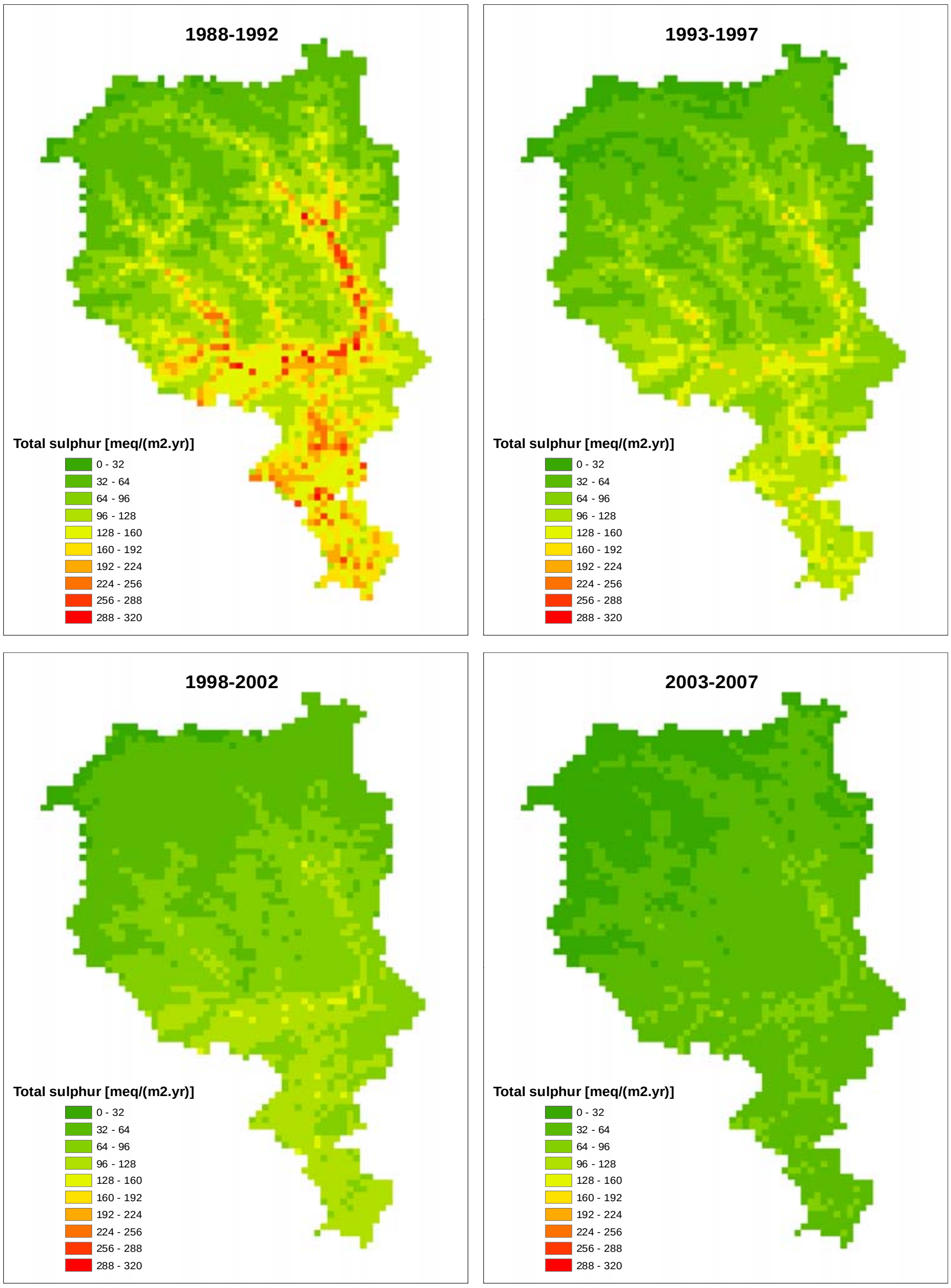
3.2 Maps

As observed in the case of the wet and dry deposition of sulphur the total deposition of sulphur also decreased consistently during the monitored period of time. The maximum deposition of sulphur decreased from 312 to 98 meq/(m².yr), while the average deposition decreased from 108 to 43 meq/(m².yr). Conversely, the deposition of nitrogen decreased much less since 1988. Moreover, during particularly wet periods as it happened in the period 1998–2002, the deposition of nitrogen can increase again to levels similar to those observed in the beginning of the monitoring period. In fact, the maximum and the average deposition of total nitrogen during all the 4 time periods were 356, 289, 324 and 264 meq/(m².yr), respectively 148, 124, 147 and 122 meq/(m².yr). Oxidized and reduced nitrogen contributed with about 50 % each to the total, although a slight increase of reduced nitrogen (from 50 % to 52 %) with respect to oxidized nitrogen (from 50 % to 48 %) over time can be observed. As a consequence of the reduced sulphur deposition the present load of acidity decreased also significantly. The maximum and the average present load of acidity decreased from 558 to 296 meq/(m^2.yr) and respectively from 206 to 120 meq/(m^2.yr).

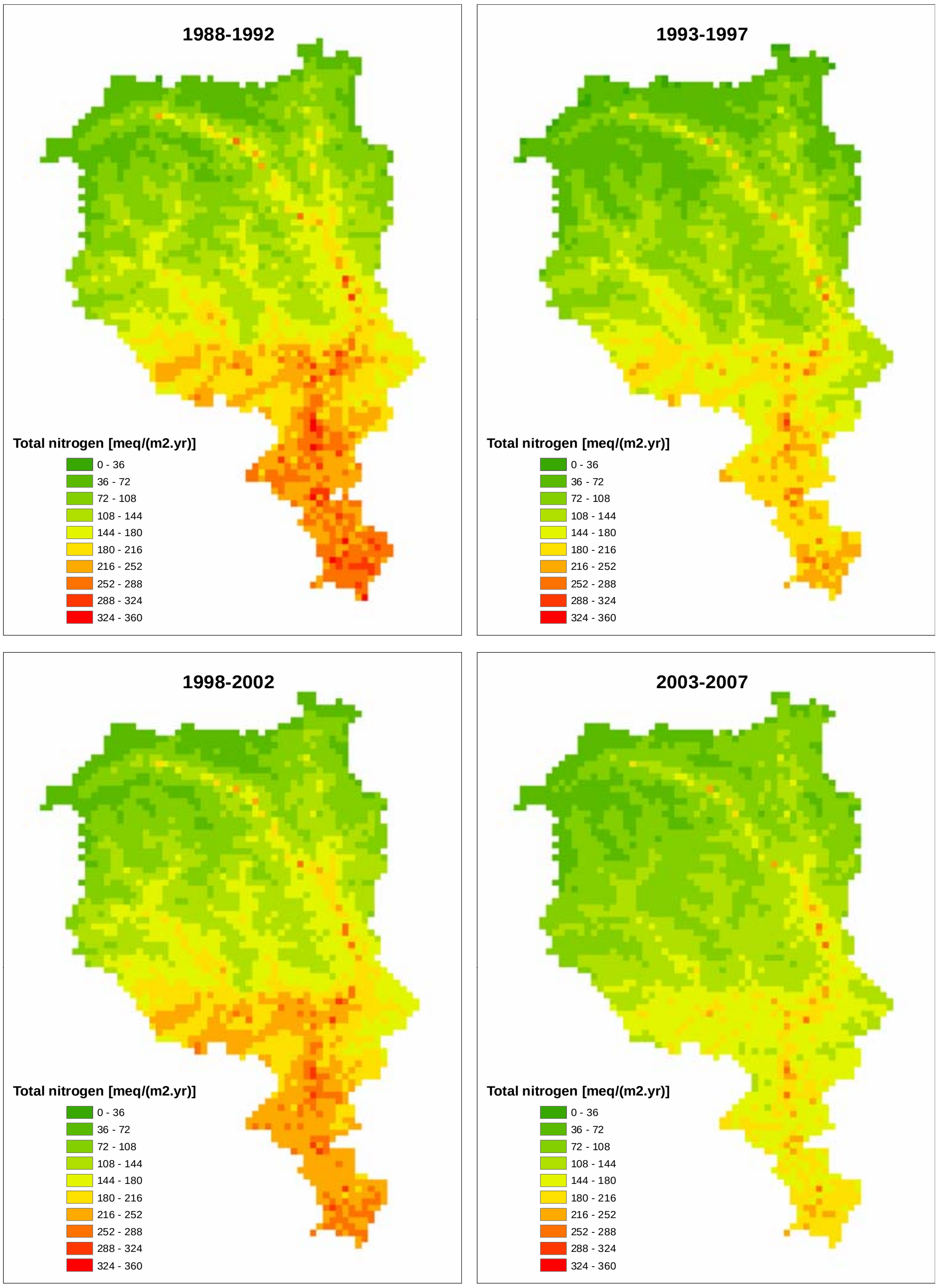
Fig. 3.2 shows how the deposition of acidifying compounds is mainly due to wet deposition. Wet deposition can contribute between 68 % and 80 % to the total deposition of acidifying compounds, depending on the amount of yearly precipitation. Dry deposition, especially that of aerosols, is therefore contributing to a lesser extent to the total deposition value. Wet deposition is also the main component of the total deposition of nitrogen: between 70 % and 77 %, depending on annual precipitations. Fig. 3.3 shows that the contribution of sulphur compounds to the total deposition of acidifying compounds decreased from 42 % in the period 1988–1993 to 26 % in the period 2003–2007. This is explained by the reduction of sulphur emissions over time. Accordingly, nitrogen compounds became more important in determining acidifying deposition. In fact, the ratio of reduced and oxidized nitrogen compounds increased from 29 % to 39 %, respectively from 29 % to 35 %.

Fig. 3.1 > Total deposition: 1988–1992, 1993–1997, 1998–2002, 2003–2007

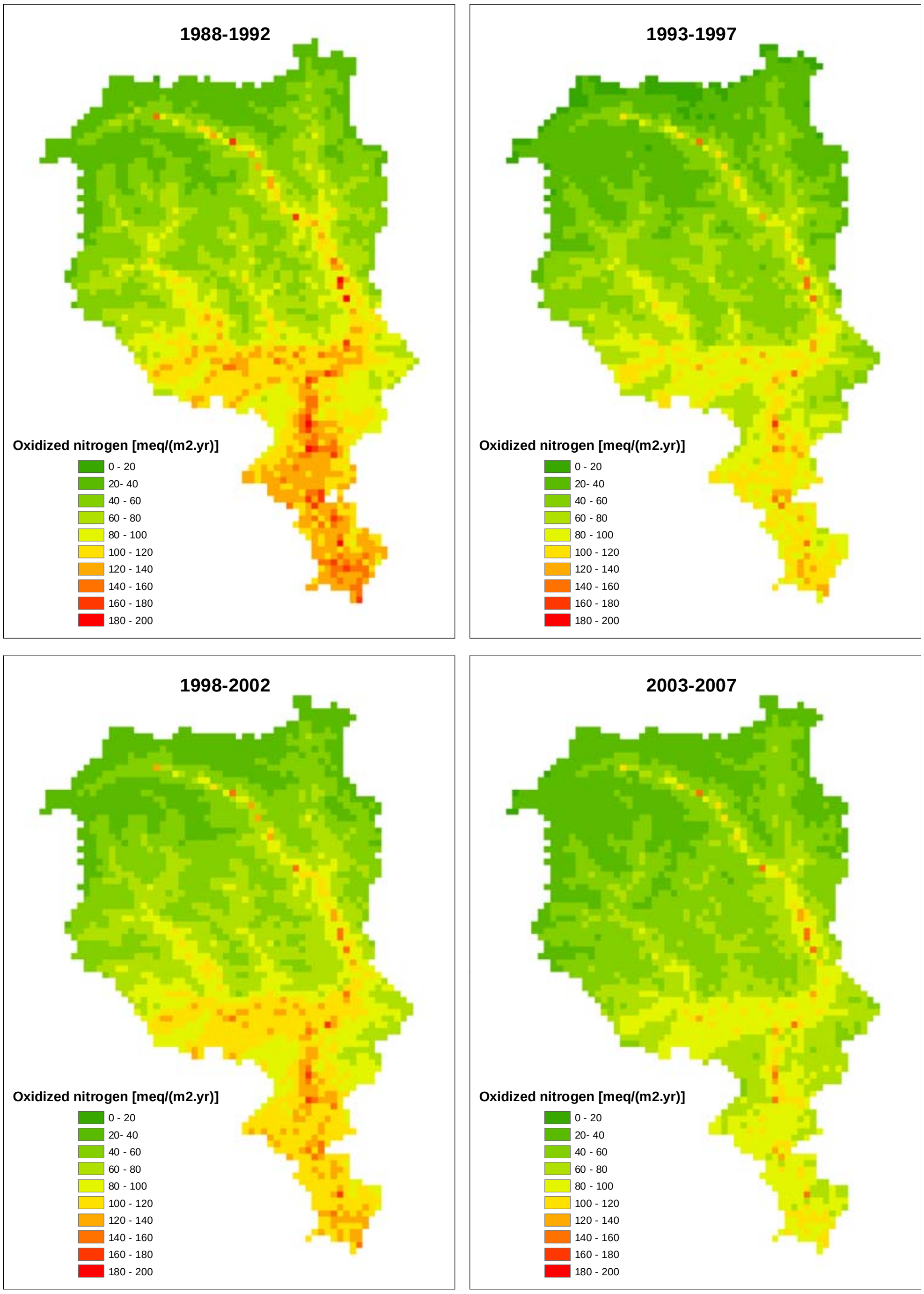
a)Total sulphur deposition



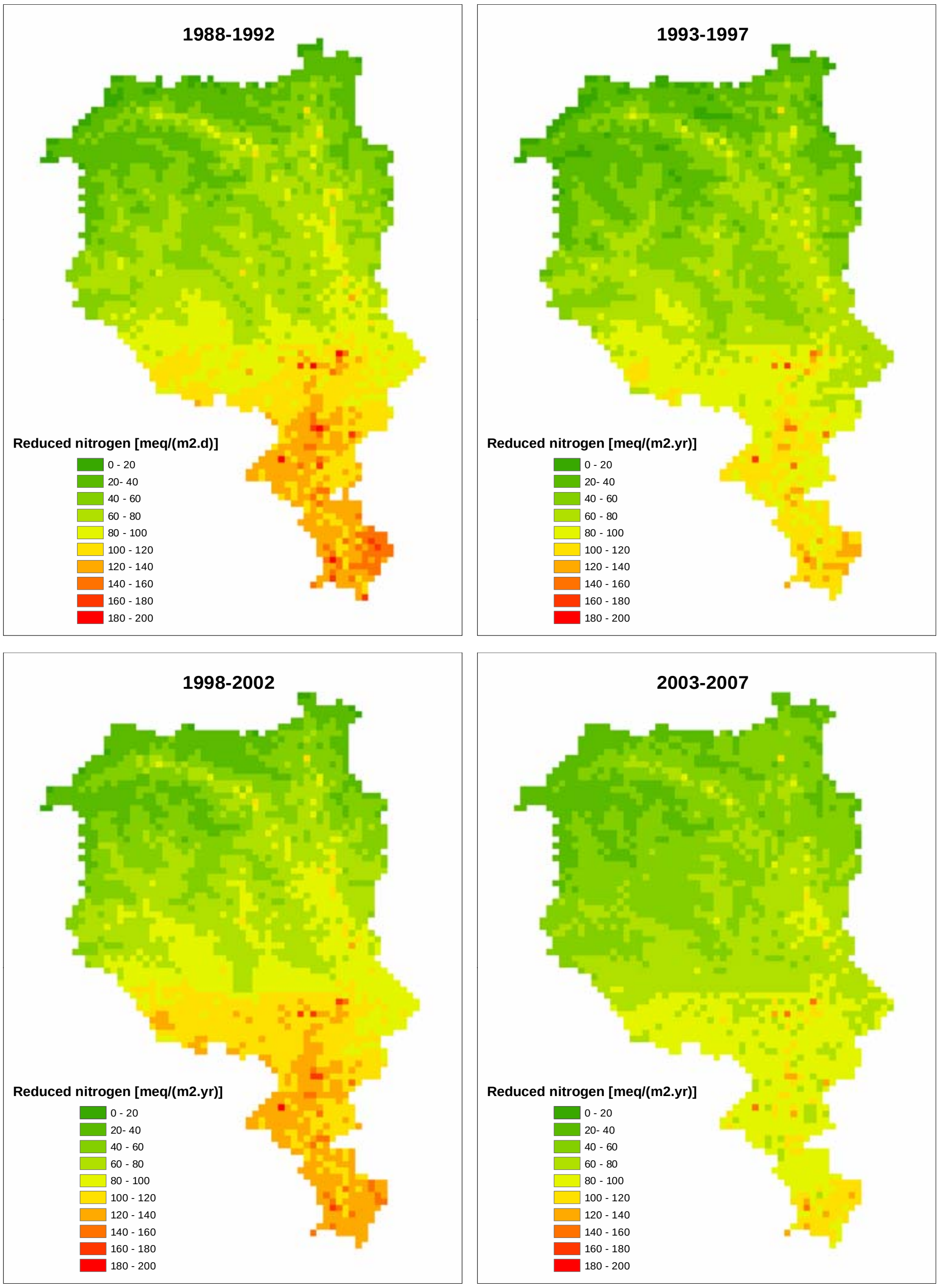
b) Total nitrogen deposition



c) Deposition of oxidized nitrogen



d) Deposition of reduced nitrogen



e) Present load of acidity

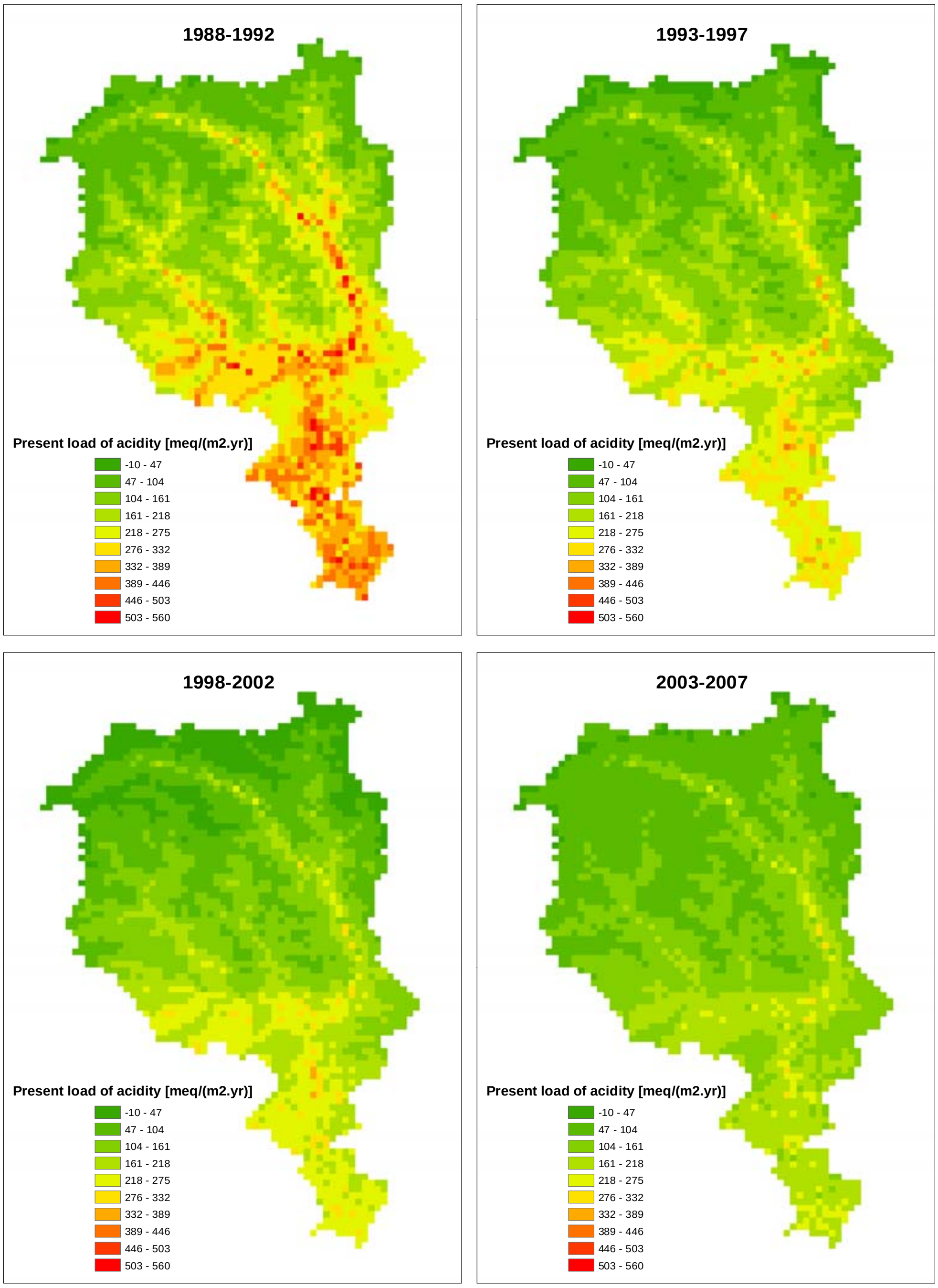


Fig. 3.2 > Contribution of wet deposition and dry deposition of gases and aerosols to total acidifying load

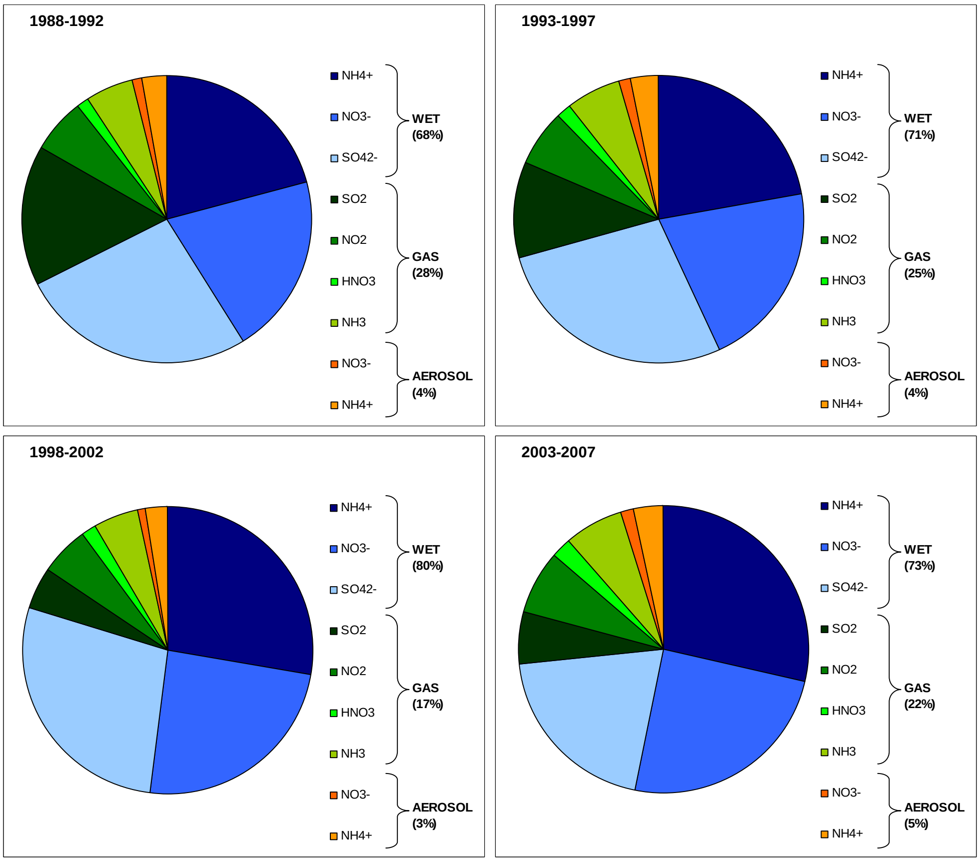
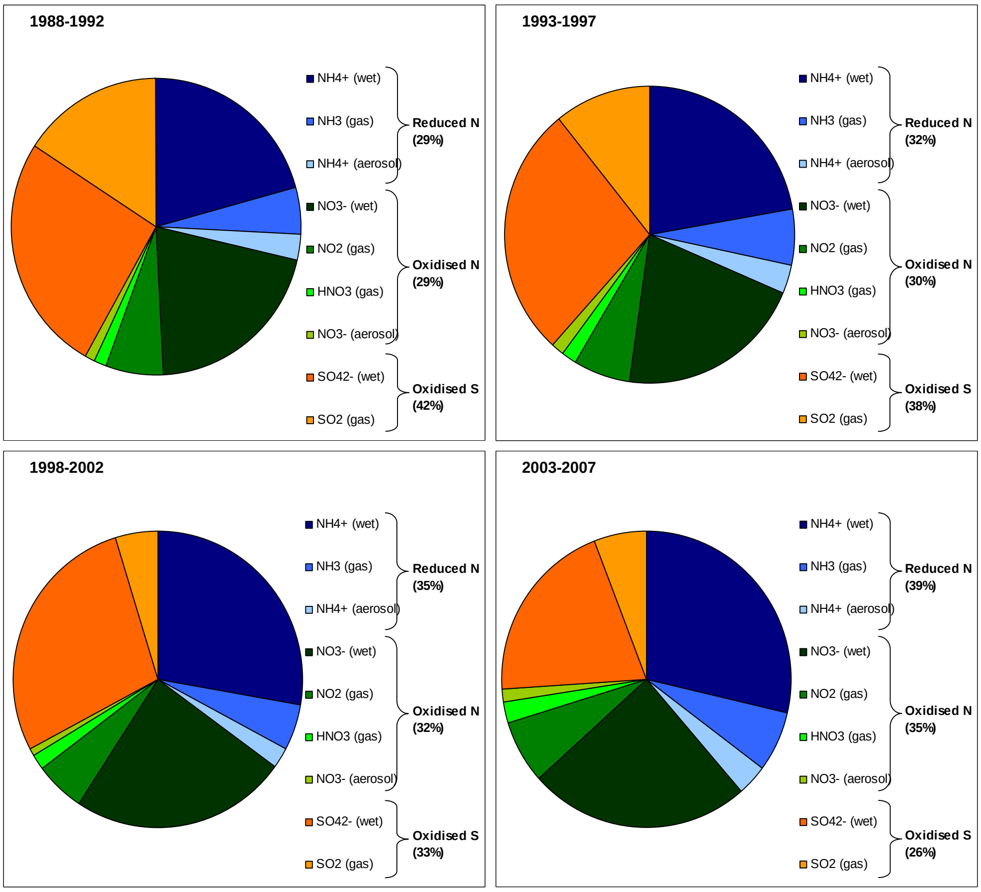


Fig. 3.3 > Contribution of reduced N, oxidised N and oxidised S to total acidifying load



4 > Conclusions

A chemical analysis of rainwater over the last 20 years in Canton Ticino shows that sulphate concentrations have decreased, reflecting the decrease of SO_2 emissions since 1980. While no significant trend could be observed for the concentrations of ammonium and nitrate, the concentrations of bicarbonate and base cations have increased and were particularly high during the years 1999, 2000 and 2002, when the amount of precipitation was higher than usual.

It is possible that rain rich years increase the probability of the occurrence of alkaline rain events. In addition, the reduction of sulphate concentration during the last two decades may have decreased the capability of rainwater of neutralizing alkaline rain events, making these more noticeable in rainwater chemistry. As a consequence of decreased sulphur emissions and of an increased number of alkaline rain events acidity has decreased and pH values have thus increased.

It has also been observed that most chemical parameters in rainwater correlate significantly with one or more of the geographic parameters latitude, longitude and altitude. Sulphate, nitrate and ammonium concentrations correlate with latitude and altitude, reflecting the transportation of these pollutants from Milan’s urban area towards north. Atmospheric currents causing rainfall are mostly directed from south-west to north-east. Therefore concentrations of base cations and bicarbonate, which increase with decreasing annual precipitation (smaller dilution of alkaline rain events on an annual base), increase along with longitude. Acidity correlated with latitude at the beginning of the monitored period (1988–1992), but has become gradually more independent of latitude and dependent on longitude after the period 1998–2002. This suggests that during the first period acidity was mainly determined by emissions of SO_2, NO_x and NH_3, whereas afterwards alkaline rain events have become much more significant.

Observations made for concentrations of chemical parameters in rainwater are not substantially different from those for wet deposition. In general, time trends with a decreasing deposition of sulphate and acidity and with an increasing deposition of base cations and bicarbonate can be observed. The geographic distribution has also remained constant. However, the particularly rain rich (1998–2002) and rain poor (2003–2007) years had visible consequences on deposition. The deposition of sulphate, nitrate and ammonium were slightly higher during the period 1998–2002 compared to the immediately previous and successive periods.

Wet deposition contributes mostly to the total deposition of nitrogen (70–77 %) and to the present load of acidity (68–80 %), while the dry deposition of gases and especially of aerosols are much less important. As a consequence of the reduced deposition of sulphur the relative importance of sulphur compounds in the total deposition of acidifying compounds has decreased from 42 % to 26 %, while that of nitrogen compounds has increased from 58 % to 74 % over the past 20 years.

> Appendix

A1 Mean annual concentrations in wet deposition

Tab. A1.1 > Mean annual concentrations in wet deposition: sampling sites

Prec. and Cond. correspond to precipitation, respectively to conductivity.

Year	Prec.	Analysed Prec.	Cond. 20 °C	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	HCO_3^{-}	NO_3^{-}	SO_4^{2-}	Cl^{-}	Acidity
	mm	%	μS cm^{-1}		meq m^{-3}									
Acquarossa														
1990	1056	61	26	4.4	18	6	20	5	40	0	45	51	29	43
1991	1201	75	17	4.6	27	6	17	3	28	14	31	38	13	10
1993	1746	91	16	4.7	32	6	9	2	34	7	31	42	12	12
1994	1432	97	13	5.0	30	11	7	1	31	11	28	40	7	-1
1995	1044	80	12	4.9	25	8	5	2	28	4	28	36	5	9
1996	1282	92	12	4.9	23	6	6	1	27	12	25	26	7	0
1997	1083	89	10	5.0	12	4	5	4	21	0	22	23	8	9
1998	1227	86	13	4.9	18	5	6	1	33	3	30	30	4	9
1999	1688	78	12	5.3	32	9	5	1	34	11	28	35	5	-6
2000	1684	89	14	5.3	60	12	9	2	26	35	27	41	7	-30
2001	1344	88	12	5.1	23	9	5	1	37	5	33	38	4	3
2002	1792	87	12	5.2	42	7	10	7	23	34	20	34	4	-28
2003	923	81	13	5.5	35	9	6	2	40	19	32	33	5	-16
2004	1241	67	9	5.5	24	7	7	3	33	16	24	23	5	-12
2005	661	77	16	5.8	49	14	14	5	61	30	46	41	5	-28
2006	1018	35	7	5.3	17	6	6	1	13	1	18	15	4	7
2007	954	85	11	5.4	24	7	7	2	39	11	30	33	4	-7
Bignasco														
2001	2099	4	8	5.3	13	3	4	2	24	6	20	17	4	-1
2002	2564	69	10	5.0	13	3	8	4	21	4	22	25	6	7
2003	1087	92	12	5.1	21	3	6	3	39	12	32	30	5	-3
2004	1663	15	10	4.9	16	2	6	5	14	4	29	18	4	9
2005	844	92	13	5.1	20	3	5	2	47	9	37	28	4	0
2006	1287	85	11	5.0	15	3	9	2	28	2	30	20	6	8
2007	1252	93	11	5.1	17	4	8	3	29	3	30	26	6	6
Monte Brè														
1995	1412	51	15	4.6	15	7	6	1	25	0	29	43	5	24
1996	1721	80	14	4.8	21	5	5	1	35	7	32	36	6	11
1997	1227	80	15	4.9	15	5	6	1	38	0	36	38	7	14

Year	Prec.	Analysed Prec.	Cond. 20 °C	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	HCO_3^{-}	NO_3^{-}	SO_4^{2-}	Cl^{-}	Acidity
	mm	%	µS cm^{-1}		meq m^{-3}									
1998	1508	86	16	4.8	23	5	9	2	43	4	37	41	7	10
1999	1699	93	15	5.0	37	7	10	3	45	8	38	43	10	1
2000	2149	93	11	5.2	31	6	10	2	28	12	28	31	7	-6
2001	1499	87	17	4.9	21	6	11	2	54	3	44	46	9	10
2002	2105	101	16	5.1	66	6	8	3	35	50	31	34	9	-42
2003	1167	90	15	5.2	25	5	10	4	53	15	45	32	9	-8
2004	1373	29	10	5.2	17	4	9	2	25	7	28	19	6	0
2005	947	92	24	4.8	29	6	20	5	75	9	69	41	20	7
2006	1304	89	15	5.2	31	5	11	2	51	15	43	33	7	-8
2007	1143	94	11	5.3	15	3	8	2	41	9	33	26	7	-4
Locarno Monti														
1982	1875	28	19	4.4	21	6	5	3	14	0	20	59	8	36
1983	1938	90	29	4.5	49	11	16	3	57	4	43	109	13	29
1984	2132	65	21	4.5	31	7	25	4	28	12	30	84	11	21
1985	1729	25	41	4.1	41	9	41	4	54	0	62	125	15	78
1988	2127	100	27	4.3	34	5	14	3	50	3	39	84	17	42
1989	1478	89	24	4.3	20	7	13	4	30	0	36	62	15	46
1990	1474	78	34	4.3	22	6	20	6	56	3	56	73	30	51
1991	1782	86	27	4.4	23	5	18	3	52	0	42	65	18	36
1993	2134	91	20	4.5	29	7	11	2	39	5	36	52	13	24
1994	1865	85	18	4.6	24	8	8	1	34	6	31	52	9	16
1995	1406	92	19	4.6	27	8	6	2	38	3	37	58	9	23
1996	1661	84	19	4.7	28	8	10	1	43	13	37	49	10	9
1997	1564	88	15	4.8	16	6	7	2	35	0	32	39	9	15
1998	1752	90	20	4.7	22	5	10	3	52	4	46	48	8	18
1999	2367	77	17	4.9	33	6	9	2	50	6	43	46	8	6
2000	2623	87	17	4.9	48	8	11	3	39	26	38	43	9	-13
2001	1754	84	20	4.7	23	5	10	1	56	6	49	49	8	15
2002	2649	94	15	5.0	44	4	6	2	38	35	30	31	6	-26
2003	1107	86	16	4.9	21	3	7	2	49	10	43	35	6	3
2004	1894	17	10	4.8	14	4	16	11	16	0	25	39	4	15
2005	1057	89	17	5.0	28	4	8	2	62	12	51	36	5	-2
2006	1629	78	13	5.0	19	4	11	2	38	5	34	28	8	5
2007	1527	85	12	5.1	15	3	5	1	45	6	37	29	5	1
Lugano														
1982	1683	24	28	4.2	16	5	4	2	22	0	27	65	10	60
1983	1453	78	33	4.3	59	13	15	4	68	4	54	123	16	45
1984	1832	83	28	4.2	33	7	18	5	29	2	31	93	15	58
1985	1380	16	42	4.1	53	12	36	5	56	0	63	118	37	86
1989	1468	80	31	4.3	28	8	18	5	51	1	55	82	18	51

Year	Prec.	Analysed Prec.	Cond. 20 °C	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	HCO_3^-	NO_3^-	SO_4^{2-}	Cl^-	Acidity
	mm	%	µS cm^{-1}											meq m^{-3}
1990	1342	95	31	4.4	28	6	23	7	64	2	59	70	29	41
1991	1288	75	26	4.4	18	6	24	7	60	0	54	70	17	39
1993	1590	84	21	4.6	29	7	11	3	46	3	42	60	12	25
1994	1703	84	18	4.8	33	12	11	2	42	9	38	59	12	7
1995	1412	84	19	4.6	26	10	8	2	41	4	37	56	8	19
1996	1721	80	17	4.8	26	8	10	2	44	6	36	49	10	10
1997	1227	96	16	4.8	19	6	8	2	44	2	38	43	9	12
1998	1508	81	19	4.7	27	6	10	3	50	7	43	48	9	10
1999	1699	77	19	4.9	44	9	13	3	53	12	43	60	12	1
2000	2149	86	16	5.0	38	7	11	2	41	16	40	42	9	-5
2001	1499	76	18	4.9	22	6	14	4	62	4	49	55	12	10
2002	2105	91	19	5.0	70	7	12	5	45	46	38	49	11	-36
2003	1167	75	23	5.1	51	9	14	6	75	27	68	57	12	-19
2004	1373	63	13	5.5	32	6	10	4	58	16	40	34	8	-13
2005	947	61	20	5.2	41	8	11	5	73	17	64	46	10	-10
2006	1304	60	19	5.2	44	13	16	6	60	16	52	46	17	-10
2007	1143	66	14	5.5	29	7	13	6	43	18	39	35	9	-15
Piotta														
1990	1281	61	23	4.5	24	5	16	4	29	9	38	48	25	26
1991	1475	78	17	4.6	19	3	20	4	32	7	32	33	15	17
1993	2005	93	13	4.7	17	4	6	1	24	2	23	33	9	16
1994	1279	93	13	4.9	27	9	8	1	25	10	26	35	9	3
1995	1235	92	11	5.0	20	6	11	1	21	1	22	32	12	9
1996	1597	78	11	5.0	13	5	8	1	25	3	22	24	8	8
1997	1345	82	11	4.9	11	3	9	1	21	0	24	23	9	12
1998	1426	90	12	4.9	13	4	8	1	27	2	24	26	6	11
1999	1722	84	10	5.1	21	4	5	1	28	6	24	26	5	2
2000	1853	86	14	5.1	61	6	9	1	23	49	26	28	9	-41
2001	1509	89	12	4.9	14	3	9	1	33	6	28	28	8	7
2002	2018	94	7	5.2	14	2	4	2	20	10	16	15	4	-3
2003	1063	88	12	5.3	20	4	9	2	45	22	29	26	9	-16
2004	1119	85	8	5.3	16	3	15	4	23	10	21	18	11	-5
2005	644	108	11	5.3	14	2	7	1	38	8	29	21	7	-3
2006	1176	81	9	5.2	16	3	9	1	23	5	25	18	9	2
2007	1313	80	9	5.3	12	2	5	1	28	7	22	20	5	-1
Robiei														
1996	2465	53	6	5.1	6	2	2	0	11	0	12	15	2	9
1997	2202	89	8	5.0	10	2	3	1	15	0	15	21	3	10
1998	2216	95	9	5.0	15	3	6	1	20	5	19	23	3	6
1999	2845	91	9	5.3	19	6	5	1	24	7	21	25	4	-1

Year	Prec.	Analysed Prec.	Cond. 20 °C	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	HCO_3^-	NO_3^-	SO_4^{2-}	Cl^-	Acidity
	mm	%	µS cm^{-1}		meq m^{-3}									
2000	3330	90	11	5.2	27	5	6	1	25	13	24	28	4	-6
2001	2258	92	12	4.9	13	3	2	1	32	2	28	31	3	11
2002	2782	72	9	5.1	10	2	3	1	27	5	21	21	2	2
2003	1625	91	9	5.3	12	2	3	1	37	7	29	22	2	-2
2004	2277	65	7	5.3	15	2	4	1	22	8	19	16	3	-3
2005	1357	91	11	5.2	17	2	2	1	53	7	40	29	2	0
2006	2146	82	8	5.1	13	2	3	1	25	3	23	18	3	4
2007	1639	100	8	5.2	10	2	3	1	29	4	24	20	3	1

Sonogno

2001	2099	11	12	4.8	7	3	6	2	35	3	26	29	6	13
2002	2782	87	11	5.1	17	5	6	6	26	19	22	22	4	-11
2003	1435	76	11	5.2	20	3	6	2	35	8	31	26	6	-2
2004	1980	43	9	5.3	12	3	9	3	32	7	25	20	5	-3
2005	1033	50	10	5.2	19	2	6	1	25	7	24	20	4	-1
2006	1858	97	10	5.1	21	7	10	3	22	10	23	21	5	-3
2007	1659	84	10	5.3	15	3	6	3	40	8	30	28	4	-4

Stabio

1990	1231	60	32	4.4	23	6	22	6	69	8	61	71	21	34
1991	1181	61	32	4.4	36	9	28	9	71	0	66	85	21	37
1993	1394	90	23	4.7	43	12	14	3	60	2	52	75	15	19
1994	1485	92	21	4.8	40	12	13	2	55	11	46	66	14	6
1995	1487	91	22	4.6	25	8	9	1	53	6	45	61	9	21
1996	1706	88	19	4.7	26	8	15	1	42	8	37	50	12	12
1997	1269	90	16	4.9	20	6	8	1	49	3	39	43	8	11
1998	1566	90	18	4.9	24	7	10	2	56	8	41	46	11	6
1999	1410	93	19	4.9	35	8	12	2	59	11	47	51	11	1
2000	2336	92	17	5.0	33	7	11	2	52	17	41	45	9	-7
2001	1250	101	19	4.9	30	7	12	2	66	11	53	54	11	3
2002	2509	75	19	5.1	67	6	10	2	54	55	36	42	11	-46
2003	1202	90	15	5.0	19	4	8	2	54	15	43	32	7	-5
2004	1364	86	12	5.2	23	5	12	6	45	13	37	34	7	-6
2005	898	100	18	5.2	25	5	10	3	75	16	55	36	9	-10
2006	1184	90	15	5.2	24	5	13	2	62	12	48	33	10	-6
2007	1183	88	13	5.4	15	4	10	4	52	13	38	31	9	-8

A2 Average concentrations in rainwater in the periods of 1988–1992, 1993–1997, 1998–2002 and 2003–2007

Tab. A2.1 > Average concentrations in rainwater: sampling sites

Prec. and Cond. correspond to precipitation, respectively to conductivity.
Values in red are estimations.

Period	Prec.	Cond. 20 °C	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	HCO_3^-	NO_3^-	SO_4^{2-}	Cl^-	Acidity
	mm	$\mu S\ cm^{-1}$		$meq\ m^{-3}$									
Acquarossa													
1988–1992	1169	21	33	23	6	19	4	34	7	37	44	21	25
1993–1997	1317	13	13	25	7	7	2	29	7	27	35	8	6
1998–2002	1547	13	7	37	8	7	3	30	19	27	36	5	-12
2003–2007	959	11	4	28	8	6	2	35	14	29	28	5	-11
Bignasco													
1988–1992	1552	14	23	10	3	9	4	25	1	26	33	9	22
1993–1997	1917	10	13	9	4	5	2	20	1	20	25	6	11
1998–2002	2144	9	8	13	3	6	3	22	5	21	21	5	3
2003–2007	1227	11	10	17	3	7	3	29	5	31	24	5	5
Monte Brè													
1988–1992	1451	21	34	18	5	9	2	42	3	42	51	10	31
1993–1997	1530	15	19	17	5	6	1	33	3	32	39	6	16
1998–2002	1792	15	10	37	6	9	2	40	17	35	38	8	-8
2003–2007	1187	14	8	23	4	11	3	47	11	42	29	9	-3
Locarno Monti													
1988–1992	1701	28	45	26	6	16	4	47	2	43	72	20	43
1993–1997	1726	18	23	25	7	9	2	38	5	35	50	10	18
1998–2002	2229	17	14	14	6	9	2	46	17	40	42	8	-3
2003–2007	1443	13	11	11	3	10	4	39	6	36	33	5	5
Lugano													
1988–1992	1451	30	45	25	7	21	6	58	1	56	74	21	44
1993–1997	1530	18	19	27	9	10	2	43	5	38	54	10	14
1998–2002	1792	18	13	42	7	12	4	49	19	42	50	11	-6
2003–2007	1187	18	5	39	9	13	5	61	19	52	43	11	-13
Piotta													
1988–1992	1375	20	29	21	4	18	4	31	8	35	40	20	21
1993–1997	1492	12	13	17	5	8	1	23	3	23	29	9	10
1998–2002	1706	11	9	25	4	7	1	26	15	23	24	6	-6
2003–2007	1063	10	6	16	3	9	2	30	10	25	20	8	-5

Period	Prec.	Cond. 20 °C	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	HCO_3^-	NO_3^-	SO_4^{2-}	Cl^-	Acidity
	mm	µS cm^{-1}		meq m^{-3}									
Robiei													
1988–1992	2362	10	17	9	2	4	1	17	0	18	23	3	17
1993–1997	2476	7	9	8	2	2	1	13	0	13	18	2	9
1998–2002	2686	10	8	18	4	5	1	26	7	23	25	3	2
2003–2007	1809	9	6	13	2	3	1	31	6	26	20	3	0
Sonogno													
1988–1992	1820	18	33	10	4	8	6	34	3	29	38	9	29
1993–1997	2245	12	18	9	5	5	3	27	3	22	29	6	15
1998–2002	2446	11	11	13	4	6	4	30	12	23	25	5	-1
2003–2007	1593	10	6	17	4	8	3	31	8	27	23	5	-2
Stabio													
1988–1992	1381	32	40	29	8	25	7	70	4	63	78	21	36
1993–1997	1468	20	20	31	9	12	2	52	6	43	59	12	14
1998–2002	1814	18	11	41	7	11	2	56	24	42	47	10	-13
2003–2007	1166	14	7	21	4	10	3	56	13	43	33	8	-7
Bellinzago (Italy)													
1988–1992	955	33	40	31	6	12	3	80	5	62	82	14	34
1993–1997	1135	24	30	23	5	10	2	53	4	46	57	11	26
1998–2002	1155	21	12	41	8	14	8	62	32	46	50	13	-20
2003–2007	849	16	7	21	5	11	4	66	20	43	36	10	-13
Devero (Italy)													
1988–1992	1488	18	34	11	2	6	3	28	1	28	33	7	34
1993–1997	1723	13	19	10	2	4	1	22	1	22	25	4	18
1998–2002	2070	12	12	19	3	11	3	26	11	24	25	10	0
2003–2007	1180	10	6	15	3	5	2	31	9	25	20	4	-3
Domodossola (Italy)													
1988–1992	1273	21	32	20	4	5	2	31	3	32	46	6	29
1993–1997	1475	16	21	17	3	5	2	28	3	27	35	5	19
1998–2002	1622	13	13	24	3	5	2	31	17	27	27	4	-4
2003–2007	1045	12	9	15	3	4	1	42	9	33	23	4	0
Graniga (Italy)													
1988–1992	1559	22	36	19	3	8	4	37	4	37	46	8	32
1993–1997	1763	15	20	17	3	5	2	30	4	28	35	5	16
1998–2002	1950	14	14	20	3	6	2	32	14	29	28	4	1
2003–2007	1309	12	9	15	3	4	1	42	12	32	23	4	-3

Period	Prec.	Cond. 20 °C	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	HCO_3^-	NO_3^-	SO_4^{2-}	Cl^-	Acidity
	mm	µS cm^{-1}											meq m^{-3}
Lunecco (Italy)													
1988–1992	2057	22	31	19	4	8	2	45	4	38	51	9	27
1993–1997	2304	19	22	19	4	9	2	39	4	34	44	9	18
1998–2002	2670	17	14	26	4	8	2	43	17	35	37	7	-2
2003–2007	1493	13	9	14	3	5	1	47	6	37	28	5	4
Pallanza (Italy)													
1988–1992	1735	30	42	23	5	11	2	61	3	49	69	11	39
1993–1997	1972	25	32	21	5	9	2	52	3	44	57	10	28
1998–2002	2189	20	18	27	4	10	3	56	15	43	44	9	3
2003–2007	1426	16	9	16	4	8	2	65	12	46	34	7	-2
S. Monte Orta (Italy)													
1993–1997	1391	32	41	26	5	10	3	70	5	57	70	10	36
1998–2002	1725	23	27	22	5	10	2	53	5	44	55	10	22
2003–2007	1846	22	22	19	5	13	3	66	6	51	52	13	16
Monte Mesma (Italy)													
2003–2007	1257	16	10	18	4	8	2	59	7	47	34	7	3
Basodino (Glacier)													
1988–1992	2362	7	7	13	5	4	2	9	3	10	16	7	4
1993–1997	1338	5	4	12	5	3	1	7	3	8	12	4	1
1998–2002	2886	4	3	11	2	3	1	5	6	7	7	2	-3
2003–2007	1809	5	3	9	3	4	1	12	7	10	8	4	-4

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