Chemistry of snow melt runoff

P. A. Waldner, H. Burch, WSL, Birmensdorf, Switzerland,

This century's increase of the ionic input by precipitation is leading to an acidity and nutrient overloads in rivers threating aquatic wildlife. In alpine catchments ionic input during winter is stored in the snowcover and released as an ionic pulse during early snow melt. In a partly forested alpine catchment a similar pulse in the runoff was measured. Calcareous soils buffered the acidity. There is a difference in the seasonal variation of the input between Alptal (prealpine) and high alpine sites. During winter the atmosphere at high alpine sites (ice core-archives) is frequently decoupled from lower layers.

Keywords: Snow chemistry, long term trends, ionic pulse, catchment runoff, sequential sampler

Im Laufe dieses Jahrhunderts führte der zunehmende Ioneneintrag mit dem Niederschlag zu beeinträchtigenden pH-Werten und Nährstoffkonzentrationen für Wasserlebewesen. In alpinen Regionen wird der winterliche Eintrag in der Schneedecke gespeichert und als Ionenschub zu Beginn der Schneeschmelze freigesetzt. Ein entsprechender Ionenschub konnte im Abfluss aus einem voralpinen, mehrheitlich bewaldeten Einzugsgebiet ebenfalls nachgewiesen werden. Kalkhaltiger Boden puffert den pH. Der Unterschied der saisonalen Variationen des Inputs zu hochalpinen Standorten wird diskutiert.

Keywords: Schneechemie, langzeitliche Veränderungen, Ionenschübe, Einzugsgebiet, Abfluss, Fraktionensammler

1 Introduction

The ionic charge in precipitation has increased during the last 100 years (Döscher et al., 1995). Acidity and nutrient charge lead to environmental problems in soils, rivers and lakes (see chapter 1.1) such as:

- the increase of acidity threatens aquatic wildlife
- danger of lake eutrophisation
- decrease of drinking water quality

In alpine environments large parts of the annual precipitation is stored in the snowcover. Released meltwater dominates runoff generation in spring. However, little is known about its chemical makeup. Have there been drastic long term changes in the input? How does the snowcover influence the ion retention and runoff load of a typical alpine catchment?

1.1 Illustrations to actual environmental problems

A number of processes control the transfer of the ionic charge (acidity and nutrients) in precipitation into the runoff of a catchment. Acidic episodes during snowmelt have been reported from rivers on the Scandinavian subcontinent (Seip & Tollan, 1985) and alpine lakes (Marchetto et al., 1995). Experiments quantified toxic effects causing observed fish diminution (Brown & Turnpenny, 1988).

Improvements in wastewater treatment raise the relevance of natural nutrient sources. In lakes, nutrient overload may cause a switch to eutrophisation. The impacts of high nitrate and ammonium concentrations in drinking water on human health is subject of controversial discussions.

1.2 Archives of the ionic charge development in precipitation

To investigate on long term changes in the input, historical concentrations have to be reconstructed with the help of natural archives (Döscher et al., 1995). Meteorological conditions for actual known archives are given at a limited number of areas:

- high alpine glaciers (in the European Alps above around 4000 m a.s.l.)
- continental ice shield in Greenland and Antarctica

To get past values for other areas, extrapolations would be necessary. Hence, the question about relations between the input at high alpine and lower areas arises.

1.3 Processes controlling ionic content of snow

During winter, the ionic charge in precipitation is stored in the snowcover. Grain coalescence and recrystallisation causes impurities within the snow to segregate at the grain surfaces, because they are not easily incorporated into the crystalline lattice (Colbeck, 1981). Freeze-thaw cycles re-enforces these processes. Microbes often populate the snowcover. Jones (1996) measured a transformation of up to 20 % of stored ammonia by microbial activity, while nitrate was not touched. Gaseous losses during snow metamorphism are not relevant for most ions.

During snowmelt, ions are released with meltwater. Johannessen & Henriksen (1978) first described the fractionation of pollutants in the snow and the occurrence of high concentrations of ionic species within the early melt

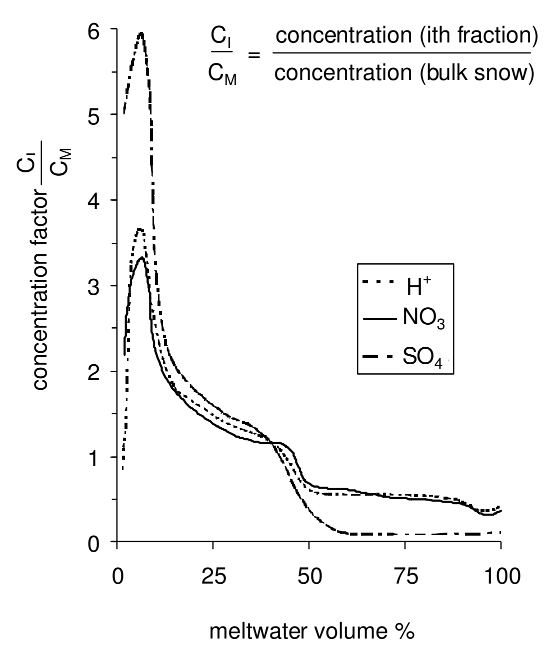

Fig. 1: Concentration of meltwater relative to bulk snow concentration in a snow lysimeter experiment (Johannessen & Henriksen, 1978).

fractions. Samples of the meltwater from a snowcover had periodically been taken with the use of a lysimeter (*Fig. 1*).

Within a catchment, different equilibrium reactions can be responsible for a buffering of acidic inputs in soils and rivers. The equilibrium between solid and liquid carbonate buffers the pH above 7 (Stumm & Morgan, 1981).

1.4 Hypothesis

This report is based on the following hypothesis:

1. There are differences between high alpine and lower areas in the seasonal variation of the nutrient charge in precipitation.
2. During early melt, ionic pulse in the meltwater produces a similar reaction in the runoff.

2 Methods

New results from partly forested, alpine catchments situated in the Alptal-Valley near Einsiedeln (Switzerland) were used to investigate these hypothesis. The experimental catchments are instrumented for long term investigations about the influence of forest on water balance, floods and nutrient budgets.

2.1 Site description

The catchments have elevation ranges from 1000 m a.s.l. up to 1600 m a.s.l. The geologic formation is Flysch, containing banks of calcareous sandstone (Frei, 1965; Hantke & al., 1967). The climate is cool and moist. Mean annual temperature is 4.5 °C. About 40 % of the 2200 mm annual precipitation is snow. Spruce-fir forest (50 %), pasture and wetland are the dominant vegetation cover (Burch, 1994).

Tab. 1: Characteristics of currently run experimental catchments in the Alptal-Valley near Einsiedeln in Switzerland (Burch, 1994).

catchment		Vogelbach	Erlenbach	Lümpenen
area	ha	155	64	93
exposition	-	ESE	W	ESE
forest	%	63	39	19
wetland	%	25	61	24
pasture	%	12	0	57
hydrologic measurements	starting year	1968	1978	1972

2.2 Instrumentation, sampling strategy and chemical analyses

The hydrologic investigations in the catchments started several decades ago. Frequent chemical analyses of bulk precipitation and snow cover have been carried out since 1975 (*Tab. 2*). Climatic stations and flow proportional runoff sampling started in 1981 and 1982 respectively.

Tab. 2: Instrumentation of the experimental catchments in the Alptal-Valley near Einsiedeln (Switzerland).

	intervall	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996
climate: temp, radiation, ..	10'							░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░
precipitation																							
- bulk	7 d	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
- only wet	7 d														▨	▨	▨	▨	▨	▨	▨	▨	▨
- sequential	10 mm															▨	▨	▨	▨	▨			
- pH (near-real time)	10'															▥	▥	▥	▥				
snow-cover	14 d	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░
streamwater sampling (flow-proportional)	7 d								☰	☰	☰	☰	☰	☰	☰	☰	☰	☰	☰	☰	☰	☰	☰

Collected samples have been stored at 4 °C and analysed in the laboratory. Several changes of the methods used to analyse these samples had been encouraged by the improvement of analytical techniques worldwide. Today element concentrations are measured with ICP-MS (inductively coupled plasma - mass spectrometry), anions with IC (ion chromatography) and ammonia with FIA (flow injected analyses).

3 Results and Interpretations

This paper focuses on the ions nitrate (NO_3^-), ammonia (NH_4^+), sulphate (SO_4^{--}) and chloride (Cl^-). For those ions the input by precipitation is most relevant for the annual nutrient budget of the catchment.

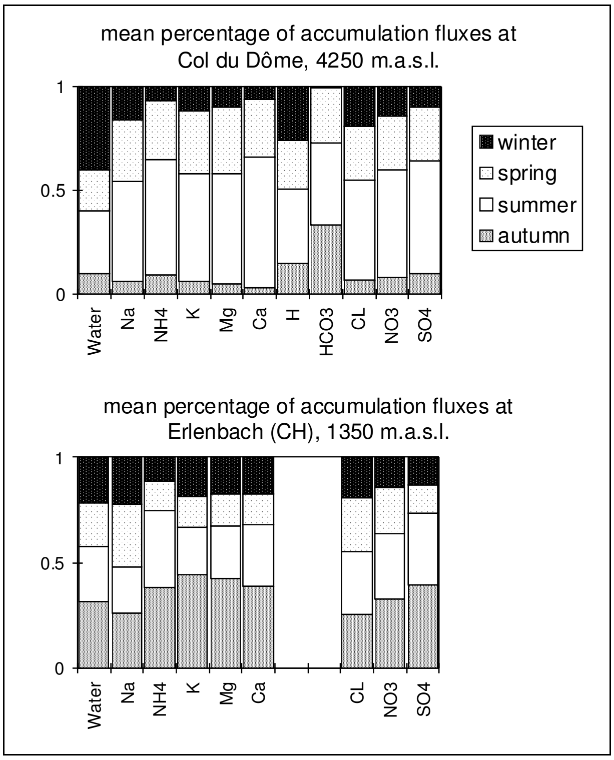

Fig. 2: Percentages of annual accumulated fluxes of water, Na, NH_4^+, K, Mg, Ca, H^+, Cl^-, NO_3^-, SO_4^{--} in the Alptal-Valley (CH), 1350 m a.s.l. and at Col du Dôme (F), 4250 m a.s.l. (Maupetit et al., 1995).

3.1 Ionic charge in precipitation

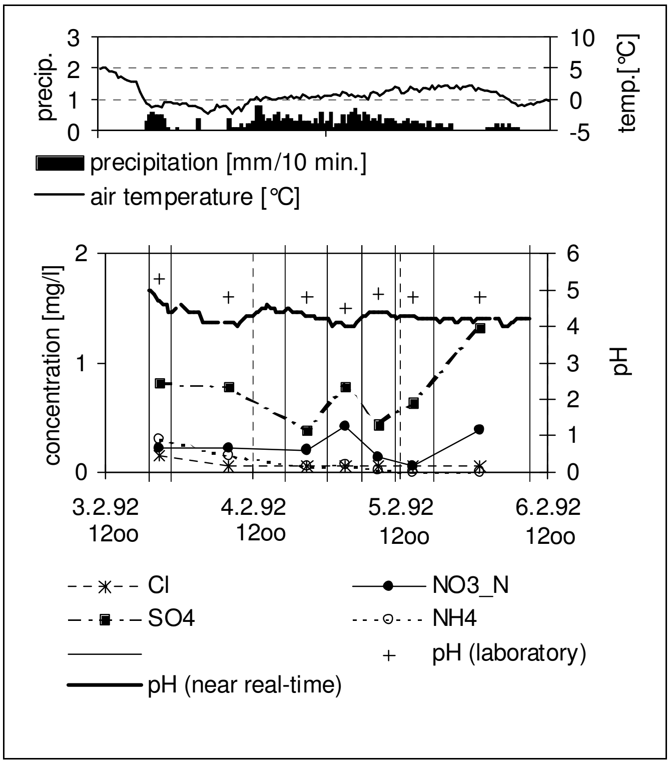

Fig. 3: Variation of pH (laboratory and near real time measurement) and ionic concentrations in precipitation in the Alptal-Valley at 1350 m a.s.l. near Einsiedeln (sum of rainfall = mm, maximum rainfall-intensity = mm/10 min.).

Fig. 2 shows a clear differences between Col du Dôme (Maupetit et al., 1995) and Alptal in the percentages of the annual fluxes accumulated during winter, spring, summer and autumn (hypotheses 1).

Maupetit et al. (1995) puts the lack of influence by polluted bottom layer air in high alpine regions during winter down to frequent inverse stratification of the atmosphere. Schwikowski (1996) pointed out that bottom layer air is mainly moving up during convective storms in spring.

Results from a sequential precipitation sampler show typical temporal variations of precipitation during a snow event (Fig. 3). A comparison between the pH of sequential samples and a near real-time pH measurement (1989-1993) indicated that the pH of precipitation-samples is influenced by the solution of alkaline dust after falling (Burch et al., 1996).

3.2 The storage of chemicals in the snowcover

A typical development of the storage in the snowcover is shown in Fig. 4. The snowcover is increasing during the winter. During a relatively short period the main melting occurs. The ionic concentrations typically decrease during the melting.

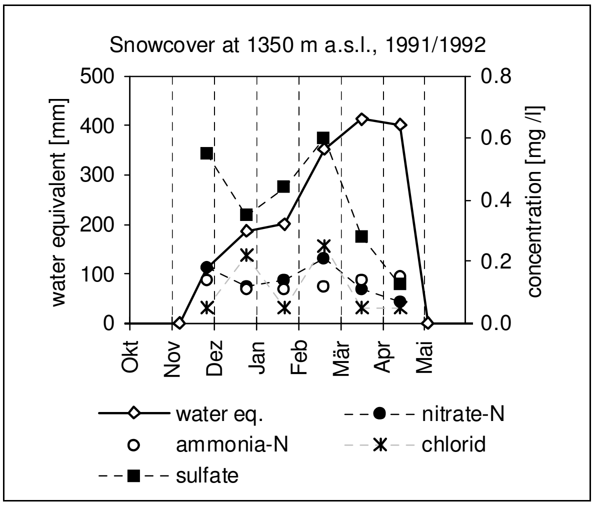

Fig. 4: Water equivalent [mm] and nitrate and ammonia concentrations [mg/l] in the snowcover in the Alptal-Valley near Einsiedeln (Switzerland).

3.3 Snowmelt and catchment runoff

Melting processes in subcatchments are not synchronous. Snowmelt induced runoff may occur throughout the winter, but mainly in spring (Fig. 6). Snowmelt is announced by typical diurnal cycles clearly shown in (Fig. 7).

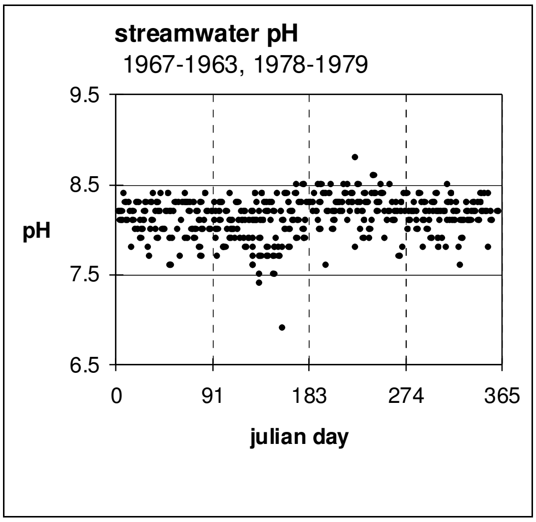

Fig. 5: pH in runoff in the Alptal-Valley (weekly grab samples).

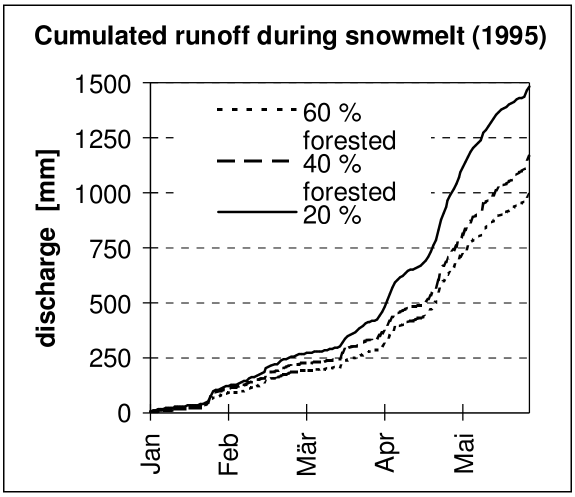

Fig. 6: Cumulated runoff of 3 different forested catchments in the Alptal-Valley during snowmelt (1995). Higher forest cover results in a higher water use in the catchment.

An intensive measurement campaign was carried out during the start of main melting period 11. - 13. April 1992 in three catchments. In spite of the mentioned lack of synchronity, a clear ionic pulse in the runoff (hypotheses 2) could be observed in one catchment (Fig. 7).

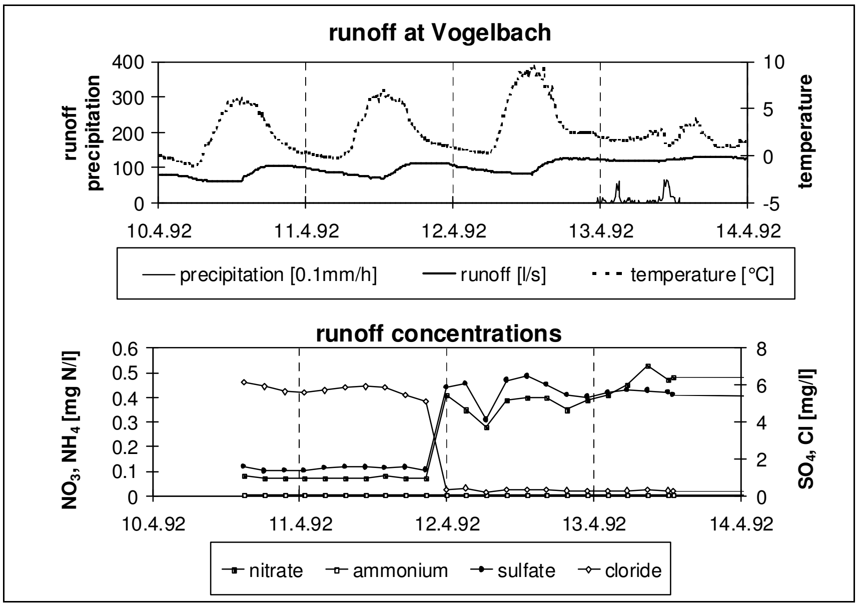

Fig. 7: Precipitation, air temperature, runoff and the concentrations of nitrate and ammonium in the Alptal-Valley at the beginning of snowmelt between 11.- 13. April 1992.

This result is a first indication of the existence of highly concentrated water flows contributing to catchment runoff. Assumingly acidity and ammonia are concentrated as well. But no pH values below 7 have been measured (Fig. 5). Only a slight tendency to deeper pH-values in spring is visible. Chloride is highly soluble. At the beginning of snowmelt the chloride in the runoff had been deluted by low concentrated meltwater. The chloride in runoff originated either from an earlier pulse or from soil water. The lack of ammonia in runoff is put down to its transformation to other forms of nitrogen in the catchment. The acidic meltwater (pH range: 3.5 - 6) is buffered mainly by solution of calcium carbonate in the soils.

4 Conclusions

A difference in the seasonal variations of the ionic charge in precipitation between high alpine and lower sites could be shown. This confirms a decoupling between high and low atmospheric layers during important periods of the year proposed in other papers. The development of the ionic charge in precipitation at lower heights seems to be only partly registered by high alpine natural archives. Extrapolations to other areas have to be based on detailed knowledge about transport processes in the atmosphere. Local investigations are helpful. Further the results indicate, that the chemical composition of the snowcover varies with height.
An ionic pulse has clearly been measured in the runoff of Vogelbach-catchment (prealpine) during the beginning of a snowmelt period. This indicates the existence of highly concentrated ionic pulses caused by snow melting in subcatchments. These pulses are an impact of the snowcover. On one hand ionic pulses represent an temporal and spatial increase of ionic concentrations. On the other hand they shorten the period during which the ionic input is available. Hence, ionic pulses influence the ion retentions in a catchment.

Summary

In alpine environments snow meltwater dominates runoff generation in spring. The ionic charge in precipitation, being stored in the snowcover, increased during this century. Meanwhile elevated nutrient concentration and acidity in aquatic systems is causing environmental problems. High alpine ice cores rarely register important periods. The seasonal variation indicates the decoupling of lower regions like Alptal (Switzerland) by inverse stratification of the atmosphere during winter. During snow metamorphism, the stored ions are segregated at the grains surface. In 1978 ionic pulses in the early melt fraction were firstly measured in laboratory and in lysimeter experiments. Despite not simultaneous melting processes in subcatchment, a clear pulse of nitrate and sulphate was measured in a catchment's runoff in spring. Assumed similar pulses of acidity and ammonia were retained in the catchment.

Zusammenfassung

In alpinen Einzugsgebieten wird der Abfluss hauptsächlich durch Schmelzwasser gebildet. Der Ioneneintrag mit dem Niederschlag stieg in diesem Jahrhundert stetig an. Gleichzeitig führten erhöhte Nährstoff- und Säurekonzentrationen in Gewässern zu Umweltproblemen. In hochalpinen Eiskernen sind wichtige Zeiträume kaum enthalten. Jahreszeitliche Variationen

deuten auf die Abkopplung von tieferen Regionen durch inverse Schichtung der Atmosphäre im Winter hin. Bei der Schneeumwandlung werden die im Schnee aufbewahrten Ionen auf die Kornoberfläche umgelagert. In Labor- und Lysimeterversuchen konnten Ionenschübe zu Beginn des Schmelzens gemessen werden. Trotz der zeitlichen Verschiebungen von Schmelzprozessen in Teileinzugsgebieten konnte im Frühling ein Nitrat- und Sulfatschub im Abfluss eines Einzugsgebietes gemessen werden. Ein entsprechender Säureschub wurde im Gebiet aufgefangen und konnte im Abfluss nicht nachgewiesen werden.

References

BROWN, D. J. A. & TURNPENNY, A. W. H., 1988: Effects on Fish. In Acid rain and Britain's natural ecosystems, eds. M. R. Ashmore, J. N. B. Bell & C. Garretty, Imperial College Centre for Environment Technology, Vail Printers Limited. London, pp. 87.

BURCH, H., 1994: Ein Rückblick auf die hydrologische Forschung der WSL im Alptal. In Gedenkschrift Hans M. Keller, Vol. 35, Schweizerische Gesellschaft für Hydrologie und Limnologie (SGHL); Eidg. Forschungsanstalt für Wald, Schnee und Landschaft (WSL): 18-32.

BURCH, H., WALDNER, P. A. & FRITSCHI, B., 1996: Variation of pH and concentration of nutrients and minerals during rain-events. 6th Conference of Experimental and Representative Basin Network (ERB), September 24-26, Strasbourg.

COLBECK, S. C., 1981: A simulation of the enrichment of atmospheric pollutants in snow cover runoff. Water Resources Research, 17(5): 1383-1388.

DÖSCHER, A., GAGGELER, H. W., SCHOTTERER, U. & SCHWIKOWSKI, M., 1995: A 130 years deposition record of sulfate, nitrate and chloride from a high-alpine glacier. Water Air and Soil Pollution, 85(2): 603-609.

FREI, R., 1965: Die Flyschbildungen in der Unterlage von Iberger Klippen und Mythen, Vol. 14, pp. 175.

HANTKE, R. et al., 1967: Geologische Karte des Kantons Zürich und seiner Nachbargebiete, 1:50000. Vierteljahresschrift der naturforschenden Gesellschaft in Zürich, 112 (2): 91-122.

JOHANNESSEN, M. & HENRIKSEN, A., 1978: Chemistry of snow meltwater: changes in concentration during melting. Water Resources Research, 14: 615-619.

JONES, H. G., 1996: Impact of snow on biology and ecology, International Symposium to Celebrate 60 Years of Snow and Avalanche Research in Davos.

MARCHETTO, A., MOSELLO, R., PSENNER, R., BENDETTA, G., BOGGERO, A., TAIT, D. & TARTARI, G. A., 1995: Factors affecting water chemistry of alpine lakes. Aquatic Sciences.

MAUPETIT, F., WAGENBACH, D., WEDDELING, P. & DELMAS, R. J., 1995: Seasonal fluxes of major ions to a high altitude cold alpine glacier. Atmospheric Environment, 29 (1): 1-9.

SCHWIKOWSKI, M., 1996: Interactions between atmosphere and cryosphere, International Symposium to Celebrate 60 Years of Snow and Avalanche Research in Davos.

SEIP, H. M. & TOLLAN, A., 1985: Acid Deposition. Facets of Hydrology, 11: 69-97.

STUMM, W. & MORGAN, J. J., 1981: Aquatic chemistry. John Wiley & Sons, New York.