

# SEASONAL, ANNUAL AND LONG-TERM VARIABILITY IN THE WATER CHEMISTRY OF A REMOTE HIGH MOUNTAIN LAKE: ACID RAIN VERSUS NATURAL CHANGES

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**Abstract.** Seasonal fluctuations as well as long-term trends in water chemistry were studied in Schwarzsee ob Sölden (Tyrol, Austria), an oligotrophic softwater lake situated at 2796 m a.s.l. The catchment is composed of granite, plagioclase and micaschists containing considerable amounts of sulphur, with little soil cover. The lake is ice covered for about nine months, during this time the deepest layers (>16m) become anoxic. During summer overturn, alkalinity (ALK) is lowest ( $-8 \mu\text{eq l}^{-1}$ ) in the whole water column, whereas pH reaches its minimum (4.88) at the surface during snowmelt. A decrease of pH from 5.8 to 5.4 during winter is caused by  $\text{CO}_2$  oversaturation, but deep water ALK increases to up to  $130 \mu\text{eq l}^{-1}$  due to in-lake ALK generation by reductive processes and base cation (BC) release. The seasonal pattern of ALK in SOS is driven by in-lake processes in winter, the snowmelting in spring and watershed processes and precipitation during summer. Since 1989 summer sulfate concentrations in SOS, originating mainly from the catchment, show a tendency to increase presumably caused by enhanced weathering. In contrast,  $\text{SO}_4^{2-}$  concentrations in other high mountain lakes which are dominated by atmospheric depositions show a decreasing trend. SOS is a good example for the complexity of interactions between catchment and in-lake processes which act at different time scales and depend on climate changes and atmospheric inputs.

**Keywords:** Acidification, alkalinity generation, weathering, atmospheric deposition, lakes.

## 1. Introduction

Remote high mountain lakes are sensitive to anthropogenic disturbances and climate change (Mosello et al. 1992). Therefore, many alpine lakes with low ALK, and situated in siliceous catchments, show different degrees of acidification (Psenner 1988; Camarero et al. 1995). The chemical composition of those lakes is mainly controlled by the chemical equilibrium of solutes with bedrock weathering products and by atmospheric deposition (Stoddard 1987; Schindler, 1988). However, superimposed to these factors, several processes like mixing, snow melting, and redox reactions in deep waters, cause seasonal variations in the water chemistry.

Paleolimnological data (Psenner and Schmidt, 1992;) show that high mountain lakes are sensitive indicators of climate change. Reconstruction of past chemical conditions using sediment cores, however, do not provide information about short-term (seasonal) processes of lake-water chemistry but mean values over several years. Information about the factors controlling e.g. ALK generation on a seasonal scale, may give important hints to elucidate long-term changes in acidification gathered by paleolimnological methods. In addition, they may allow us to predict ecosystem changes resulting from different climate and deposition scenarios.

Accordingly, the main aim of this paper was to study the factors controlling the dynamics of ALK generation in a high mountain lake in the light of seasonal and interannual changes. Moreover, we discuss recent trends of parameters relevant to acidification.

## 2. Materials and methods

Schwarzsee ob Sölden (SOS) is an ultra-oligotrophic high mountain lake with an area of 3.05 ha and a maximum depth of 17.5 m, situated in the Ötztal Alps (46°57'57'' N, 10°56'46'' E) at 2796 m a.s.l. The lake has no direct inflow or outflow and the water renewal time, based on the annual wet deposition, is ca. 1.1 yr. The catchment area (ca. 18 ha) consists of slowly weathering minerals such as biotite, granite, plagioclase, amphibolite and hornblende with considerable amounts of sulphur ranging from 211 to 3400 ppm. The main area of the catchment consists of undulating bare rock with a scarce and acidic soil cover. Due to the fact that the lake is covered by ice during ca. 9 months (November until July) the snow and ice cover have an important influence on its hydrology and biogeochemistry. Snowfall accounts for most of the annual precipitation and the major wet flux is from the storage and release of snowpack meltwater.

The lake was sampled at irregular time intervals since 1985 and monthly from January 1993 to September 1994. Samples were collected with a Patalas-Schindler sampler at the deepest part of the lake from 0, 1.5, 3, 6, 9, 12 and 15 m. In order to distinguish between atmospheric input, dilution, terrestrial catchment and redox processes 2 water layers were considered separately. Surface layers comprise depths from 0 to 1.5 m and bottom layers 15-16.5 m corresponding to 7 % of the lake volume. Temperature, conductivity and pH were measured in the field while the samples for major ions, ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), iron (II) ( $\text{Fe}^{2+}$ ) and reactive silica (DRSi) were analyzed in the laboratory. The chemical analysis and the methods used are cited elsewhere (Marchetto et al., 1995). Production of ALK in deep waters was calculated from changes in the ionic charge balance between base cations (BC) and acid anions (AA) and compared this with measured ALK changes:

$$\Delta\text{ALK} = \Delta [\text{Ca}^{2+}] + \Delta [\text{Mg}^{2+}] + \Delta [\text{Na}^+] + \Delta [\text{K}^+] + \Delta [\text{NH}_4^+] - \Delta [\text{SO}_4^{2-}] - \Delta [\text{Cl}^-] - \Delta [\text{NO}_3^-]$$

## 3. Results and Discussion

### 3.1 SURFACE LAYERS

During the ice covered period, ALK increased whereas pH decreased slightly due to a 2 to 20 fold  $\text{CO}_2$  oversaturation under ice. The maximum ALK ( $7 \mu\text{eq l}^{-1}$ ) was observed at the beginning of May (Figure 1).

During this period, the measured change of ALK was  $-9 \mu\text{eq l}^{-1}$  corresponding to the dilution of BC and  $\text{SO}_4^{2-}$  (50 and 20 %, respectively) and the input of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  (9, 16 and 5%, respectively). The main annual fluctuation of ALK in the surface layers was  $14 \mu\text{eq l}^{-1}$  while in the deep water it was ca. 10 times higher ( $137 \mu\text{eq l}^{-1}$ ).

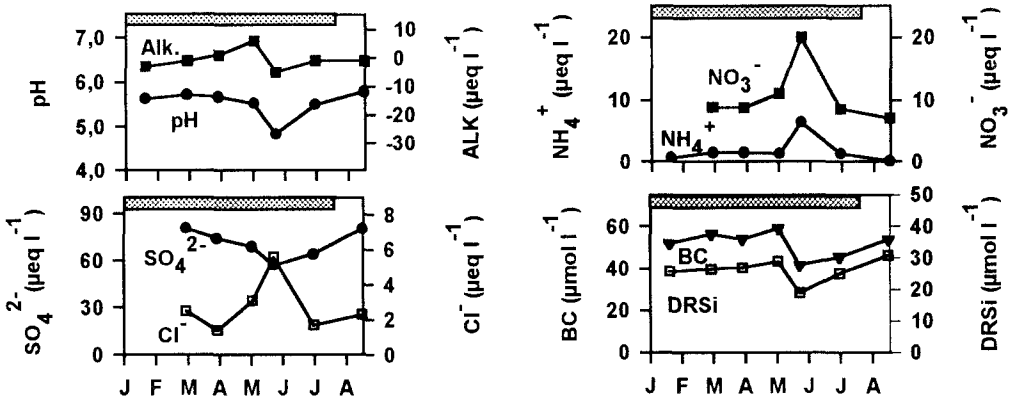


Fig 1. Time series plots for pH, Alkalinity,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , basic cations (BC) and dissolved reactive silica (DRSi) in surface water samples (0-1.5 m) from January 1993 until August 1994 in Schwarzzsee ob Sölden (SOS). The filled bars represent the ice covered period.

### 3.2 BOTTOM LAYERS

The dissolved oxygen ( $\text{O}_2$ ) concentration was  $10.3 \text{ mg l}^{-1}$  in August 1993 decreasing to  $0.5 \text{ mg l}^{-1}$  during the ice covered period in April (Figure 2). The associated change in redox conditions led to an increase in  $\text{NH}_4^+$ ,  $\text{Fe}^{2+}$  and major BC.

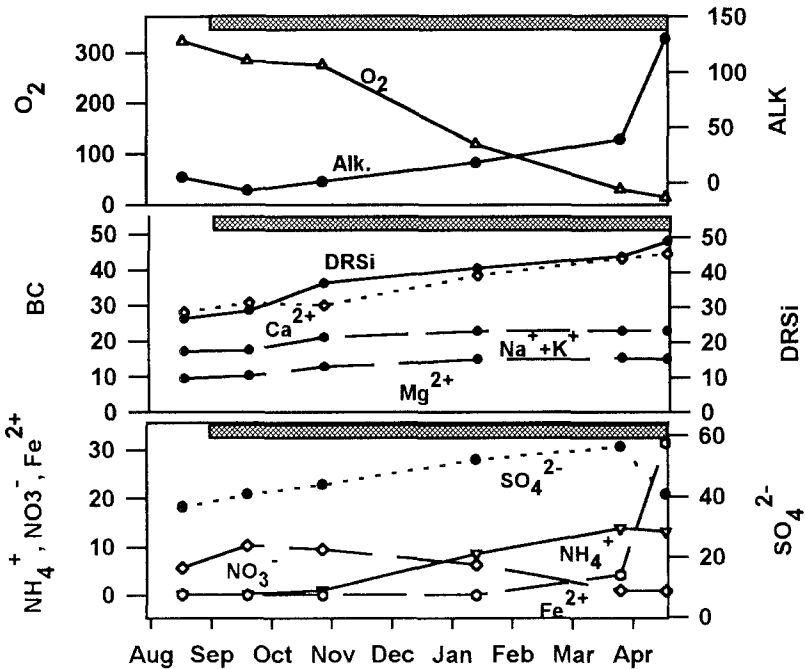


Fig. 2. Concentrations of  $\text{O}_2$ , Alkalinity,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+ + \text{K}^+$ , DRSi,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Fe}^{2+}$  and  $\text{NH}_4^+$  (in  $\mu\text{mol l}^{-1}$ ) determined from 15 m depth from August 1993 to April 1994 for SOS. The filled bars represent the ice covered period.

Correspondingly, measured ALK increased continuously from  $-7 \mu\text{eq l}^{-1}$  in August to  $130 \mu\text{eq l}^{-1}$  in April. As ALK generation in the catchment during the ice and snow covered period is low (Psenner and Catalan, 1994), we assume that in SOS the increase in ALK is mainly due to in-lake processes. Decomposition of organic matter caused an ALK loss of  $36.9 \mu\text{eq l}^{-1}$  from August 1993 to April 1994.  $\text{NO}_3^-$  concentrations increased due to nitrification processes from 5.8 in August to  $10.4 \mu\text{eq l}^{-1}$  in September leading to an ALK loss of  $9.2 \mu\text{eq l}^{-1}$ . At the same time the pH decreased by 0.7 units. After the build-up of the ice cover, reduction processes (denitrification or reduction to ammonium) caused a continuous decrease of  $\text{NO}_3^-$ , generating  $9.4 \mu\text{eq l}^{-1}$  of ALK until April.  $\text{NH}_4^+$  increased from 0.2 in summer to  $14.0 \mu\text{eq l}^{-1}$  in March (Figure 2), thus generating  $13.8 \mu\text{eq l}^{-1}$  of ALK.

$\text{Fe}^{2+}$  was low during summer ( $0.2 \mu\text{eq l}^{-1}$ ) and also during early winter when  $\text{O}_2$  was still present. From March to April the  $\text{Fe}^{2+}$  concentration increased from  $8.6 \mu\text{eq l}^{-1}$  to  $63 \mu\text{eq l}^{-1}$ . The ALK increase due to iron reduction between August and April was  $63 \mu\text{eq l}^{-1}$ .  $\text{SO}_4^{2-}$  concentrations increased from August to the end of March by  $39.6 \mu\text{eq l}^{-1}$  (from 72 to  $112 \mu\text{eq l}^{-1}$ ) and decreased by  $31.4 \mu\text{eq l}^{-1}$  in the following month when  $\text{O}_2$  was  $\leq 0.5 \text{ mg l}^{-1}$ . As reduced sulfur, mainly in the form of pyrite, is present in SOS sediments (Tessadri, pers. comm.) we assume that the increase of  $39.6 \mu\text{eq SO}_4^{2-}$  due to oxidation of pyrite led to an increase of 39.6 equivalents of  $\text{H}^+$  ions that are neutralized by exchange with alkaline and earthalkaline ions of the minerals present in SOS sediments.

The increase in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from August 1993 to March 1994 of  $46 \mu\text{eq l}^{-1}$  led to an ALK generation of  $46 \mu\text{eq l}^{-1}$ . The increase of  $\text{Na}^+$  and  $\text{K}^+$  contributed with 5 and  $1 \mu\text{eq l}^{-1}$  of ALK respectively, and the increase of DRSi was  $23 \mu\text{mol l}^{-1}$ .

From October 1993 to March 1994, BC release was the main ALK generation process ( $\text{Ca}^{2+}$  23%,  $\text{Mg}^{2+}$  8% and  $\text{Na}^+ + \text{K}^+$  3%) with contributions from nitrate reduction (33%), Cl<sup>-</sup> (10%) and reduction of Fe (23%) (Figure 3). However, in April 1994 when  $\text{O}_2$  was lowest ( $0.5 \text{ mg l}^{-1}$ ) the relative importance of those processes changed. Redox reactions involving nitrogen did not play any considerable role, whereas reduction of Fe became the most important ALK contributor (57%) followed by the reduction of  $\text{SO}_4^{2-}$  (32%) and the release of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (10% and 1% respectively). ALK generation calculated from changes in the ion balance differed from measured ALK by 2.5%. This may be due to the presence of organic acids that are included in the ion-balance calculation but not in the measured ALK as well as analytical errors and the fact that reduction of manganese was not considered in the calculations.

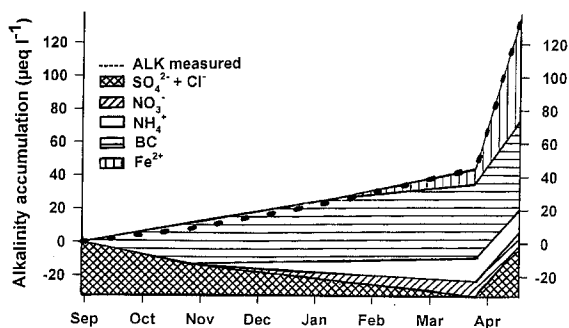


Fig. 3. ALK changes at 15 m depth in SOS (September 1993 to April 1994). The areas under the lines represent the relative contribution of different ions to the ALK generated or consumed. Measured ALK is indicated by a dashed line.

## 3.3 ANNUAL CHANGES OF ACIDITY AND CHEMICAL COMPOSITION

Long-term studies on deposition chemistry since 1985 have shown that concentrations of  $\text{SO}_4^{2-}$  in rain and snow decreased in the Northern hemisphere as a consequence of a reduction on sulfur emissions (Mosello et al, 1985). On the other hand,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  have become an important source for acidity of rainwater, as shown by several studies made in Norway and Spain (Mosello et al., 1985, Psenner and Catalan, 1994;).

Surprisingly, summer  $\text{SO}_4^{2-}$  concentrations in SOS lake water have increased since 1985 (Figure 4), whereas pH, ALK or  $\text{NO}_3^-$  concentrations do not show any clear trend. At the same time, the BC and Si, typical weathering products, increased. In contrast to this increase in  $\text{SO}_4^{2-}$  we did not observe this trend in two other acid sensitive high mountain lakes situated in the same valley but with different geologic characteristics (Wögrath and Psenner, 1995). Therefore, we conclude that the increase of  $\text{SO}_4^{2-}$  is due to enhanced weathering of pyrite in the catchment and decreased  $\text{SO}_4^{2-}$  reduction in the lake, as a result of direct and indirect effects of increasing air temperatures, e. g. better  $\text{O}_2$  saturation due to longer ice free periods during the last years. Paleolimnological investigations of sediments from SOS have shown a tight coupling between air temperature and lake acidification (Koinig, unpub.).

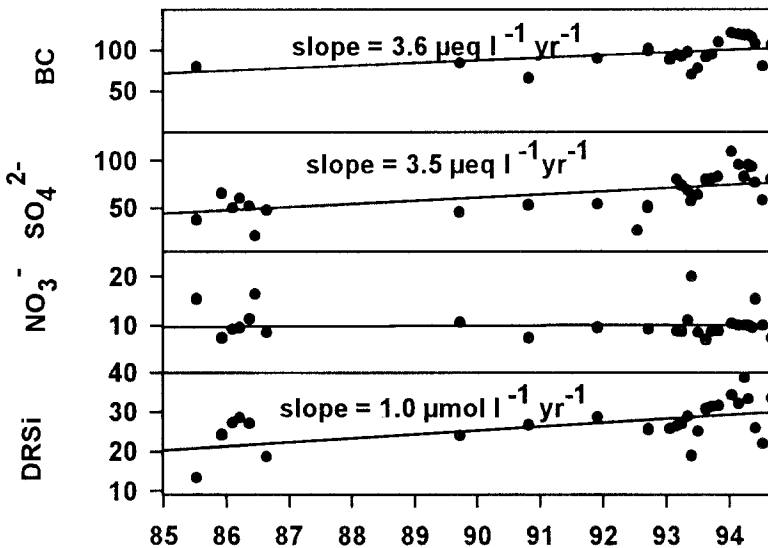


Fig. 4. Trends in the concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , DRSi and base cations (BC) from 1985 through 1994 in the surface waters of SOS. The annual increase was calculated from the slope of the linear regression.

## 4. Conclusions

The seasonal pattern of ALK in SOS is driven by in-lake processes in winter, dilution of BC and peaks of AA associated with snowmelting in spring, and weathering in the terrestrial catchment and precipitation during summer. In-lake processes in winter show a clear sequence depending

on the redox conditions in deep water layers. From October to March, reduction of N compounds as well as release of BC generate most of the ALK. When  $O_2$  falls below  $1 \text{ mg l}^{-1}$ , Fe reduction becomes the main contributor for ALK generation.  $SO_4^{2-}$  concentrations increase from October to March due to pyrite oxidation and decrease afterwards caused by reducing conditions. During snowmelt, ALK decreases due to the dilution of BC and input of AA, mainly  $NO_3^-$ . The summer concentrations of  $SO_4^{2-}$  have been increasing in SOS since 1985 but did not cause a decrease of pH or ALK because they were balanced by a corresponding increase in BC. As the bedrocks of SOS contain considerable amounts of sulfur the increase of air temperatures observed since 1985 may have led to enhanced weathering of pyrite in the catchment. The  $H^+$  ions resulting from this oxidation may have been neutralized by ion exchange or mineral dissolution, thus explaining the increase of BC. Increasing air temperatures will result in a shorter ice covered period. This may improve the oxygen conditions at the bottom layers and thus sulfur stored in the sediments during winter can be oxidized. On the other hand, higher water temperatures and longer ice free periods may enhance production and decomposition rates of organic matter which could eventually lower the redox potential.

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