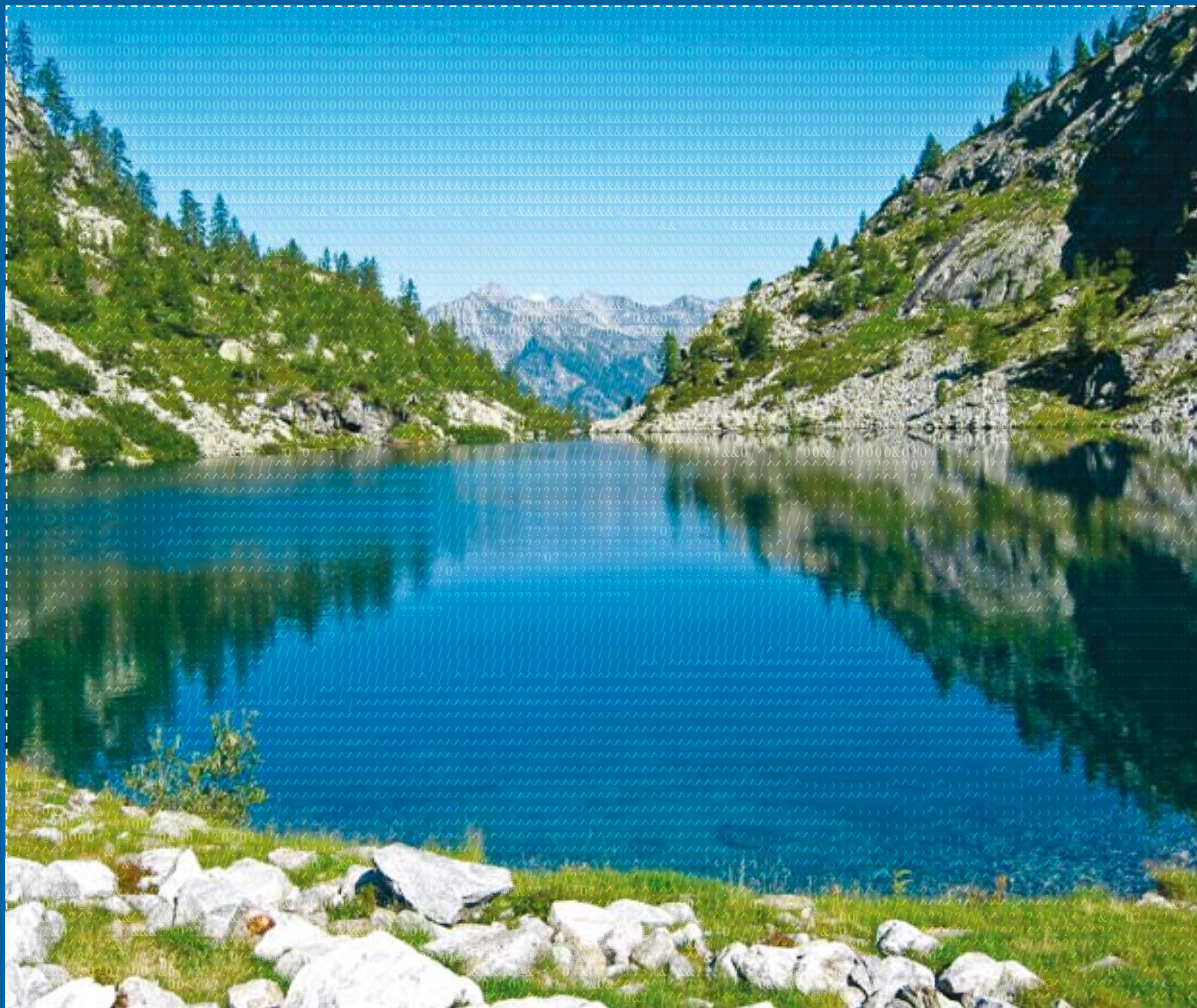19
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> Impacts of Air Pollution on Alpine Lakes and Rivers

Chemistry and biology in Alpine lakes and rivers in Southern Switzerland related to acidification from long-range transboundary air pollution: Monitoring results from 1980-2004

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Chemistry and biology in Alpine lakes and rivers in Southern Switzerland related to acidification from long-range transboundary air pollution: Monitoring results from 1980-2004

Mit deutscher Zusammenfassung – Avec résumé en français – Con riassunto in italiano

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> Abstracts

Switzerland joined the International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes under the Convention on Long-Range Transboundary Air Pollution (UNECE) in 2000. However, monitoring of Alpine mountain lakes started already in 1980. Trend analyses on the key variables involved in acidification processes were performed. Sulphate concentrations decreased and alkalinity increased significantly in most studied lakes, while base cation and nitrate trends are small and mostly insignificant. Seasonal variations of the same parameters were analyzed for three Alpine rivers. Seasonal variations of alkalinity, base cation and sulphate concentrations correlate negatively with the river discharge, while a positive correlation was found for the concentrations of dissolved aluminium. The nitrate concentrations on the other hand were difficult to predict In both lakes and rivers macroinvertebrates were utilized as bioindicators for the level of acidification. Applying the evaluation system proposed by Braukmann and Biss (2004) for rivers, acidification classes corresponding well with the measured river pH values were obtained.

Seit dem Jahre 2000 nimmt die Schweiz an den Arbeiten des Internationalen Kooperativen Programms zur Beurteilung und Überwachung der Versauerung von Fliessgewässern und Seen der Konvention über weiträumige grenzüberschreitende Luftverunreinigung (UNECE) teil. Alpine Bergseen werden allerdings schon seit 1980 untersucht. So konnten bei den für die Versauerungsprozesse wichtigsten Parametern Trendanalysen durchgeführt werden. Seit den achtziger Jahren kann in den meisten untersuchten Seen eine signifikante Abnahme der Sulfatkonzentrationen und eine Zunahme der Alkalinität festgestellt werden, während die Trends bei den basischen Kationen und beim Nitrat meistens klein und nicht signifikant sind. Für dieselben Parameter wurde die Saisonalität in drei alpinen Fliessgewässern untersucht. Die saisonalen Variationen der Alkalinität sowie der Konzentrationen von basischen Kationen und Sulfat korrelieren negativ mit der Abflussmenge. Eine positive Korrelation mit dem Abfluss wurde stattdessen für die Aluminiumkonzentrationen gefunden. Sowohl in den Seen als auch in den Fliessgewässern wurden Makroinvertebraten als Bioindikatoren für den Versauerungsgrad untersucht. Bei Anwendung des von Braukmann und Biss (2004) für Fliessgewässer entwickelten Bewertungssystems konnten den Flüssen Säureklassen zugeordnet werden, die gut mit den gemessenen pH-Werten übereinstimmen.

La Suisse participe depuis l'an 2000 aux travaux du programme international concerté d'évaluation et de surveillance de l'acidification des cours d'eau et des lacs dans le cadre de la Convention sur la pollution atmosphérique transfrontière à longue distance (CEE-ONU). Les lacs alpins ont toutefois déjà fait l'objet d'études depuis 1980. Des analyses de tendances pour les principaux paramètres intervenant dans les processus d'acidification ont ainsi été menées. Dans la plupart des lacs étudiés, une baisse significative de la concentration de sulfate ainsi qu'une augmentation de l'alcalinité ont été constatées, alors que l'évolution des concentrations de cations basiques et de nitrate a été faible et non significative. Les variations saisonnières ont également été étudiées dans trois cours d'eau alpins pour les mêmes paramètres. Ainsi, les variations saisonnières de l'alcalinité, des concentrations de cations basiques et de sulfate sont corrélées négativement avec le volume écoulé alors que la corrélation avec les concentrations d'aluminium dissous est positive. Des macroinvertébrés ont été utilisés comme indicateurs du degré d'acidité tant dans les lacs que les cours d'eau. En appliquant la méthode d'évaluation proposée par Braukmann et Biss (2004), des classes d'acidité, qui correspondent aux valeurs de pH mesurées, ont été attribuées aux cours d'eau.

La Svizzera ha aderito nel 2000 al Programma internazionale di cooperazione per la valutazione e il monitoraggio dell'acidificazione nei corsi d'acqua e nei laghi della Convenzione per l' inquinamento atmosferico transfrontaliero a lunga distanza della CEE/ONU. Tuttavia il monitoraggio dei laghetti alpini é iniziato già nel 1980. Per i parametri chiave coinvolti nel processo di acidificazione é stata fatta un'analisi delle tendenze. Dagli anni ottanta le concentrazioni di solfato sono diminuite e l'alcalinità è aumentata in modo significativo nella maggior parte dei laghetti, mentre sono piccoli e prevalentemente non significativi i trend delle concentrazioni di nitrato e dei cationi basici. Per gli stessi parametri é stata studiata la variabilità stagionale in tre corsi d'acqua. Le variazioni stagionali dell'alcalinità e delle concentrazioni di solfato e dei cationi basici correlano negativamente con la portata dei fiumi. È stata invece trovata una correlazione positiva tra le concentrazioni di alluminio disciolto e la portata. Sia per i laghetti che per i corsi d'acqua sono stati utilizzati i macroinvertebrati come bioindicatori del grado di acidificazione. Applicando il sistema di valutazione sviluppato da Braukmann e Biss (2004) per i corsi d'acqua, si è potuto attribuire ai fiumi delle classi di acidificazione che corrispondono bene ai valori di pH misurati.

> Preface

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 in southern Switzerland belong to such sensitive receptors since they are mainly located on crystalline bedrocks with low weathering rates. It is of interest to know how such sensitive ecosystems react over time on changing deposition of acidifying air pollutants resulting from the implementation of international emission control programmes.

In the year 2000 Switzerland joined the activities of the International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters) operating under the Working Group on Effects of the Convention. But already since 1980 Alpine lakes at high altitudes in southern Switzerland are regularly monitored by the Cantone Ticino.

The objectives of ICP Waters are to assess, on a regional basis, the degree and geographical extent of acidification of surface waters. Together with the results from other countries, the data from the survey of Alpine lakes and rivers at high altitudes in southern Switzerland contribute to fulfil the tasks of ICP Waters. Trend analyses of important chemical parameters linked with acidification are presented in this report as well as the occurrence of invertebrate fauna indicating the status of acidification. The report also contains results from the analysis of some persistent organic pollutants and heavy metals in fishes.

We express our warm thanks and appreciation to the Cantone Ticino for carrying out the survey of Alpine lakes and rivers at high altitudes and for participating in the work of ICP Waters.

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> Summary

Trend analyses of the key parameters involved in acidification processes measured in 20 Alpine lakes during the period 1980–2004 reveal significant decreasing sulphate (15 out of 20) and increasing alkalinity trends (14 out of 20) in most studied lakes, while trends for base cation and nitrate are small and mostly insignificant. The average increase in alkalinity between 1980 and 2004 was 0.012 meq l^{-1}. Today 2 lakes out of 20 are acid (alkalinity < 0 meq l^{-1}), 13 sensitive to acidification (0 meq l^{-1} < alkalinity < 0.05 meq l^{-1}) and 5 have low alkalinities but are not sensitive to acidification (0.05 meq l^{-1} < alkalinity < 0.2 meq l^{-1}). Differently, in the 1980's 4 lakes were acid, 14 were sensitive to acidification and 2 had low alkalinities. The average increase of pH during the same time period was 0.3. Nowadays only 3 lakes out of 20 have an average pH below 6, while in the 1980's 8 lakes had an average pH that may be defined critical for aluminium dissolution.

Differences in average water chemistry of river Maggia, Vedeggio and Verzasca can mainly be explained by differences in catchment area and geology. Seasonal variations of alkalinity, base cation and sulphate concentrations are negatively correlated with the river discharge: with increasing discharge alkalinity and concentrations of sulphate and base cation approach a minimum that is specific for each river. pH never decreased below 6 and lowest alkalinities measured during high flow events were 0.08 meq l^{-1} in river Maggia, 0.07 meq l^{-1} in river Vedeggio and 0.03 meq l^{-1} in river Verzasca. Differently, dissolved aluminium concentrations are positively correlated with the river discharge, while nitrate concentrations are more difficult to predict. It was estimated that 60–80% of the alkalinity decrease during high flow events is caused by dilution of ground- and river water with rain water, while the remaining 20–40% is consumed by titration of acid anions. The increase of the nitrate fraction in river water during higher discharge is the main cause for alkalinity consumption.

Macronvertebrate samples collected in the littoral and effluent of 4 Alpine lakes between 2000 and 2004 are poor in species and typical for this ecosystem. The predominant orders are *Diptera*, *Plecoptera* and *Oligochaeta*. The higher taxa number and EPT index (= number of families in the orders *Ephemeroptera*, *Plecoptera* und *Trichoptera)* in the lakes Laghetto Superiore (60, 12) and Laghetto Inferiore (51, 10) with respect to Lago Tomè (31, 8) and Lago del Starlaresc da Sgiof (31, 3) seem to reflect their higher average pH (6.4–6.5 compared to 5.6–5.2). The same is indicated by the presence of acid sensitiver species in Laghetto Superiore and Inferiore *(Baetis alpinus, Crenobia alpina, Pisidium Casertanum* and other *Ephemeroptera)*. Macroinvertebrate population sampled in river Maggia (Mag), Vedeggio (Ved) and Verzasca (Ver) in the same period is very different from that observed in lakes. Both the total number of taxa (Mag: 113, Ved: 122, Ver: 94) and the EPT index (Mag: 21, Ved: 21, Ver: 17) are higher. In addition, the dominating orders are *Ephemeroptera, Plecoptera* and *Diptera*. Applying the categorisation system proposed by Braukmann and Biss (2004) for rivers, acidification classes that correspond well with the measured river pH's are obtained. In

fact, for most macroinvertebrate samples an acidification class of 2 was obtained, corresponding to a pH around 6.5–7.0, indicating predominantly neutral to episodically weakly acidic rivers.

Results from HCB, HCH, PCB, DDT and metal analyses in fish muscle from Laghetto Superiore and Laghetto Inferiore in the period 2000–2004 correspond well with what reported for other European mountain lakes, confirming the importance of transport through the atmosphere for the distribution of these parameters.

> Zusammenfassung

Trendanalysen von wesentlichen Parametern, die im Zusammenhang mit Versauerungsprozessen zwischen 1980 und 2004 in 20 alpinen Bergseen gemessen wurden, ergeben in den meisten Seen eine signifikante Abnahme der Sulfatkonzentration und eine signifikante Zunahme der Alkalinität (15 resp. 14 von 20 Seen), während sich die Trends der basischen Kationen- und Nitratkonzentrationen als nicht signifikant und unbedeutend erweisen. Zwischen 1980 und 2004 ist die Alkalinität im Durchschnitt um 0.012 meq l^{-1} gestiegen. Heutzutage sind 2 von 20 Seen sauer (Alkalinität <0 meq l^{-1}), 13 sind säureempfindlich (0 meq $l^{-1}<$ Alkalinität <0.05 meq l^{-1}) und 5 haben eine niedrige Alkalinität, sind aber nicht säureempfindlich (0.05 meq $l^{-1}<$ Alkalinität < 0.2 meq l^{-1}). In den 1980er Jahren waren noch 4 Seen sauer, 14 säureempfindlich und 2 hatten eine niedrige Alkalinität. Während der gleichen Zeitperiode nahmen die pH-Werte im Durchschnitt um 0.3 Einheiten zu. Zurzeit haben nur noch 3 von 20 Seen einen durchschnittlichen pH-Wert unter 6, während in den 1980er Jahren noch 8 Seen einen pH-Wert hatten, der bezüglich der Aluminiumauflösung als kritisch zu betrachten ist.

Die Unterschiede zwischen den Durchschnittswerten von chemischen Parametern der Flüsse Maggia, Vedeggio und Verzasca werden im Wesentlichen von der Grösse und der Geologie der jeweiligen Einzugsgebiete bestimmt. Die saisonalen Variationen der Alkalinität und der Konzentrationen der basischen Kationen und des Sulfats korrelieren negativ mit dem Abflussvolumen. Dabei nähern sich die Alkalinität und die Konzentrationen von Sulfat und basischen Kationen bei zunehmenden Abflussvolumina einem flussspezifischen Minimum. Die pH-Werte der untersuchten Flüsse sanken nie unter 6 und die niedrigsten gemessenen Alkalinitätswerte betrugen in der Maggia 0.08 meq l^{-1}, im Vedeggio 0.07 meq l^{-1} und in der Verzasca 0.03 meq l^{-1}. Anders die Konzentrationen des gelösten Aluminiums, die positiv mit dem Abflussvolumen korrelieren. Schwierig vorherzusehen sind stattdessen die Nitratkonzentrationen. Es wurde abgeschätzt, dass 60–80% der Alkalinitätsabnahme während Hochwasserereignissen der Verdünnung von Grund- und Flusswasser mit Regenwasser zuzuschreiben ist, während die restlichen 20–40% die Folge eines Alkalinitätsverbrauchs durch Titration von sauren Anionen sind. Es wurde zudem beobachtet, dass der Alkalinitätsverbrauch zum grössten Teil durch die Zunahme der Nitratfraktion während Hochwasserereignissen verursacht wird.

Die Zusammensetzung der Makroinvertebraten, die von 2000 bis 2004 im Littoral und Abfluss von 4 alpinen Bergseen gesammelt wurden, ist artenarm und typisch für dieses Oekosystem. Die meistvertretenen Gattungen sind *Diptera, Plecoptera* und *Oligochaeta*. Die grössere Anzahl Taxa und der höhere ETP Index (=Anzahl Familien in den Gattungen *Ephemeroptera, Plecoptera* und *Trichoptera)* in den Seen Laghetto Superiore (60; 12) und Laghetto Inferiore (51; 10) im Vergleich zu Lago Tomè (31; 8) und Lago del Starlaresc da Sgiof (31; 3) scheinen im Zusammenhang mit den mittleren höheren pH-Werten der ersten beiden zu stehen (6.4–6.5 gegenüber 5.2–5.6). Das Gleiche kann aus dem Vorkommen einer grösseren Anzahl säuresensibler Arten in den

Seen Laghetto Superiore und Inferiore geschlossen werden *(Baetis alpinus, Crenobia alpina, Pisidium Casertanum* und andere *Ephemeroptera)*. Die zur gleichen Zeit in den Flüssen Maggia (Mag), Vedeggio (Ved) und Verzasca (Ver) gesammelten Populationen der Makroinvertebraten unterscheiden sich stark von jenen in den Seen. Sowohl die Anzahl Taxa (Mag: 113, Ved: 122, Ver: 94) wie auch der EPT Index (Mag: 21, Ved: 21, Ver: 17) waren deutlich grösser. Am meisten vertreten sind die Gattungen *Ephemeroptera, Plecoptera* und *Diptera*. Bei der Anwendung der von Braukmann und Biss (2004) vorgeschlagenen Evaluationsmethode erhält man Säureklassen, die gut mit den gemessenen pH-Werte übereinstimmen. Tatsächlich konnten die meisten Makroinvertebratenproben einer Säureklasse 2 zugeordnet werden, was einem durchschnittlichen pH-Wert von 6.5–7 entspricht und typisch für vorwiegend neutrale und nur episodisch leicht saure Gewässer ist.

Die im Muskelfleisch von Fischen zwischen 2000 und 2004 in 2 Bergseen (Laghetto Superiore, Laghetto Inferiore) gemessenen Konzentrationen der persistenten organischen Verbindungen HCB, HCH, PCB und DDT sowie einiger Schwermetalle sind mit Literaturwerten von anderen europäischen Bergseen vergleichbar und bestätigen die Wichtigkeit des atmosphärischen Transportes in der Verbreitung dieser Substanzen.

> Resumé

L'analyse des tendances des principaux paramètres intervenant dans les processus d'acidification, mesurés dans 20 lacs alpins entre 1980 et 2004, mettent en évidence une baisse significative de la concentration de sulfate et une augmentation significative de l'alcalinité dans la plupart des lacs (respectivement dans 15 et 14 des 20 lacs), alors que l'évolution des concentrations de cations basiques et de nitrate est peu importante et non significative. L'alcalinité a augmenté en moyenne de 0.012 méq l^{-1} entre 1980 et 2004. Aujourd'hui, 2 des 20 lacs sont acides (alcalinité < 0 méq l^{-1}), 13 sont sensibles aux acides (0 < alcalinité 0.05 méq l^{-1}) et 5 sont faiblement alcalins mais non sensibles aux acides (0.05 < alcalinité < 0.2 méq l^{-1}). Dans les années 80, 4 lacs étaient encore acides, 14 sensibles aux acides et 2 avaient une faible alcalinité. Pendant la même période, le pH des lacs a augmenté en moyenne de 0,3 unité. Actuellement, seuls 3 lacs sur 20 ont un pH moyen inférieur à 6, alors que dans les années 1980, 8 lacs avaient encore un pH considéré comme critique du point de vue de la dissolution de l'aluminium.

La grandeur et la géologie des bassins versants déterminent dans une large mesure les différences entre les valeurs chimiques moyennes de la Maggia, du Vedeggio et de la Verzasca. Les variations saisonnières de l'alcalinité et des concentrations de cations basiques et de sulfate sont négativement corrélées avec le volume écoulé, de manière qu'avec une augmentation du volume écoulé l'alcalinité et les concentrations de cations basiques et de sulfate s'approchent d'un minimum qui est spécifique de chaque cours d'eau. Le pH des cours d'eau examinés ne descendait jamais en dessous de 6. Les valeurs les plus faibles mesurées pour l'alcalinité étaient de 0,08 méq l^{-1} dans la Maggia, de 0,07 méq l^{-1} dans le Vedeggio et de 0,03 méq l^{-1} dans la Verzasca. Différemment, les concentrations d'aluminium dissous corrèlent négativement avec les concentrations d'aluminium et le concentrations de nitrate sont difficiles de prédire. On a estimé que 60 à 80% de la baisse de l'alcalinité lors des crues était imputable à la dilution des eaux souterraines et des eaux des rivières par de l'eau de pluie, alors que les 20 à 40% restants découlaient d'une consommation d'alcalinité par titration des anions acides. On a en outre observé que la consommation d'alcalinité est en majeure partie due à l'augmentation de la fraction de nitrate pendant les crues.

La composition des macroinvertébrés recueillis entre 2000 et 2004 sur le littoral et dans l'émissaire de 4 lacs alpins est pauvre en espèces et typique de cet écosystème. Les ordres les mieux représentés sont *Diptera*, *Plecoptera* et *Oligochaeta*. Le nombre plus important de taxa et l'indice ETP plus élevé (= nombre de familles dans les ordres *Ephemeroptera*, *Plecoptera* et *Trichoptera)* relevés dans les lacs Laghetto Superiore (60; 12) et Laghetto Inferiore (51; 10), en comparaison du Lago Tomè (31; 8) et du Lago del Starlaresc da Sgiof (31; 3), semblent être liés aux pH moyens plus élevés des deux premiers (6.4 à 6.5 par rapport à 5.2 à 5.6). On peut tirer la même conclusion en ce qui concerne la présence d'un nombre plus important d'espèces sensibles aux acides dans le Laghetto Superiore et le Laghetto Inferiore *(Baetis alpinus, Crenobia alpina,*

Pisidium Casertanum et autres *Ephemeroptera).* Les populations de macroinvertébrés recensées au cours de la même période dans la Maggia (Mag), le Vedeggio (Ved) et la Verzasca (Ver) sont très différentes de celles des lacs. Le nombre de taxa (Mag: 113, Ved: 122, Ver: 94) ainsi que l'indice EPT (Mag: 21, Ved: 21, Ver: 17) étaient nettement plus élevés. Les ordres les plus représentés sont *Ephemeroptera, Plecoptera* et *Diptera*. En appliquant la méthode d'évaluation proposée par Braukmann et Biss (2004), on obtient des classes d'acidification qui correspondent bien aux valeurs de pH mésurés. En effet, on a obtenu une classe d'acidification égal a 2 pour la plupart des échantillons de macroinvertébrés, ce qui correspond à un pH moyen de 6,5 à 7, typique des eaux principalement neutres avec seulement quelques épisodes de faible acidité.

Les concentrations des composés organiques persistants (HCB, HCH, PCB et DDT) et des différents métaux lourds mesurées dans la chair des poissons dans 2 lacs alpins (Laghetto Superiore et Laghetto Inferiore) entre 2000 et 2004 sont comparables aux valeurs citées dans la littérature pour d'autres lacs de montagne européens et confirment l'importance du transport atmosphérique dans la dissémination de ces substances.

> **Riassunto**

Le analisi dei trend dei principali parametri coinvolti nei processi di acidificazione e misurati in 20 laghetti alpini tra il 1980 e il 2004 evidenziano una significativa diminuzione delle concentrazioni di solfato e un significativo aumento dell'alcalinità nella maggior parte dei laghetti (15, rispettivamente 14 laghetti su 20), mentre sono trascurabili e non significativi i trend delle concentrazioni di cationi basici e di nitrato. Tra il 1980 e il 2004 l'aumento medio di alcalinità é stato di 0.012 meq l^{-1}. Oggi 2 laghetti su 20 sono acidi (alcalinità <0 meq l^{-1}), 13 sensibili all'acidificazione (0 meq l^{-1}<alcalinità<0.05 meq l^{-1}) e 5 hanno una alcalinità bassa senza però essere sensibili all'acidificazione (0.05 meq l^{-1}<alcalinità<0.2 meq l^{-1}). Negli anni 1980, invece, i laghetti acidi, sensibili e con bassa alcalinità erano rispettivamente 4, 14 e 2. Durante lo stesso periodo l'aumento medio del pH é stato di 0.3. Attualmente soltanto 3 laghetti su 20 hanno un pH medio inferiore a 6, negli anni 1980, invece, ben 8 laghetti avevano un pH medio che può essere considerato critico in relazione alla dissoluzion dell'alluminio.

La dimensione e la geologia del bacino imbrifero determinano in larga misura le differenze dei valori chimici medi delle acque dei fiumi Maggia, Vedeggio e Verzasca. Le variazioni stagionali dell'alcalinità e delle concentrazioni di cationi basici e di solfato correlano negativamente con la portata del fiume, di modo che con l'aumentare della portata l'alcalinità e le concentrazioni di solfato e di cationi basici si avvicinano sempre di più ad un minimo specifico per ogni corso d'acqua. Il pH non é mai sceso sotto il 6 e i valori minimi di alcalinità erano 0.08 meq l^{-1} nella Maggia, 0.07 meq l^{-1} nel Vedeggio e 0.03 meq l^{-1} nella Verzasca. Al contrario, correlano positivamente con la portata le concentrazioni di alluminio disciolto. Sono invece difficili da predire le concentrazioni di nitrato. È stato stimato che il 60–80% della diminuzione dell'alcalinità durante eventi di piena può essere attribuito alla diluizione delle acque sotterranee e dei corsi d'acqua con acqua piovana, mentre il rimanente 20–40% é dovuto al consumo di alcalinità durante la titolazione di anioni acidi. È stato inoltre osservato che l'aumento della frazione di nitrato durante eventi di piena é la causa principale del consumo di alcalinità.

I campioni di macroinvertebrati raccolti tra il 2000 e il 2004 lungo il litorale e nell'emissario di 4 laghetti alpini sono poveri di specie e tipici per questo ecosistema. Gli ordini maggiormente rappresentati sono i *Diptera, Plecoptera* e *Oligochaeta*. Il più alto numero di taxa e indice EPT (= numero di famiglie negli ordini *Ephemeroptera, Plecoptera* e *Trichoptera*) nel Laghetto Superiore (60, 12) e Inferiore (51, 10) rispetto al Lago Tomè (31, 8) e al Lago del Starlaresc da Sgiof (31, 3) sembra riflettere il più alto pH medio dei primi due (6.4- 6.5 rispetto a 5.6- 5.2). Lo stesso fenomeno viene sottolineato dalla presenza di specie maggiormente sensibili all'acidificazione nel Laghetto Superiore e Inferiore *(Baetis alpinus, Crenobia alpina, Pisidium Casertanum* e altri *Ephemeroptera)*. La popolazione di macroinvertebrati campionati nello stesso periodo nei fiumi Maggia (Mag), Vedeggio (Ved) e Verzasca (Ver) si differenzia molto

da quella trovata nei laghetti. Sono infatti più grandi sia il numero di taxa (Mag: 113, Ved: 122, Ver: 94) che l'indice EPT (Mag: 21, Ved: 21, Ver: 17). Inoltre, gli ordini maggiormente rappresentati sono *Ephemeroptera, Plecoptera* e *Diptera*. Appliccando il metodo di valutazione proposto da Braukmann e Biss (2004), si ottengono classi di acidificazione che corrispondono bene ai valori di pH misurati. Infatti, è stato ottenuto una classe di acidificazione pari a 2 per la maggior parte dei campioni di macroinvertebrati, corrispondente a un pH di 6.5–7 e indicante acque prevalentemente neutre caratterizzate da singoli episodi di debole acidità.

I risultati delle analisi di HCB, HCH, PCB, DDT e metalli nella parte edibile di pesci pescati nel Laghetto Superiore e Inferiore tra il 2000 e il 2004 corrispondono ai valori riportati per altri laghetti di montagna europei, confermando l'importanza del trasporto atmosferico nella distribuzione di queste sostanze.

> Introduction

The International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters) was established under the United Nations Economic Commission for Europe's Convention on Long-Range Transboundary Air Pollution (LRTAP) in 1985, when it was recognised that acidification of freshwater systems provided some of the earliest evidence of the damage caused by sulphur emissions. The monitoring programme is designed to assess, on a regional basis, the degree and geographical extent of acidification of surface waters. The data collected should provide information on exposure/response relationships under different conditions and correlate changes in acid deposition with the physical, chemical and biological status of lakes and streams. The Programme is planned and coordinated by a Task Force under the leadership of Norway. Up to now chemical and site data from more than 200 catchments in 24 countries in Europe and North America are available in the database of the Programme Centre. Switzerland joined the Programme in 2000, although monitoring of Alpine lakes started already at the beginning of the 1980's. Since then 4 annual reports have been published (LSA, 2000–2003).

1 > Study site description

The study area is located in the Central Alps in the northern part of canton Ticino, Switzerland (Fig. 1.1). In order to study the influence of transboundary air pollution, the freshwater systems were selected in remote areas far from local pollution sources. Precipitation in this region is mainly determined by warm, humid air masses originating from the Mediterranean Sea, passing over the Po Plain and colliding with the Alps. Since the study area's lithology is dominated by base-poor rocks especially gneiss, its freshwaters are sensitive to acidification. For the monitoring programme 20 Alpine lakes and 3 rivers were chosen. The lake's watersheds are constituted mainly by bare rocks with vegetation often confined to small areas of Alpine meadow. The selected Alpine lakes are situated between an altitude of 1690 m and 2580 m and are characterized by intensive irradiation, a short vegetation period, a long period of ice coverage and by low nutrient concentrations. The sampling points of the selected rivers are located at lower altitudes (610–918 m), implying larger catchment areas and therefore less sensitivity toward acidification than lakes. The main geographic, morphometric and geologic parameters of the monitored lakes and rivers are shown in Tab. 1.1 and 1.2, respectively.

Fig. 1.1   > Lake and river sampling points in canton Ticino, Switzerland.

Tab. 1.1   > Main geographic, morphometric and geologic parameters of the monitored lakes (personal communication from Meteotest).

Long and Lat stay for longitude and latitude, respectively and Alt. for altitude.

Lake name	Long E CH	Lat N CH	Long E	Lat N	Alt.	Catchment area	Lake area	Max depth		Characterization watershed surface		Calcareous rocks
	m	m			m a.s.l.	ha	ha	m	% rock	% vegetation	% water	%
Lago di Tomè	696280	135398	8,691	46,364	1692	294	5.8	38	57	41	2	0.0
Lago di Sascòla	687175	126413	8,571	46,284	1740	90	3.2	5	16	81	4	1.7
Lago d'Alzasca	688363	124488	8,585	46,267	1855	110	10.4	40	20	70	9	0.0
Lago del Starlaresc da Sgiof	702905	125605	8,777	46,276	1875	23	1.1	6	29	67	5	0.0
Lago di Sfille	681525	124213	8,496	46,265	1909	63	2.8	12	30	65	4	0.0
Laghi dei Pozzöi	679613	124200	8,472	46,265	1955	33	1.1	4	30	66	3	0.0
Lago di Mognòla	696075	142875	8,690	46,431	2003	197	5.4	11	73	24	3	0.0
Laghetto Inferiore	688627	147855	8,594	46,477	2074	182	5.6	33	65	27	8	0.0
Laghetto Superiore	688020	147835	8,587	46,477	2128	125	8.3	29	65	29	7	0.0
Lago d'Orsalìa	683513	132613	8,524	46,340	2143	41	2.6	16	89	5	6	0.0
Lago della Crosa	680375	136050	8,483	46,370	2153	194	16.9	70	72	20	9	0.0
Laghetto d'Antabia	681038	137675	8,492	46,387	2189	82	6.8	16	83	8	8	0.0
Lago dei Porchieirsc	700450	136888	8,745	46,377	2190	43	1.5	7	69	28	3	0.0
Lago Leit	698525	146800	8,722	46,466	2260	52	2.7	13	75	20	5	0.0
Lago di Morghirolo	698200	145175	8,718	46,451	2264	166	11.9	28	74	19	7	0.0
Schwarzsee	681963	132188	8,503	46,335	2315	24	0.3	7	77	22	1	0.0
Lago della Froda	686025	143788	8,559	46,441	2363	67	2.0	17	88	9	3	0.0
Lago Nero	684588	144813	8,541	46,449	2387	72	12.7	68	59	23	18	0.0
Lago Barone	700975	139813	8,753	46,404	2391	51	6.6	56	65	22	13	0.0
Laghetto Gardiscio	701275	142675	8,757	46,429	2580	12	1.1	10	84	7	9	0.0

Tab. 1.2   > Main geographic, morphometric and hydrologic parameters of the monitored rivers.

Long and Lat stay for longitude and latitude, respectively.

River name	Sampling site	Long CH	Lat CH	Long E	Lat N	Altitude	Catchment area	Annual mean water discharge
		m	m			m a.s.l.	km²	m³ s⁻¹
Maggia	Brontallo	692125	134375	8,64	46,36	610	ca. 189	ca. 2.5 (1982–2003)*
Verzasca	Sonogno	704200	134825	8,79	46,36	918	ca. 27	ca. 1.6 (1990–2003)
Vedeggio	Isone	719900	109800	8,99	46,13	740	20	0.9 (1980–2004)

* estimated water discharge without influence of water extraction for hydropower generation.

2 | > Water chemistry

Origin of acid precipitation

From the beginning of the industrial revolution in the middle of the 19th century the
continuous increase of fossil energy consumption (combustion of petrol, coal and gas)
has caused rising emissions of sulphur dioxide and nitrogen oxides (SO_2 and NO_x). In
the atmosphere these gases can oxidize to sulphate and nitrate acids causing acid
precipitations. Besides the above described mechanism, due to intensification of agri-
culture, also the emissions of ammonia (NH_3) contributes to acid precipitation. Al-
though ammonia itself reacts as a base in the atmosphere (NH_4^+), during assimilation
by plants the temporary bound proton is released to the environment again. In addition,
in soils and waters ammonia can be oxidized by microorganisms to nitrate, liberating
two protons. In this way, ammonia can contribute to the acidification of soils and
waters.

**Fig. 2.1   > Annual sulphur dioxide, nitrogen oxides and ammonia emissions in Switzerland from 1900 to
2010.**

Dashed lines indicate estimate values.
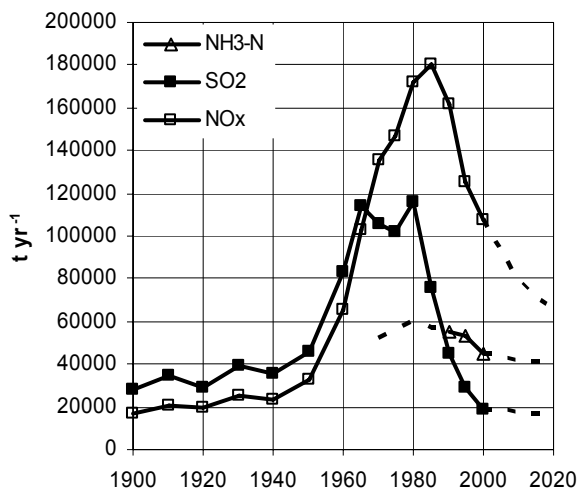
Source: BUWAL. 2005.

In Fig. 2.1 the sulphur dioxide, nitrogen oxides and ammonia emissions in Switzerland
from 1900 to 2010 are shown. The sulphur dioxide and nitrogen oxides emission
started to increase steeply after the second world war. Sulphur dioxide reached its
maximum between 1965 and 1980, while nitrogen oxides peaked around 1985. After-
wards, both sulphur and nitrogen oxides decreased continuously until 2000. The reduc-
tion 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 carbon with other fossil fuels. The inversion of tendency of the nitrogen oxides emissions after 1985 was mainly determined by the application of catalytic converters to cars.

2.2   Mechanisms of freshwater acidification

Acidification can be defined as a reduction of the acid neutralizing capacity of soils or waters. The acid neutralizing capacity is also known as alkalinity (Alk) and indicates the sensitivity of a water system toward acidification. It can be expressed as (Sigg and Stumm, 1989):

$$[Alk]=[HCO_3^-]+2*[CO_3^{2-}]+[OH^-]-[H^+] \qquad \text{(eq. 1)}$$

or

$$[Alk]=[Na^+]+[K^+]+2*[Mg^{2+}]+2*[Ca^{2+}]+[NH_4^+]-[Cl^-]-2*[SO_4^{2-}]-[NO_3^-] \qquad \text{(eq. 2)}$$

for pH<8.2:

$$[Alk]\cong[HCO_3^-]-[H^+] \qquad \text{(eq. 3)}$$

Distilled water, that equilibrates with CO_2 of a non polluted atmosphere, has a pH of 5.65. At this pH, proton and bicarbonate concentrations are equal and alkalinity becomes zero (Sigg and Stumm, 1989). We consider freshwaters acidic when [Alk]<0 meq l^{-1}, sensitive to acidification when 0<[Alk]<0.05 meq l^{-1} and with low alkalinity but not sensitive to acidification when 0.05 <[Alk]<0.2 meq l^{-1} (Mosello et al., 1993). The critical alkalinity value, below which acid deposition exceeds the critical load (i.e. the load which will leave a lake alkalinity that ensures fish development, Henriksen et al. 1990, 1995) was fixed at 0.02 meq l–1.

Alkalinity is the result of complex interactions between wet and dry deposition and the soil and rocks of the watershed and biologic processes. The involved chemical and biological reactions can be divided in weathering reactions, ion-exchange reactions, redox processes and the formation and degradation of biomass and humus (Stumm et al., 1983). Weathering reactions consume protons and release base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+). Carbonates (lime, dolomite) are weathered faster than aluminium silicates or aluminium oxides. Ion-exchange reactions at the surface of clay minerals or humus have the same effect than weathering but are faster (minutes compared to hours or days) and have a smaller pool of exchangeable bases. In the long run, chemical weathering is the rate-limiting step in the supply of base cations for export from the watershed. Reduction processes also increase alkalinity (e.g. denitrification, sulphate reduction), while oxidation reactions (e.g. nitrification, oxidation of hydrosulphide) reduce alkalinity. Production of biomass can increase alkalinity if nitrate is assimilated, while it can decrease alkalinity if ammonia is assimilated. It can be concluded that oligotrophic freshwaters that are poor in carbonates and electrolytes are particularly sensitive to acidification. Such waters can be found in areas with weathering resistant underground (granite, gneiss) with a thin soil surface. In Switzerland high mountain regions have often these characteristics.

2.3   Sampling procedure

Between 1980 and 2000 surface water samples of 20 lakes were collected every 2 to 5 years mostly at the beginning of autumn. After 2000 surface water sampling occurred twice a year (beginning of summer and beginning of autumn). Surface water was collected directly from the helicopter.

In addition, after 1996 also water profiles, especially of Laghetto Inferiore and Laghetto Superiore were taken. After 2000, water profiles of Laghetto Inferiore, Laghetto Superiore, Lago di Tomè and Lago Lago del Starlaresc da Sgiof were sampled regularly at least twice a year (at the end of winter, when surface water was still frozen, and in summer).

River water has been sampled monthly since 2000.

2.4   Chemical analyses

Measured parameters, analytical methods, quantification limits and conservation methods are resumed in Tab 2.1. The quality of the data was assured by participating regularly at national and international intercalibrations tests. In addition, data were accepted only if the calculation of the ionic balance and the comparison of the measured with the calculated conductivity gave good to discrete results (Tartari and Mosello, 1997). Furthermore, the data were checked for outliers. If available, as for metals and organic carbon, we compared the dissolved with the total concentrations.

Tab. 2.1   > Measured parameters, conservation methods, analytical methods, accuracy and quantification limits.

CA, PC, GF, PP stay for cellulose acetate, polycarbonate, glass fibre and polypropylene, respectively. CFA stays for continuous flow analyzer and ICP-OES for inductively coupled plasma atomic-emission spectroscopy.

Parameter	Filtration	Conservation	Method	Accuracy
pH	No	No	potentiometry	0.02
conductivity	No	No	Kolrausch bridge (20 °C)	$0.5\ \mu S\ cm^{-1}$
alkalinity	No	No	potentiometric Gran titration**	$0.001\ meq\ l^{-1}$
				Quantification limit
Ca^{2+}	CA filter	PP bottle, 4 °C*	ion cromatography	$0.010\ mg\ l^{-1}$
Mg^{2+}	CA filter	PP bottle, 4 °C*	ion cromatography	$0.005\ mg\ l^{-1}$
Na^+	CA filter	PP bottle, 4 °C*	ion cromatography	$0.005\ mg\ l^{-1}$
K^+	CA filter	PP bottle, 4 °C*	ion cromatography	$0.010\ mg\ l^{-1}$
NH_4^+	CA filter	PP bottle, 4 °C*	CFA (spectrophotometry)	$3\ \mu g\ N\ l^{-1}$
SO_4^{2+}	CA filter	PP bottle, 4 °C*	ion cromatography	$0.005\ mg\ l^{-1}$
NO_3^-	CA filter	PP bottle, 4 °C**	ion cromatography	$0.010\ mg\ N\ l^{-1}$
NO_2^-	CA filter	PP bottle, 4 °C*	CFA (spectrophotometry)	$1\ \mu g\ N\ l^{-1}$
Cl^-	CA filter	PP bottle, 4 °C*	ion cromatography	$0.010\ mg\ l^{-1}$
soluble reactive P	CA filter	PP bottle, 4 °C*	CFA (spectrophotometry)	$4\ \mu g\ P\ l^{-1}$
soluble reactive Si	CA filter	PP bottle, 4 °C*	ICP-OES with ultrasonic nebulizer	$0.003\ mg\ Si\ l^{-1}$
total N	No	glass bottle, immediate mineralisation	persulphate digestion, spectrophotometry	$0.01\ mg\ N\ l^{-1}$
total P	No	glass bottle, immediate mineralisation	persulphate digestion, CFA (spectrophotometry)	$4\ \mu g\ P\ l^{-1}$
DOC	PC filter	brown glass bottle, + H_3PO_4	UV-Persulfate	$0.05\ mg\ C\ l^{-1}$
O_2	No	No	Winkler method	$0.5\ mg\ O_2\ l^{-1}$
chlorophyll a	GF filter	glass bottle, +ethanol, 4 °C	ethanol extraction, spectrophotometry	$0.1\ \mu g\ l^{-1}$
soluble Al	PC filter	acid washed PP bottle, +HNO₃, 4 °C	CFA (spectrophotometry)	$3\ \mu g\ l^{-1}$
total Al	No	acid washed PP bottle, +HNO₃, 4 °C	CFA (spectrophotometry))	$3\ \mu g\ l^{-1}$
soluble Cu	PC filter	acid washed PP bottle, +HNO₃, 4 °C	ICP-OES with ultrasonic nebulizer	$1\ \mu g\ l^{-1}$
total Cu	No	acid washed PP bottle, +HNO₃, 4 °C	ICP-OES with ultrasonic nebulizer	$1\ \mu g\ l^{-1}$
soluble Zn	PC filter	acid washed PP bottle, +HNO₃, 4 °C	ICP-OES with ultrasonic nebulizer	$1\ \mu g\ l^{-1}$
total Zn	No	acid washed PP bottle, +HNO₃, 4 °C	ICP-OES with ultrasonic nebulizer	$1\ \mu g\ l^{-1}$
soluble Pb	PC filter	acid washed PP bottle, +HNO₃, 4 °C	ICP-OES with ultrasonic nebulizer	$0.5\ \mu g\ l^{-1}$
total Pb	No	acid washed PP bottle, +HNO₃, 4 °C	ICP-OES with ultrasonic nebulizer	$0.5\ \mu g\ l^{-1}$
soluble Cd	PC filter	acid washed PP bottle, +HNO₃, 4 °C	ICP-OES with ultrasonic nebulizer	$0.5\ \mu g\ l^{-1}$
total Cd	No	acid washed PP bottle, +HNO₃, 4 °C	ICP-OES with ultrasonic nebulizer	$0.5\ \mu g\ l^{-1}$

*between July 2004 and December 2004 samples were frozen. ** The so obtained alkalinity is called Gran Alkalinity.

2.5 Acidification effects on Alpine lakes between 1980 and 2004

2.5.1 Surface water chemistry of 20 lakes between 2000 and 2004

Tab. 2.2 shows the mean values of the main parameters measured in surface water of 20 lakes monitored at the beginning of summer (mid June to mid July) and in autumn (mid September to beginning of November), both after overturn between 2000 and 2004. Dependent on the lake and the parameter the sample number varied between 7 and 10 (data not shown). The chemical water composition is typical for carbonate poor mountain regions: low conductivity, alkalinity and pH and small nutrient and DOC concentrations. Average conductivity at 20 °C varies between 7.8 and 18.3 μS cm^{-1}, alkalinity between –0.010 and 0.067 meq l^{-1}, pH between 5.2 and 6.9, sulphate between 1.08 and 3.67 mg l^{-1}, nitrate between 0.12 and 0.47 mg N l^{-1}, dissolved organic carbon between 0.14 and 0.70 mg C l^{-1}, reactive dissolved silica between 0.37 and 1.22 mg Si l^{-1} and total aluminium between <12.8 and 100.9 μg l^{-1}. Ortho-phosphate is always smaller than the quantification limit of 4.3 P μg l^{-1} and ammonia and nitrite is neglectable small compared to nitrate.

Chemistry of Alpine lakes is the result of numerous physical, chemical and biological reactions occurring in the catchment. These are influenced by many parameters like deposition, catchment area and slope, watershed surface type (vegetation, bare rock), soil, geology and temperature.

If we assume that calcium and magnesium originate exclusively from carbonate, in areas with no acidification the sum of calcium and magnesium should equal alkalinity (Alk $\cong$ [HCO_3^-]).

Therefore, an alkalinity that is smaller than the sum of calcium and magnesium concentrations would indicate a consumption of alkalinity. In our study area the estimated consumption varied from 0.025 to 0.071 meq l^{-1} and was on average 0.039 meq l^{-1} (Fig. 2.2a). Similar values were reported by Niederhauser (1993). However, Fig. 2.2b seems to suggest that the sum of calcium and magnesium concentrations is not completely independent of sulphate concentrations, indicating that carbonate is not the only calcium and magnesium source and that sulphur components can also contribute.

Calcium and/or magnesium sulphates can originate from dry deposition of aerosols, from deposition of dust (e.g. from the Sahara) or from sulphur containing rocks in the catchment. Since carbonate seems not to be the only calcium and magnesium source, the before calculated alkalinity consumption must be considered as an overestimation.

Tab. 2.2 > Average surface water concentrations measured between 2000 and 2004 in 20 Alpine lakes.

Average values with some or all single values below the quantification limit were preceded with <.

Lake name	pH	Cond. (µS cm⁻¹)	Alk. (meq l⁻¹)	Ca²⁺ (mg l⁻¹)	Mg²⁺ (mg l⁻¹)	Na⁺ (mg l⁻¹)	K⁺ (mg l⁻¹)	NH₄⁺ (mg N l⁻¹)	SO₄²⁻ (mg l⁻¹)	NO₃⁻ (mg N l⁻¹)	Cl⁻ (mg l⁻¹)	NO₂⁻ (µg N l⁻¹)	o-PO₄ (µg P l⁻¹)	Ntot (mg N l⁻¹)	Ptot (µg P l⁻¹)	DOC (mg C l⁻¹)	Si (mg l⁻¹)	Aldissolved (µg l⁻¹)	Altot (µg l⁻¹)	Cudissolved (µg l⁻¹)	Cutot (µg l⁻¹)	Zndissolved (µg l⁻¹)	Zntotal (µg l⁻¹)
Lago di Tomè	5.6	9.6	0.002	0.93	0.08	0.31	0.14	0.02	1.59	0.47	0.14	3	<4.3	0.56	<4.5	0.27	0.81	44.2	67.5	<2.2	<4.2	6.1	9.1
Lago di Sascòla	6.1	10.1	0.014	0.94	0.15	0.33	0.31	0.02	1.61	0.40	0.15	3	<4.3	0.48	<4.3	0.54	0.78	<23.9	32.5	<1.5	<1.9	3.0	4.5
Lago d'Alzasca	6.8	15.7	0.072	1.88	0.21	0.49	0.43	0.02	2.17	0.27	0.16	3	<4.3	0.36	<4.3	0.47	1.16	<11.3	<14.4	<1.7	<2.1	3.5	3.8
Lago del Starlaresc da Sgiof	5.2	10.4	–0.010	0.67	0.11	0.34	0.19	0.03	1.62	0.42	0.21	2	<4.3	0.56	<4.3	0.70	0.70	88.9	100.9	<2.3	<5.6	11.9	32.9
Lago di Sfille	6.4	9.5	0.025	1.06	0.11	0.37	0.12	0.02	1.59	0.23	0.16	2	<4.3	0.33	<4.3	0.55	0.86	24.7	33.1	<2.4	<2.5	2.8	5.3
Laghi dei Pozzöi	6.5	8.9	0.032	0.96	0.11	0.35	0.16	0.01	1.47	0.12	0.14	1	<4.3	0.23	<4.3	0.66	0.83	18.9	26.1	<1.6	<1.9	1.5	3.6
Lago di Mognòla	6.8	15.7	0.052	1.72	0.24	0.54	0.43	0.01	2.98	0.28	0.12	2	<4.3	0.36	<4.9	0.27	1.22	<12.7	23.7	<1.7	<1.9	2.0	2.9
Laghetto Inferiore	6.5	9.8	0.028	1.08	0.10	0.29	0.32	0.02	1.55	0.27	0.10	3	<4.3	0.33	<4.3	0.30	0.58	<10.5	13.9	<2.3	<2.2	2.3	5.1
Laghetto Superiore	6.4	9.1	0.025	0.96	0.09	0.25	0.28	0.03	1.38	0.26	0.10	2	<4.3	0.32	<4.3	0.26	0.53	<11.4	15.5	<1.4	<2.4	2.1	5.6
Lago d'Orsalia	6.3	9.6	0.023	1.10	0.08	0.29	0.16	0.13	1.24	0.40	0.12	2	<4.3	0.46	<4.3	0.26	0.72	<13.7	23.1	<1.5	<2.2	1.8	4.2
Lago della Crosa	6.3	7.8	0.017	0.86	0.07	0.26	0.14	0.01	1.08	0.27	0.13	3	<4.3	0.37	<4.3	0.27	0.68	<10.1	<12.8	<1.4	<1.5	1.5	2.6
Laghetto d'Antabia	6.9	13.5	0.067	1.76	0.07	0.42	0.26	0.05	1.25	0.33	0.13	3	<4.3	0.43	<4.3	0.26	1.10	<10.5	<15.9	<1.4	<1.7	1.8	2.4
Lago dei Porchieirsc	6.8	18.3	0.060	2.40	0.14	0.43	0.38	0.02	3.56	0.33	0.13	2	<4.3	0.38	<4.3	0.24	1.21	<11.3	16.3	<1.6	<2.8	3.4	4.7
Lago Leit	6.4	14.1	0.023	1.44	0.25	0.35	0.38	0.02	3.67	0.21	0.11	2	<4.3	0.29	<4.5	0.37	0.74	<12.3	39.3	<1.4	<1.7	2.8	4.1
Lago di Morghirolo	6.6	11.2	0.032	1.17	0.16	0.29	0.36	0.02	2.11	0.21	0.11	2	<4.3	0.30	<4.3	0.33	0.72	<12.1	25.7	<2.1	<2.0	1.6	2.6
Schwarzsee	6.5	11.7	0.038	1.42	0.10	0.31	0.24	0.02	1.54	0.35	0.14	2	<4.3	0.43	<4.3	0.26	0.83	<16.3	24.1	<1.6	<2.2	1.7	3.9
Lago della Froda	6.7	12.2	0.046	1.57	0.15	0.27	0.21	0.01	1.91	0.22	0.09	2	<4.3	0.30	<5.8	0.66	0.57	<13.2	<16.7	<2.0	<2.6	2.0	4.1
Lago Nero	6.8	14.6	0.012	1.87	0.10	0.34	0.38	0.01	2.58	0.16	0.10	2	<4.3	0.30	<6.9	0.30	0.55	<11.1	<14.0	<1.8	<1.8	<1.6	1.8
Lago Barone	6.0	9.1	0.012	1.02	0.10	0.26	0.19	0.02	1.75	0.32	0.13	2	<4.3	0.44	<4.7	0.38	0.60	<12.4	22.4	<1.5	<1.8	4.5	4.1
Laghetto Gardiscio	5.3	7.9	–0.006	0.50	0.09	0.18	0.22	0.03	1.62	0.22	0.11	1	<4.3	0.32	<4.3	0.14	0.37	52.9	67.7	<1.4	<1.8	3.8	5.4

Fig. 2.2   > a) Mean alkalinity and b) SO$_4^{2-}$ concentrations vs. Ca^{2+}+Mg^{2+} concentrations for 20 Alpine lakes.
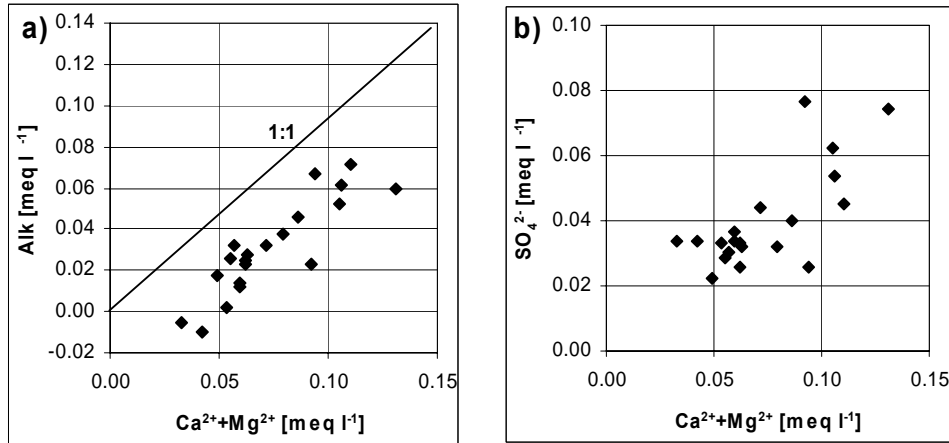
The alkalinity consumption in the lake's watershed determines its alkalinity and pH. Out of 20, 2 lakes (Lago del Starlaresc da Sgiof and Laghetto Gardiscio) are acidic (Alk < 0 meq l^{-1}) with average pH's of 5.2 and 5.3, 13 are sensitive to acidification (Alk < 0.05 meq l^{-1}) and 5 have low alkalinities (< 0.2 meq l^{-1}) but are not sensitive to acidification. For Lago del Starlaresc da Sgiof it must also be mentioned that the lake is surrounded by a raised bog that may decrease titration of acid rain in the catchment (reduced contact with the soil). Alkalinity and pH correlate closely. It is known, that in open systems, with water in equilibrium with the atmosphere, pH can be represented as a linear function of the logarithm of the bicarbonate concentration (Sigg and Stumm, 1989):

$$pH=\log[HCO_3^-]+11.3 \text{ (for 25}°C)\qquad\qquad\text{(eq. 4)}$$

Calculating the bicarbonate concentrations with equation 3, it is possible to plot the average pH values of Tab. 2.2 against log[HCO$_3^-$]. The result is shown in Fig. 2.3a. For pH > 5.5 a linear relationship, very close to that reported in literature, can be observed (pH = log[HCO$_3^-$] + 11.2). However, for acid lakes the calculated bicarbonate concentrations seem to be too low. It is reported that at pH<6 the release of metals from soils or sediments as a consequence of weathering processes becomes more and more important. Consequently aluminium hydroxides can influence alkalinity. In Niederhauser (1993) the equation for calculating alkalinity was modified as follows:

$$Alk=[HCO_3^-]-[H^+]-3*[Al^{3+}]-2*[Al(OH)^{2+}]-[Al(OH)_2^+]\qquad\qquad\text{(eq. 5)}$$

In Fig. 2.3b the bicarbonate concentrations of the 3 lakes with the lowest pH were corrected considering the dissolved aluminium concentrations specified in equation 5. The so obtained points fit very well with the linear regression line, confirming the importance of aluminium in determining alkalinity at low pH's.

Fig. 2.3   > a) Mean pH without consideration of Al. and b) pH with consideration of Al. vs. log[HCO$_3$] for 20 Alpine lakes.

a) $y = 1.14x + 11.63$

b) $y = 1.12x + 11.52$
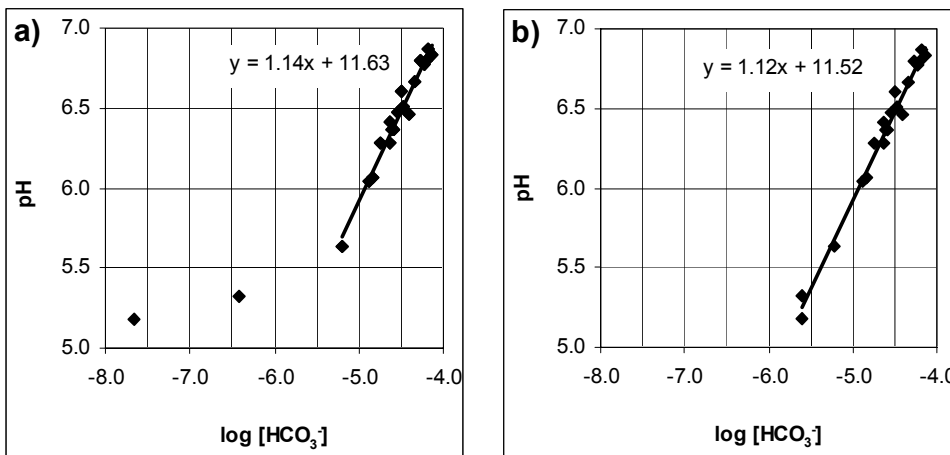
The previously mentioned release of aluminium at low pH is particularly important because of its toxic effects on organisms. As expected from theory (Sigg and Stumm, 1989), drawing the average aluminium concentrations against the mean pH a negative exponential correlation is obtained (Fig. 2.4): Al increases with decreasing pH and lakes with the lowest pH have the highest aluminium concentrations.

Fig. 2.4   > Mean aluminium concentrations vs. pH for 20 Alpine lakes.
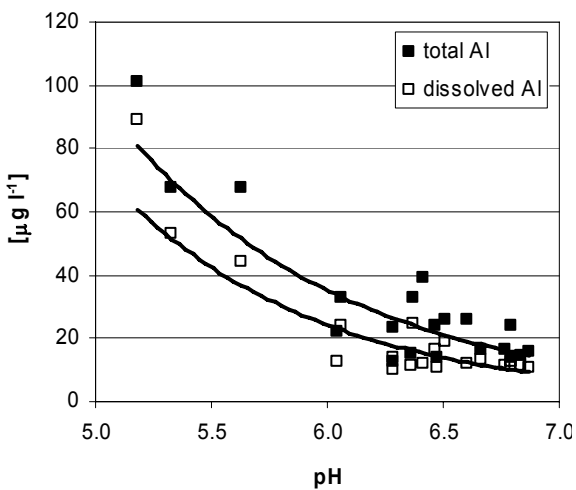
Aluminium is normally not soluble and is bound to silica at pH 7.0. As acidity increases aluminium becomes more soluble and is released from the soil. Toxicity of aluminium is mainly due to its soluble form which predominates in the pH range 5.0 – 5.5. In fact, above pH 6 most organisms do not suffer adverse effects, while between pH 6 and 5.5 lake acidity can lead to a decline and elimination of the most sensitive species like crustaceans, molluscs, particularly sensitive insects (ex: *Ephemeroptera),* plankton (ex: *Daphnia)* and fish (trout, salmon). Damages increase as pH goes from 5.5 to 5. At pH 5, 75% of all fish species disappear. When lake pH goes under 5, only the most resistant fish, insect and plankton species can survive and the bottom of the lake or river becomes covered with undecayed material and the near-shore areas may be dominated by mosses (Petri-Heil, 1986).

Originally it was assumed that such changes were a response to the direct effects of acidity but it was subsequently shown that also the indirect effect of low pH, coupled with an increase in the concentration of aluminium, is important. Ionoregulatory effects of aluminium and H^+ ions have been shown to be the main reasons for the damage of the invertebrate population. For fish ionoregulatory effects of aluminium and H^+ are important at low pH (< 5.5), while respiratory effects of aluminium are more important at moderately acid condition (pH 5 to 6) due to precipitation of aluminium hydroxides onto the gills surface (Gensemer and Playle, 1999).

The Swiss law for water protection does not indicate a concentration limit for aluminium in surface waters. Therefore, in order to better judge the measured aluminium concentrations, we compared them with the concentration limits existing in the USA. The chronic U.S. National Ambient Water Quality Criteria (USEPA, 1988) for total aluminium at a pH of 6.5–9 is 87 μg l^{-1}, indicating that the average value over four days should not exceed this value more than once every three years. However, since aluminium seems to be more toxic at low pH's it results that in acid waters the acceptable chronic value of total aluminium may be even lower. It follows that aluminium concentrations in our 3 most acid lakes are probably high enough for causing toxic effects on organisms.

2.5.2 Seasonal influence on lake profiles 2000–2001

In order to find the best sampling season for trend analyses, the yearly dynamic of the main physical and chemical was investigated. For that purpose two lakes were chosen to represent lakes that mix completely twice a year (dimictic: Laghetto Superiore) and lakes that mix only partially with the lower layer never mixing with the upper layer (meromictic: Laghetto Inferiore) (Pradella, 2001). Between April 2000 and February 2001 for each lake 7 water profiles were sampled: 3 with (5.5.2000, 14.2.2001, 10.4.2001) and 4 without ice coverage (5.7.2000, 8.8.2000, 8.9.2000, 4.10.2000).

Temperature, conductivity (20°C) and oxygen and the calculated density profiles are shown in Fig. 2.5. Density profiles were calculated from temperature and conductivity profiles.

Fig. 2.5   > Temperature, conductivity (20°C), density and oxygen profiles in Laghetto Inferiore and Laghetto Superiore from May 2000 to April 2001.
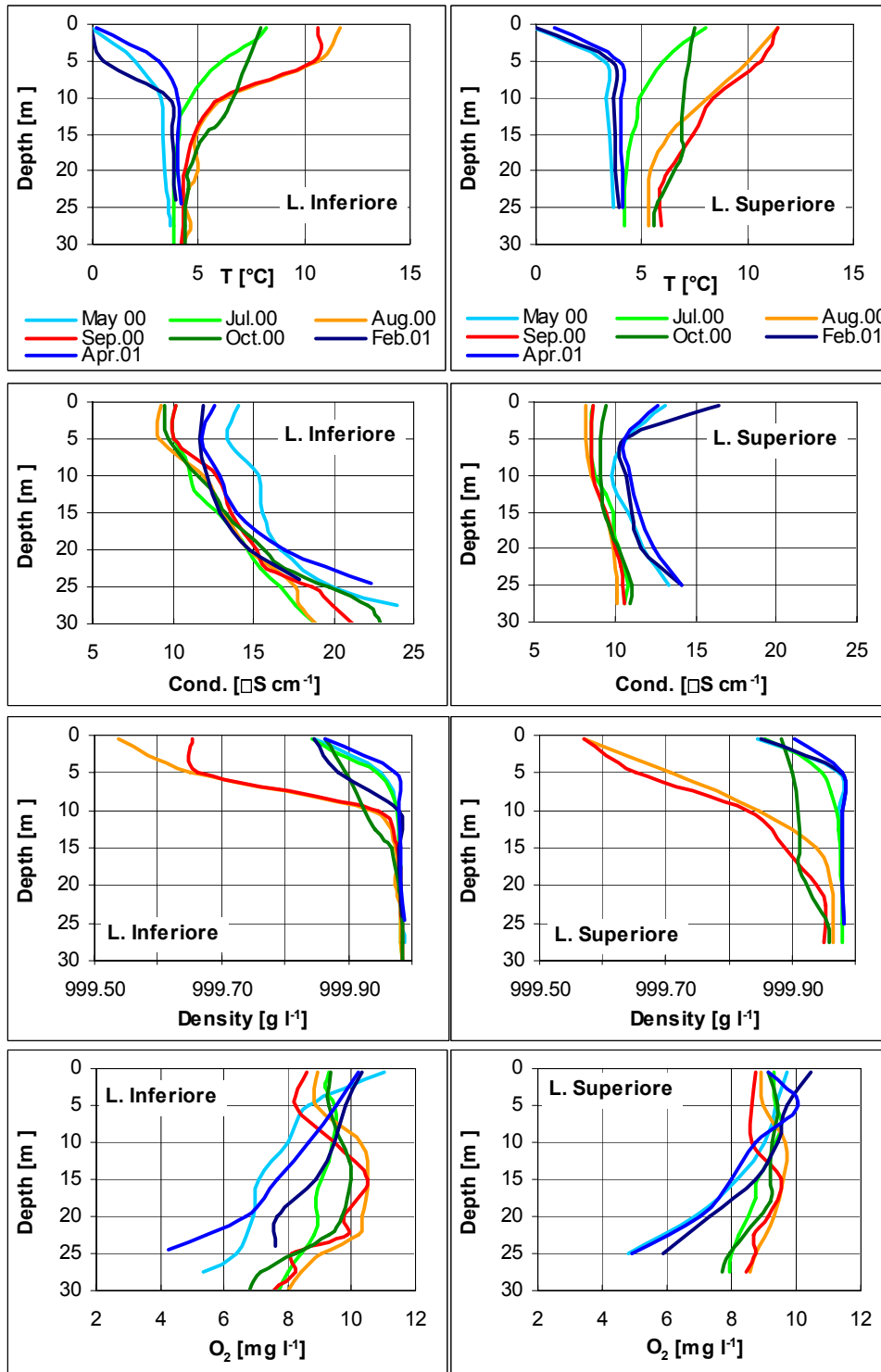
Temperature profiles of the two lakes are very similar. During winter stagnation, when surface water is frozen (November to June), temperature increases gradually from 0 °C to 3–4 °C m in Laghetto Superiore between 0 and 5 m depth and in Laghetto Inferiore between 0 and 10 m depth. Below these depths temperature remains constant. During summer stagnation (mid July to mid September) the epilimnion (0–5 m) is characterized by temperatures of about 11°C in both lakes, while in the hypolimnion temperatures are higher in Laghetto Superiore (5–6°C) than in Laghetto Inferiore (4–5°C) indicating that in Laghetto Superiore thermal energy could reach greater depths. The same is suggested by the thicker metalimnion layer in Laghetto Superiore (5–20 m) with respect to Laghetto Inferiore (5–15 m). A higher light absorption in Laghetto Inferiore is probably the reason of this difference. In fact, the measured Secchi depth (=depth to which a black and white disc is visible when lowered into water to estimate water clarity) is lower and chlorophyll-a concentrations higher in Laghetto Inferiore (Secchi depth: 13.5–14 m, chlorophyll-a: 2–3.5 $\mu g\ l^{-1}$ at 20 m and 7 $\mu g\ l^{-1}$ at 30 m) than in Laghetto Superiore (Secchi depth: 16–17 m, chlorophyll-a: 1.5–2 $\mu g\ l^{-1}$ at 25 m and 2–2.5 $\mu g\ l^{-1}$ at 28 m). The higher chlorophyll-a concentrations in Laghetto Inferiore may be caused by higher nutrient concentrations in bottom water, but in both lakes chlorophyll-a concentrations, Secchi depth and P concentrations are typical for oligotrophic lakes. These data show that maximum productivity occurs close to the lake bottom. This is typical for high altitude lakes with low nutrients concentrations, where light inhibits plankton growth at smaller depths. Interestingly, maximum productivity does not overlap with maximum oxygen concentrations (10–20 m). The reason is probably connected with the fact that where highest oxygen production occurs (photosynthesis at the bottom) also highest mineralization of organic material takes place. Another interpretation of the same phenomena is given by Ohlendorf et al. (2000): "The observation that highest chlorophyll-a values occur at the lake bottom, whereas the pH and O_2 maxima occurring at the same time were detected between 6 m and 9 m depth, might indicate that the algal bloom was already over and that the algae had settled to the bottom by the time of sampling. However, high chlorophyll-a values might also be the result of picoplankton activity in the bottom water (Hodell et al., 1998)."

Temperature profiles of July and October show a situation shortly after winter and summer stagnation, respectively. In the July profile it can be observed that temperature started to increase at the surface but is still close to the winter situation at greater depths. The opposite can be observed in the October profile: surface water starts to cool down while deeper layers still remain at summer temperatures. These results suggest that the July profile was sampled shortly after spring overturn and the October profile shortly before fall overturn.

The main parameters determining conductivity are calcium (30%), sulphate (25%), bicarbonate (15%) and nitrate (10%). Conductivity profiles differ greatly between Laghetto Superiore and Laghetto Inferiore. Conductivity in Laghetto Inferiore is constant in the first 5 m (9–10 $\mu S\ cm^{-1}$) and increases continuously toward the deepest point (19–23 $\mu S\ cm^{-1}$) in all ice free profiles, while winter-spring profiles are characterized by higher values at the surface (10–15 $\mu S\ cm^{-1}$) but were similar to summer-fall profiles at deeper layers (> 20 m). In Laghetto Superiore the difference between sur-

face and bottom water is much less pronounced and deep water conductivity (10–14 μS cm^{-1}) is smaller than in Laghetto Inferiore. Differently than what observed for temperature profiles, no great difference exists between the conductivity profiles of summer stagnation and those close to overturn. The higher conductivity immediately below the ice cover is due the water freezing process, while the increase toward bottom waters especially in winter in Laghetto Superiore and during the whole year in Laghetto Inferiore is probably caused by mineralisation processes of organic material in deep water layers. This phenomena results more pronounced in Laghetto Inferiore, because of the occurrence of only partial mixing processes in the water column (meromixis) between winter and summer stagnations, leading to an accumulation of salts in deep water layers not participating the overturn (from 20–25 to 30 m depth). The meromixis of Laghetto Inferiore is also evidenced by the almost constant temperature (3.7–4.4 °C) and the high density of bottom water during the whole year, while in Laghetto Superiore a difference between summer and winter bottom temperature is visible (from 3.7–4.1 °C in winter to 5.3–5.9 °C in summer), showing that thermal energy from the surface reaches even the deepest water layers. The meromixis of Laghetto Inferiore is probably caused by its particular morphometry. In fact, although Laghetto Inferiore and Laghetto Superiore, have similar maximum depths (33 m and 29 m, respectively), Laghetto Inferiore has a slightly smaller surface area (5.2 ha) than Laghetto Superiore (8.3 ha) and has two conic depressions at the bottom (below 15 m), while Laghetto Superiore has a more regular morphometry (Pradella, 2001). Those differences imply that in Laghetto Superiore the friction area of wind energy is greater and together with the more regular morphometry during periods with no thermal stratification internal mixing processes can reach more easily bottom waters than in Laghetto Inferiore.

Sulphate, nitrate and reactive dissolved silica profiles of Laghetto Superiore and Laghetto Inferiore are shown in Fig. 2.6. Sulphate and silica profiles are very similar to the conductivity profiles discussed before: increasing concentrations from the surface toward the bottom due to meromixis in Lago Inferiore and more constant profiles in Laghetto Superiore with higher concentrations under the ice cover due to the concentration effect of freezing and higher concentrations at the bottom due to mineralization of organic matter in the winter-spring profiles (in Laghetto Inferiore also already in October). Nitrate profiles are slightly different and are characterized by the almost not existence of a vertical gradient especially in the summer-autumn profiles in Laghetto Inferiore probably caused by nitrogen assimilation at the bottom water (and/or denitrification in the sediment, where oxygen is absent). The influence of mineralization in winter and assimilation in summer is shown by the higher concentrations of nitrate in winter bottom water compared to the summer-fall situation.

Fig. 2.6 > Sulphate, nitrate and reactive dissolved silica profiles in Laghetto Inferiore and Laghetto Superiore from May 2000 to April 2001.
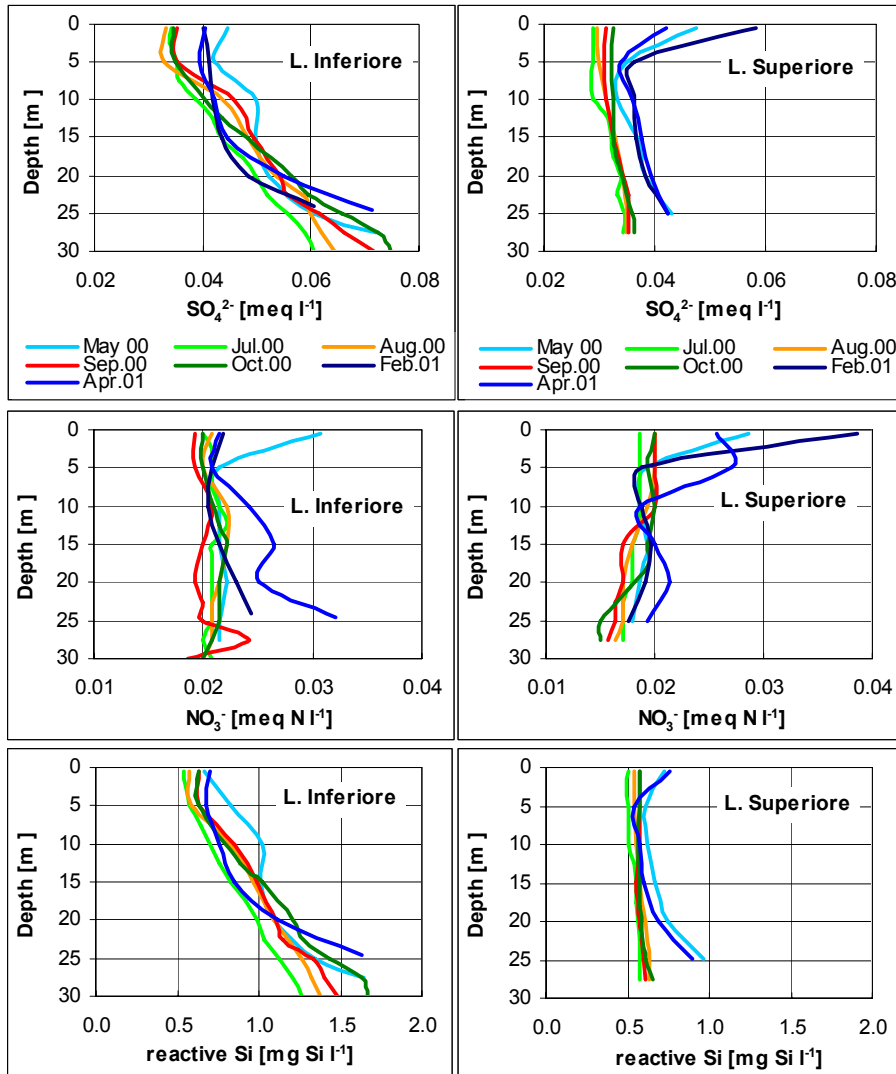
Base cation (sum of calcium and magnesium , > 85 % calcium), Gran alkalinity and pH are shown in Fig. 2.7. Base cation profiles are similar to those of conductivity, sulphate and silica. Because of meromixis in Laghetto Inferiore the increase of base cation toward the lake bottom is much more pronounced than in Laghetto Superiore. The concentration increase immediately below the ice cover can again be explained by the concentration effect of the freezing process. Differently, the concentration increase in winter-spring bottom water, especially in Laghetto Superiore, is probably caused by dissolution of calcium carbonate from the sediment because of the production of CO_2 from mineralization processes. In summer CO_2 production from mineralization over-laps with CO_2 consumption from photosynthesis.

Fig. 2.7   > Base cation, Gran alkalinity and pH profiles in Laghetto Inferiore and Laghetto Superiore from May 2000 to April 2001.
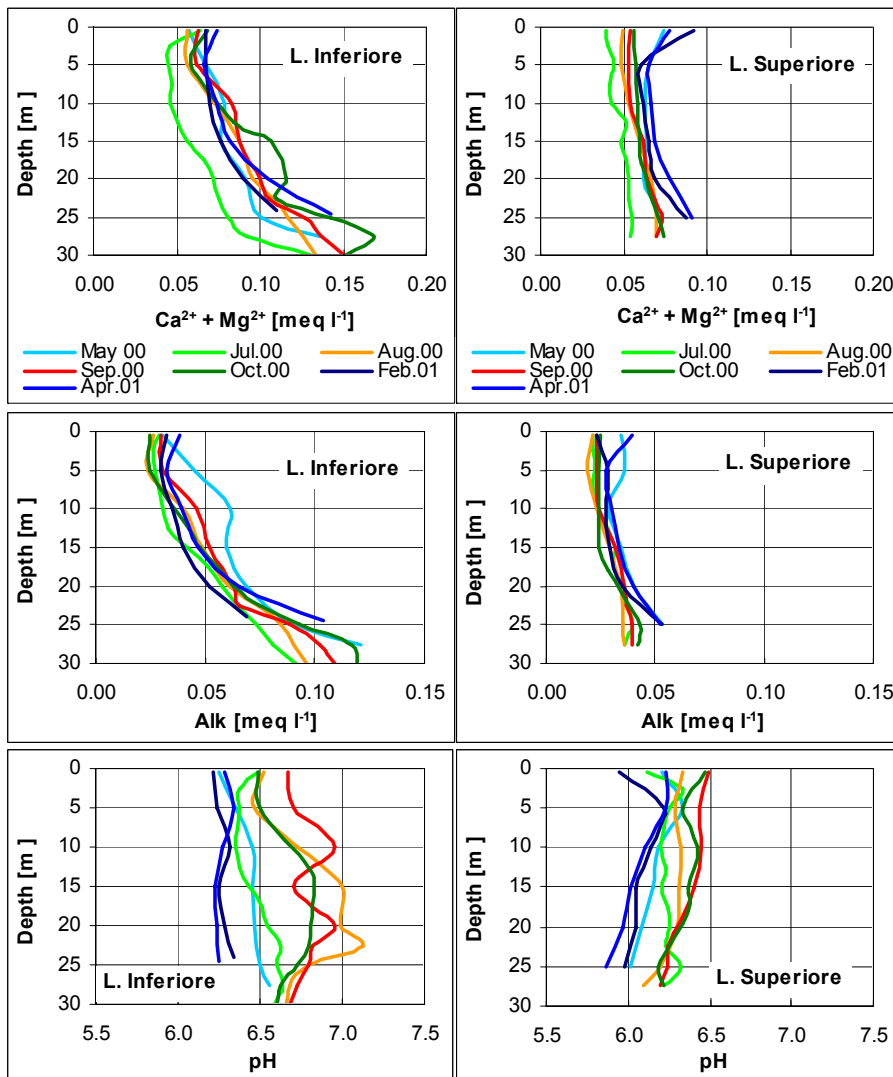
A net production of CO_2 in bottom water is also shown by decrease of pH in bottom waters in months with ice coverage. Interestingly, comparing the oxygen profiles from August to October with the pH profile, it appears that the layers with maximum pH and maximum oxygen concentrations correspond quite well. Again, the phenomena can be explained by photosynthetic activity at the lake bottom that produces O_2 and consumes CO_2. We probably can't find maximum pH and O_2 concentrations at the bottom because of the local overlap of mineralisation of organic matter (O_2 consumption and CO_2 production).

Alkalinity profiles look also similar to sulphate and base cation profiles. This is not surprising because alkalinity can also be expressed as the difference between base cation and acid anions (eq. 2). Therefore the alkalinity increase toward the bottom in Laghetto Superiore mainly during ice coverage and in Laghetto Inferiore during the whole year can be explained by a higher calcium increase with respect to sulphate (other base cation and acid anion are less relevant). This indicates a production of alkalinity in bottom water also known as "internal alkalinity production" and is probably caused by a combination of calcium carbonate dissolution and nitrate and sulphate assimilation and/or nitrate and sulphate reduction in anoxic sediments.

This chapter showed that the main parameters involved in acidification processes (sulphate, nitrate, base cation, alkalinity and pH) vary in a lake during the seasons, depending on the depth and on the lake type. To obtain representative data for calculating trend analyses it is therefore useful to take samples shortly after overturn situations (here beginning of summer and beginning of autumn) when the water column is mixed most. In literature autumn samples are preferred because the water column is not influenced by acidification events due to snow melt. However, for the July data shown here an acidification effect in the surface water of the lakes due to snow melt can not be observed. As a consequence, we decided to utilize for our trend analyses (see next chapter) not only data from the beginning of fall but also from the beginning of summer. Finally, as a result of what observed in this chapter it was also decided to interrupt yearly monitoring of lake profiles for the next 4–5 years and increase instead monitoring of surface water from 2 to 3 times a year (1 during spring overturn and 2 during autumn overturn).

2.5.3 Trends in surface water chemistry of 20 Alpine lakes between 1980 and 2004

Trend analyses can provide important information of the geographic extent of acidification and recovery of lakes and streams (Skjelvåle, 2003). In the last 20–25 years there has been a substantial reduction in the emissions of sulphur and in some countries also in nitrogen oxides (Vestreng, 2003). As a consequence there has been an improvement of the quality of atmospheric deposition. In fact, in the last 20 years a decrease in sulphate deposition and therefore also in acidity deposition have been observed in many European sites (Schöpp et al. 2003). The aim of this chapter is to verify if deposition trends are reflected in trends of surface water chemistry. Trend analyses were performed on the key variables involved in acidification and recovery: alkalinity (Gran alkalinity), pH, sulphate, nitrate, base cations (calcium + magnesium) and reactive dissolved silica. Dissolved organic carbon concentrations are small and are not important in determining alkalinity and are therefore not discussed. The analyses cover the period 1980–2004 and, according to the observations exposed in the previous chapter, surface water data from the beginning of summer and the beginning of autumn are utilized.

2.5.3.1 Statistical methods used for the trend analyses.

For each site and parameter we utilized the Mann-Kendall test to detect temporal trends (Dietz and Kileen, 1981). The two sided test for the null hypothesis that no trend is

present was rejected for p-values below 0.05. In addition we quantified trends with the method of Sen (Sen, 1968). Results are shown in Tab. 2.3.

2.5.3.2   Sulphate trends

Sulphate, beside nitrate, is the main acid anion in acid deposition. Trends in sulphate concentrations are significant in 15 out of 20 lakes. The trend is significantly negative in 14 lakes and significantly positive in 1 lake (Lago Leit). The absence of decreasing sulphate concentrations in 6 lakes may be attributed to increased weathering of sulphur containing rocks, resulting from climate warming (Rogora, 2004) or leakage of old sulphate stored in the catchment. In fact, 5 of those 6 lakes are characterized by relatively high sulphate concentrations (mean 2000–2004: 2.11–3.67 mg l^{-1}, Tab. 2.2). Lago Barone is the only lake with no significant decreasing sulphate trend and with not particularly high sulphate concentrations. However, the p-value resulting from the Mann-Kendall test of this lake is small (0.095) and the rate of the trend high (–0.61 μeq l^{-1} yr^{-1}) compared to the values of the other 4 lakes with no significant trend (p: 0.471–0.773; rate: –0.12 to 0.13 μeq l^{-1} yr^{-1}), suggesting that its trend is close to be significant. The median sulphate reduction rate is –0.89 μeq l^{-1} yr^{-1}. This rate is smaller than previously reported for the European alps (–1.80 μeq l^{-1}; Skjelvåle, 2003). The decrease of sulphate concentrations started at the beginning of the eighties, quickly after the beginning of the improvement of the air sulphur oxides concentrations, suggesting a fast chemical response of the lakes. The thin soil and the relatively small sulphur storage, typical for high altitudes, surely contributed to the rapid response in most of the studied lakes.

2.5.3.3   Nitrate trends

In any of the 20 lakes a significant nitrate trend can be detected and the median nitrate trend is low (–0.06 μeq l^{-1} yr^{-1}). This disagrees with observations in Skjelvåle (2003), where a positive nitrate trend was indicated for the Alpine regions. Interestingly, the mean nitrate trend is almost 15 times lower than the sulphate trend, although the emission reductions of SO_2 (ca. 100 teq yr^{-1}) and NO_x (ca. 90 teq yr^{-1}) in canton Ticino were estimated to be in the same range (SPAAS, 2003). However, the fact that in canton Ticino the decrease of SO_2 concentrations in the atmosphere (1.6 μeq m^{-3}) is four times higher than the decrease in NO_x concentrations (0.4 μeq m^{-3}) may indicate that NO_x concentrations in canton Ticino are influenced by air masses coming from the south (Italy), where reduction of NO_x emissions started later (CH: 1985, I: 1992) and is percentually lower (CH: –49%, I: –32%) (Vestreng, 2003). In addition, those air masses are also enriched with ammonia from livestock and cultivated lands. In fact, from the 1980's to nowadays no trend in nitrogen compounds in rain water has been observed (Mosello et al., 2000). On the contrary, increasing nitrogen trends were reported for rivers (Mosello et al., 2001) and reveal the presence of increasing nitrogen saturation in soils or the effect of recent climate warming on soil mineralization, causing increased nitrate leaching. Both phenomena, transboundary air pollution and increased nitrogen leaching from soils, may explain the difference between trends of Swiss nitrogen emission into the atmosphere and nitrate concentrations in Alpine lakes.

Tab. 2.3 > Results from trend analyses of 20 Alpine lakes monitored between 1980–2004.

For each site are indicated the range of the number of data points (depending on the parameter), the calculated trends (Sen's method), the p-value from the Mann-Kendall test (significant trends in red) and for each parameter the median trend and the number of sites with significant positive or negative or no trend are shown.

Lake name	no.	SO_4^{2-} trends µeq l⁻¹ yr⁻¹	SO_4^{2-} trends p-value	NO_3^- trends µeq l⁻¹ yr⁻¹	NO_3^- trends p-value	$Ca^{2+}+Mg^{2+}$ trends µeq l⁻¹ yr⁻¹	$Ca^{2+}+Mg^{2+}$ trends p-value	Alk trends µeq l⁻¹ yr⁻¹	Alk trends p-value	H^+ trends µeq l⁻¹ yr⁻¹	H^+ trends p-value	Si trends µg Si l⁻¹ yr⁻¹	Si trends p-value
Lago di Tomè	14–15	-0.99	0.0008	0.12	0.5820	-0.24	0.2503	0.25	0.0468	-0.12	0.6507	8.0	0.0256
Lago di Sascòla	12–15	-1.16	0.0055	-0.05	0.8820	-0.39	0.1250	0.70	0.0013	-0.07	0.0093	9.3	0.2404
Lago d'Alzasca	13–17	-0.94	0.0039	-0.04	0.7095	0.24	0.5641	1.15	0.0050	0.00	0.1081	4.9	0.7133
Lago del Starlaresc da Sgiof	13–15	-1.59	0.0003	0.40	0.4279	-0.22	0.5190	0.25	0.3205	-0.44	0.0238	11.1	0.0101
Lago di Sfille	12–17	-1.19	0.0002	-0.04	0.5326	-0.61	0.2165	0.45	0.0625	-0.01	0.3131	4.9	0.2426
Laghi dei Pozzöi	12–16	-1.14	0.0069	-0.30	0.1251	-0.49	0.1497	0.95	0.0148	-0.01	0.3291	0.8	0.9452
Lago di Mognola	13–17	0.13	0.7729	0.00	0.8030	0.33	0.8691	-0.09	0.8040	0.00	0.5030	8.0	0.5822
Laghetto Inferiore	18–22	-1.07	0.0000	-0.29	0.1739	-0.33	0.3974	0.41	0.5716	0.00	0.3081	-3.5	0.3211
Laghetto Superiore	14–18	-0.98	0.0000	-0.14	0.2532	0.07	0.7909	1.11	0.0044	-0.02	0.2351	5.3	0.0615
Lago d'Orsalia	12–16	-1.09	0.0307	0.24	0.3905	0.41	0.3219	1.21	0.0003	-0.07	0.0028	10.7	0.0732
Lago della Crosa	13–16	-0.83	0.0000	-0.02	0.4605	-0.15	0.3439	0.83	0.0002	-0.03	0.1207	3.7	0.0232
Laghetto d'Antabia	10–13	-0.63	0.0015	0.02	0.8055	0.90	0.0381	1.57	0.0031	0.00	0.1381	10.9	0.0196
Lago dei Porchieirsc	9–11	0.06	0.7548	-0.14	0.3850	0.84	0.9379	1.20	0.0423	-0.02	0.0112	8.6	0.6002
Lago Leit	12–14	1.14	0.0004	-0.16	0.0990	1.82	0.0002	0.70	0.0010	-0.03	0.0018	4.8	0.1916
Lago di Morghirolo	13–16	-0.12	0.4713	-0.17	0.1592	0.52	0.0132	0.93	0.0039	-0.02	0.0334	0.79	0.4268
Schwarzsee	12–16	-1.02	0.0307	-0.10	0.6842	-0.38	0.6525	0.97	0.0581	-0.01	0.2553	9.3	0.1139
Lago della Froda	12–16	-0.64	0.0272	-0.18	0.1140	0.14	0.7187	1.09	0.0039	-0.01	0.0123	-0.8	0.6754
Lago Nero	13–18	-0.07	0.5442	-0.06	0.3395	0.09	0.7332	0.84	0.0056	0.00	0.7015	-13.6	0.0027
Lago Barone	14–16	-0.61	0.0954	0.02	0.7856	0.45	0.1258	0.84	0.0090	-0.05	0.2019	5.6	0.2052
Laghetto Gardiscio	13–16	-0.39	0.0169	-0.13	0.2963	0.07	0.7187	0.25	0.0909	-0.29	0.0255	0.0	0.7560
n° increasing trend		1		0		3		14		0		4	
no trend		5		20		17		6		12		15	
n° decreasing trend		14		0		0		0		8		1	
median		-0.89		-0.06		0.08		0.84		-0.02		5.1	

2.5.3.4   Base cation trends

Base cations (Ca^{2+} and Mg^{2+}) are mobilised by weathering and cation exchange reactions that neutralise acids in the watershed. They respond indirectly to changes in sulphate and nitrate concentrations. Without other base cation influencing phenomena, by decreasing acid anions concentrations (mainly sulphate), base cations are expected to decrease. However, in the last few years an increase of the occurrence of alkaline rain episodes (probably due to climatic effects) has been observed and it is likely that calcareous Saharian dust, rich in base cation, is responsible for it (Rogora et al. 2004). Increased weathering, resulting from recent climate warming may also contribute to increased base cation concentrations (Rogora, 2004). As reported elsewhere for European Alps (Skjelvåle, 2003), for $Ca^{2+}+Mg^{2+}$ no regional trend can be observed. At our study site only 3 lakes out of 20 have a significant increasing trend. The median rate is low: 0.08 µeq l^{-1} yr^{-1}. The absence of a significant base cation trend in most lakes may be explained, as mentioned before, by the fact that base cations are controlled by both base cation decreasing and increasing mechanisms.
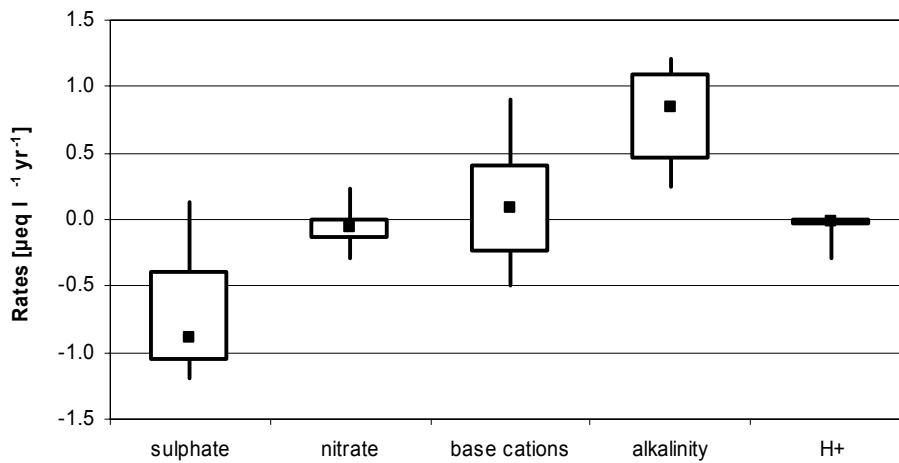
2.5.3.5   Alkalinity trends

When rates of $Ca^{2+}+Mg^{2+}$ decline are equal, or nearly equal, to rates of sulphate and nitrate reduction, then recovery (increasing alkalinity and pH) is prevented (see eq. 2). Subtracting the median acid anions trends (–0.89 and –0.06 µeq l^{-1} yr^{-1}) from the median base cation trend (0.08 µeq l^{-1} yr^{-1}) we obtain a figure (1.03 µeq l^{-1} yr^{-1}) that suggests a positive alkalinity trend at our study site (see also Fig. 2.8). In fact, we can find a significant positive alkalinity trend in most lakes (14). Surprisingly, with exception of Lago di Mognòla, those lakes not showing a significant alkalinity trend (Lago di Sfille, Schwarzsee, Laghetto Gardiscio, Lago del Starlaresc da Sgiof, Laghetto Inferiore) have at the same time significant sulphate reducing trends. In 3 lakes (Lago di Sfille, Schwarzsee, Laghetto Gardiscio) this apparent contradiction can be explained by positive alkalinity trend that are almost significant (p: 0.0581–0.0909). The opposite is observed for Lago Barone: almost significant increasing sulphate trend toward significant positive alkalinity trend. In Lago del Starlaresc da Sgiof (acid lake) the sulphate reduction led to a significant pH reduction (H^+ trend: 0.44 µeq l^{-1} yr^{-1}) probably not compensated by an increase of bicarbonate concentrations and therefore inhibiting a significant alkalinity increase. For Laghetto Inferiore the difference between the behaviour of sulphate concentrations (reduction trend) and alkalinity (no trend) can not be explained. This surprises even more when comparing the rates of the trends with those of Laghetto Superiore, that is connected with Laghetto Inferiore by the outflow of the latter. Laghetto Superiore has a significant sulphate trend in the same range (–0.98 µeq l^{-1} yr^{-1}) as in Laghetto Inferiore (–1.07 µeq l^{-1} yr^{-1}) and a significant increasing alkalinity trend (1.11 µeq l^{-1} yr^{-1}) reflecting the sulphate trend. Interestingly, Lago Leit, although having a significant increasing sulphate trend, has a significantly positive alkalinity trend. In this case increasing sulphate concentrations are compensated by a significant increase in base cation concentrations. The same phenomena explains the significant alkalinity increase in Lago di Morghirolo although no significant sulphate increasing trend can be detected. A significant alkalinity increase not being accompanied by a significant sulphate decrease is also observed in Lago dei Porchieirsc and

Lago Nero. In the first lake the small number of data points, especially before 2000 (2 sampling dates) is probably the reason for this incongruence, in the latter no reasonable explanation can be found.

Fig. 2.8 > Distribution of sulphate, nitrate, base cation and H$^+$ rates of the trends calculated for the study site.

Each box shows the range of the trends (25th to 75th percentile, with line at median). The confidence intervals indicate 10th and 90th percentiles.

In Fig. 2.9 average alkalinity values in the 1980's are compared with average values between 2000 and 2004. It appears that, although not in all lakes a significant positive alkalinity trend can be detected, in almost all lakes an alkalinity increase from the 1980's to nowadays can be observed. The average increase was 0.012 meq l^{-1}. In the 1980's 4 lakes were acidic (today 2), 14 were sensitive to acidification (today 13) and 2 had low alkalinities but were not acid sensitive (today 5). In terms of critical load exceedances it can be observed that today 6 lakes have an average alkalinity that is below the critical value (0.020 meq l^{-1}) while they were 13 in the 1980's.

Fig. 2.9 > Average alkalinity in the 1980's and between 2000 and 2004 in 20 Alpine lakes.
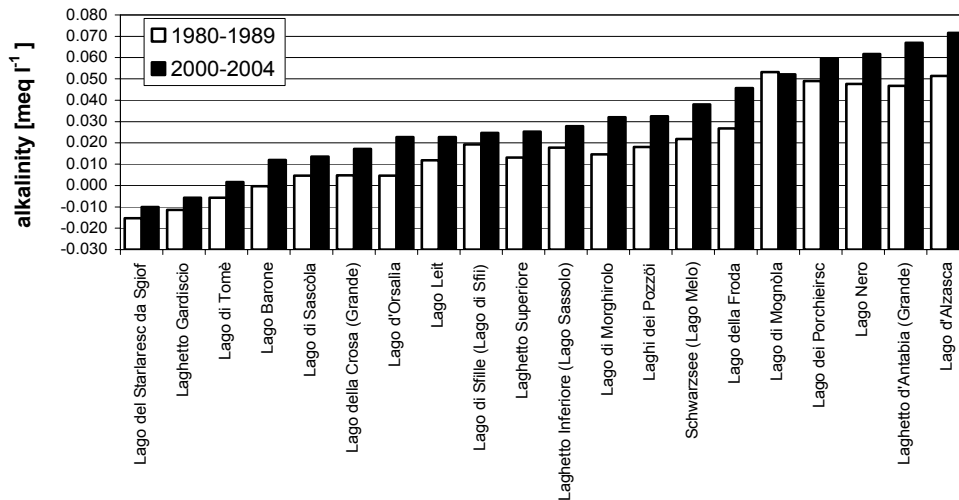
#### 2.5.3.6   H$^+$ trnds

The median H$^+$ trend is low (–0.02 µeq l^{-1} yr^{-1}) and only 8 lakes have a significant decreasing trend. Plotting the calculated H$^+$ trend against the average H$^+$ concentrations during the whole monitoring period a correlation between the two variables appears (Fig. 2.10): higher H$^+$ decrease at higher H$^+$ concentrations or in other words higher H$^+$ decrease at lower pH. This phenomena is probably caused by the high buffer capacity of bicarbonate containing water around pH=6.3 (5.8–6.8). This implies that in the pH range ≈4.3–6.3, the same sulphate decrease generates a higher H$^+$ decrease at lower than at higher pH.

Fig. 2.10   **> H^+ trends vs. average H^+ concentrations of the period 1980–2004 for 20 Alpine lakes.**
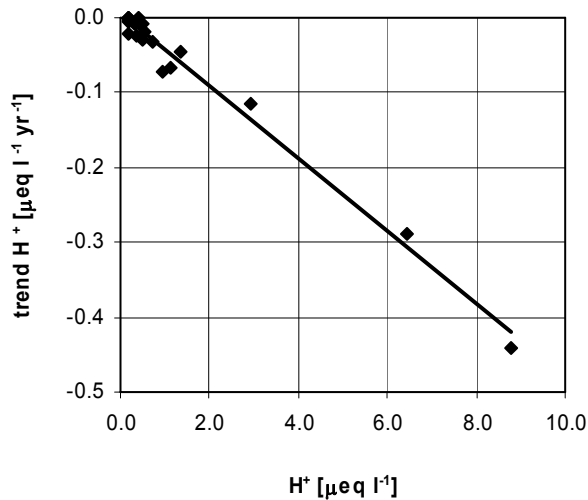
The pH improvement in our lakes becomes evident when comparing the average pH in the 1980's with those of the years 2000–2004 (Fig. 2.11). The increase of pH was on average 0.3. In the 1980's 8 out of 20 lakes had an average pH<6, while nowadays only 3 lakes have pH values that are critical for aluminium dissolution (ch. 3.4.1). To better interpret the observed pH improvement it would be useful to know how pH's were before lake acidification begun. As far as we know, pH reconstructions exists only for Lago Leit. Marchetto and Lami (1994) estimated from chrysophycean scale a pH decrease from ca. 6.8 to 5.6 (pH decrease = 1.2). However, our pH measurements indicate that in Lago Leit pH generally did not decreased below pH 6, indicating that the pH decrease estimated by Marchetto and Lami (1994) is probably slightly overestimated.

Fig. 2.11   > Average pH in the 1980's and between 2000 and 2004 in 20 Alpine lakes.
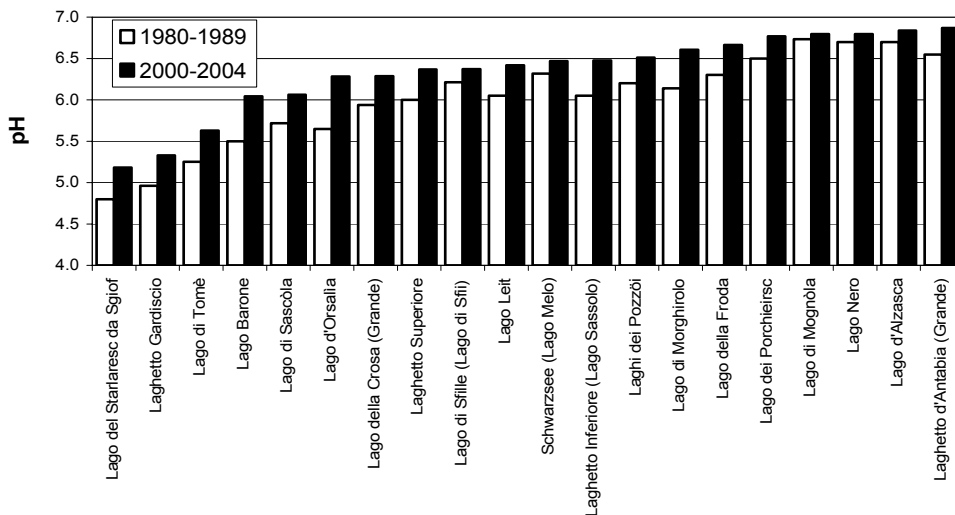
Niederhauser (1993) reconstructed the pH's of other two Alpine lakes, that are not included in our monitoring list, from diatom scales (Langsee and Lago della Zòta). The pH of Langsee probably ranged between 5.7 and 5.9 until 1900 and decreased to 5.1 (1990–1991) in the 20th century. Similar results were obtained for Lago della Zòta: pH's of 5.7–5.8 before 1900 and decrease to 5.0 (1991). The mentioned literature data therefore suggest a pH decrease in the 20th century in Alpine acid sensitive lakes around 0.6–0.8 units. From the previous pH increase estimation (0.3 units) it results that our lakes did still not completely recover.

2.5.3.7   Soluble reactive silica trends

Reactive silica concentrations originate from weathering of silica containing rocks (mainly gneiss) in the catchment area (see ch. 2.2). The silica release from a catchment is pH dependent (Scheffer and Schachtschabel, 2002): depending on the rock, at pH's <5–8 silica release decreases with increasing pH because of decreasing weathering rates, while at pH's >5–8 the release of silica increases because of increased solubility. In addition, it is known that climate warming may also increase weathering rates and therefore the silica release. It results that soluble reactive silica concentrations in lakes depend on different parameters and it becomes difficult to estimate the result of a trend analyses. The median soluble reactive silica trend at our monitoring site is positive (5.1 μg Si l^{-1} yr^{-1}). However, in most lakes (15) a significant trend can not be observed: 4 lakes have significantly increasing trends (Lago di Tomè, Lago del Starlaresc da Sgiof, Lago della Crosa, Laghetto d'Antabia) and 2 lakes almost significantly trends (Laghetto Superiore, Lago d'Orsalìa). Significantly decreasing trends can only be observed in Lago Nero.

| 2.5.4 | **Discussion and conclusions** |

Significant decreasing sulphate and increasing alkalinity trends were found in most studied lakes, while trends for base cation and nitrate were small and mostly insignificant. The average increase in alkalinity between 1980 and 2004 was 0.012 meq l^{-1}, while the average pH increase during the same time period was 0.3.

As writes Skjelvåle (2003) "the uncertainties in future chemical recovery mainly relate to the effects of climate change and the future behaviour of nitrogen in the ecosystem". Due to decreased SO_2 emissions, the importance of nitrogen to freshwater acidification becomes more and more determinant. Therefore, uncertainties in the evolution of nitrogen emissions make it difficult to predict future trends in freshwater recovery. Probably, because of increasing nitrogen leakage out of the soil (Mosello et al., 2001), due to increased nitrogen saturation level or increased mineralisation because of climate warming, if nitrogen deposition remains constant or increases, further recovery from declined sulphate export may be delayed and in the worst case already obtained recovery may be nullified. On the other side, climate warming may increase the number of alkaline rain episodes (containing Saharian dust) and enhance weathering reactions, that buffer better acid precipitation, increasing alkalinity and pH.

In consideration of the uncertainities connected with the future development of parameters determing water acidity, it is important to continue monitoring of alpine lakes.

2.6 | **Acidification effects on rivers between 2000 and 2004**

2.6.1 | **Chemical characterization of 3 Alpine rivers between 2000 and 2004**

Concentrations of the main physical and chemical parameters of the rivers Maggia, Vedeggio and Verzasca measured between 2000 and 2004 are shown in Tab. 2.4. Dependent on the river and the parameter the sample number varied between 54 and 64 (data not shown).

Average alkalinity is highest in river Maggia (0.279 meq l^{-1}) followed by river Vedeggio (0.144 meq l^{-1}) and river Verzasca (0.059 meq l^{-1}). Based on these data River Verzasca and river Vedeggio have low alkalinities (0.050–0.200 meq l^{-1}), but no river is sensitive to acidification. The same is suggested by minimum alkalinities that are always > 0 meq l^{-1}. Average pH values vary between 6.7 and 7.4. It follows that the sampled rivers are less acidic than most Alpine lakes. This can be explained by the lower altitudes of the rivers sampling point and therefore the larger catchment areas and longer water residence times that increases neutralization of deposited acids through weathering. In fact, the concentrations of base cation, acid anion, reactive dissolved silica and conductivity at 20°C are also mostly higher in rivers than in Alpine lakes. As a consequence of the higher pH, dissolved aluminium concentrations in rivers (<12 µeq l^{-1}) are lower than in most lakes. Average dissolved organic carbon ranges between 0.39 and 0.55 mg C l^{-1}. Ortho-phosphate concentration is low (<4.7 P µg l^{-1}) and ammonia and nitrite are neglectable small compared to nitrate.

As observed for Alpine lakes, also water chemistry of rivers is the result of numerous physical, chemical and biological reactions occurring in the catchment. These are influenced by many parameters like deposition, catchment area and slope, watershed surface type (vegetation, bare rock), soil, geology, temperature. However, the parameters being probably responsible most for water quality differences in the 3 rivers are the catchments area and geology. In fact, highest alkalinity, pH and conductivity, all parameters that are proportional to weathering activity in the watershed, are measured in river Maggia, whose catchment area is 7 and 10 times larger than the watersheds of river Verzasca and Vedeggio, respectively. Surprisingly, river Vedeggio has higher pH and conductivity values and higher alkalinity, base cations, acid anions and soluble reactive silica concentrations than river Verzasca, although their catchment areas are in the same range. Similarly to the catchment of river Maggia, the watersheds of river Vedeggio and Verzasca are very poor in carbonate containing rocks, but while the catchment of river Verzasca is characterized by the presence of rather new rocks that were formed during the orogenesis of the alps (60 millions years ago), the geology of the catchment of river Vedeggio is much older (300 millions to 2.5 milliards years) and therefore much more weathered and fractured increasing the surface that can interact with water from precipitations. This may be the cause for higher weathering activity in the catchment of river Vedeggio, being responsible for higher river alkalinity and pH.

Tab. 2.4 > Average, minimum and maximum concentrations in 3 Alpine rivers between 2000 and 200.

Average values with some or all single values below the quantification limit were preceded with.

Parameter	Unit	Maggia			Vedeggio			Verzasca		
		Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
pH		7.4	6.5	7.8	7.0	6.2	7.4	6.7	6.2	7.3
Cond. (20 °C	μS cm^{-1}	55.7	21.5	73.2	41.0	23.7	51.1	22.0	14.5	26.9
Alk.	meq l^{-1}	0.279	0.081	0.377	0.144	0.068	0.186	0.059	0.030	0.113
Ca^{2+}	mg l^{-1}	7.56	2.99	10.55	4.42	2.54	5.97	2.58	1.58	3.70
Mg^{2+}	mg l^{-1}	0.64	0.29	0.91	0.90	0.57	1.23	0.22	0.15	0.31
Na$^+$	mg l^{-1}	1.61	0.64	2.10	1.64	0.93	2.63	0.70	0.44	0.93
K$^+$	mg l^{-1}	1.46	0.64	1.96	0.57	0.01	0.87	0.53	0.35	0.78
NH$_4^+$	mg N l^{-1}	<0.05	0.00	0.17	0.05	0.00	0.28	0.04	0.00	0.19
SO$_4^{2-}$	mg l^{-1}	9.05	3.03	13.5	6.22	3.59	9.09	3.60	1.64	5.34
NO$_3^-$	mg N l^{-1}	0.55	0.35	2.10	1.05	0.74	1.42	0.71	0.40	1.11
Cl$^-$	mg l^{-1}	1.02	0.16	2.04	0.91	0.38	1.35	0.30	0.02	1.04
NO$_2^-$	μg N l^{-1}	2	0	5	1	0	5	1	0	5
o-PO$_4$	μg P l^{-1}	4.7	1.0	12.5	<4.3	<2	7	<4.6	<1.0	14.3
Ntot	mg N l^{-1}	0.60	0.35	0.98	1.11	0.86	1.56	0.77	0.39	1.27
Ptot	μg P l^{-1}	<5.7	<4.3	15.0	<6.5	<4.3	38.7	<5.7	<4.3	15.6
DOC	mg C l^{-1}	0.54	0.19	1.99	0.55	0.22	1.73	0.39	0.12	1.14
Si	mg Si l^{-1}	2.36	0.69	3.39	3.37	1.10	4.12	1.79	0.72	2.29
Al$_{dissolved}$	μg l^{-1}	<12	<3	55	<11	<0	52	<11	<3	49
Al$_{total}$	μg l^{-1}	<16	<5	91	<42	<5	881	<16	<3	216
Cu$_{dissolved}$	μg l^{-1}	<1.5	<1.0	2.4	<1.6	<1.0	3.7	<1.5	<1.0	2.8
Cu$_{total}$	μg l^{-1}	<1.7	<1.0	4.7	<1.8	<1.0	3.7	<1.7	<1.0	2.8
Zn$_{dissolved}$	μg l^{-1}	<3.1	<0.5	28.2	<2.1	<0.5	9.2	<2.7	<0.5	7.8
Zn$_{total}$	μg l^{-1}	<3.6	0.5	26.2	<3.5	<0.5	21.8	<3.8	<0.5	20.1

2.6.2 Seasonal variation of chemical parameters in Alpine rivers

It is known that the temporal variability of river water quality is strongly related to the river hydrograph (NIVA, 1996). This is also the reason why rivers were sampled at monthly intervals. In the following paragraphs we discuss the seasonal variations of the key variables involved in acidification and recovery. In particular the dependency of alkalinity (Gran alkalinity), pH, sulphate, nitrate and base cations (calcium+magnesium +sodium+potassium) on the daily mean discharge is discussed. Dissolved organic carbon concentrations are small, not important in determining alkalinity and are therefore not presented. Daily average discharge values of river Vedeggio at Isone (sampling point) are published in IST (2000–2004). For river Verzasca discharge is measured only at Lavertezzo (BWG, 2000–2004). In order to estimate the discharge at Sonogno (sampling site) the daily mean discharge at Lavertezzo was divided by the catchment area of this station (186 km^2) and multiplied by the catchment area of the river Verzasca at Sonogno (27 km^2). For river Maggia discharge is measured at Bignasco.

However, the discharge of river Maggia is highly influenced by water extraction for hydropower generation, so that its real discharge does not represent natural hydrology in the catchment. Therefore, we estimated a virtual discharge without the influence of hydropower generation of river Maggia at Brontallo (sampling point) normalizing the discharge of river Verzasca at Lavertezzo to the catchment area of river Maggia (189 km^2).

2.6.2.1   Sulphate

Plotting sulphate concentrations against the daily mean discharge, a decreasing potential function can be plotted through the data points in all three rivers (Fig. 2.12a). This correlation indicates that sulphate concentrations in the watershed get more and more diluted as precipitation and therefore discharge increase. This is not surprising. In fact, annual mean sulphate concentrations in wet deposition at the monitored area (0.02–0.03 meq l^{-1}; SAEFL, 2001) is 3, 4–6, and 6–8 times smaller than average concentrations in river Verzasca, Vedeggio and Maggia, respectively. In addition, with increasing duration of a precipitation event, the river discharge also often increases and the atmosphere becomes cleaner and sulphate concentrations in wet deposition decrease. As a result ground- and surface-water in the watershed get diluted even more with increasing discharge. Fig. 3.12a also shows that sulphate concentrations don't decrease below a minimum concentration that is specific for each river (Maggia: 0.07 meq l^{-1}, Vedeggio: 0.08 meq l^{-1}, Verzasca: 0.04 meq l^{-1}).

2.6.2.2   Base cation

Similarly to sulphate concentrations, also base cation concentrations decrease potentially with increasing discharge (Fig. 2.12b). The explanation of this phenomena is the same as described in the previous paragraph for sulphate concentrations. Since base cation concentrations in wet deposition (annual mean: 0.03–0.04 meq l^{-1}; SAEFL, 2001) are a factor 5–6, 10–13 and 13–18 smaller than average concentrations in river Verzasca, Vedeggio and Maggia, base cation concentrations in ground- and surface-water get more and more diluted as precipitation and therefore discharge increase. Minimum base cation concentrations are 0.22 meq l^{-1} in river Maggia, 0.23 meq l^{-1} in river Vedeggio and 0.12 meq l^{-1} in river Verzasca .

Fig. 2.12   > a) Sulphate and b) base cations concentrations vs. discharge in river Maggia, Vedeggio and Verzasca during the sampling period 2000–2004.
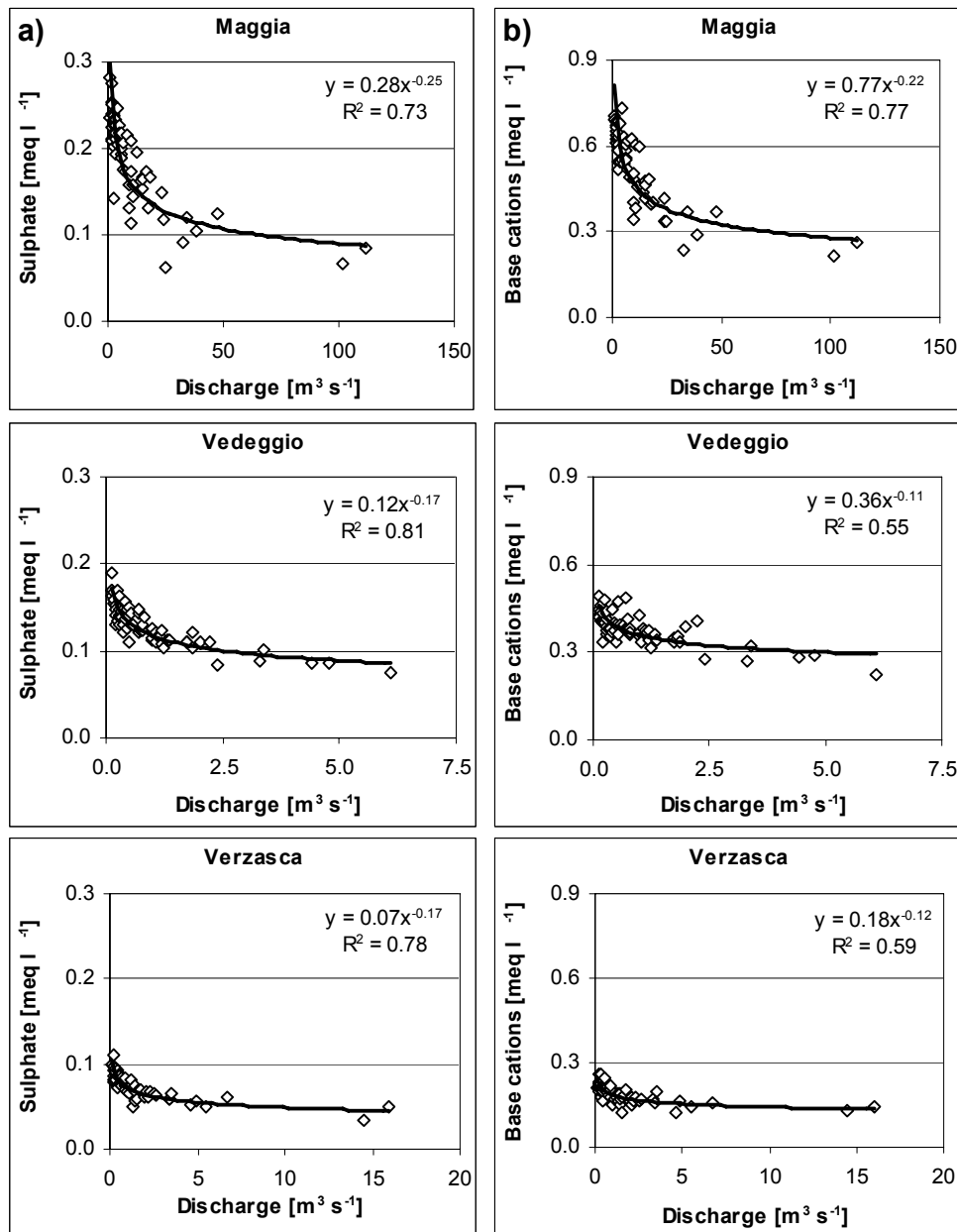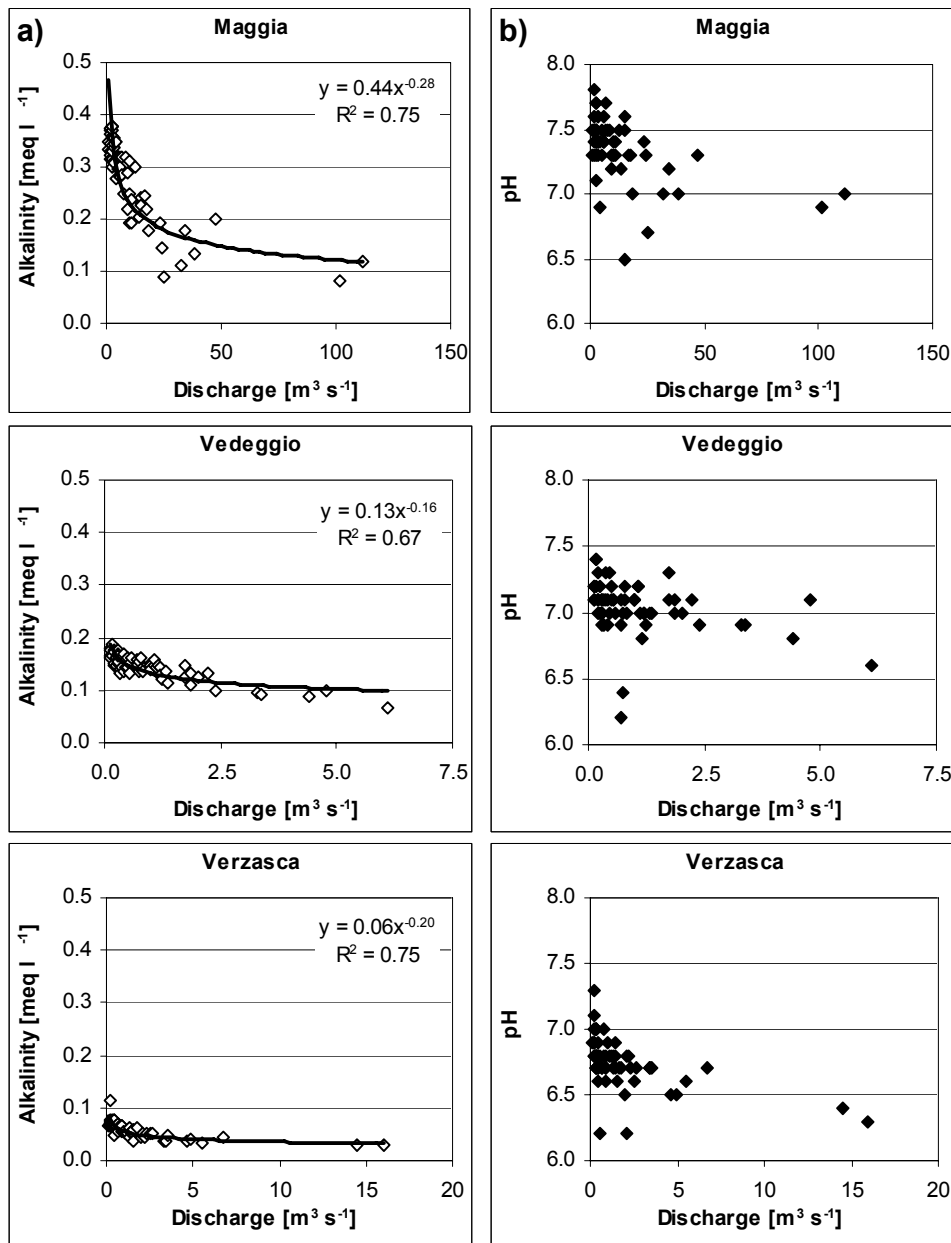

2.6.2.3   Alkalinity

A very good correlation can also be found between alkalinity and daily mean discharge (Fig. 2.13a). Like sulphate and base cations concentrations, alkalinity in river water decrease potentially with increasing discharge. The limit below which alkalinity seems

not to fall is 0.08, 0.07, 0.03 meq l^{-1} in river Maggia, Vedeggio and Verzasca, respectively. Since wet deposition is most of the time acidic (annual mean acidity: 0.010–0.015 meq l^{-1}; SAEFL, 2001), a dilution effect as described for sulphate and base cation concentration is very probable. However, the occurrence of acid precipitation also suggests an alkalinity loss due to titration of strong acids.

Fig. 2.13   > a) Alkalinity and b) pH vs. discharge in river Maggia, Vedeggio and Verzasca during the sampling period 2000–2004.

2.6.2.4   pH

The very good correlation between alkalinity and discharge would suggest a pH decrease with increasing river discharge as well. pH and discharge values are shown in Fig. 2.13b. Although the correlation between the two variables is not as good as observed for alkalinity, sulphate and base cation concentrations, the data seem to effectively suggest a pH decrease with increasing discharge.

This means that pH drops are most probable during precipitation events. However, pH seems never to decrease below pH 6 in any of the monitored river. Considering this and the correlation between pH and aluminium observed for Alpine lakes (Fig. 2.4), it follows that aluminium concentrations probably never reach critical values in the monitored rivers. Plotting the concentrations of dissolved aluminium measured in rivers against the pH (Fig. 2.14a), it results that most values in the pH range between 6 and 8 are below 20 μg l^{-1} and correspond well with lake data in Fig. 2.4. However, in the same pH range some values are clearly above 20 μg l^{-1} and can therefore not be explained with the pH alone. The situation becomes clearer when drawing the concentrations of dissolved aluminium versus the river discharges (Fig. 2.14b), where the existence of a positive linear correlation between the two parameters, that is typical for each river, immediately appears. It is possible that aluminium concentrations increase with increasing discharge because of enhanced transport of previously in soil accumulated aluminium.

Fig. 2.14   > a) Dissolved Al and b) pH vs. discharge in river Maggia, Vedeggio and Verzasca during the sampling period 2000–2004.
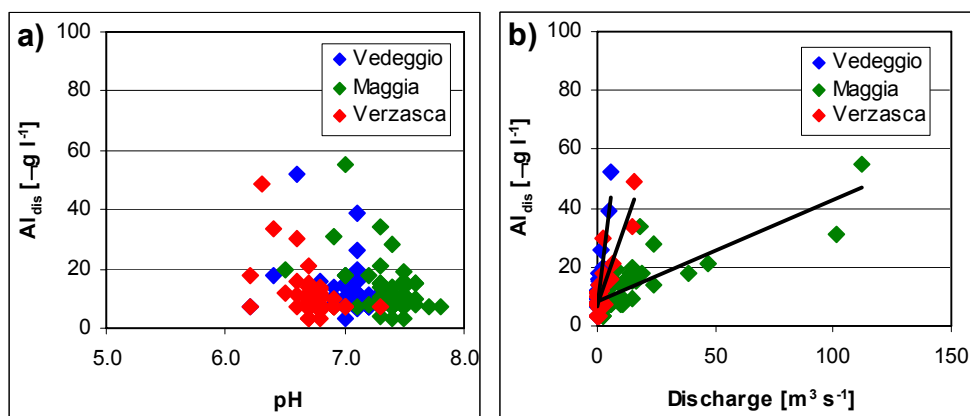
2.6.2.5   Nitrate

Nitrate concentrations apparently do not correlate with the river discharge (Fig. 2.15a). Substituting the equations of alkalinity, sulphate and base cation concentrations found in the previous paragraphs in equation 2, it is possible to calculate the sum of nitrate and chloride concentrations ($\sum(NO_3^-+Cl^-)$) as a function of the river discharge (Fig. 2.15b). Similarly to nitrate, chloride didn't correlate with the discharge (data not shown). The model yields $\sum(NO_3^-+Cl^-)$ concentrations that increase slightly with increasing flow at small discharges, reaching a maximum value, and then slightly decrease with increasing water flow at higher discharge values. Fig. 2.15b also shows that the measured $\sum(NO_3^-+Cl^-)$ concentrations scatter around the modelled values. The dynamic of $\sum(NO_3^-+Cl^-)$ becomes clearer when comparing concentrations in wet deposition with those in river water. $\sum(NO_3^-+Cl^-)$ concentrations are on average 0.07 meq l^{-1} in river Maggia, 0.10 meq l^{-1} in river Vedeggio and 0.06 meq l^{-1} in river Verzasca, with nitrate being the main compound (Maggia: 58%, Vedeggio: 75%, Verzasca: 87%). While in river water ammonia concentrations are insignificant, their concentrations in wet deposition are in the same range as nitrate. Therefore, since in surface water ammonia is easily oxidized to nitrate, $\sum(NO_3^-+Cl^-)$ in river water is compared with the sum of the yearly mean ammonia, nitrate and chloride concentrations in wet deposition (0.03–0.07 meq l^{-1}, 84–92% $NH_4^++NO_3^-$). It results that nitrate and chloride concentrations in wet deposition and in river water are in the same range. This explains why $\sum(NO_3^-+Cl^-)$ concentrations in river water do not correlate greatly with the discharge. In fact, during precipitation events $\sum(NO_3^-+Cl^-)$ in river water gets neither consistently diluted nor concentrated so that variations in concentrations are also the consequence of other variables. It is probable that at the beginning of a rain event, especially if they are anticipated by long dry periods, initially $\sum(NO_3^-+Cl^-)$ concentrations increase with increasing discharge because of higher concentrations in rain water due to a more polluted atmosphere and/or because of leakage of the before accumulated mobile nitrate from the soils (i.e. from mineralization of organic matter). On the other side, if rain events last longer, the discharge may still increase but $\sum(NO_3^-+Cl^-)$ concentrations in river water probably decrease because the atmosphere gets cleaner. Modelled values seem to follow such a dynamic. However, every rain event is unique in its combination of precipitation intensity, duration of the rainless period before and time length of the event itself.

In addition, small variations in the concentrations of pollutants in the atmosphere may also depend on numerous factors (traffic, season, atmospheric currents, …). Moreover, nitrate and ammonia that reach the earth surface undergo a variety of physical, chemical and biological processes, that are themselves influenced by numerous variables like season, meteorology, vegetation, soil, temperature …, that determine nitrogen concentrations in river water. As a consequence, it is not surprising that $\sum(NO_3^-+Cl^-)$ is difficult to predict.

Fig. 2.15   > a) Measured nitrate and b) measured and modelled nitrate + chloride concentrations vs. discharge in river Maggia, Vedeggio and Verzasca during the sampling period 2000–2004.
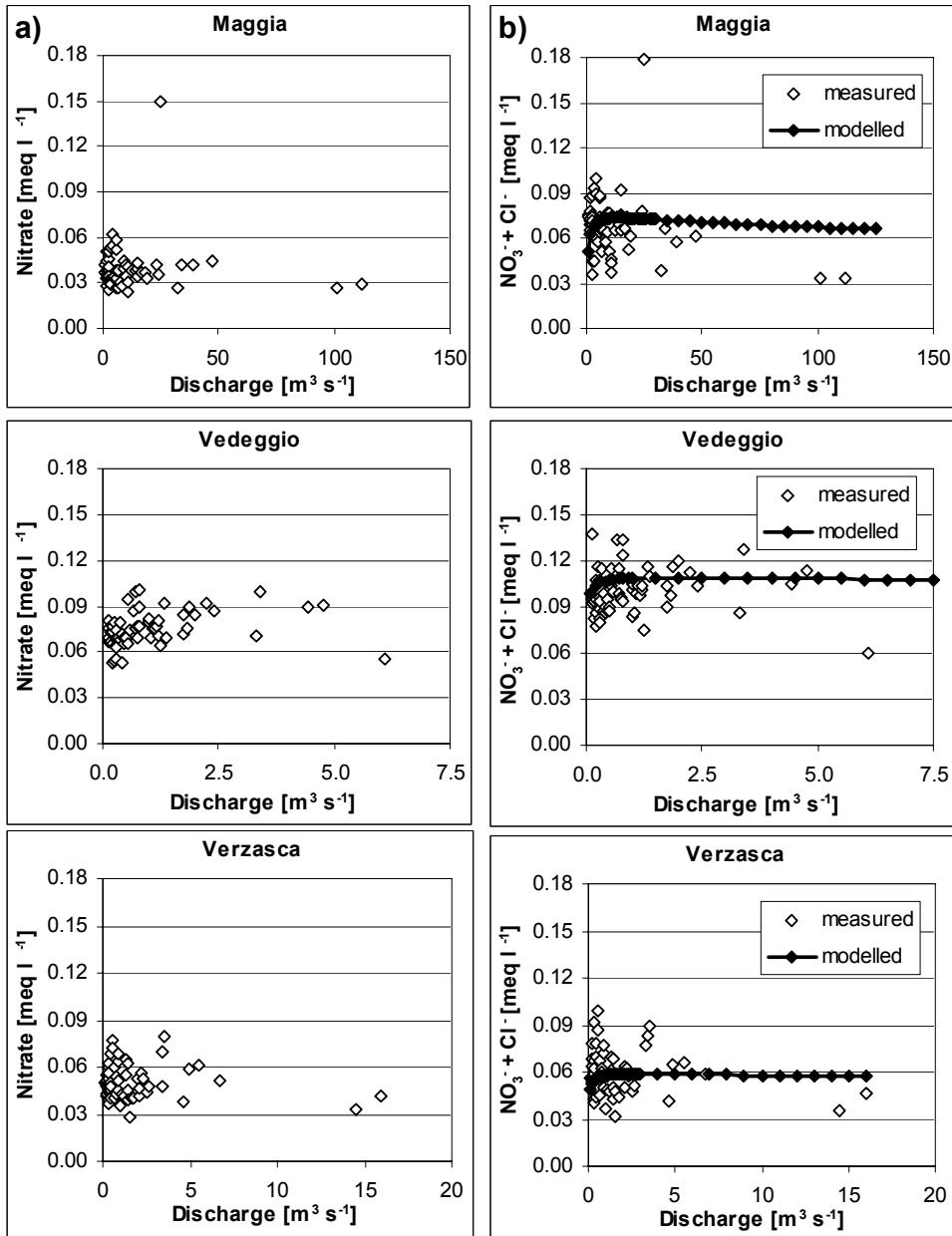
2.6.2.6   Alkalinity loss during rain events

It has been suggested that alkalinity decreases with increasing discharge partly because of dilution and partly because of titration of strong acids during rain events. As applied by Lepori et al. (2003a) and proposed by Kahl et al. (1992), assuming that in the absence of strong acids alkalinity (mainly bicarbonate) behaves similarly than base cation because of their common origin, the percentage alkalinity loss due to dilution can be estimated as follows:

$$[Alk_{pre\text{-}event}\text{-}(BC_{event}/BC_{pre\text{-}event})*Alk_{pre\text{-}event}]/\Delta Alk*100 \qquad\qquad\qquad (eq.\ 6)$$

where BC_{event}, $BC_{pre\text{-}event}$, $Alk_{pre\text{-}event}$, ΔAlk indicate base cation during a precipitation event, base cation before a precipitation event, alkalinity before a precipitation event and the difference between alkalinity before and after a rain event, respectively.

Unfortunately, since river water was sampled only once a month, the time resolution of the data was insufficient to study the variation of river water chemistry during single precipitation events. However, in order to roughly estimate the percentage losses of alkalinity because of dilution and titration, for each river a discharge limit was fixed, below which discharge was considered as base flow and above which discharge was assumed to be influenced by a precipitation event. For river Maggia, Vedeggio and Verzasca this limit was fixed at 5, 0.5 and 0.7 $m^3\ s^{-1}$, respectively. Calculating an average base flow alkalinity and base cation concentration and comparing them with alkalinity and base cation concentrations during high flow events as described in equation 6, for river Maggia, Vedeggio and Verzasca average percentage losses of alkalinity due to dilution of 70–80% are obtained, indicating titration losses of 30–20%. Similar alkalinity losses due to titration are obtained with base cation and alkalinity values calculated with the correlation equations shown in Fig. 2.12b and 2.13a: average values are 16% in river Maggia, 26% in river Vedeggio and 37% in river Verzasca.

It is possible to identify the acid anions responsible for alkalinity consumption by comparing the concentration fractions of sulphate/Σanions, nitrate/Σanions, chloride/Σanions and alkalinity/Σcations in river water during base flow, with high flow conditions. If dilution is the only cause for alkalinity reduction, the alkalinity fraction would not change. The difference in alkalinity fraction multiplied with the sum of cations corresponds to the amount of alkalinity lost due to titration. Since Σanions = Σcations and $Alk = [Na^+] + [K^+] + 2*[Mg^{2+}] + 2*[Ca^{2+}] + [NH_4^+] - [Cl^-] - 2*[SO_4^{2-}] - [NO_3^-]$, the sum of alkalinity and all anion fractions should be one, although small discrepancies occur because of analytical imprecision and the omission of ionic species. A decline in alkalinity fraction must therefore be accompanied by a concomitant increase of one or more anion fractions, which identify the acid anions causing it (Lepori et al., 2003a). For the modelled and measured river water concentrations, differences of alkalinity and anion fractions between base and high flow conditions were multiplied with the sum of cations and anions, respectively. Modelled alkalinity, sulphate and nitrate+chloride concentrations were obtained from the correlation equations described in the former paragraphs. For modelled and measured values, results as a function of discharge are shown in Fig. 2.16.

Fig. 2.16 > a) Modelled (bar graph) and b) measured (scatter plot) contribution of acid anions to alkalinity loss because of titration during precipitation events in river Maggia, Vedeggio and Verzasca during the sampling period 2000–2004.
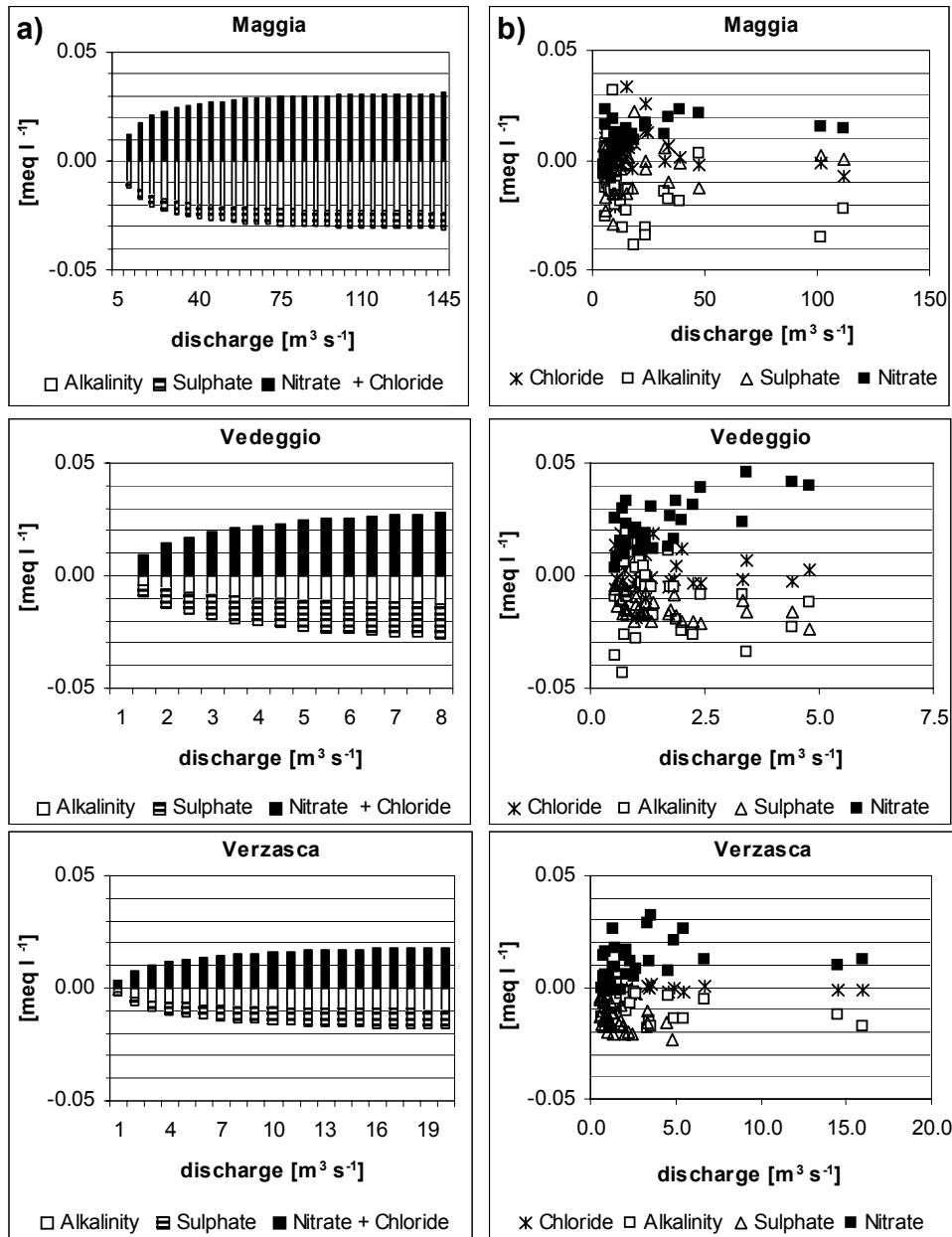
The positive nitrate + chloride values and negative alkalinity and sulphate values in Fig. 2.16a indicate that nitrate+chloride fractions increase during precipitation events while alkalinity and sulphate fractions decrease, suggesting that nitrate and chloride are responsible for alkalinity consumption through titration. The same is indicated by the measured values shown in Fig. 2.16b, where it appears that, especially for higher discharge, nitrate is the main anion that causes titration.

2.6.3   **Discussion and conclusions**

Because of the small database we did not consider the influence of seasons when correlating the river chemistry with the discharge. It is probable that correlating the variables for each season individually, better correlation coefficient would have been found and seasonal differences may have been observed (Lepori et al., 2003a). More-over, it is clear that the division of the dataset in base flow and high flow conditions with the simple application of a discharge limit can give only rough indications concerning differences in water chemistry during base flow and high flow conditions. Better and more correct results would have been obtained collecting water samples at short time intervals before and during single precipitation events. Real discharge values for river Maggia and Verzasca instead of those estimated would also have produced more precise results. However, in spite of these uncertainties the analyses of river chemistry data permitted to make several considerations.

It was observed, that differences in average river water chemistry in the monitored area were caused by differences in catchment area (> area > mean water residence time> weathering > alkalinity, and conductivity) and geology (> weatherable>alkalinity and conductivity). Variations of alkalinity, base cation and sulphate concentrations were negatively correlated with the river discharge mostly because of dilution of ground- and river-water with rain water, aluminium concentrations were positively correlated with the river discharge, while nitrate concentrations were more difficult to predict. The studied rivers never became acidic. Lowest alkalinities, measured during high flow events, were 0.08 meq l^{-1} in river Maggia, 0.07 meq l^{-1} in river Vedeggio and 0.03 meq l^{-1} in river Verzasca. pH never decreased below 6 in all rivers. However, the results also suggest that smaller rivers with smaller catchment areas and therefore with a lower weathering capacity, may acidify and get enriched with toxic aluminium concentrations during high flow events. In fact, Lepori et al. (2003b) showed that severe episodes of acidification can affect macroinvertebrate assemblages in streams in the southern Swiss Alps. Since nitrate was shown to be the main cause for alkalinity consumption during high flow events, the future degree of acidification of Alpine rivers will largely depend on the future development of nitrogen emissions into the atmosphere and nitrate leakage from soils, where leakage may increase due to increased nitrogen saturation level and/or increased mineralisation because of climate warming.

3 > Macroinvertebrates as indicators for acidification

3.1 Introduction

As reported in Raddum et al. (2004), ICP Waters documented widespread improvements in surface water chemistry in response to emission control programs and decreasing acid deposition. However, the ultimate goal of emission control programmes is biological recovery, e.g. the return of acid sensitive species that have disappeared and the restoration of biological functions that have been impaired during the course of acidification. To study biological recovery at sites with acidification problems ICP Waters decided to include in its programme also the monitoring of macroinvertebrates as bioindicators.

Macroinvertebrates are small animals without backbones that are still big enough to be seen with the naked eye. They live all or part of their life cycle in or on the sediment of a water body. Examples include insect larvae, snails, crayfish, worms, mussels, leeches and acarines. Since they can be found in most surface waters, colonize all available substrates, can relatively easily be identified and have a life span that ranges from several months to a number of years, macroinvertebrates are now used successfully in almost all parts of the world as bioindicators for the level of water pollution caused by oxygen depleting organic components from effluents. The response of macroinvertebrates to water acidity is often precisely the reverse of their indicator properties for effluent pollution. A range of oxygen-dependent cold-water organisms which react very sensitively to pollution from effluents are astonishingly tolerant to low pH values. This situation demanded the development of a new form of indication system (Braukmann and Biss, 2004). In the following paragraphs two simple models to determine the level of acidification of rivers and lakes by using sensitive aquatic organisms are summarized. Although our time series of macroinvertebrate data is not long enough to study biological recovery as a response of an improvement of acid deposition, we tried to apply both method to our macroinvertebrate data set, to test if they can be utilized to characterize Swiss Alpine rivers.

3.1.1 Acidification categories of Raddum

The model was presented first in 1984 (Raddum and Fjellheim, 1984) and described by Raddum et al. (1988) as follows:

"The model especially focuses on sensitive invertebrate species. Each of the localities within a watershed is given a score (scale 0–1) depending on presence/absence of organisms indicating different levels of acidity.

The acidification number is estimated by the use of a hierarchical system. Indicator organisms with the same tolerance to acidity are assigned the same acidification number. There are four levels of tolerance:

> Category a) species tolerating pH >5.5–6.0 are given the number 1
> Category b) species tolerating pH >5.0–5.5 are given the number 0.5
> Category c) species tolerating pH > 4.7 are given the number 0.25
> Category d) species tolerating pH < 4.7 are given the number 0.

The acidification number is calculated as follows:

If a sample contains one or more species of category a) the locality gets the score 1 (less acidified). If species of category a) are missing, species of category b) may be present, indicating acid episodes down to pH 5.0. In this case the locality is considered moderately acidified and is given a score of 0. At more pronounced level of acidification, small mussels may still be found if acid episodes do not exceed pH 4.7. This results in a score of 0.25. If only category d) species are present, the locality is considered highly acidified and is given a score of 0."

The main advantages of this categorisation system are its possible application to both river and lake ecosystems and the fact that only qualitative and not quantitative data are needed. The fact, that it was developed on the basis of a Norwegian data set, is the main disadvantage for us, because the population of macroinvertebrates in the Swiss Alps might differ greatly from that of Scandinavian countries.

3.1.2   Acidification classes of Braukmann and Biss

A five class biological classification system of different degrees of acidity using benthic macroinvertebrates was developed by Braukmann and Biss (2004) for German rivers. The classes are characterized in Tab. 3.1.

To evaluate and assess the acidity of a sample, a cumulative addition process is employed. The taxa of a sample are sorted first by their specific acid indexes (from 1 to 5), than from higher to smaller dominance values (number of individuals in the specific taxa divided by the total number of individuals in all taxa). The dominance values are then added cumulatively from class 1 to 5 up to a dominance of 10%. The acid index of the taxa, where a dominance of 10% is reached, indicate the degree of acidification of a river.

Unfortunately, the categorisation system of Braukmann and Biss has been developed only for rivers and, similarly to that of Raddum, it was developed on a data set not including the Alps, but only the mountain region of Baden-Württemberg in Germany (primarily Black Forest and Odenwald). However, considering the fact that in the studied area also typical Alpine species have been found (*Perla grandis, Rhithrogena hybrida, Baetis alpinus),* the class-system of Braukmann and Biss might also be utilized to characterize Alpine streams.

Tab. 3.1   > Five-class system published by Braukmann and Biss (2004).

Class	Acid status	pH	Biological factors
1	Continuously neutral (not acidic)	6.5- >7.0, not <6.0	Acid-sensitive organisms
2	Predominantly neutral to episodically weakly acidic	around 6.5–7.0, rarely <5.5	Moderately acid-sensitive organisms
3	Periodically critically acidic	6.5–5.5, sometimes below	Acid-tolerant organisms
4	Periodically strongly acidic	around 5.5, often below 5.0, rarely till 4.3	Acid-resistant organisms
5	Continuously extremely acidic	<5.5 to 4.3, often below	Very acid-resistant organisms

3.2   Methods

Macroinvertebrate samples were collected by "kicksampling" as indicated in the ICP Waters Manual (NIVA, 1996) from 2000 to 2004. Sampling in river Maggia, Vedeggio and Verzasca occurred from 5 to 8 times a year, while in lakes (Laghetto Inferiore, Laghetto Superiore, Lago di Tomè, Lago del Starlaresc da Sgiof) samples were collected from the littoral and the emissary between 1 and 5 times a year. Macroinvertebrates were conserved in 70% ethanol. In the following presentation of the results samples from the littoral and the lake outlet were considered as one single sample.

3.3   Results and discussion

3.3.1   Lakes

As reported before, macroinvertebrates were sampled in 4 Alpine lakes, that are all characterized by extreme conditions: high altitudes, low temperatures, long ice cover, low nutrient concentrations, pH and alkalinity. Lago di Tomè (LT) and Lago del Starlaresc da Sgiof (LST) are among the monitored lakes with the lowest pH (average: 5.6 and 5.2, respectively), while pH of Laghetto Inferiore (LI) and Laghetto Superiore (LSU) can be defined as average (mean: 6.5 and 6.4, respectively) (see ch. 2.4.1). Because of the high altitudes and therefore extreme physical-chemical conditions the population of macroinvertebrates in Alpine lakes is expected to be generally poor (Fjellheim et al., 2000; Hieber, 2002; Marchetto et al., 2004), however, differences in the population of macroinvertebrates may reflect differences in pH and alkalinity between the lakes.

Tab. 3.2   > Number of samples, individuals and taxa, EPT index and average abundances of the main macroinvertebrate groups in 4 Alpine lakes in the years 2000 to 2004.

Laghetto Inferiore	2000	2001	2002	2003	2004	Average 2000–2004	Total 2000–2004
no. of samples	5	3	3	3	3		17
Total no. individuals	577	269	492	2460	3374		7172
no. taxa	17	20	16	31	36		51
EPT index	4	4	3	9	9		10
Ephemeroptera	0 %	0 %	0 %	1 %	2 %	1 %	
Plecoptera	17 %	34 %	19 %	12 %	11 %	19 %	
Trichoptera	1 %	7 %	0 %	2 %	2 %	2 %	
Diptera	47 %	33 %	52 %	65 %	48 %	49 %	
Coleoptera	3 %	0 %	1 %	0.9 %	1 %	1 %	
Oligochaeta	22 %	25 %	20 %	18 %	30 %	23 %	
Others	10 %	2 %	4 %	2 %	7 %	5 %	

Laghetto Superiore	2000	2001	2002	2003	2004	Average 2000–2004	Total 2000–2004
no. of samples	4	3	3	3	3		16
Total no. individuals	394	210	482	3020	3762		7868
no. taxa	23	18	19	36	36		60
EPT index	5	5	4	12	9		12
Ephemeroptera	0 %	0 %	0 %	5 %	4 %	2 %	
Plecoptera	30 %	29 %	16 %	19 %	12 %	21 %	
Trichoptera	6 %	9 %	3 %	3 %	2 %	5 %	
Diptera	28 %	33 %	38 %	52 %	57 %	41 %	
Coleoptera	3 %	0 %	1 %	1 %	1 %	1 %	
Oligochaeta	30 %	26 %	39 %	18 %	15 %	26 %	
Others	3 %	4 %	4 %	3 %	10 %	5 %	

Lago di Tomè		2001	2002	2003	2004	Average 2001–2004	Total 2001–2004
no. of samples		2	2	2	1		7
Total no. individuals		222	384	572	443		1621
no. taxa		11	15	21	19		31
EPT index		4	5	6	5		8
Ephemeroptera		0 %	0 %	0 %	0 %	0 %	
Plecoptera		17 %	27 %	33 %	44 %	30 %	
Trichoptera		9 %	5 %	9 %	3 %	6 %	
Diptera		36 %	43 %	47 %	47 %	43 %	
Coleoptera		0 %	1 %	2 %	2 %	1 %	
Oligochaeta		8 %	23 %	5 %	0 %	9 %	
Others		30 %	2 %	3 %	4 %	10 %	

Lago del Starlaresc da Sgiof	2001	2002	2003	2004	Average 2000–2004	Total 2000–2004
no. of samples	2	2	2	1		7
Total no. individuals	99	915	1207	785		3006
no. taxa	8	14	18	19		31
EPT index	2	2	3	2		3
Ephemeroptera	0 %	0 %	0 %	0 %	0 %	
Plecoptera	0 %	1 %	1 %	3 %	1 %	
Trichoptera	11 %	4 %	3 %	0 %	5 %	
Diptera	64 %	84 %	85 %	67 %	75 %	
Coleoptera	1 %	1 %	0 %	0 %	1 %	
Oligochaeta	3 %	4 %	3 %	3 %	3 %	
Others	21 %	6 %	8 %	26 %	15 %	

Tab. 3.2 reports the number of samples, individuals and taxa, the EPT index (= number of families in the order *Ephemeroptera, Plecoptera, Trichoptera)* and the average abundances of the main macroinvertebrate groups in 4 Alpine lakes in the years 2000 to 2004. The taxa richness is often regarded as indicator for the "health" of a biological community. The number of identified taxa are higher in LI and LSU (51 and 60, respectively) than in LT and LST (both 31). The EPT index is also often used as water quality indicator because macroinvertebrates belonging to the orders of *Ephemeroptera, Plecoptera* and *Trichoptera* are highly sensitive to pollution. Therefore a high EPT index stays for high water quality, whereas a low EPT index suggests that water may be polluted. The average EPT index at our sampling sites is generally low. However, it indicates a better water quality in LI and LSU, especially if compared with LST. The similarity between LI and LSU is also evidenced by their similar relative abundance of the main macroinvertebrate groups. *Diptera* (LI: 49 %, LSU: 43 %), represented mainly by *Chironomidae,* is the dominant group in both lakes followed by *Oligochaeta* (LI: 23 %, LSU: 26 %) and *Plecoptera* (LI: 19 %, LSU: 19 %). *Chironomidae* dominated also in LT and LST. In fact, the relative abundance of *Diptera* is 43 % and 75 % in LT and LST, respectively. The widespread diffusion of *Oligochaeta* and the acid tolerant *Chironomidae* is typical for Alpine lake and lake outlets (Fjellheim et al., 2000; Hieber, 2002; Marchetto et al., 2004). The average relative abundance of *Chironomidae* larvae is high (LI: 34 %, LSU: 38 %, LT: 40 %, LST: 63 %) indicating a low varied invertebrate population. The order *Ephemeroptera,* to which belong many of the most acid sensitive species, is absent in LT and LST and only few organisms of it are found in LI and LSU. Low pH's may not necessarily be the reason. In fact, its absence in Alpine lakes and lake outlets is quite common (Hieber, 2002). Especially in LST their absence may be connected with the often missing current in the outlet. With exception of LST the order *Plecoptera* is well represented, especially in LT (30 %). The higher relative abundance of *"Other"* invertebrate groups (15 %) in LST is interesting. This is principally due to the presence of *Odonata* and *Heteroptera (Corixidae)* found almost exclusively at this site, most probably because of its wetland characteristics.

Tab. 3.3   > Highest "Raddum categories" in 4 Alpine lakes in the years 2000 to 2004.

	2000	2001	2002	2003	2004
Laghetto Inferiore	d	b	b	b	b
Laghetto Superiore	c	b	b	a	a
Lago di Tomè		d	d	d	d
Lago del Starlaresc da Sgiof		d	d	d	d

The acidification categories of Raddum (Tab. 3.3) seem to reflect the chemistry of lakes in suggesting better pH conditions in LI and LSU with respect to LT and LST. In fact, while in LT and LST the category was constantly *d,* in LI and LSU in the last few years values between *b* (because of the presence of *Crenobia alpina*) and *a* (because of the presence of *Baetis alpinus)* were obtained. The mussel *Pisidium Casertanum* with a "Raddum index" of 0.25, determining a category of type *c,* is also only present in LI and LSU. However, according to Raddum and Fjellheim (1984) those values would correspond to pH's of > 5.0–5.5 to >5.5–6.0 in LI, of >5.0–5.5 in LSU and of < 4.7 in LT and LST, with exception of LI all definitely too low compared to measured values. A possible explanation may be a delay of biological with respect to chemical recovery. However, we doubt it. In fact, even in the 1980's, when pH's reached their lowest levels, pH's of LT and LST were not below 4.7 (LT: 5.3, LST: 4.8) and average pH's of LI and LSU were 6.1 and 6.0, respectively. We therefore think that the difference between the measured pH's and these indicated by the categories of Raddum , is mainly due to the inadequacy of the "Raddum categorisation system" in describing Alpine lakes and lake outlets biology, primarily because of its natural poorness in taxa and among these also acid sensitive taxa (e.g. *Ephemeroptera)* and the fact that the index was developed on the basis of a Norwegian data-set.

3.3.2 **Rivers**

Macroinvertebrates were sampled in river Maggia, Vedeggio and Verzasca. Compared to the Alpine lakes discussed in the previous chapter, these rivers are characterized by being situated at much lower altitudes, having therefore larger catchments areas, that are responsible for higher average weathering rates. As a consequence these rivers are richer in nutrient concentrations and have higher average pH's than lakes (see ch. 2.4). In fact, average pH in river Maggia, Vedeggio and Verzasca are 7.4, 7.0 and 6.7, respectively (ch. 2.4). However, during high flow pH can decrease close to average pH values in lakes: 6.5 in river Maggia and 6.2 in river Vedeggio and Verzasca. Tab. 3.4 reports the number of samples, individuals and taxa, the EPT index and the average abundances of the main macroinvertebrate groups in the 3 monitored Alpine rivers in the years 2000 to 2004. The difference to lakes is immediately visible. In fact, the total taxa number and the EPT index are both higher in rivers than in lakes: the taxa number by a factor 2–3 and the EPT index by a factor 2–7. The relative abundances of the main macroinvertebrate groups differ also greatly between lakes and rivers. *Plecoptera* and

Diptera are still well represented in rivers, but *Oligochaeta* almost completely disappear and *Ephemeroptera* become, especially in river Maggia and Vedeggio, the dominant order. However, as already observed in the previous chapter the poor representation of *Ephemeroptera* and the abundance of *Oligochaeta* in Alpine lakes and lake outlets is probably to a certain amount typical for this ecosystem, making a direct comparison between acidification effects in rivers and lakes on the basis of macroinvertebrate community structure difficult.

Differences between rivers themselves are not so pronounced. The number of taxa is highest in river Vedeggio (122) followed by river Maggia (113) and river Verzasca (94) and the EPT index is higher in river Maggia and Vedeggio (21) with respect to river Verzasca (17). Both total taxa and EPT index seem to suggest better living condition in river Maggia and Vedeggio compared to river Verzasca. It's hard to say if this is related to the lower pH values in river Verzasca or other maybe local reasons. The best represented orders are *Ephemeroptera* (Maggia: 39%, Vedeggio: 31%, Verzasca: 45%) followed by *Plecoptera* (Maggia: 24%, Vedeggio: 32%, Verzasca: 18%). *Diptera* and *Coleoptera* are also well represented (Maggia: 23 and 7%, Vedeggio: 15 and 10%, Verzasca: 13 and 19%, respectively). A discrete number of *Trichoptera* was only found in river Vedeggio (10%) and, as already mentioned, *Oligochaeta* were not captured in rivers.

Tab. 3.4   > Number of samples, individuals and taxa, EPT index and average abundances of the main macroinvertebrate groups in 3 Alpine rivers in the years 2000 to 2004.

Maggia	2000	2001	2002	2003	2004	Average 2000–2004	Total 2000–2004
no. of samples	8	6	6	6	5		32
Total no. individuals	2247	1507	2833	5320	5120		17027
no. taxa	56	44	57	63	61		113
EPT index	14	12	13	18	17		21
Ephemeroptera	35 %	28 %	50 %	40 %	40 %	39 %	
Plecoptera	35 %	20 %	31 %	23 %	12 %	24 %	
Trichoptera	4 %	1 %	4 %	4 %	8 %	4 %	
Diptera	19 %	39 %	8 %	25 %	24 %	23 %	
Coleoptera	4 %	8 %	7 %	5 %	12 %	7 %	
Oligochaeta	0 %	0 %	0 %	1 %	0 %	0 %	
Others	2 %	4 %	1 %	3 %	3 %	3 %	

Vedeggio	2000	2001	2002	2003	2004	Average 2000–2004	Total 2000–2004
no. of samples	8	6	6	6	5		32
Total no. individuals	1578	1934	1789	3687	3081		12069
no. taxa	66	64	51	61	60		122
EPT index	14	16	12	16	14		21
Ephemeroptera	35 %	39 %	31 %	18 %	31 %	31 %	
Plecoptera	28 %	28 %	38 %	44 %	22 %	32 %	
Trichoptera	11 %	4 %	8 %	15 %	14 %	10 %	
Diptera	16 %	9 %	9 %	21 %	23 %	15 %	
Coleoptera	8 %	20 %	12 %	2 %	9 %	10 %	
Oligochaeta	0 %	0 %	0 %	0 %	1 %	0 %	
Others	1 %	1 %	1 %	0 %	1 %	1 %	

Verzasca	2000	2001	2002	2003	2004	Average 2000–2004	Total 2000–2004
no. of samples	8	6	6	6	5		32
Total no. individuals	1574	2258	2570	3761	4269		14432
no. taxa	48	46	46	51	48		94
EPT index	12	13	12	14	11		17
Ephemeroptera	46 %	45 %	36 %	41 %	55 %	45 %	
Plecoptera	18 %	18 %	25 %	18 %	11 %	18 %	
Trichoptera	3 %	4 %	3 %	4 %	2 %	3 %	
Diptera	12 %	8 %	10 %	19 %	12 %	13 %	
Coleoptera	18 %	22 %	23 %	14 %	18 %	19 %	
Oligochaeta	0 %	1 %	0 %	0 %	0 %	0 %	
Others	3 %	2 %	2 %	3 %	1 %	2 %	

Irrelevant differences between the studied rivers are also observed with respect to the calculated acidification classes (Tab. 3.5). The acidification category of Raddum is mainly of type *a* (Maggia: 98%, Vedeggio: 100%, Verzasca: 98%), indicating pH's >5.5–6.0, which actually corresponds to what measured. The classes of Braukmann and Biss are most of the times of type 2 (Maggia: 90%, Vedeggio: 90%, Verzasca: 94%) and of type 1 in all other cases, suggesting a predominantly neutral to episodically weakly acid water quality corresponding to pH's normally around 6.5–7.0 and rarely below 5.5. However, measured pH's would correspond better to type 1 (continuously neutral, never below 6.0). The reason of this divergence is probably either the fact, that the class system has not been developed on the basis of an Alpine macroinvertebrate data-set but on data from Germany, or a delay of biological recovery with respect to chemical recovery. It is interesting to observe that all sampled organisms with a "Raddum index" of 1, determining the less acidic category *(a),* belong to the genus *Baetis.* We found *Alainites muticus, Baetis alpinus Baetis fuscatus Baetis melanonyx, Baetis niger, Baetis rhodani and Baetis lutheri.* It is worth to mention that according to Braukmann and Biss these species do not belong to the most acid sensitive but to the moderately acid sensitive ones. Species that were found at our sites, that were even more acid sensitive according to Braukmann and Biss (2004) are *Ephemerella ignita, Rhithrogena hybrida, Habroleptoides confusa and Perla sp.,* all species that were not considered by Fjellheim and Raddum (1990), when developing their acid categorisation system. Interestingly, the smaller number of taxa with a "Braukmann and Biss index" of 2 in river Verzasca (19) with respect to river Maggia (31) and Vedeggio (32), is the only evidence based on observation made on acid indexes, that seems to suggest a lower pH in river Verzasca.

Tab. 3.5   > Distribution of "Raddum" and "Braukmann and Biss" classes in 3 Alpine rivers in the years 2000 to 2004.

Rivers		2000	2001	2002	2003	2004	Total 2000–2004
Maggia	Samples with "Raddum category"=*a*	88%	100%	100%	100%	100%	98%
	no. of taxa with "Raddum category"=*a*	4	4	4	5	4	6
	Samples with "Braukmann and Biss class"=1	13%	0%	0%	0%	40%	10%
	Samples with "Braukmann and Biss class"=2	88%	100%	100%	100%	60%	90%
	no. of taxa with "Braukmann and Biss class"=1	5	3	4	3	4	6
	no. of taxa with "Braukmann and Biss class"=2	19	12	15	15	17	31
Vedeggio	Samples with "Raddum category"= *a*	100%	100%	100%	100%	100%	100%
	no. of taxa with "Raddum category"= *a*	5	5	4	4	4	6
	Samples with "Braukmann and Biss class"=1	0%	0%	50%	0%	0%	10%
	Samples with "Braukmann and Biss class"=2	100%	100%	50%	100%	100%	90%
	no. of taxa with "Braukmann and Biss class"=1	6	3	3	3	5	7
	no. of taxa with "Braukmann and Biss class"=2	15	16	18	17	16	32
Verzasca	Samples with "Raddum category"= *a*	88%	100%	100%	100%	100%	98%
	no. of taxa with "Raddum category"= *a*	4	2	2	4	4	5
	Samples with "Braukmann and Biss class"=1	13%	17%	0%	0%	0%	6%
	Samples with "Braukmann and Biss class"=2	88%	83%	100%	100%	100%	94%
	no. of taxa with "Braukmann and Biss class"=1	4	3	3	3	2	4
	no. of taxa with "Braukmann and Biss class"=2	11	10	12	10	12	19

Discussion and conclusions

In general, we can conclude that in Alpine lakes the higher pH in LI and LSU with respect to LT and LST seems to be the main cause for the presence of acid more sensitive taxa in the firsts *(Baetis alpinus, Crenobia alpina, Pisidium casertanum* and other *Ephemeroptera).* The same is indicated by the higher taxa richness and EPT index in LI and LSU. However, the pH's indicated by the acidification category of Raddum underestimate the measured values, probably because of the natural taxa poorness of Alpine lake ecosystems. Since we don't have historical macroinvertebrate data and we don't know how their populations were before anthropogenic acidification, in order to verify the previous assumption and try to calibrate the categorisation of the "Raddum indexes" to our study site, it would be useful to study in addition to the actual macroinvertebrate monitoring programme also the macroinvertebrate community in an Alpine lake with neutral pH.

River macroinvertebrate population is very different from that observed in lakes. Both the total number of taxa and the EPT index are higher. However, because the monitored lakes and rivers represent 2 very different ecosystems, a direct comparison of their degree of acidification based on macroinvertebrate information, is in our opinion, not reasonable. With exception of the total taxa number, EPT index and number of taxa with a "Braukmann and Biss class" of 2, that are slightly lower in river Verzasca with respect to river Maggia and Vedeggio suggesting lower pH's in the first, macroinvertebrate data do not differ greatly between the 3 rivers. pH's indicated by the acidification categories correspond quite well with measured values. Only the pH minimas indicated by the "Braukmann and Biss class" was slightly too small. However, it must be added that the categorisation system of Braukmann and Biss has a higher pH resolution in the pH range typical for our rivers making acid typology errors easier but less severe. In fact, according to the categorisation of Raddum all surface waters with pH's > 5.5–6.0 belong to the same class, while in Braukmann and Biss (2004) the same pH range is defined by 3 categories. This characteristic makes the "Braukmann and Biss indexes" a better tool to interpret macroinvertebrate data from our rivers.

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

Introduction

Persistent organic pollutants (POP's) and metals are chemical substances that persist in the environment, bioaccumulate through the food web and pause a risk of causing effects to human health and the environment (UNEP definition). Nowadays, the production and the release of POP's into the environment has been restricted or banned in many developed countries (Aahrus protocol), but in some developing countries their usage is still allowed or unregulated. The discovery of the occurrence of relatively high concentrations of POP 's in polar regions, considered as pristine areas, a few decades ago, was at first surprising. The transport mechanism was explained by Wania and Mackay (1993) in the 90ties: as a result of the positive correlation between vapour pressure and temperature and dependent on their volatility, POP's can be transported for long distances through the atmosphere from warm (low latitude) to cold regions (high latitude). This latitudinal fractionation of organic compound is known as global fractionation process. Since temperature decreases not only with latitude but also with altitude it was expected that accumulation of POP's occurs also in mountain regions. This hypothesis has been confirmed by numerous publications: POP's in remote mountain regions could be detected in atmospheric deposition (Carrera et al. 2002, Fernanández and Grimalt 2003), in snow (Blais et al. 1998, Carrera et al. 2001, Fernanández and Grimalt 2003), in surface waters (Fernanández and Grimalt 2003, Galassi et al. 1997, Vilanova et al. 2001), in sediments (Fernanández and Grimalt 2003, Galassi et al. 1997, Grimalt et al. 2001, Grimalt et al. 2004), in soils (Grimalt et al. 2004), in fish (Catalan et al. 2004, Grimalt et al. 2001, Hofer et al. 2001, Rognerud et al. 2001, Schmid et al. 2005, Vives et al. 2004) and in zooplankton (Galassi et al. 1997).

In order to quantify the contamination of DDT's , PCB's, HCB's, HCH and metals in the Swiss Alps, we determined its concentrations in fish muscle from two Alpine lakes and three Alpine rivers. We compared our results with literature data and discussed their possible origin.

Sampling procedure

Fish were collected in 2 Alpine lakes (Laghetto Inferiore, Laghetto Superiore) and three Alpine rivers (Maggia, Vedeggio, Verzasca) from 2000 to 2004. In lakes fish were caught by angling, while in rivers they were captured by electrofishing. Rainbow trout *(Oncorhynchus mykiss)* was the dominant fish species in lakes, while in streams brown trout *(Salmo trutta fario)* prevailed. Sampling occurred twice a year (summer and autumn) in 2000 and 2001 and only once a year (autumn) from 2002 to 2003. All fish were measured for length and weight and aged by scale analysis.

Chemical analyses

For every sampling site and sampling date a homogenized sample of fish muscle was prepared. Organochlorine compounds were extracted and isolated as described in Steinwandter (1985). The so obtained extracts were first purified by gelchromatography and then purified further and fractionated on a silicagel column. The extraction efficiency was determined by addition of a known amount of PCB–167. Organochlorine compounds were then determined by gas chromatography with electron capture detection and in case verified by MS. A DB–5 column was used with hydrogen as the carrier gas and PCB–198 was used as an internal standard. The lipid content was determined gravimetrically after extraction with cyclohexane: ethylacetate.

Metal analyses was performed according to the Swiss manual for food analyses (BAG, 2005). In particular, fish samples for metal analyses were either mineralised or combusted and the metals were measured with AAS and ICP-OES.

Fish population characteristics

The average fish number for each sampling and the average fish weight, length, conditioning index, age and lipid content are shown in Tab. 4.1. The average sampled fish number is 15 for river Maggia, 13 for river Vedeggio, 15 for river Verzasca, 13 in Laghetto Inferiore and 18 in Laghetto Superiore. The average fish weight is slightly higher in rivers (from 84 to 109 g) than in lakes (72 and 73g). Fish length, conditioning index, age and lipid content are similar in rivers and in lakes. Mean length, conditioning index, age and lipid content are 20–22 cm, 0.98–1.02, 36–41 months, 1.4–1.7% in rivers and 19 and 20 cm, 0.99 and 0.93, 35 and 34 months, 1.4 and 1.1% in lakes. The percentage of fish having a conditioning index lower than 1 is 44% in river Maggia, 45% in river Vedeggio, 60% in river Verzasca, 59% in Laghetto Inferiore and 82% in Laghetto Superiore indicating a not ideal physical state especially in lakes and in river Verzasca.

Tab. 4.1   > Mean and standard deviation of the fish number for each sampling and average and standard deviation of weight, length, conditioning index (C.I.), age and lipid fraction in muscle of fish sampled in Laghetto Inferiore, Laghetto Superiore and river Maggia, Vedeggio and Verzasca from 2000 to 2004.

	Laghetto Inferiore	Laghetto Superiore	Maggia	Vedeggio	Verzasca
Number of fish	13±6	18±3	15±3	13±2	15±2
Weight (g)	72±26	73±28	109±23	91±29	84±23
Length (g)	19.1±2.3	19.7±2.2	21.9±1.4	20.5±2.3	20.3±1.9
C.I.	0.99±0.08	0.93±0.10	1.02±0.09	1.02±0.09	0.98±0.10
Age (month)	35±7	34±7	38±7	36±8	41±9
lipid (%)	1.4±0.6	1.1±0.4	1.7±0.4	1.7±0.2	1.4±0.4

4.3.2   POP's in fish muscle

Average and relative PCB concentrations between 2000 and 2004 measured in fish muscle are shown in Fig. 4.1a and Fig. 4.1b, respectively. Average total PCB concentrations are twice as high in lakes (Laghetto Inferiore: 10 µg kg^{-1}, Laghetto Superiore:14 µg kg^{-1}) than in rivers (Maggia: 6 µg kg^{-1}, Vedeggio: 7 µg kg^{-1}, Verzasca: 6 µg kg^{-1}). Less volatile cogeners PCB–180, PCB–153 and PCB–138 prevail in lakes and in rivers (Fig. 5.1b): in lakes the distribution is on average 29% PCB–180, 38% PCB–153, 29% PCB–138, 4% PCB–101, 1% PCB–52, 0% PCB–28 and in rivers 18% PCB–180, 38% PCB–153, 32% PCB–138, 9% PCB–101, 2% PCB–5 2, 2% PCB–28.

Fig. 4.1   > a) Concentrations (µg kg^{-1} wet weight) and b) relative concentrations (%) of PCB's in fish muscle: *Oncorhynchus mykiss* **in lakes (L. Inferiore and L. Superiore) and** *Salmo trutta fario* **in rivers (Maggia, Vedeggio, Verzasca).**
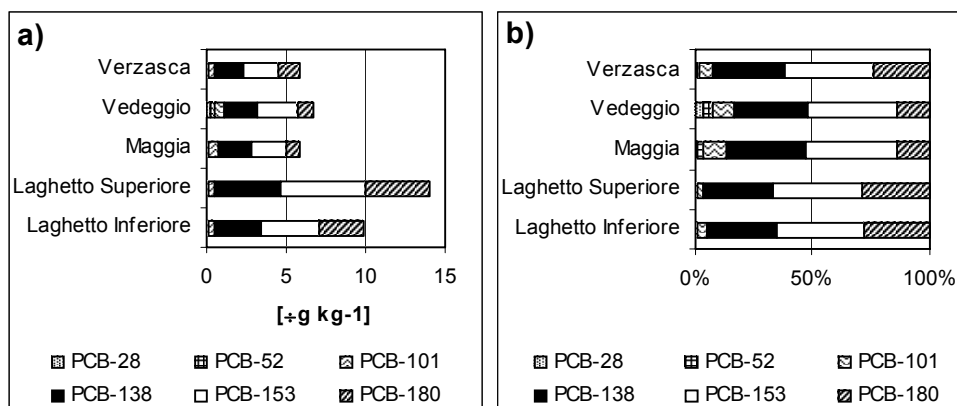
Average total DDT concentrations between 2000 and 2004 are three times higher in fish muscle from lakes than from rivers: 9 μg kg^{-1} in Laghetto Superiore, 8 μg kg^{-1} in Laghetto Inferiore, 2 μg kg^{-1} in the rivers Maggia and Verzasca and 3 μg kg^{-1} in river Vedeggio (Fig. 5.4a). DDE prevails over DDT and DDD (Fig. 4.2b): in lakes the distribution is on average 70% DDE, 20% DDT, 11% DDD and in rivers 62% DDE, 19% DDT, 19% DDD.

Average HCB and HCH concentrations in fish muscle of Alpine lakes are low. Average HCB range between 0.10 and 0.14 μg kg^{-1} in rivers and 0.08–0.11 μg kg^{-1} in lakes, while average HCH rage between 0.04 and 0.13 μg kg^{-1} in rivers and between 0.01 and 0.02 μg kg^{-1} in lakes.

Fig. 4.2   > a) Concentrations (μg kg^{-1} wet weight) and b) relative concentrations (%) of DDT in fish muscle: *Oncorhynchus mykiss* **in lakes (L. Inferiore and L. Superiore) and** *Salmo trutta fario* **in rivers (Maggia, Vedeggio, Verzasca).**
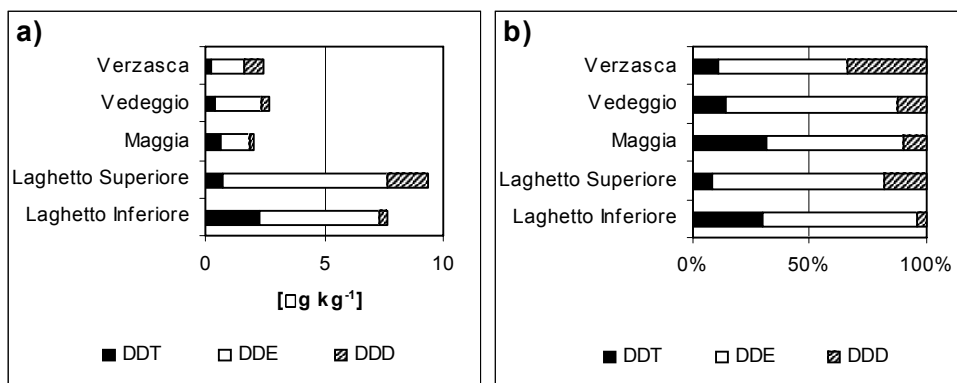
4.3.3   Metals in fish muscle

Average metal concentrations and their standard deviation measured in fish muscle between 2000 and 2004 are shown in Tab. 4.2. In general no great differences can be observed between metal concentrations in rivers and lakes. Only concentrations of lead appear to be 4 to 6 times higher in lakes than in rivers.

Tab. 4.2 > Average metal concentrations with standard deviation (mg kg⁻¹ wet weight) measured in fish from Laghetto Inferiore, Laghetto Superiore and river Maggia, Vedeggio and Verzasca between 2000 and 2004.

	Laghetto Inferiore	Laghetto Superiore	Maggia	Vedeggio	Verzasca
Al (mg kg⁻¹)	0.87 ± 0.45	1.09 ± 0.27	1.11 ± 0.66	1.28 ± 1.15	1.03 ± 1.07
Cd (mg kg⁻¹)	0.02 ± 0.01	0.03 ± 0.02	0.01 ± 0.00	0.01 ± 0.00	0.03 ± 0.02
Cr (mg kg⁻¹)	0.24 ± 0.09	0.33 ± 0.16	0.14 ± 0.04	0.29 ± 0.20	0.33 ± 0.16
Hg (mg kg⁻¹)	0.03 ± 0.01	0.04 ± 0.02	0.02 ± 0.01	0.03 ± 0.01	0.05 ± 0.01
Ni (mg kg⁻¹)	0.16 ± 0.11	0.19 ± 0.08	0.09 ± 0.02	0.14 ± 0.05	0.16 ± 0.05
Pb (mg kg⁻¹)	0.08 ± 0.03	0.12 ± 0.05	0.02 ± 0.01	0.03 ± 0.02	0.02 ± 0.01
Cu (mg kg⁻¹)	0.36 ± 0.04	0.37 ± 0.08	0.38 ± 0.04	0.50 ± 0.08	0.39 ± 0.06
Zn (mg kg⁻¹)	5.63 ± 1.50	7.25 ± 1.56	5.54 ± 0.92	5.48 ± 0.96	6.04 ± 0.72

4.4 Discussion and conclusion

Comparing our DDT and PCB data from Alpine lakes with those from Alpine rivers it appears that concentrations in rivers are smaller. Unfortunately, this observation is difficult to interpret because rivers and lakes are two completely different ecosystems (different food web, sediments, morphology, temperature, …). However, the evidence of accumulation of contaminants like HCB, PCB's and DDT's in fish muscle originating from Alpine rivers and lakes, far from local pollution, can in both cases only be explained by atmospheric deposition (cold condensation).

HCB, PCB and DDT concentrations in fish muscle from Laghetto Superiore and Laghetto Inferiore are in the same range as reported for other European mountain lakes (Grimalt et al. 2001, Hofer et al. 2001. Rognerud et al. 2001, Schmid et al. 2005, Vives et al. 2004). In particular, a good correspondence could be found for DDE concentrations predicted from the positive correlations between concentrations and latitude in Hofer et al. 2001 and with the concentrations of HCB, DDE and PCB predicted from the positive correlations between concentrations and altitude in Grimalt et al. (2001). Also the speciation of the before mentioned pollutants corresponds to literature data (Grimalt et al. 2001, Vives et al. 2004).

Schmid et al. 2005 concluded in their study that concentrations of PCB in fish from water systems with (Alpine lakes) and without input from water treatment plants (Swiss plateau lakes) are similar, indicating that the input to Swiss water systems is mainly caused by atmospheric deposition. We also compared our data from the Alpine lakes Laghetto Superiore and Laghetto Inferiore with data from Lago Maggiore (Cipais, 2003), a close by situated lake (Fig. 1), whose chemistry is influenced by inputs from water treatment plants and by DDT, Hg and As polluted groundwater originating from a Italian contaminated site (where once DDT was produced), which is now in remediation. We compared fish from Alpine lakes *(Oncorhynchus mykiss)* with fish

species from Lago Maggiore with similar lipid content *(Scardinius erythrophthalmus, Leuciscus cephalus, Perca fluviatilis).*

HCB concentrations in fish from Lago Maggiore are on average 1 µg kg^{-1} and vary between 1 µg kg^{-1} and 17 µg kg^{-1} and are therefore a factor 10 to 100 higher than in Laghetto Superiore and Laghetto Inferiore. HCB sources in the Lago Maggiore area may be the reason for this difference.

The sum of the PCB cogeners in Lago Maggiore are in the same range as measured in fish from Laghetto Superiore and Laghetto Inferiore and are on average 15 µg kg^{-1} and vary between 3 µg kg^{-1} and 49 µg kg^{-1}. Different than in Alpine lakes is the speciation of PCB cogeners in Lago Maggiore. In fact, more volatile cogeners are more abundant in Lago Maggiore: 4% PCB 180, 19% PCB 153, 34% PCB 118, 15% PCB 101, 17% PCB 52, 11% PCB 28. Since more volatile PCB cogeners normally tend to accumulate at higher latitude (Wania and Mackay, 1993), our results suggest that there may be local pollution sources of PCB in the area of Lago Maggiore.

DDT concentrations in fish muscle from Lago Maggiore are a factor 3–4 higher than concentrations in Lago Superiore and Lago Inferiore. They are on average 23 µg kg^{-1} and vary between 5 µg kg^{-1} and 43 µg kg^{-1}. The speciation is also different: DDE is as important as DDD (12% DDT, 48% DDE, 41% DDD), while in Alpine lakes DDE dominates. The higher DDT concentrations in Lago Maggiore are most certainly due to the influence of the contaminated site, mentioned before and the presence of important amounts of DDD may be caused by anaerobic degradation of DDT in the soil or in the sediments around and in Lago Maggiore (Cipais, 2003).

The fact, that the concentrations of HCB, PCB and DDT and the speciation of PCB and DDT in Alpine lakes are in the same range as reported in literature for other European mountain lakes and different from what found in Lago Maggiore, suggests that local atmospheric pollution sources are neglectable in determining HCB, PCB and DDT concentrations in fish from close by situated Alpine lakes.

Similarly as done for POP's, in order to compare metal concentrations in fish muscle from Alpine lakes with a lake that may be influenced by local pollution sources, the measured metal data were compared with concentrations in fish sampled in Lago Maggiore. Metals concentrations in fish muscle from Lago Maggiore were published by Laboratorio cantonale (2000–2004). Average metals concentrations in *Coregonus macrophthalmus* and *Alosa fallax lacustris* from Lago Maggiore are 0.01 mg kg^{-1} and 0.00 mg kg^{-1} for Cd, 0.14 mg kg^{-1} and 0.08 mg kg^{-1} for Cr, 0.23 mg kg^{-1} and 0.12 mg kg^{-1} for Hg, 0.03 mg kg^{-1} and 0.02 mg kg^{-1} Pb, 0.64 mg kg^{-1} and 0.32 for Cu, 6.34 mg kg^{-1} and 4.11 mg kg^{-1} for Zn. It results that Cu and Zn concentrations in fish from Alpine lakes are in the same range as in Lago Maggiore. Higher concentrations are found for Hg (factor 3–8) in Lago Maggiore, suggesting local sources. Difficult to explain are the smaller Cr (factor 2–3), Cd (factor 2–3) and Pb (factor 3–6) concentrations in fish from Lago Maggiore. However, higher concentrations of Pb and Cd in fish from soft water with respect to hard water Alpine lakes, that are in the same range as found at our study site, were also reported in Hofer et al. (2001) and Köck et al. (1995).

An increased uptake of Cd and Pb through the gills that is enhanced by the low calcium level was postulated.

This chapter showed that, although concentrations of POP's and metals in fish muscle from Alpine surface waters are low and not a problem for fish consumption, their occurrence in areas far from local pollution sources indicates that these substances origin from atmospheric deposition. After having studied the concentrations of POP's and metals in fish muscle during 5 years and seeing that the concentrations of those parameters change extremely slowly we decided to interrupt the monitoring of POP's and metals in fish muscle for the next 5 years.

> Acknowledgements

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Tables

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