

Acid Rain Research

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**Critical loads of
acidity to lakes
in the Polish
Tatra Mountains**

Final report



NIVA 

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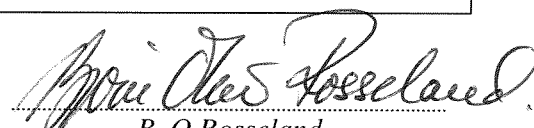
Abstract

Major chemical compounds in precipitation and runoff have been intensively followed in two Polish, Tatra Mountain lakes (Dlugi Staw and Zielony Staw) since January 1993, to assess the degree of impact of acid precipitation. Since July 1995, even nitrogen and sulphur compounds in air have been measured, which means that most focus have been put on the year July 1995 - June 1996. Based on a dynamic, combined nitrogen and sulphur model (FAB), critical loads (CL) are exceeded for both lakes. While substantial reductions of S and/or N are needed to reach CL at Dlugi Staw, only minor reductions are needed to obtain CL-level at Zielony Staw. Based on a nitrogen saturation index, both watersheds are in chronic stages of N-saturation. As long as the inputs of acid compounds are high, episodes particularly related to spring melt, may cause chemical conditions critical for aquatic life even at Zielony Staw with high acid neutralising capacity (ANC). This is primarily because the outlet and inlet streams might be totally dominated by melt water during such episodes, which means that organisms living in these streams have small changes to avoid episodes with extreme water quality. Because of far higher ANC at Zielony Staw, such episodes are both more uncommon and less extreme at this site compared with at Dlugi Staw. A surface water survey in the Karkonosze Mountains autumn 1995, documented strong impacts of atmospheric inputs of both S- and N-compounds. in this area. Thus, CL is exceeded for all investigated sites.

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Critical loads of acidity to lakes in the Polish Tatra Mountains

Final Report

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PREFACE

As part of the Agreement on Environmental Co-operation between Norway and Poland, a project "A case study on estimating Critical Loads of acidity to lakes in the Tatra Mountains in Poland" was established in 1991 with participants from the Institute for Ecology of Industrial Areas in Katowice, the Tatra Mountain National Park and the Norwegian Institute for Water Research (NIVA). The intention of the project was to collect samples from the Polish Tatra Mountains, compare their water chemistry with Norwegian lakes and to calculate their critical loads of acidity and their exceedance. The following up of this first work was a project with biweekly sampling of two lakes and precipitation sampling on a weekly basis in the Polish Tatras called "Critical Loads of acidity to lakes in the Polish Tatra Mountains - A study of the yearly variations in the precipitation and water chemistry". The project extension on precipitation sampling brought Norwegian Institute for Air Research (NILU) into the Co-operative work. The project was launched after a Norwegian visit to the Tatras in August 1992, where the activities were discussed, and the NILU precipitation sampler was placed close to the investigated lakes. The results have so far been published in two NIVA-reports (Acid Rain Research Report 29/1992 and 33/1993), while the final report will be present here. Beside a chemical evaluation of data for the whole project period, chemical fluxes in two lakes (Długi Staw and Zielony Staw) have been focused on because that was a primary goal for the last part of the project. To do such evaluations, monitoring of runoff as well ambient air concentration measurements have been added to the sampling programme the last year.

The Polish Tatra Mountains are situated on the boundary to Slovakia. This study is focused on lakes located in the granitic area of the mountains, where acidification sensitive lakes were expected to be found. Analyses of lake water started autumn 1991, wet-deposition analyses (and precipitation amounts) in January 1993, and runoff logging and analyses of air concentrations in July 1995. The monitoring programme terminated in July 1996.

The project activities for the Norwegian team has been financed by the Norwegian Ministry of Foreign Affairs.

ABSTRACT

Earlier studies have indicated that the general acidification status of the fresh water resources in the Tatra Mountains are similar to those found in similar geological settings and similar atmospheric deposition patterns in Europe and North-America. The critical load of acidity is exceeded in several lakes in the area. The main difference between the comparable areas is the great importance of nitrogen deposition in the Tatra Mountains. Two watersheds, Dlugi Staw and Zielony Staw have been followed in more detail from autumn 1992. This report is primarily evaluating data from January 1994 to June 1996, with most focus on the period July 1995 to June 1996, where we have data on total atmospheric inputs and runoff outputs.

The leakage of sulphur (S) by runoff was 90% and 95% at Dlugi Staw and Zielony Staw, respectively, while the corresponding leakage of nitrogen (N) were 57% and 39%. The leakage of N is lower than earlier reported, but in earlier reports dry-deposition was not included. About 16% of the S-inputs and 20% of N-inputs enter the catchments as dry-deposition, the remaining 80-84% as wet-deposition.

At present neither of the lakes are exceeded with respect to sulphur, according to the steady state SSWC-model for critical load (CL) calculations. However, by also accounting for nitrate leakage, CL is exceeded for Dlugi Staw, while Zielony Staw still can tolerate further acid inputs. Based on the process-oriented First-Order Acidity Balance (FAB) model, CL is exceeded for both Dlugi Staw and Zielony Staw. However, while substantial reductions of S and/or N are needed to reach the CL-level at Dlugi Staw, only minor reductions are needed to obtain the CL-level at Zielony Staw. Since the FAB-model shows the worst case scenario when all inputs of N and S will be transformed to acidity, it is important to mention that the lake water chemistry in Zielony Staw at present is below the CL-level estimated by the FAB-model.

Based on the nitrogen saturation classes given by Stoddard (1994), the watershed Dlugi Staw is close to the 3rd Stage and Zielony Staw in the 2nd Stage of N-saturation. This means that both watersheds are in chronic stages of N-saturation.

As long as the inputs of acid compounds are high, episodes particularly related to spring melt, may continue to cause water chemical conditions critical for aquatic life even in the well buffered Zielony Staw catchment, even though the lake water chemistry at this site shows that CL is still not exceeded with respect to inputs of N- and S-compounds. However, this chemically extreme melt water will be transported as an uppermost water layer through the lake. Accordingly, large parts of the lake will still have good water quality where organisms as fish can move into. On the other side, the outlet and inlet streams might be totally dominated by this melt water, which means that organisms being in streams have small changes to avoid extreme water quality episodes. Because of far higher acid neutralising capacity at Zielony Staw, such episodes are both more uncommon and less extreme at Zielony Staw compared to Dlugi Staw.

Another 9 watersheds from the Karkonosze Mountains were sampled in September 1995. The intention of this survey was to give a first CL calculation for this area. Unfortunately, we have no runoff data from these sites, which is necessary for satisfactory CL-calculations. However, the water chemistry in this area reflects strong impacts of atmospheric inputs of both S- and N-compounds. Thus, CL is exceeded at all investigated sites.

1. INTRODUCTION

There has been considerable scientific and political interest in determining the effects of acidic deposition on various environments. Beyond the linkage of atmospheric deposition of strong acids to effects on forests, lakes, crops, human health and materials, one of the important issues have been in evaluating and setting limits on the deposition of acidic compounds. These limits, or the *critical loads* of acids to an environment, is defined as "*the highest deposition of acidifying compounds that will not cause changes leading to long term harmful effects on ecosystem structure and function*" (Nilsson and Grennfelt, 1988).

Criteria for "unacceptable change" are set relative to effects on terrestrial and aquatic organisms. Both sulphur and nitrogen contribute to the total input of acidifying compounds to an ecosystem. The ratio of sulphur to nitrogen can, therefore, vary without changing the critical load for acidifying compounds. The purpose of determining critical loads is to set goals for future deposition rates of acidifying compounds such that the environment is protected. Critical loads are determined separately for different receptors, such as soils and lakes.

Critical loads for the acidification of surface waters have been most thoroughly studied with respect to sulphur. Critical loads of sulphur were exceeded long ago in large regions in Norway and in many other countries, and the effects are manifested in the form of acidic fishless lakes.

Under the auspices of the Convention on Long-Range Transboundary Air Pollution (the "Geneva Convention"), a "Task Force for Mapping the Critical Loads and the Areas where the Critical Loads are Exceeded" has been formed. A manual for calculating critical loads and their exceedance both for forest soils and for surface waters has been worked out (Sverdrup *et al.* 1990). Norway has mapped the critical loads of acidity and the exceedance for sulphur to surface water, and a project under the Nordic Council of Ministers has mapped critical loads and their exceedance for surface waters for the three Nordic countries Finland, Norway and Sweden (Henriksen *et al.* 1990).

During the work of the Task Force on Mapping, contact between Poland and Norway has been established. As part of the Agreement on Environmental Co-operation between Norway and Poland, the project "A case study on estimating Critical Loads of acidity to lakes in the Tatra Mountains in Poland" was launched in 1991 with participants from the Institute of Environmental Protection in Katowice, the Tatra Mountain National Park and the Norwegian Institute for Water Research. The intention of the project was to collect samples from the Polish Tatra Mountains, compare their water chemistry with Norwegian lakes and to calculate their critical loads of acidity and their exceedance. The project results were reported in 1992 (Henriksen *et al.*, 1992a). The following up of this first Co-operative work is a project with biweekly sampling of two lakes and precipitation sampling on a weekly basis in the Polish Tatra called "Critical Loads of acidity to lakes in the Polish Tatra Mountains. A study of the yearly variations in the precipitation and water chemistry". The first year of this project was reported in 1993 together with a discussion of future joint activities for the Polish and Norwegian groups (Wathne *et al.* 1993). Beside a chemical evaluation of data for the whole project period, chemical fluxes in two lakes (Dlugi Staw and Zielony Staw) will be focused since this was a primary goal for the last part of the project. To do such evaluations, monitoring of runoff as well as air concentrations were included in the sampling programme in 1995/96.

2. MATERIAL AND METHODS

Definitions of critical loads and acid neutralising capacity, calculation of non-marine concentration of SO₄ and basecations are given in earlier reports (Henriksen *et al.*, 1992a; Wathne *et al.*, 1993), as well as description of the geology, climate, catchment flora, and biology of aquatic systems. Thus, this will not be presented in this report.

2.1 Site description

The Tatra Mountains are situated on the border between Poland and Slovakia. It is a mountain ridge, 53 kilometre long and 18 kilometre wide, with the highest summit of 2663 m.a.s.l. in Slovakia, and 2499 m in Poland. Within the Karpaty formation, the Tatra Mountains create the highest mountain massif. Characteristic feature is young glacial relief. Complex structure of nape and differentiated relief in which forms created in subtropical climate as well as those created in a very cold climate by glaciers have been preserved, are typical for the Tatra Mountains. Due to very high elevation, low temperatures and high precipitation levels characterise the Tatra Mountains. Another distinctive features for that region are frequent, strong winds, transporting dusts and pollutants emitted into atmosphere. The diversity of flora in the Tatra Mountains is strictly connected with the climatic zones existing in that terrain. Processing physical and chemical erosion caused by atmospheric precipitation has resulted in creating numerable vaulcluses, springs, streams, creeks, brooks and lakes, which chemical composition is closely connected with the geologic-lithological characteristics of the catchment basin.

The location of the Tatra Mountains in Poland as well as a detailed map of the study area is present in the report by Wathne *et al.* (1993, Figure 1, p 8). The study area has been reduced to the part of the Polish Tatra Mountains with crystalline core where the mineralisation of surface waters is very weak, resulting in sensibility to acid deposition from the atmosphere. The selected lakes are located in the area of Hala Gasienicowa, i.e. Dlugi Staw and Zielony Staw. Dlugi Staw was selected because of its significant degree of acidification, while Zielony Staw was selected because of its rich biological life. Essential catchment specific data are presented in Table 1.

Table I. Lake and catchment specific data for the two Polish sites, Dlugi Staw and Zielony Staw.

Parameter	Site	
	Dlugi Staw	Zielony Staw
Latitude	49°13'42" N	49°13'30" N
Longitude	37°40'42" E	37°41'30" E
Lake altitude	1783 m.a.s.l.	1671 m.a.s.l.
Lake area	0.0158 km ²	0.0384 km ²
Max depth	10.6 m	15.1 m
Mean depth	5.06 m	6.8 m
Volume	0.081*10 ⁶ m ³	0.261*10 ⁶ m ³
Retention time	34 days	4.8 mths
Ice free period	May/Jul -Sep/Nov	May/Jun - Oct/Nov
Catchment area	0.66 km ²	0.50 km ²
Catchment geology	Granitoids covered by moraine	Granitoids partly limestone, covered by moraine
Catchment soil	Primitive soil/podsolic soil	Primitive soil/podsolic soil
Catchment vegetation	Dwarf pine, alpine meadows, rocks	Dwarf pine, alpine meadows, rocks
Annual precipitation	1837 mm	1795 mm
Annual runoff	49 L km ⁻² sec ⁻¹	49 L km ⁻² sec ⁻¹
Remarks	No fish (Brook trout stocked in 1990)	Brook trout and brown trout

Fish from Zielony Staw seems to be affected by water chemical conditions as low pH, and fish death has been observed during high flow periods both at spring (May 1991) and during heavy rain episodes following draught periods (Byrcyn *et al.*, 1992). Lake Dlugi Staw was populated by brook trout, but this originally stocked population disappeared in the sixties. Another brook trout population was stocked in Dlugi Staw in 1990. As a part of the AL:PE 2 project, both brown trout and brook trout have been found in Lake Zielony Staw (Wathne *et al.*, 1996).

2.2 Precipitation station and precipitation analysis

The sampling station for precipitation is situated in Hala Gasienicowa, in a station of the Institute of Meteorology and Water Management, nearby the investigated lakes. The meteorological station is located at the upper timberline (1520 m.a.s.l.). A short description of deposition data from earlier years, including data from Hala Gasienicowa from September 1992 to September 1993 and data from Chopok, Stara Lesna and Liesek in Slovakia from 1992 are presented in Wathne *et al.* (1993).

In addition to precipitation and wet-deposition chemistry, air concentrations of S- and N- compounds have been measured during the period July 1995 - June 1996. The sampler for gas and aerosol particles was situated at the meteorological station Kasprowy Wierch about 2000 m.a.s.l., while the diffusive (passive) sampler for nitrogen dioxide was situated in Hala Gasienicowa together with the precipitation sampler.

The precipitation chemistry and precipitation amounts are determined by bulk sampling on a weekly basis. The sampling equipment (NILU precipitation sampler) is made of polyethylene and has an opening of 200 mm. The opening is about 2 m above the surface. The sampler was rinsed with deionized water every week, including weeks without precipitation. The sampling and measurement of precipitation amount was performed by local observers and the samples were sent to NILU by ordinary mail for chemical analysis. After arriving at NILU, samples were stored at 5°C and analysed on a monthly basis. The precipitation samples were analysed for the ions SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+} by ionchromatography whereas pH ($-\log [\text{H}^+]$) and electrolytic conductivity were determined by potentiometry and conductometry, respectively.

Air concentrations of sulphur dioxide (SO_2), sulphate (SO_4), $\Sigma\text{HNO}_3 + \text{NO}_3$ and $\Sigma\text{NH}_4^+ + \text{NH}_3$ were determined by the use of an open face, three stage filterpack sampler (flowrate of 16 L min^{-1}). The filterpack consists of a Teflon filter (Zeflour $2\mu\text{m}$) for the determination of particles, an alkaline impregnated Whatman 40 filter (KOH and glycerol) and finally an acidic impregnated Whatman 40 filter (Oxalic acid) for the sampling of acidic (SO_2 and HNO_3) and alkaline (NH_3) gases, respectively. Extracts of the filters were analysed for sulphate and nitrate by ionchromatography, and for ammonium by spectrophotometry (Indophenol method).

Nitrogen dioxide (NO_2) was sampled by passive (diffusive) sampling where NO_2 is absorbed on a NaI impregnated Whatman 40 filter behind a stainless steel net (Ferm, 1991). Extracts of the filters are analysed for nitrite by spectrophotometry (Griess method). The samplers are exposed for 14 or 28 days. The results shown are mean values for two parallel samples.

All samples in this program, excluding nitrogen dioxide, were taken, analysed and quality assured according to the EMEP manual for sampling and chemical analysis (EMEP, 1995). The samples were analysed at NILU who has an accreditation for these methods according to the standard NS-EN 45001.

2.3 Hydrology station and runoff analysis

The post-glacial lakes of the Tatra Mountains are situated above the upper forest. They are supplied with small, usually seasonal streams, collecting the flowing rain waters and by waters from old firn reservoirs as well as retained in fissures and small pools of morainic covers. There are about 40 lakes in the Polish Tatras of a joint area of 80 hectares and a volume of ca 40 million cubic metres. None of them is more than 35 hectares in area and 80 m deep. Generally, the water levels of the Tatra Mountain Lakes are in most cases balanced, with differences amounting to several tens of centimetres. Maximal water level appears in periods of snow melt and after rich rainfalls, usually with one day delay. The lowest water level is usually observable in autumn and winter. Morphological and hydrological parameters of studied lakes presented in Table I differ to a certain degree, from that present in Wathne *et al.* (1993), based on data from Lajczak (1980) and Szafer (1962). Both lakes are supplied with waters from springs and episodic and seasonal creeks of different efficiency, and Kot (1993) have shown that there are seasonal episodes with low pH during high flow events even at Zielony Staw, which have the highest acid neutralising capacity of the two sites investigated.

The runoff station was located at the outlet of Lake Zielony Staw. Runoff, through a rectangular V-notch weir (2030 mm wide), have been monitored continuously from July 1995 to July 1996. Runoff water was collected biweekly (average: 17 ± 10 days) by local observers. Water was collected on acid washed high density polypropylene bottles, and the samples were sent to NIVA by ordinary mail for chemical analyses. After arriving at NIVA, samples were stored at 4°C and analysed after a few days. The main physical and chemical parameters measured were: pH, conductivity (κ_{25}), Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , SO_4^{2-} , NO_3^- , Cl^- , alkalinity, total nitrogen (TN), H_4SiO_4 (as $\text{SiO}_2 \text{ L}^{-1}$), and total organic carbon (TOC), as well as reactive Al (RAL) and non-labile Al (ILAL). Based on these two Al-fraction we can estimate the concentration of labile Al (LAL) which primarily represent the acute toxic Al-forms, i.e. the low molecular inorganic Al-species.

All analyses were conducted at the Norwegian Institute for Water Research (NIVA), according to EN-45000 standards. The NIVA laboratories are accredited according to these standards.

As mentioned earlier, runoff was continuously logged from July 1995 to July 1996. However, due to different problems, only runoff data exists for the periods 12-7-1995 to 08-08-1995 and from 17-10-1995 to 17-01-1996. Thus, data from essential runoff rich periods, like spring melt, are lacking. As long as the primary goal for the last year survey was to study fluxes of N- and S-compounds, we have tried to calculate the runoff during the periods where no data exists. At Dlugi Staw a very good correlation was found between runoff and the concentration of Si (silicon, or silicic acid). However, only 5 measurements of Si was conducted within the period where real runoff data were available. Unfortunately, no Si-values exist from the high flow period in the middle of July 1995. Therefore, we assumed that the lowest Si-concentration recorded at Dlugi Staw ($1.1 \text{ mg SiO}_2 \text{ L}^{-1}$) occurred at the highest flowrate ($15.2 \text{ L m}^{-2} \text{ day}^{-1}$). Thus, based on 5 real data points and 1 artificial, we calculated a "best fit" equation between runoff and [Si]. The equation is presented in Figure 1. By this equation we further calculated runoff from January 1 1994 to July 31 1996, on the basis of the biweekly Si-analyses. We have used measured runoff values when available, and estimated values for the remaining period (Figure 2).

The original air, precipitation and runoff chemistry data are presented in Appendix.

We further assume identical area-specific runoff ($\text{L m}^{-2} \text{ yr}^{-1}$) from both Dlugi and Zielony Staw. Since runoff primarily is calculated on the basis of Si chemistry, we only have biweekly calculated runoff data. Accordingly, annual runoff is estimated by the following equation:

$$\Sigma ((R_1+R_2)/2)(t_2-t_1) + ((R_2+R_3)/2)(t_3-t_2) + ((R_{n-1}+R_n)/2)(t_n-t_{n-1}). \quad (\text{I})$$

where

R_{n-1} : runoff at time t_{n-1}

R_n : runoff at time t_n

(t_n-t_{n-1}) : number of days between t_n and t_{n-1}

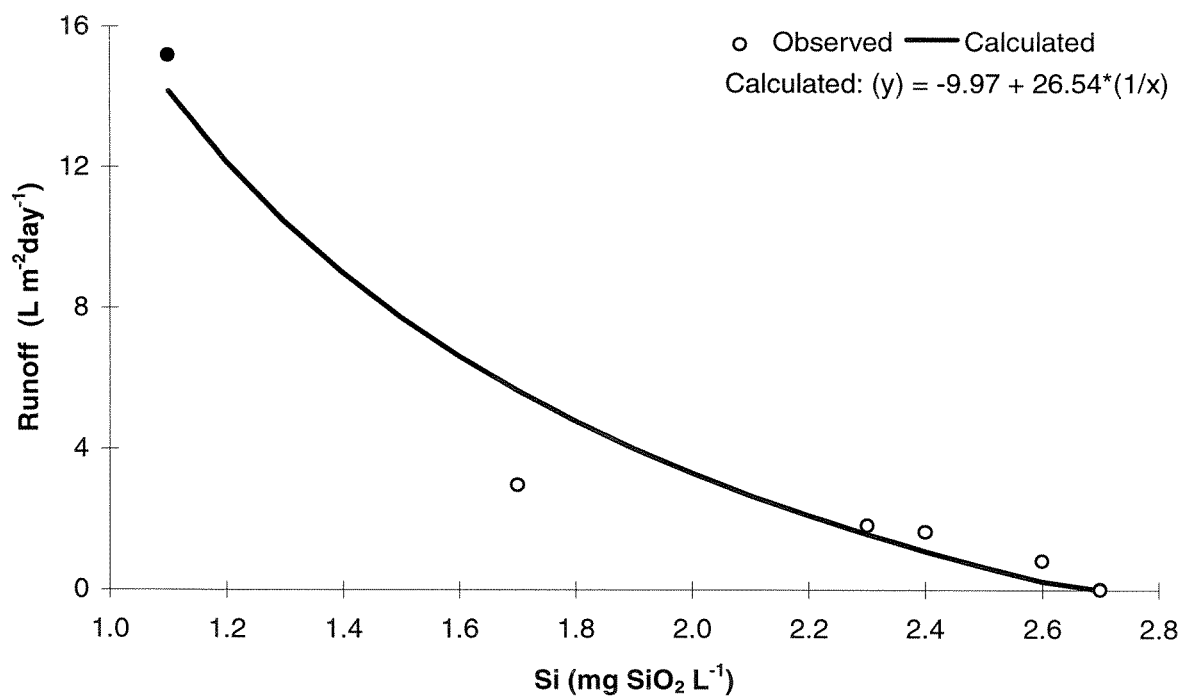


Figure 1. The relationship between the concentration of silicon (Si) and runoff at Dlugi Staw, based on 5 observed (open circles) and 1 artificially introduced value (filled circle). The artificial point relies on the assumption that the highest runoff measured occurred simultaneously with the lowest Si-concentration measured.

3. RESULTS

3.1 Hydrology

The amount of precipitation were collected weekly, while runoff was continuously monitored (logged). However, due to lack of runoff data for long periods, runoff is largely calculated based on the biweekly analysis of Si (See Chapter 2.3).

3.1.1 Precipitation

The annual amounts of precipitation were 975 mm, 1369 mm, and 1367 mm in 1993, 1994 and 1995 respectively, while for the year July 1 1995 to June 30 1996, the precipitation amount was 1276 mm. Average amount for the 3 calendar year was 1237 mm, which > 30% lower than the annual estimates present in Table 1. The fact that the weather station is located at 1520 m.a.s.l., compared with the lakes located at 1783 m.a.s.l. (Dlugi Staw) and 1671 m.a.s.l. (Zielony Staw), might be one explanation for the lower amounts of precipitation measured at Hala Gasienicowa. Hess (1968) found a correlation between altitude and precipitation in the Tatra Mountains. Recalculation data from Hala Gasienicowa (average : 1667 mm) using Hess' correlation gives as multiyear average precipitation of 1837 mm and 1795 mm for Dlugi Staw and Zielony Staw respectively. By simply using this relationships, the annual precipitation amounts at Dlugi and Zielony Staw is 1.102 (1837/1667) and 1.077 (1795/1667) times higher compared with what measured at Hala Gasienicowa. Thus, average amounts for the 3 calendar years are 1363 mm and 1332 mm at Dlugi and Zielony Staw respectively. Accordingly, the annual average precipitation during this 3 year period is 26% lower compared with the multiyear averages presented in Table I.

During the period of monitoring, high amounts of precipitation often occur during spring and early summer (primarily in May and June) and during autumn. Highest monthly inputs of water were recorded in September 1995 (252 mm) and in May 1996 (250 mm). Lowest amounts normally occur during the main winter period (November - February), when the precipitation normally enters as snow. However, snow is probably relatively normal even in March and April and sometimes even in May, all three months exhibiting relatively high precipitation inputs. Thus, a relatively thick snow pack, combined with relatively high inputs of water during spring, often cause extreme high flow periods during snow melt.

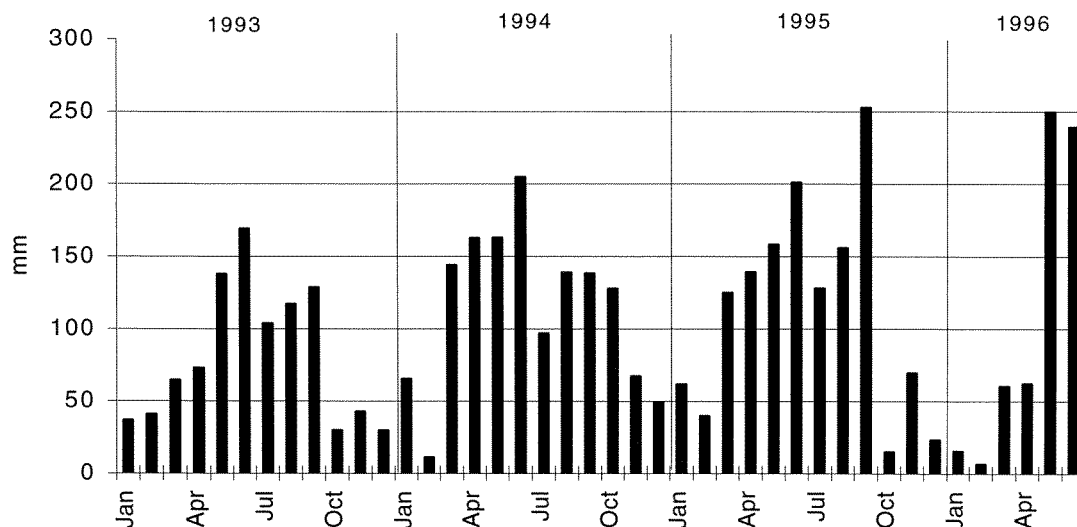


Figure 2. Monthly precipitation amounts at the weather station Hala Gasienicowa, from January 1993 to June 1996.

3.1.2 Runoff

Based on the runoff curve in Figure 3, annual runoff was $1058 \text{ L m}^{-2} \text{ yr}^{-1}$ (or mm), 1145 mm and 1240 mm for 1994, 1995 and for the period July 1, 1995 - June 30, 1996. Recalculation of precipitation (see Ch. 3.1.1) resulted in a total input of water during 1994 and 1995 of 3015 mm and 2946 mm at Dlugi and Zielony Staw respectively. Total runoff during the two years was 2203 mm, which gives an annual evapotranspiration for the period of 27% and 25%, i.e. runoff coefficients of 0.73 and 0.75 at Dlugi Staw and Zielony Staw, respectively. This is lower runoff coefficients (runoff/precipitation) compared with what earlier reported (Lajczak, 1988) for the Tatra Mountains (0.83) and for the crystalline Tatras (0.86). The rather high runoff coefficient values at Dlugi and Zielony Staw are attributed to rather low evapotranspiration under the conditions of low temperature, high humidity related to frequent precipitation and rapid water runoff (See Wathne *et al.*, 1993). Rapid water runoff means that high flow periods may be difficult to reveal on the basis of biweekly data. This may lead to a certain underestimation of runoff by our calculation method. However, the runoff coefficients for 1995/96 (July 1, 1995 to June 30, 1996) were 0.88 and 0.90 at Dlugi and Zielony Staw, respectively. This may indicate that the period July 1 - June 30 is a better water year compared with the calendar year (See comments on water year in Ch. 3.3).

High flow periods normally occur during spring and early summer (May, June), as a combination of snow melt and high precipitation inputs. In addition an extreme high flow period was recorded in July 1995. This have to be due to a very intensive rainfall event, since the flow died very fast (Figure 3) and the total amount of precipitation this period was not very extreme (Figure 2). The very high precipitation input in September 1995 (See Figure 2) occurred in a period when the runoff recorder were out of function. During the same period, our Si-based runoff estimates were very weak, because only one Si-analysis exists during this high flow event.

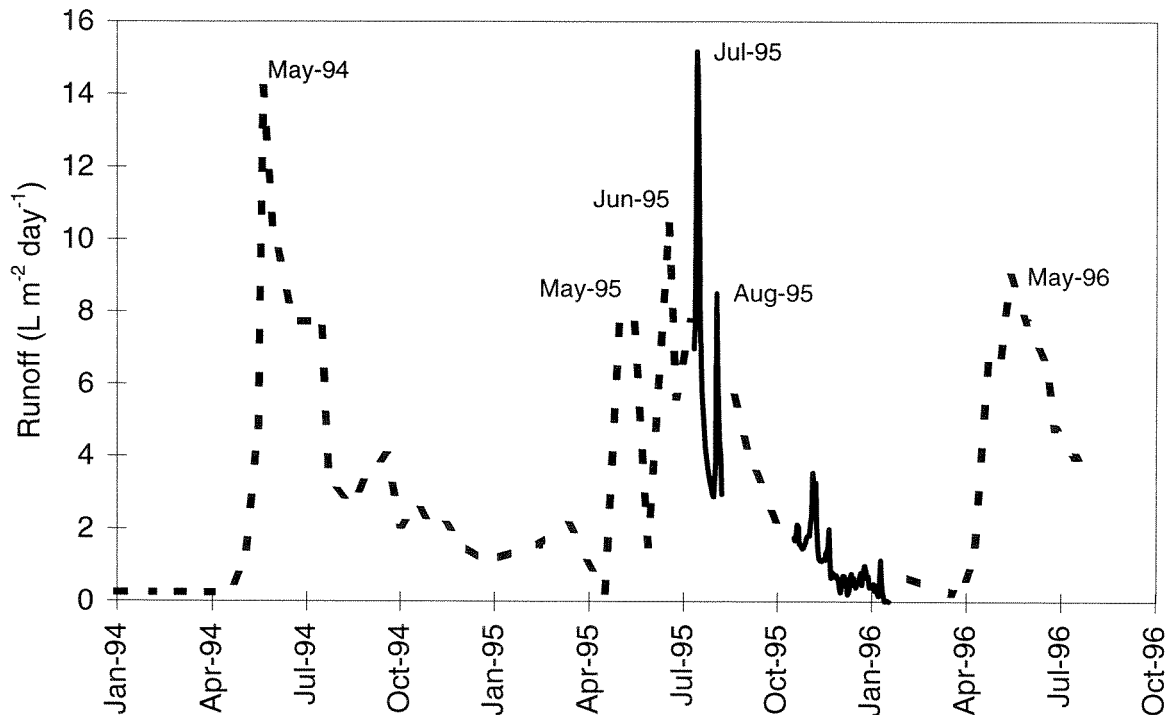


Figure 3. Calculated (dotted line) and recorded (continuous line) runoff at the runoff station at the outlet of Lake Zielony Staw. The method for runoff calculation is presented in Chapter 2.3.

3.2 Chemistry

3.2.1 Air-concentrations

Air concentrations of different nitrogen and sulphur compounds have been measured from August 1995 to June 1996. For mass balance purpose we have calculated the concentrations for July 1995, to obtain a full year of dry-deposition data. The concentrations for July 1995, is estimated as the mean value for August 1995 and June 1996. Only NO_2 data is lacking for June 1996, and the NO_2 -concentration for this month is therefore assumed to be as for May 1996. Thus, we have a full year for mass balance calculations for both N and S.

SO_2 -gas was the predominant S-compound in air, with maximum concentration in February and March ($3.7\text{-}4.0 \mu\text{g S m}^{-3}$), while the concentration of SO_4 -particles were at its highest during summer, June -August ($1.1\text{-}1.2 \mu\text{g S m}^{-3}$). The highest concentration of $\Sigma\text{HNO}_3 + \text{NO}_3$ and $\Sigma\text{NH}_4 + \text{NH}_3$ also occurred during the summer season, i.e. April -August, while the concentration of NO_2 -gas was at the highest during the winter, December-February (Figure 4 and 5).

Based on concentrations averages, SO_2 -gas constituted 69% and SO_4 -particles 31% of the total concentration of sulphur in air (Figure 6), while the corresponding percent distribution for nitrogen compounds were: $\Sigma\text{NH}_4 + \text{NH}_3$ (43%), NO_2 (37%), $\Sigma\text{NO}_3 + \text{HNO}_3$ (20%). We assume that NO_3 , HNO_3 , NH_4 , and NH_3 each constitutes 50 % of the $\Sigma\text{NO}_3 + \text{HNO}_3$ and $\Sigma\text{NH}_4 + \text{NH}_3$, respectively.

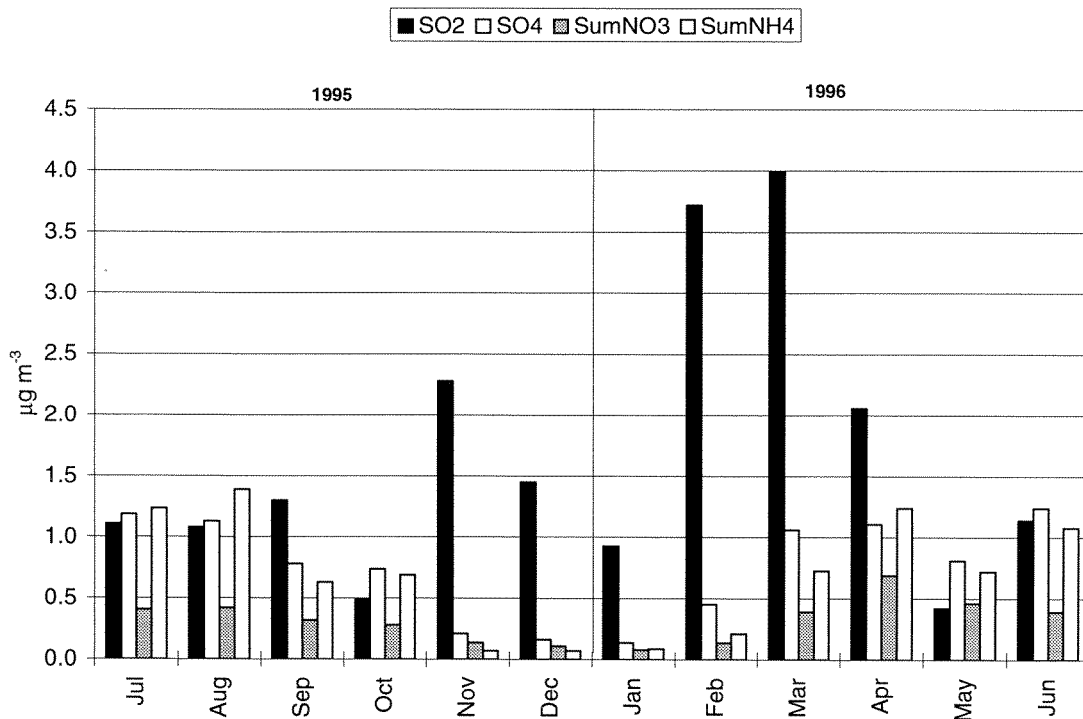


Figure 4. Air concentration of nitrogen and sulphur compounds ($\mu\text{g N or S m}^{-3}$) from July 1995 to June 1996. $\text{SumNO}_3 = \Sigma\text{HNO}_3 + \text{NO}_3$, where 50% is assumed being NO_3 , 50% HNO_3 . $\text{SumNH}_4 = \Sigma\text{NH}_4 + \text{NH}_3$, where 50% is assumed being NH_4 , 50% NH_3 . Data are from the meteorological station Kasprowy Wierch about 2000 m.a.s.l..

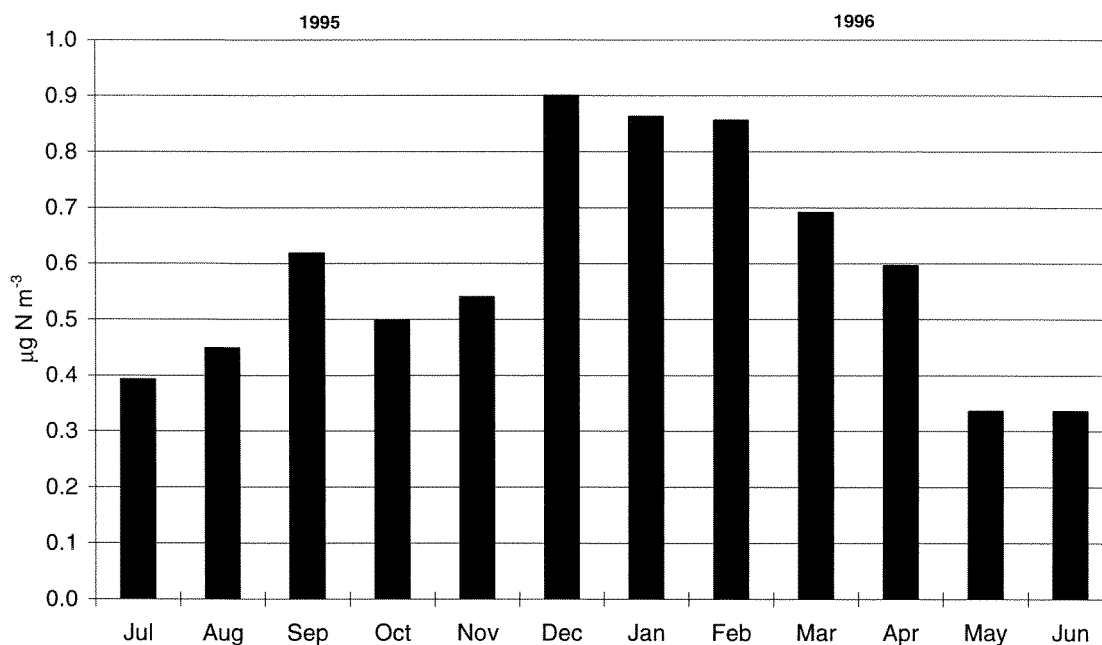


Figure 5. Concentration of NO₂ in air (µg m⁻³) from July 1995 to June 1996. The diffusive (passive) sampler for nitrogen dioxide was situated in Hala Gasienicowa, the same site where wet-deposition measurements were conducted.

The mean value for the whole period for SO₂-gas (1.66 µg S m⁻³) is 5-6 times higher than at the Norwegian station Birkenes in 1995, and 15% higher than at the EMEP site Chopok in Slovakia for 1994 (Table II). For SO₄-particles, the concentration was slightly higher at Chopok, while Birkenes was 23% lower. The concentration of the ΣNO₃ + HNO₃ was very similar at Kasprowy Wierch compared with both Birkenes and Chopok, while the concentration of ΣNH₄ + NH₃ was 26% higher at Kasprowy Wierch than at Birkenes. For NO₂-gas, the concentration was somewhat lower compared with at Birkenes, and less than half (56%) the concentration at Chopok.

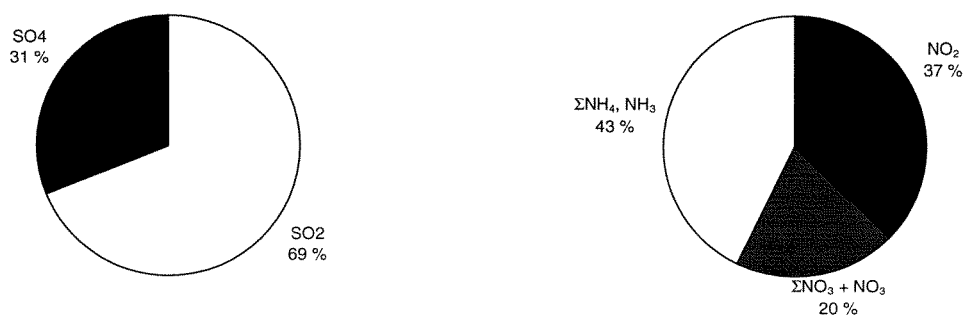


Figure 6. The percent contribution of different compounds of N and S in air, based on their annual mean concentrations.

Table II. Annual mean \pm SD and median value of dry-deposition compounds at the meteorological station Hala Gasienicowa and Kasprowy Wierch (NO_2), and annual mean values at Birkenes, Norway and Chopok, Slovakia.

Site	$\mu\text{g S m}^{-3}$		$\mu\text{g N m}^{-3}$				
	SO_2	SO_4	NO_2	NO_3	HNO_3	NH_3	NH_4
Hala, 95/96							
<i>Mean</i>	1.66	0.75	0.59	0.16	0.16	0.34	0.34
<i>SD</i>	1.16	0.42	0.20	0.09	0.09	0.24	0.24
<i>Median</i>	1.22	0.80	0.57	0.18	0.18	0.35	0.35
Birkenes, 95	0.31	0.58	0.68	0.23	0.08	0.04	0.50
Chopok, 94	3.06	1.03	1.54	0.18	0.18		
Chopok, 93	1.43	0.80	1.53	0.15	0.15		

Dry-deposition fluxes

Dry deposition fluxes is estimated on the basis of the deposition velocities (cm sec^{-1}) presented in Table III.

Due to the lower deposition velocity of gases like SO_2 and NO_2 , they play a less important role for fluxes of N and S compared with their concentrations. While SO_2 -gas on average constituted 69% of the concentration of sulphur in dry deposition, it constitutes 57% of the annual inputs of sulphur. Accordingly, while NO_2 gas constituted 37% of dry-N based on annual concentration averages, it only constitutes 15% of the annual deposition of nitrogen in dry-deposition. In addition to NO_2 , HNO_3 , NH_3 , NH_4 and NO_3 constitute 39%, 20%, 19% and 8% of the total annual dry-depositions of N in 1995/96.

Due to the far higher dry-deposition velocities during the summer period (May-September), the highest depositions of all S- and N-compounds occur within the summer season. For the year 1995/96, total dry-deposition inputs of S- and N-compounds were $213 \text{ mg S m}^{-2} \text{ yr}^{-1}$ and $261 \text{ mg N m}^{-2} \text{ yr}^{-1}$ (Table IV).

Table III. The applied dry-deposition velocities (cm sec^{-1}) of nitrogen and sulphur compounds during summer (May-September) and winter (October-April). In Norway, dry-deposition in April is normally calculated on the basis of "summer" dry-deposition velocities, but because the Polish sites are located at high altitude and have snow even in April, "winter" dry-deposition velocities are used even for April.

	SO_2	SO_4^{2-}	NO_2	NO_3^-	HNO_3	NH_3	NH_4^+
Summer	0.7	0.6	0.5	0.6	2.5	0.7	0.6
Winter	0.1	0.2	0.1	0.2	1.5	0.1	0.2

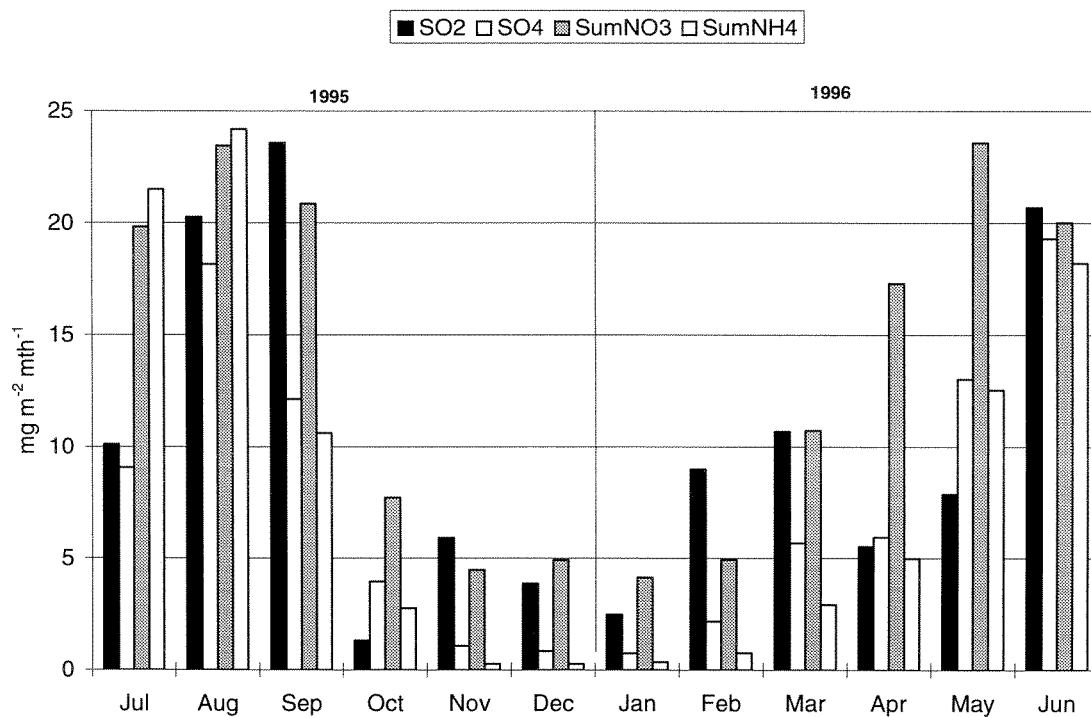


Figure 7. Monthly fluxes of dry-deposition compounds of nitrogen and sulphur ($\text{mg N or S m}^{-2} \text{mth}^{-1}$) from July 1995 to June 1996. Data are from the meteorological station Kasprowy Wierch.

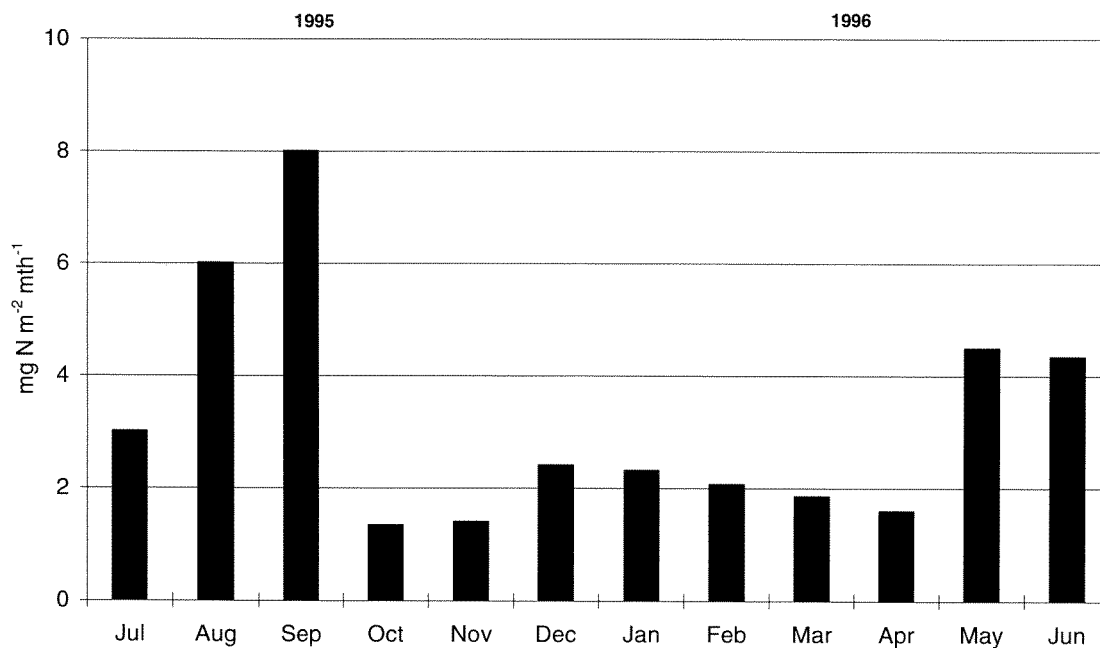


Figure 8. Estimated dry-deposition of NO_2 -gas ($\text{mg N m}^{-2} \text{mth}^{-1}$) from July 1995 to June 1996. The diffusive (passive) sampler for nitrogen dioxide was located at Hala Gasienicowa.

Table IV. Annual inputs (July 1 1995 - June 30, 1996) of dry-deposition compounds ($\text{mg N or S m}^{-2} \text{ yr}^{-1}$), based on data from the weather-station Hala Gasienicowa and Kasprowy Wierch (NO_2).

SO_2	SO_4	NO_2	NO_3	HNO_3	NH_4	NH_3	$\Sigma\text{Sulphur}$	$\Sigma\text{Nitrogen}$
121	92	39	21	102	48	51	213	261

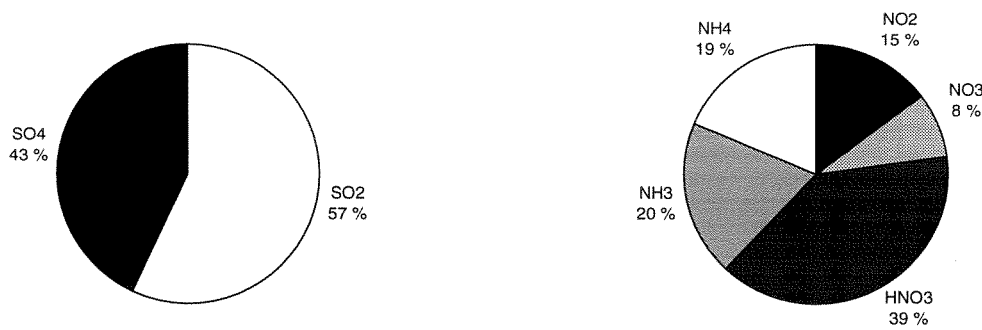


Figure 9. The distribution (%) of dry-deposition compounds of N and S, based on their total annual inputs.

3.2.2 Precipitation chemistry

The yearly mean concentrations of major cations and anions in precipitation are present in Table V. On equivalent basis the concentrations of S and N in wet-deposition is almost equal at Hala Gasienicowa, i.e. S/N ratio of 1.06 ± 0.10 (annual average for the period September 1992 to June 1996). The annual mean concentration of SO_4^{2-} , NO_3^- and NH_4^+ at Hala Gasienicowa is lower than at the nearest EMEP sites: Chopok, Stara Lesna and Liesek in Slovakia. Compared with Birkenes, Southern Norway, the concentration of SO_4^{2-} in wet-deposition at Hala Gasienicowa is higher, while NO_3^- is lower. The concentration of NH_4^+ is about the same as at Birkenes, except in 1994 where the concentration was much lower than at Birkenes (Table V). The pH in precipitation is very similar at Birkenes and Hala Gasienicowa, while the concentrations of primarily terrestrial derived base cations (Ca^{2+} and K^+) are far higher at Hala Gasienicowa. On the other hand, since Birkenes is located much closer to the sea compared with Hala Gasienicowa, the concentration of typically marine derived basecations (Na^+ and Mg^{2+}) are much higher at Birkenes. Birkenes normally receive higher total amounts of basecations, primarily as neutral salts. Accordingly, Birkenes exhibit larger variations in base cation inputs, due to frequent seasalt events.

The concentration of N and S in precipitation were usually highest in the spring months, but also in October 1995 the concentrations were high (Figure 10), but during this particular month the amount of precipitation was extremely low (Figure 11).

Table V. Annual weighted mean concentration of major cations and anions in precipitation at Hala Gasienicowa, Poland and Birkenes, Southern Norway.

Station	Year	pH -log[H ⁺]	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	mg L ⁻¹			
							NH ₄ ⁺ -N	SO ₄ ²⁻ -S	NO ₃ ⁻ -N	Cl ⁻
Hala G.	1993	4.35	0.34	0.05	0.19	0.40	0.52	1.21	0.44	0.60
	1994	4.52	0.35	0.05	0.17	0.13	0.39	0.92	0.33	0.31
	1995	4.57	0.42	0.04	0.24	0.84	0.43	0.82	0.32	1.02
Birkenes	1993	4.37	0.15	0.23	1.98	0.12	0.51	0.92	0.55	3.62
	1994	4.48	0.15	0.12	0.92	0.06	0.51	0.69	0.55	1.69
	1995	4.47	0.09	0.14	1.21	0.08	0.42	0.61	0.48	2.06
	Year	H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	μeq L ⁻¹			
Hala G.	1993	45	17	4	8	10	37	76	32	16
	1994	30	17	4	7	3	28	57	24	9
	1995	27	21	4	11	21	31	51	23	29
Birkenes	1993	43	7	19	86	3	36	59	39	102
	1994	33	7	10	40	2	36	44	39	48
	1995	34	5	12	53	2	30	39	35	58

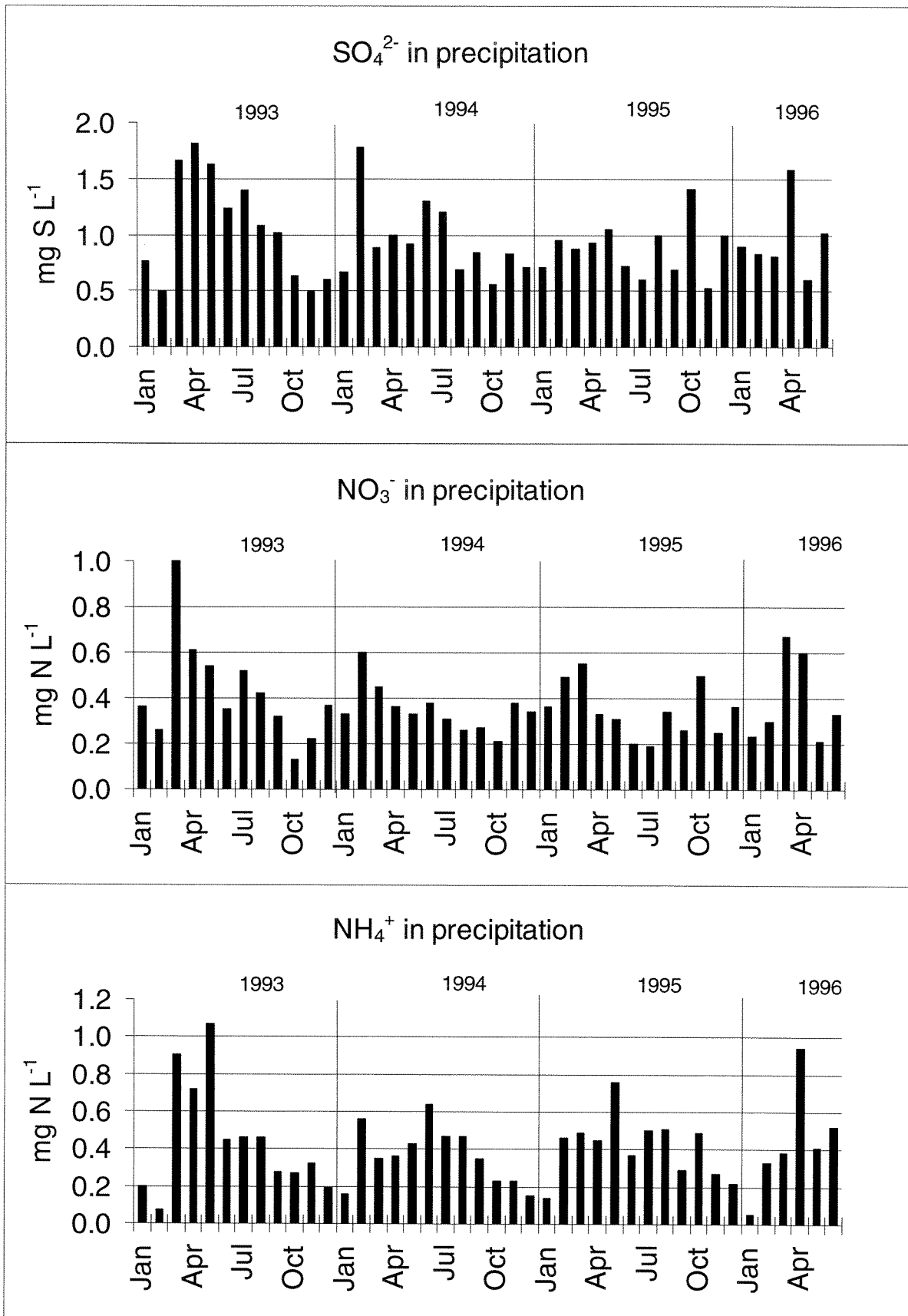


Figure 10. Monthly weighted concentrations of SO₄²⁻, NO₃⁻, and NH₄⁺ in wet-deposition (precipitation) at the meteorological station Hala Gasienicowa.

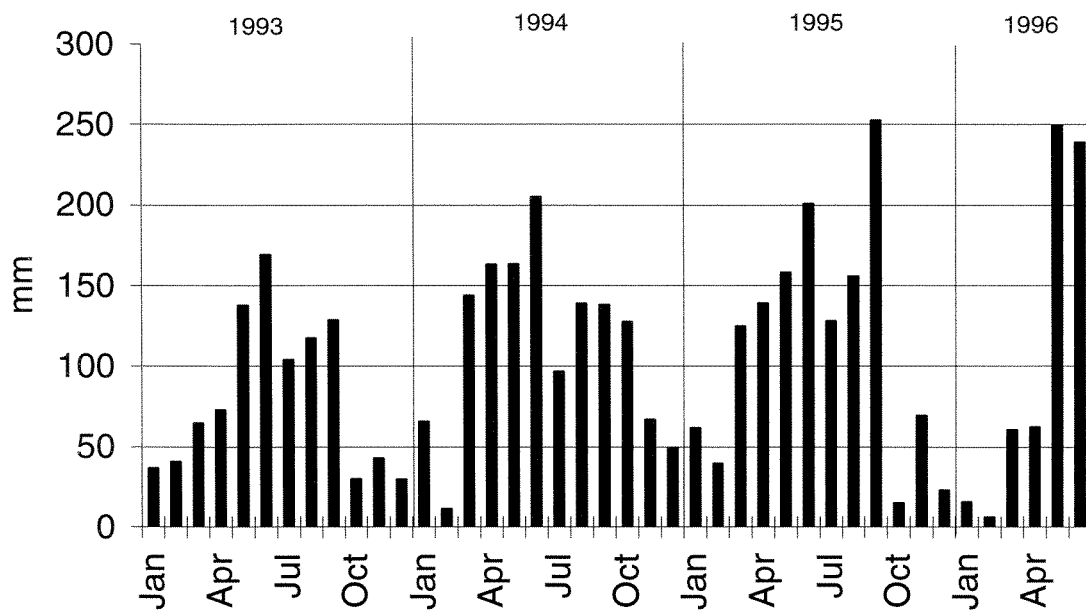


Figure 11. Monthly amounts of precipitation at the meteorological station Hala Gasienicowa.

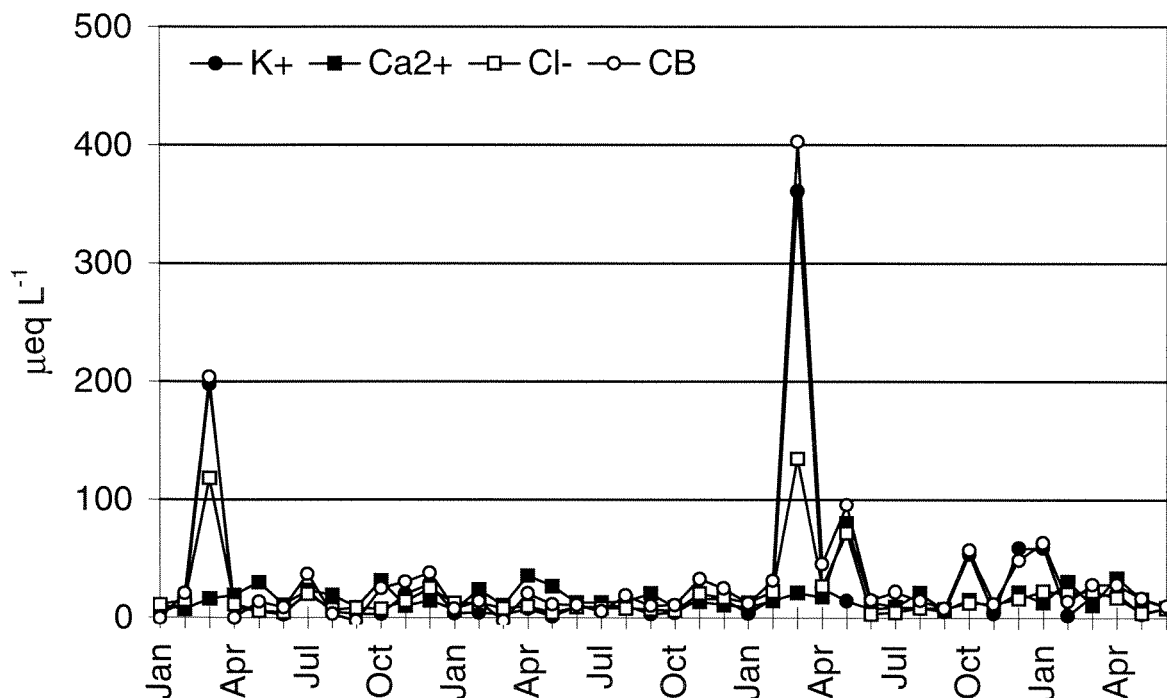


Figure 12. Concentration of K⁺, Ca²⁺, Cl⁻ and charge balance (CB : ΣCations - ΣAnions) at the meteorological station Hala Gasienicowa during the period January 1993 - June 1996.

During the monitoring period, 3 months exhibited extreme imbalance between cations and anions (Figure 12), i.e. in March 1993 and 1995, and in May 1995. Excess of cations during these months were 203, 403 and 95 $\mu\text{eq L}^{-1}$, respectively. Median charge balance during the whole monitoring period was (CB; $\Sigma\text{Cations} - \Sigma\text{Anions}$) 16 $\mu\text{eq L}^{-1}$. This confirms the extreme imbalances or excess of cations during these 3 months. During the same 3 months, the Cl^{-} -concentration was also extremely high (Figure 12), while SO_4^{2-} was relatively high only in March 1993 (Figure 10). Because pH was relatively low during the same months, 4.11, 4.43 and 4.84, acid buffering or acid neutralising anions as HCO_3^{-} , OH^{-} and SiO_4^{4-} , can not be the actual counter ions for these cation excess. Other actual anions might be PO_4^{3-} , F^{-} and organic acid anions, but those compounds have never been measured. There are no acidifying step prior to the analysis of base cations, which could have been an reasonable analytical reason. It still might be analytical explanations, but so far we have not revealed such. The amounts of precipitation during the 3 months were relatively high, i.e. 64.4, 125 and 158 mm, so it is neither an effect of minor precipitation inputs. All together, we believe that this imbalance is a result of high inputs of base cation particles with one or several unknown counterions. Unfortunately, we have no data to support this argument, but based on information from our collaborating scientists in Poland, these events are always connected with southern winds (SSW, SSE), i.e. from Slovakia. Thus, these episodes may reflect impacts from special industrial point source (s) in Slovakia. The chemical composition of this (or these) emission(s) should therefore easily be revealed.

Wet-deposition fluxes

Due to the higher precipitation amounts at Hala Gasienicowa compared with at Stara Lesna and Liesek, wet-deposition fluxes of compounds were generally higher at Hala Gasienicowa, but the fluxes were generally lower compared with at Chopok. One exception is a somewhat higher NO_3^{-} -deposition in 1994 at Hala Gasienicowa, which might be because Hala Gasienicowa received about 30% more precipitation than Chopok this year. Annual precipitation at Hala Gasienicowa in 1993, 1994 and 1995 were 973, 1369, and 1368 mm respectively, while the deposition of S varied from 1.12 to 1.26 $\text{g m}^{-2} \text{yr}^{-1}$ (Table VI). Annual precipitation at Birkenes was 1245 mm (1993), 1397 (1994) and 1411 mm (1995), and the annual depositions of S varied from 0.74 to 0.96 $\text{g m}^{-2} \text{yr}^{-1}$. Regarding wet-deposition of N-compounds (ΣNO_3 , NH_4), Hala Gasienicowa annually received from 0.94 to 1.03 $\text{g N m}^{-2} \text{yr}^{-1}$ during 1993-1995, while at Birkenes 1.27 to 1.48 $\text{g N m}^{-2} \text{yr}^{-1}$. Thus, while the amount of precipitation and inputs of N-compounds are slightly higher at Birkenes, the inputs of sulphur at Birkenes is somewhat lower compared with at Hala Gasienicowa. The inputs of H^{+} -ions are also very similar at both sites. Since the amounts of precipitation is relatively similar at both sites, the comparison of basecations between the two sites gives the same conclusion as for the concentration comparisons, i.e. higher inputs of terrestrial derived compounds (Ca^{2+} , K^{+}) at Hala Gasienicowa, while higher inputs of typically more marine base cations (Na^{+} and Mg^{2+}) at Birkenes.

As expected, highest wet-deposition fluxes at Hala Gasienicowa occur as a direct result of large precipitation amounts (compare Figure 11 and Figure 13).

Table VI. Annual inputs of water (mm) and major cations and anions ($\text{g m}^{-2} \text{yr}^{-1}$) in precipitation at Hala Gasienicowa, Poland and Birkenes, Southern Norway. H^{+} is in $\text{meq m}^{-2} \text{yr}^{-1}$.

Station	Year	mm	H^{+}	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	$\text{NH}_4^{+}\text{-N}$	$\text{SO}_4^{2-}\text{-S}$	$\text{NO}_3^{-}\text{-N}$	Cl^{-}
Hala	1993	973	44	0.33	0.05	0.19	0.39	0.51	1.18	0.43	0.58
	1994	1369	42	0.47	0.07	0.23	0.18	0.54	1.26	0.46	0.43
	1995	1368	37	0.57	0.06	0.34	1.15	0.59	1.12	0.44	1.39
Birkenes	1993	1245	54	0.18	0.29	2.47	0.15	0.63	0.96	0.68	4.51
	1994	1397	46	0.21	0.16	1.29	0.08	0.71	0.89	0.77	2.36
	1995	1411	47	0.13	0.20	1.71	0.11	0.59	0.74	0.68	2.91

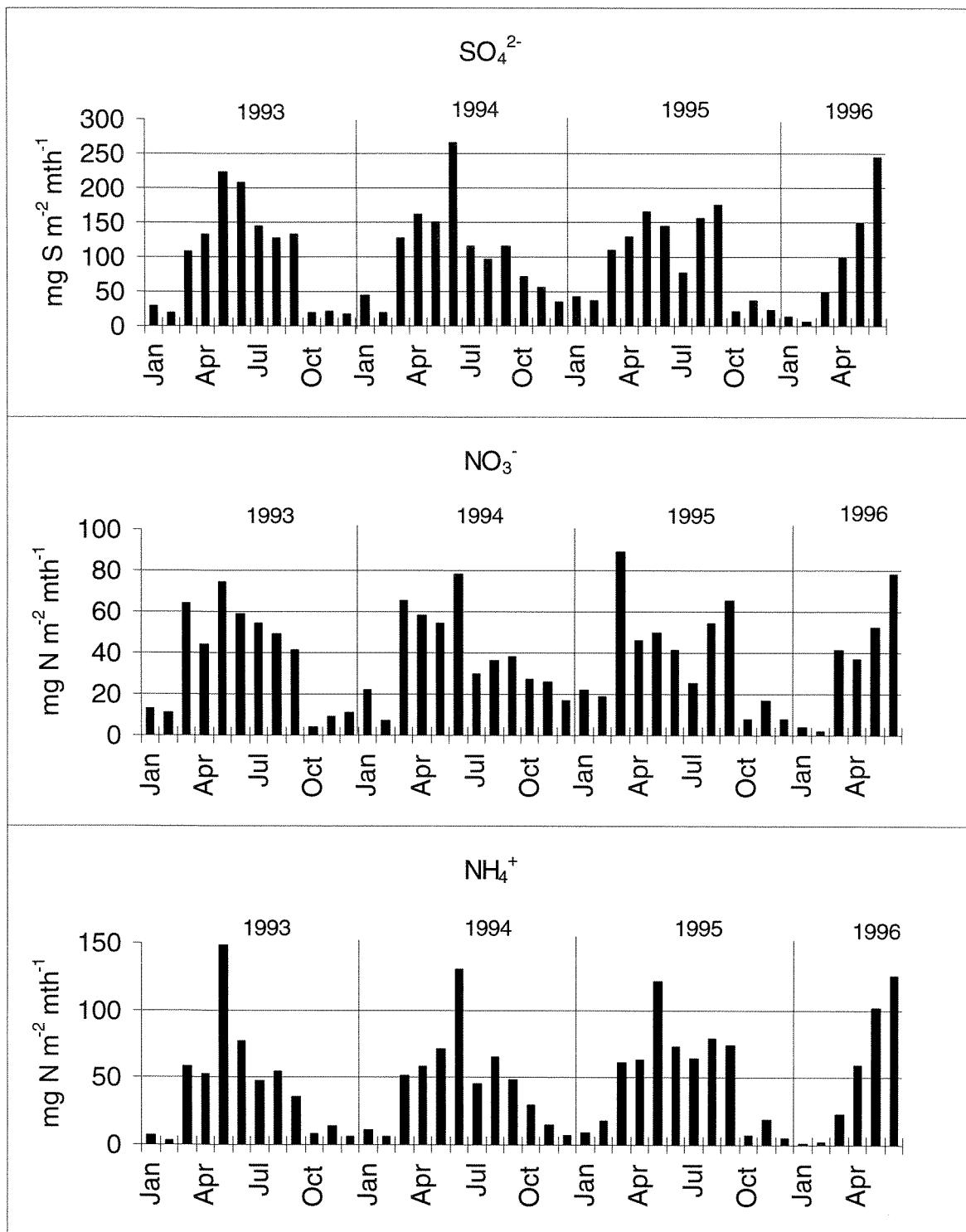


Figure 13. Monthly inputs of SO_4^{2-} , NO_3^- , and NH_4^+ by wet-deposition (precipitation) at the weather-station Hala Gasienicowa.

3.2.3 Runoff

Annual weighted mean concentrations of major chemical compounds in Dlugi Staw and Zielony Staw are presented in Table VII and VIII. As also commented on in earlier reports, concentrations of basecations and thereby alkalinity, are higher in runoff water from Zielony Staw compared with Dlugi Staw (Figure 14). The SO_4^{2-} -concentrations are similar, mirroring similar deposition of sulphur at the two sites as well as sulphate acts as a conservative ion, i.e. input \approx output (Table IX). The NO_3^- -concentration is normally significantly higher in the runoff from Dlugi Staw compared with Zielony Staw.

As shown in Figure 15, Zielony often exhibit water chemical changes due to snow melt earlier at spring compared with Dlugi Staw. This can be illustrated by ANC, which was at its lowest during springmelt at Zielony, May 4 (1994), May 2 (1995), May 4 (1996). The corresponding ANC extremes at Dlugi Staw occurred May 22 (1994), May 16 (1995) and May 14 (1996). The fact that spring melt seems to occur somewhat earlier at Zielony Staw may be because Zielony Staw is located at a latitude about 112 m lower than Dlugi Staw.

During spring 1996, an extreme water chemical episode occurred early April, with ANC of $-10 \mu\text{eq L}^{-1}$ at Dlugi Staw and as low as $-28 \mu\text{eq L}^{-1}$ at Zielony. Due to difficult sampling conditions, the sample at Zielony Staw was taken at the outlet. Accordingly this sample was highly dominated by melt water passing through the lake as a uppermost surface layer. This occurs because melt water has a temperature near 0°C and thereby lower density than the "original" lake water which normally at that time has temperatures about $3\text{-}4^\circ\text{C}$ relatively close to the surface.

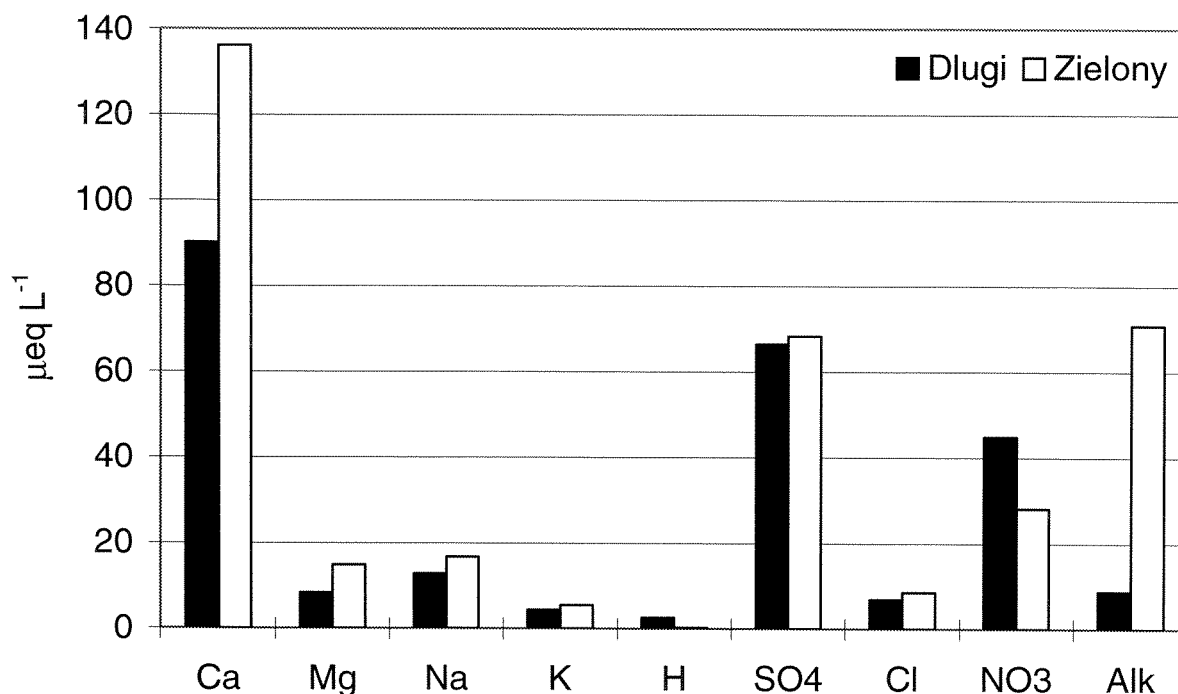


Figure 14. Weighted mean concentrations of major chemical compounds in Dlugi Staw and Zielony Staw during 1994 and 1995.

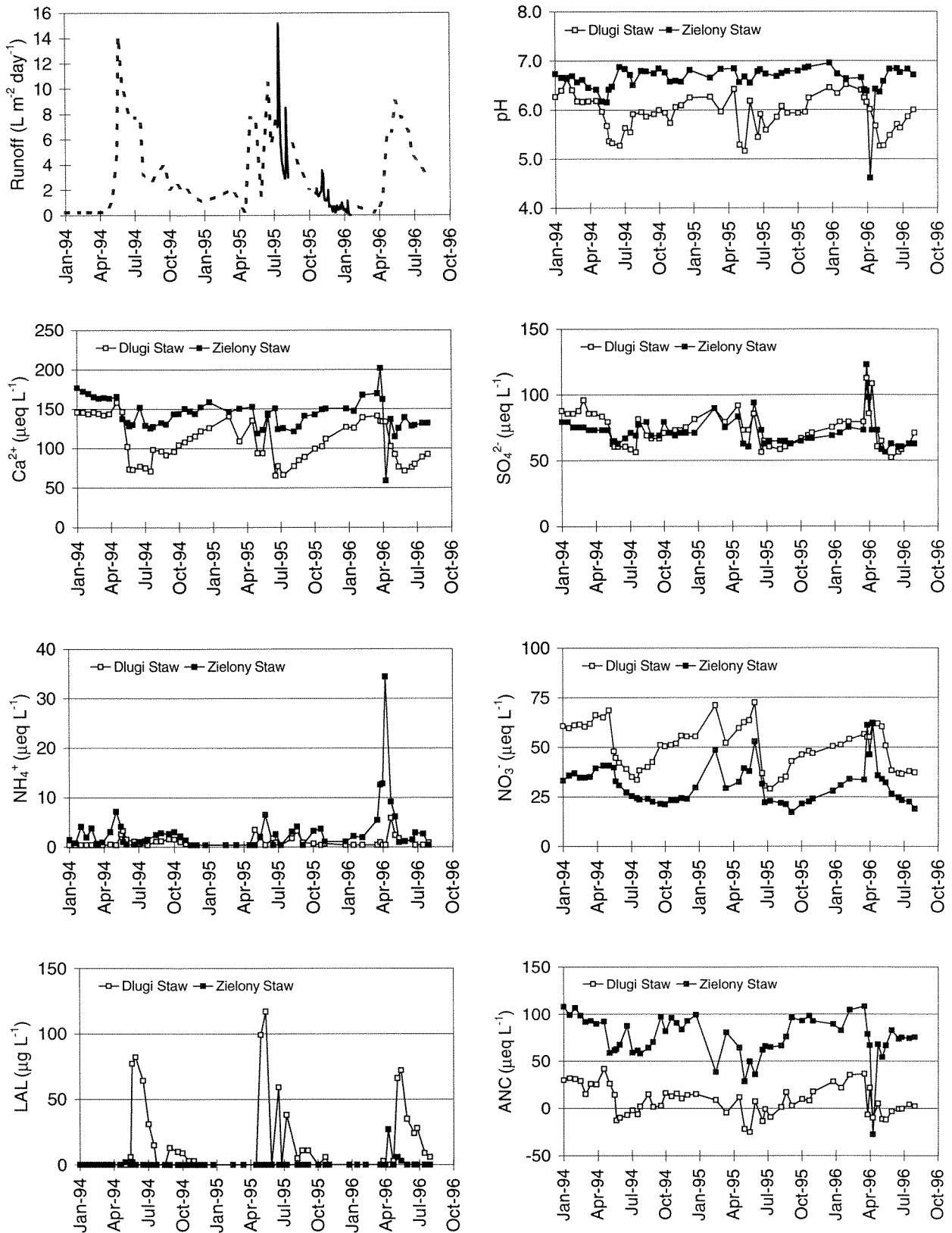


Figure 15. Runoff and major chemical parameters in lake water from Dlugi Staw and Zielony Staw. Runoff: ---- : calculated values; — : measured values. LAL: labile aluminium, primarily representing inorganic low molecular weight Al-forms; ANC: Acid neutralising capacity.

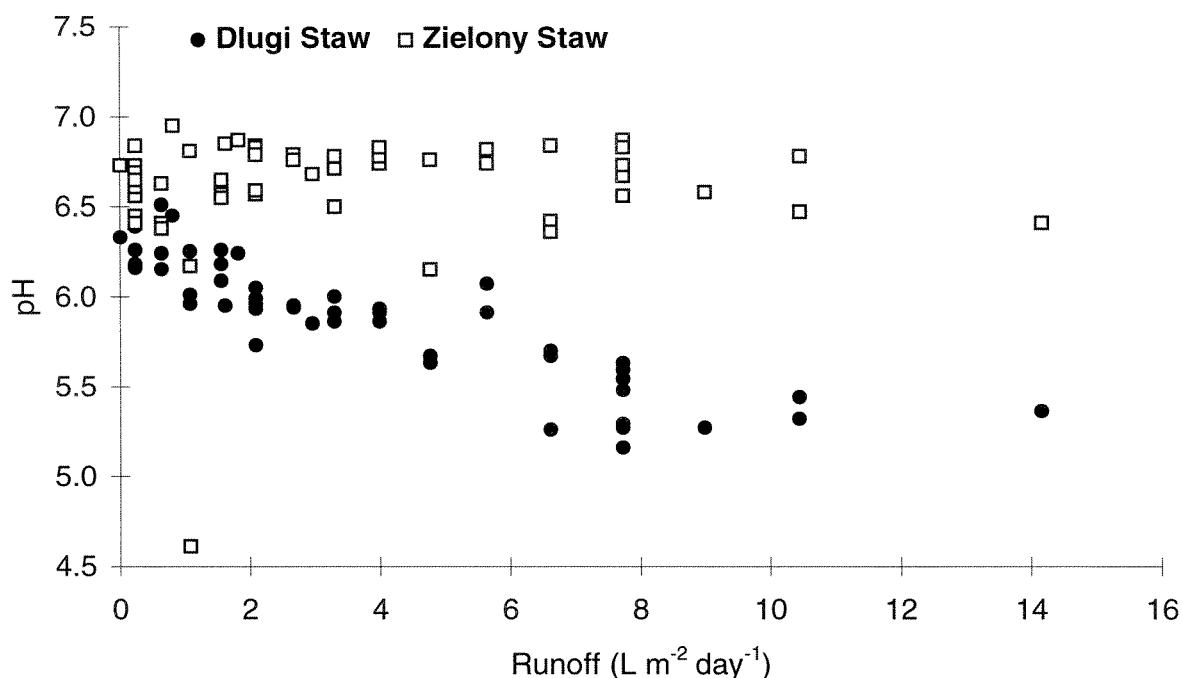


Figure 16. The relationship between pH and runoff at Dlugi Staw and Zielony Staw.

In addition to latitude differences, the Dlugi Staw catchment has less vegetation cover and steeper surroundings. All together this results in shorter contact time of water within the Dlugi Staw catchment, in other words, less time for physico-chemical water-catchment interactions. This is reflected in the water chemistry by lower ANC, lower base cation concentrations and alkalinity (Table VII and VIII). Another factor for this differences are geological differences. As present in Table I, both catchments contain granitoids, covered by moraine, but the Zielony Staw catchment also contain areas with limestone. This may also be of great importance for the higher pH buffering capacity of this catchment. The better pH-buffering capacity at Zielony Staw compared with Dlugi Staw is illustrated in Figure 16.

For the biology, shorter residence time of water within the catchment, means less time or reduced possibility for nutrients like nitrogen compounds to be assimilated by plants and micro-organisms. Less vegetation cover will further amplify this effect. This is the probably the major factors for the generally higher leakage of NO_3^- by runoff from Dlugi Staw compared with Zielony Staw.

Severe water chemical conditions do primarily occur during spring melt, normally with a somewhat higher concentration of most ions during the initial spring melt, followed by a dilution of most ions as runoff increases. At high flow only $[\text{H}^+]$ seems to increase (pH-lowering), which means that the concentration of base cations decreases more than the decrease in strong acid anions. The concentration of weak acid anions is very low in the two watersheds and therefore of minor importance for the water pH. Runoff during an initial hydrological high-flow period is often "old water" which has been kept in the catchment for a relatively long time, and pressed out by the very new water entering the catchment by the last rain or by snow that melts. This effect is often called the piston-effect, a phenomenon which is earlier described by several authors (e.g. Johannessen *et al.*, 1980). This effect explains why higher concentrations of most ions occur during the initial melting period. However, this piston effect occur only for a short time period.

Table VII. Annual weighted means, maximum and minimum concentrations of major cations and anions in Dlugi Staw and Zielony Staw during January 1994 to June 1996.

Station	Year	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺ -N	SO ₄ ²⁻ -S	NO ₃ ⁻ -N	Cl ⁻	Alk
		-log[H ⁺]	mg L ⁻¹								
Dlugi Staw	1994	5.56	1.79	0.09	0.31	0.13	0.018	1.04	0.62	0.23	
	1995	5.61	1.82	0.11	0.28	0.13	0.021	1.08	0.64	0.26	
	<i>max</i>	6.64	3.17	0.17	0.50	0.23	0.082	1.80	1.02	0.40	
<i>min</i>	5.16	1.31	0.04	0.17	0.10	< 0.005	0.83	0.41	0.10		
Zielony Staw	1994	6.59	2.75	0.17	0.41	0.16	0.020	1.10	0.38	0.21	
	1995	6.72	2.71	0.19	0.36	0.17	0.020	1.08	0.40	0.39	
	<i>max</i>	6.96	4.04	0.30	0.66	0.36	0.481	1.97	0.87	0.90	
<i>min</i>	4.61	1.18	0.11	0.26	0.14	< 0.005	0.90	0.24	0.20		
	Year	H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺ -N	SO ₄ ²⁻ -S	NO ₃ ⁻ -N	Cl ⁻	Alk
		μeq L ⁻¹									
Dlugi Staw	1994	2.78	89.4	7.8	13.7	4.5	1.2	65.3	44.0	6.4	8.9
	1995	2.47	90.8	8.8	12.1	4.3	1.3	67.5	45.8	7.4	8.8
	<i>max</i>	6.92	158	14.0	21.8	7.6	5.9	113	72.5	11.3	32.8
<i>min</i>	0.23	65.4	3.3	7.4	3.3	< 0.4	52.1	28.9	2.8	-0.3	
Zielony Staw	1994	0.26	137	14.0	18.0	5.4	1.4	69.0	27.4	6.0	72.2
	1995	0.19	135	15.7	15.6	5.7	1.4	67.7	28.9	11.0	69.5
	<i>max</i>	24.5	202	24.7	28.7	12.0	34.4	123	62.1	25.4	97.8
<i>min</i>	0.11	58.9	9.1	11.3	4.7	< 0.4	56.3	17.1	5.6	7.9	

Table VIII. Annual weighted means, maximum and minimum values of important chemical parameters in Dlugi Staw and Zielony Staw during January 1994 to June 1996. BC = ΣBase cations; CB = Charge balance.

	Year	RAL	ILAL	LAL	Si	BC	ANC	ΣCations	ΣAnions	CB
		μg L ⁻¹		mg SiO ₂ L ⁻¹		μeq L ⁻¹				
Dlugi Staw	1994	43	10	33	1.71	122	0.8	123	125	-2
	1995	45	10	35	1.78	133	-3.3	124	129	-5
	<i>max</i>	127	10	117	2.70	198	41.8	199	210	14
<i>min</i>	< 10	< 10	0	1.10	83.3	-25.0	92	99	-37	
Zielony Staw	1994	10	10	0	1.65	185	73.6	176	175	1
	1995	10	10	0	1.65	198	66.3	174	177	-3
	<i>max</i>	37	10	27	2.10	267	108	280	299	23
<i>min</i>	< 10	< 10	0	0.40	87.1	-28.0	149	156	-19	

The pH, LAL (labile aluminium) and ANC are key chemical parameter describing water toxicity. According to these parameters, the most severe chemical episode at Dlugi Staw occurred May 16 1995, with pH, ANC and LAL at 5.16, -25.1 μeq L⁻¹ and 117 μg L⁻¹. Such water chemical conditions are today well known being harmful aquatic organisms like salmonids. How critical depends on factors as animal species, the life-history stage, adaptation etc. The most severe conditions at Zielony Staw was recorded April 9 1996, with pH as low as 4.61. Simultaneously ANC was -28 μeq L⁻¹ and LAL at 27 μg L⁻¹. Also these conditions should be harmful to most salmonids, and might therefore have caused problems for the brook trout population in the lake. On the other side, this water was primarily melt water (See earlier comments) which normally has a temperature ≈ 0°C, while the temperature of the upper lake water normally is somewhat higher. Accordingly, due to lower density of melt water, it will pass through the lake as a uppermost layer. Thus, there might be a large lake volume left with biological acceptable or good water quality where organisms as fish can move into. On the other side, the outlet streams might be totally dominated by melt water during such episodes,

which means that there are small changes for organisms in the streams to avoid such extreme chemistry.

The high flow period during autumn 1995, related to high precipitation inputs (highest in September, i.e. 252 mm), lead to a certain lowering in pH and ANC and a small increase in LAL at Dlugi Staw, while no severe chemical changes occurred at Zielony Staw. This may indicate that autumn episodes related to high precipitation inputs normally are less biological harmful episodes compared with episodes related to snow melt. The water chemistry measured during episodes during January 1, 1994 to June 30, 1996 are almost of the same order as earlier recorded during 1992 and 1993 (Wathne *et al.*, 1993), both at Dlugi Staw and Zielony Staw.

In the report by Wathne *et al.* (1993), a comparison was made between Tatra Mountain lakes and alpine lakes in southern Norway (830 - 1150 m.a.s.l.) with similar concentrations of calcium and sulphate. The water chemistry of the selected lakes were very similar for the two countries, except for the concentrations of NO_3^- and alkalinity. The NO_3^- -concentrations in the Tatra lakes were much higher than in Norway, and the alkalinity lower. As a consequence of the latter, the pH of the lakes are lower in the Tatra Mountain lakes (pH 5.49) compared with the Norwegian lakes (pH 6.62). Thus, the Tatra Lakes seem more acidified than the Norwegian lakes, and the difference is primarily because of higher nitrate concentrations in the Tatra Mountain lakes.

3.3 Fluxes of major chemical compounds

One major goal with last year survey was to assess the fluxes of chemical compounds, primarily N- and S-compounds within the Dlugi Staw and Zielony Staw catchments. Thus, in addition to the ongoing precipitation recording and analysis of chemical compounds in wet-deposition and runoff, runoff recording as well as dry-deposition measurements were conducted the last year (July 1995 - June 1996, named 95/96).

The annual inputs of S and N compounds in wet-deposition presented in Table VI. To account for the fact that the weather station are located at some distance from the lakes, we have multiplied the wet-deposition fluxes at Hala Gasienicowa with the factor 1.102 (Dlugi Staw) and 1.077 (Zielony Staw). These factors are based on recalculation of precipitation according to Hess (1968), described in more detail in Chapter 3.1.1. Effluxes or annual outputs from the lakes are calculated in accordance with the equation (I) presented in Chapter 2.3.

Annual inputs of S-compounds in dry-deposition ($\Sigma\text{SO}_4, \text{SO}_2$) was $0.213 \text{ g S m}^{-2} \text{ yr}^{-1}$, while inputs of oxidised ($\Sigma\text{NO}_3, \text{HNO}_3 + \text{NO}_2$) and reduced ($\Sigma\text{NH}_4, \text{NH}_3$) N-compounds by dry-deposition were $0.162 \text{ g N m}^{-2} \text{ yr}^{-1}$ and $0.099 \text{ g N m}^{-2} \text{ yr}^{-1}$, respectively. Dry-deposition of S- and N-compounds are assumed to be identical at the two sites.

Annual inputs of sulphur by wet-deposition were $1.155 \text{ g S m}^{-2} \text{ yr}^{-1}$ at Dlugi Staw and $1.129 \text{ g S m}^{-2} \text{ yr}^{-1}$ at Zielony Staw. This gives a total annual input (wet + dry) of $1.368 \text{ g S m}^{-2} \text{ yr}^{-1}$ at Dlugi Staw and $1.342 \text{ g S m}^{-2} \text{ yr}^{-1}$ at Zielony Staw during 1995/96 (Table IX).

Inputs of NO_3 and NH_4 by wet deposition were $0.431 \text{ g N m}^{-2} \text{ yr}^{-1}$ and $0.617 \text{ g N m}^{-2} \text{ yr}^{-1}$ at Dlugi Staw, and $0.421 \text{ g N m}^{-2} \text{ yr}^{-1}$ (as NO_3) and $0.603 \text{ g N m}^{-2} \text{ yr}^{-1}$ (as NH_4) at Zielony Staw. Thus, the total input (wet + dry) of N-compounds during 1995/96 was $1.1309 \text{ g N m}^{-2} \text{ yr}^{-1}$ at Dlugi Staw and $1.285 \text{ g N m}^{-2} \text{ yr}^{-1}$ at Zielony Staw (Table IX). About 84% of sulphur and 80% of nitrogen enters the catchments as wet-deposition.

Annual runoff of S- and N-compounds from Dlugi Staw were $1.224 \text{ g S m}^{-2} \text{ yr}^{-1}$ and $0.752 \text{ g N m}^{-2} \text{ yr}^{-1}$, while at Zielony Staw $1.269 \text{ g S m}^{-2} \text{ yr}^{-1}$ and $0.500 \text{ g N m}^{-2} \text{ yr}^{-1}$ (See Figure 17 and 18). Thus, the leakage of sulphur is 89.5% and 94.6% at Dlugi Staw and Zielony Staw, respectively. If sulphate is a fully conservative ion, the leakage should be 100 %. Reasons for a certain lower leakage might be due to at least three factors:

1) Runoff from the watersheds are largely dependant on: (a) Amount of precipitation; (b) Amount of water stored in the snow pack; (c) Amount of storage opportunity in the soil and thereby the amount of water stored in the soil at any time. (d) Evapotranspiration during summer.

The calendar year (January 1 to December 31) is therefore very seldom the best water-year. We have not enough data to confirm if the year July 1 - June 30 is ideal for annual flux estimates at Dlugi and Zielony Staw. The ideal water year is that successive 12-month period that most consistently, year after year, gives the highest correlation between precipitation and runoff.

2) Estimates of dry-deposition fluxes rely on the deposition velocity constants applied for the different gases and particles (Table III). The velocities depend on surface characteristics and are relatively uncertain. However, the relatively large amount of precipitation makes wet-deposition as predominant contributor to the total deposition. This further makes the dry-deposition estimates less crucial. There are also uncertainties in our estimation of precipitation at the two sites according to Hess (1968).

3) We have largely calculated runoff on the basis of Si-concentration in runoff, except for 5 recordings, were measured runoff data existed simultaneously with water samples.

For the year 1995/96, the leakage of N-compounds by runoff was 57% and 39% at Dlugi Staw and Zielony Staw, respectively. As earlier mentioned, the high leakage is probably a combination of several factors like i) The amount of N entering the catchments is too high for the total plant and microbial demand of this element; ii) The contact time of water within the catchment is too short for the nitrogen to be assimilated by plant and micro-organisms.

Table IX. Annual fluxes ($\text{g m}^{-2} \text{ yr}^{-1}$) of N- and S-compounds in Dlugi Staw and Zielony Staw catchments during 1995/96.

	Dlugi Staw		Zielony Staw	
	S	N	S	N
Input (wet-dry)	1.368	1.309	1.342	1.285
Output	1.224	0.752	1.269	0.500
Input-Output	0.144	0.557	0.073	0.785
Leakage (%)	89.5%	57.4%	94.6%	38.9%

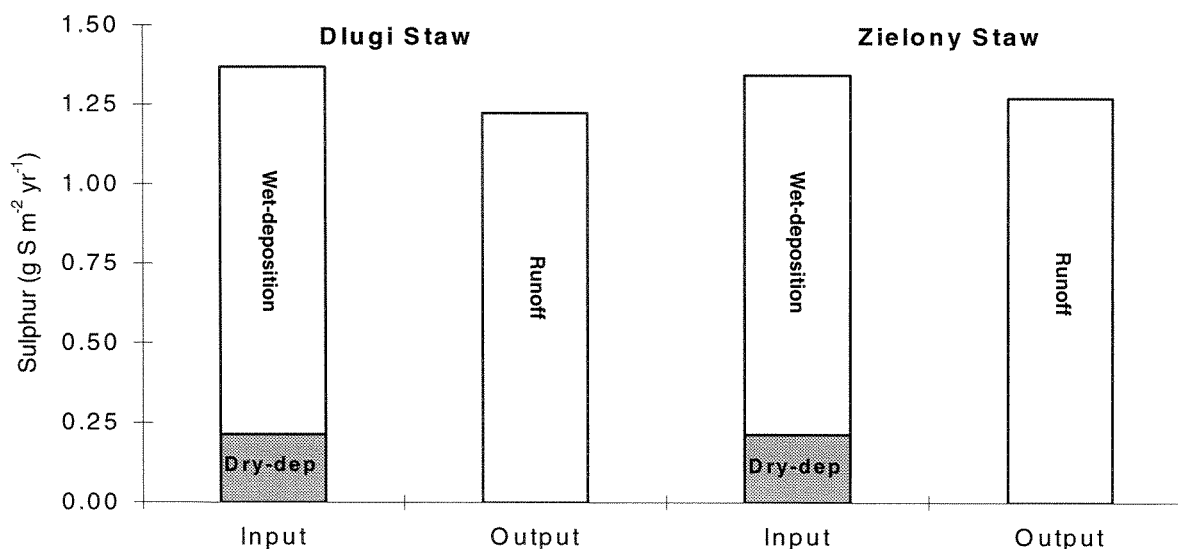


Figure 17. Annual input (wet- and dry deposition) and output (runoff) of inorganic sulphur ($\text{g S m}^{-2} \text{ yr}^{-1}$) at Dlugi Staw and Zielony Staw during the year July 1, 1995 to June 30, 1996.

The most exiting with the flux calculations, is the higher effluxes of oxidised nitrogen compounds (NO_3^-) compared with influxes ($\Sigma\text{NO}_3, \text{HNO}_3, \text{NO}_2$) at Dlugi Staw (Figure 18, Table X). This is earlier reported by Rzychon and Worsztynowicz (1995). They further claimed that Dlugi Staw belongs to the 3rd Stage of nitrogen saturation, based on the N-saturation status index given by Stoddard (1994). At this stage, no sinks exist in the watershed and all inputs, as well as mineralised nitrogen, are lost from the system, either through denitrification or by runoff. Mineralisation and oxidation of inorganic NH_4^+ to NO_3^- supplies nitrogen in a such degree that NO_3^- -concentration may exceed those in deposition. Stoddard (1994) also characterised watersheds in Stage 3 as net source of N rather than a sink. By this criteria Dlugi Staw is not at Stage 3, since the total influx of nitrogen at Dlugi Staw, is still much higher than the total efflux (Figure 18). Typically seasonal NO_3^- pattern at Stage 3 are runoff concentrations at all seasons in excess of concentration attributable to deposition and evapotranspiration. Based on this criteria, Dlugi Staw belongs to Stage 3, even though, dry-deposition is excluded (Figure 19). Zielony is earlier reported being in stage 2 (Rzychon and Worsztynowicz, 1995), but long periods of the year, the NO_3^- concentration in runoff is higher than in wet-deposition even here. However, the runoff water from both sites still show seasonal changes, with lowest concentrations during the primary production period (Figure 15).

In runoff water from both lakes the NH_4^+ -concentration is normally very low, even though NH_4^+ is the major N-compound in deposition. This is normal, since NH_4^+ in surface waters are rarely elevated at any seasons because of soil cation exchange, low mobility, and competition among vegetation, mycorrhizal roots, and nitrifiers, all contributing to watershed NH_4^+ retention. High $[\text{NH}_4^+]$ always occur in relation to early stage of high flow periods, primarily during snow melt (Figure 15).

On average, 92.8% of the H^+ from wet-deposition in 1995/96 was neutralised/buffered by biogeochemical processes within the watershed of Dlugi Staw, while 98.5% at Zielony Staw. Higher acid neutralising capacity (ANC) at Zielony is due to longer water residence time and to a certain degree due to slightly better geological conditions. This is well illustrated by the 1.75 times higher annual flux of geological derived base cations in runoff from Zielony Staw (Table X).

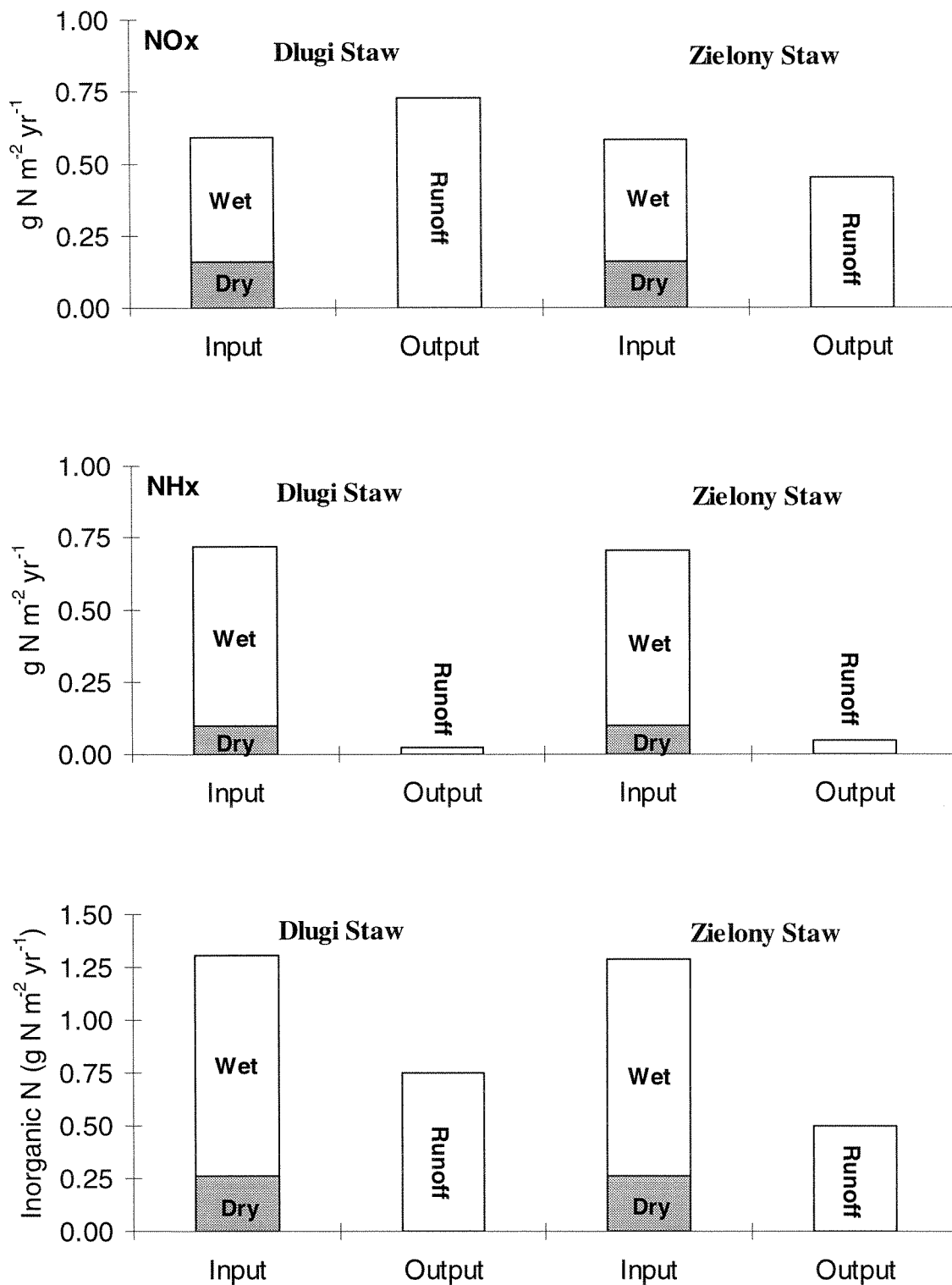


Figure 18. Annual input (wet- and dry deposition) and output (runoff) of reduced inorganic N-compounds (NHx), oxidised inorganic compounds (NOx), total inorganic N ($\Sigma\text{NHx,NOx}$) at Dlugi Staw and Zielony Staw during the year July 1, 1995 to June 30, 1996.

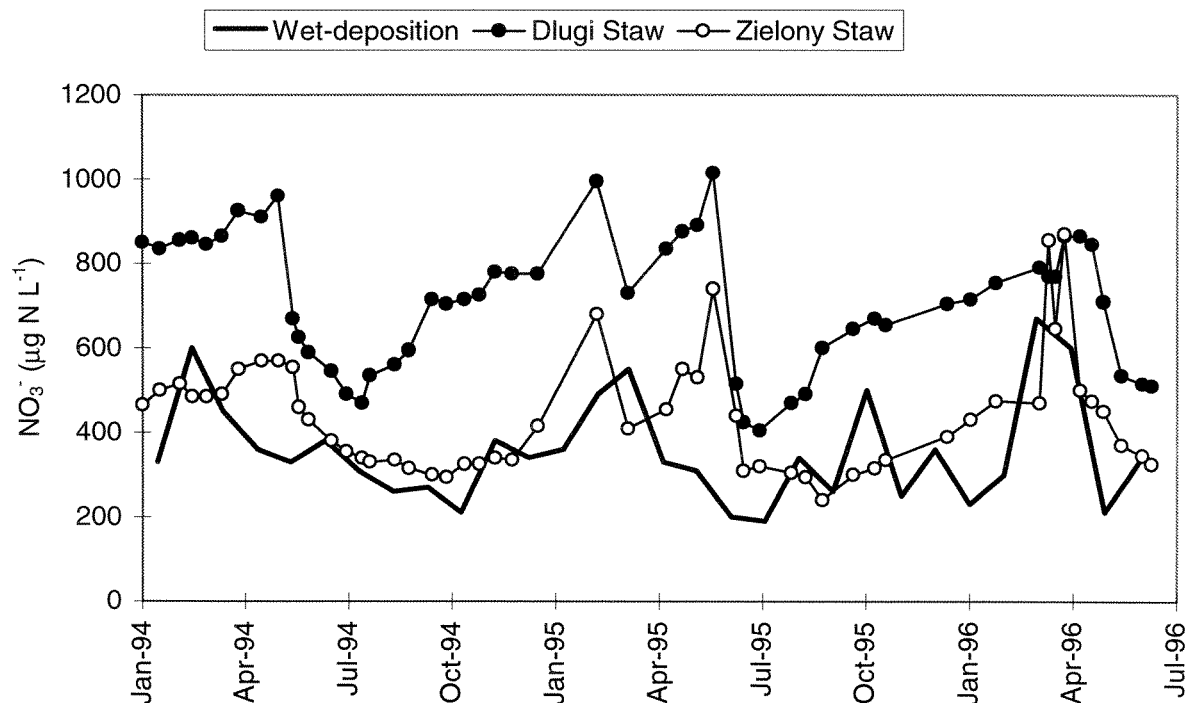


Figure 19. Concentration of NO_3^- in wet-deposition and in Dlugi Staw and Zielony Staw during January 1994 to June 1996.

Table X. Annual fluxes ($\text{meq m}^{-2} \text{ yr}^{-1}$) of chemical compounds at Dlugi Staw and Zielony Staw during 1995/96. a: Wet-deposition only; b: Aluminium is estimated as Al^{3+} , which is an overestimation of this elements on equivalent basis; c: Both wet and dry, i.e. all inputs of sulphur is calculated as SO_4^{2-} , all NH_x as NH_4^+ , and all NO_x as NO_3^- . BC = Base cations ($\Sigma\text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{K}^+$).

		a	a	b	c	c	c	a
		H^+	BC	Al^{3+}	NH_4^+	SO_4^{2-}	NO_3^-	Cl ⁻
Dlugi	Input	40.0	35.5		51.2	85.5	42.4	12.1
	Output	2.9	135	3.5	1.8	76.5	51.9	7.7
	Net	37.1	-99.5	-3.5	49.4	9.0	-9.5	4.4
Zielony	Input	39.1	34.7		50.2	83.9	41.7	11.9
	Output	0.6	209	0.1	3.4	79.3	32.3	8.9
	Net	38.5	-174	-0.1	46.8	4.6	9.4	3.0

3.4 Critical load calculations

Critical loads (CL) have been widely accepted as a basis for control strategies for regional air pollution. In order to gain more insight in the magnitude and spatial variation of CL, the UN/ECE Executive Body of the Convention on Long-Range Transboundary Air Pollution (LRTRAP) has set up a Task Force on Mapping Critical Levels/Loads under the Working Group on Effects. The data from individual countries are collected, mapped and reported by the Co-ordination Centre for Effects (CCE), located at the National Institute of Public Health and the Environment (RIVM) in Bilthoven, the Netherlands.

In the Lökeberg meeting document (Grennfelt and Törnelöf, 1992), two models for calculating CL of surface waters with respect to acidifying depositions (both S and N) were presented, one empirical and one process oriented. The first model, the Steady-State Water Chemistry (SSWC) model (Henriksen et al. 1992b, 1995), enables the calculation of critical loads of acidity and present exceedance of incoming total acidity (including nitrogen) over CL. The process-oriented First-Order Acidity Balance (FAB) model (Posch *et al.* 1996) allows the simultaneous calculation of CL of acidifying N and S deposition and their exceedance. The FAB model is based on the steady-state mass balance principle widely used in many models for computing CL for forest soils. The new nitrogen protocol will most likely be based on results from the FAB model applied both to forest soils and surface waters. The SSWC-model includes both S and N acidity, in such a way that present N-leaching (N_{leach}) is considered in the calculation of critical load exceedance (present Ex_{Ac}), while the FAB model also consider the potential N acidity of the deposition.

Based on annual weighted deposition and lake-water chemistry data for 1995/96 at Dlugi Staw and Zielony Staw, we have calculated CL for S and N by both the SSWC-model and the FAB-model. As shown in Table XI, Zielony Staw has the highest critical load because of higher weathering rate in the catchment. By this SSWC-model, at present none of the lakes are exceeded with respect to sulphur only. By adding present nitrate leaching into the model, CL is exceeded for Dlugi Staw, while Zielony Staw still can tolerate further acid inputs.

Table XI. Critical loads and present critical load exceedances for Dlugi Staw and Zielony Staw based on the SSWC-model. Units: $meq\ m^{-2}\ yr^{-1}$.

Lake	Critical load	Sulphur	Sulphur + Nitrogen
Dlugi Staw	95	-10	42
Zielony Staw	164	-80	-48

Based on the FAB-model, the CL is exceeded for Dlugi Staw, by only evaluating S. Thus, CL is far more exceeded at this site when both nitrogen and sulphur deposition are evaluated together. The fact that the CL of this lake is exceeded even by S alone, means that a reduction in S-deposition by $\approx 6\%$ (i.e. from $85.5\ meq\ m^{-2}\ yr^{-1}$ to $80.6\ meq\ m^{-2}\ yr^{-1}$) is necessary to obtain a situation where it is possible to chose whether you can reduce either N or S or both in order to reach the CL-level for this lake (Figure 20). It is important to underline that the FAB-model is a process oriented steady state model, and relies on the assumption that the present total inputs of both S and N (- a: $2.7\ meq\ N\ m^{-2}\ yr^{-1}$, see Figure 20) are able to leave the catchment as mobile NO_3^- and SO_4^{2-} once in the future. This means that the model shows the potential acidity of the S and N inputs of today. The difference from this worst case scenario and the chemical situation in the lake today, is illustrated as the difference between the precipitation points and the runoff points in Figure 20. However, as well illustrated in Figure 20, substantial reductions of S and/or N is needed to reach the CL-level for Dlugi Staw, even based on the lake water chemistry of today.

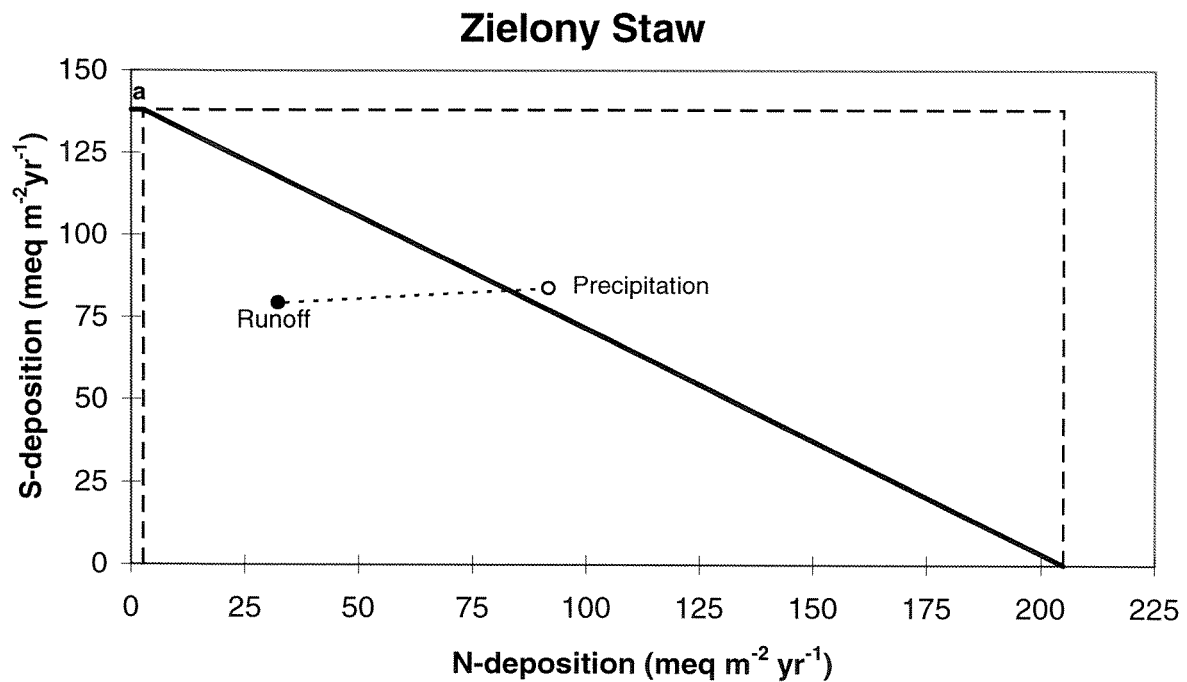
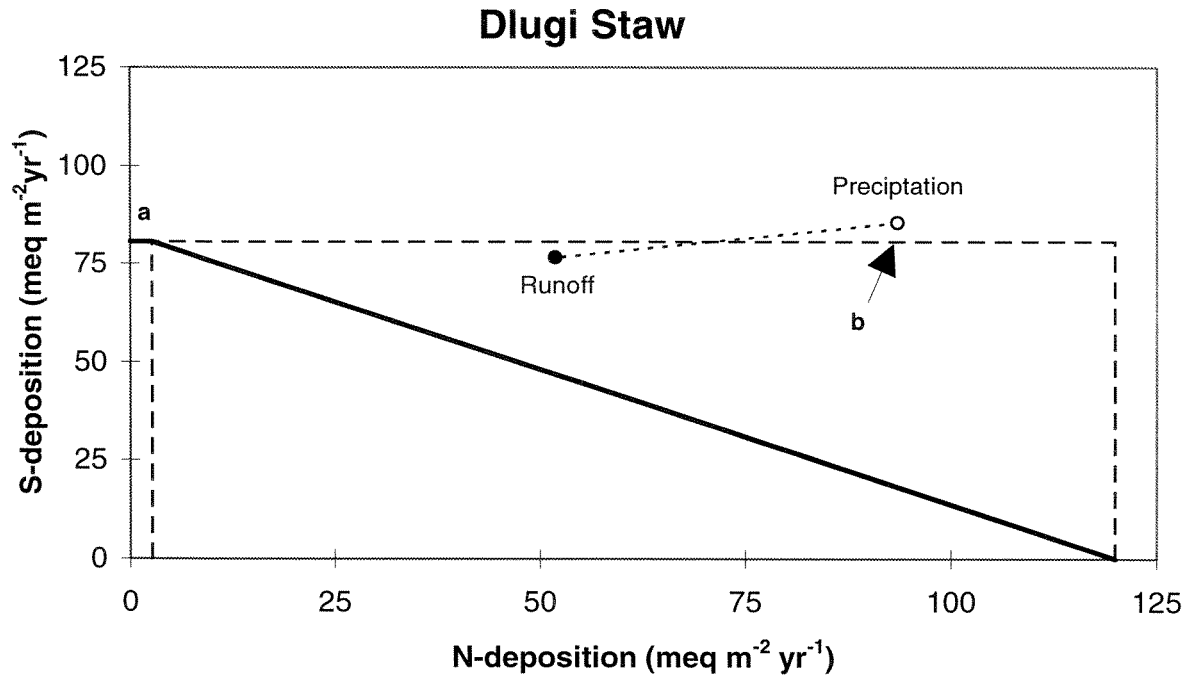


Figure 20. Critical loads of nitrogen and sulphur at Dlugi and Zielony Staw, based on data from July 1, 1995 to June 31, 1996. The heavy continuous line is the calculated critical load function for the catchment, or the no exceedance line for sulphur and nitrogen inputs. **a**: minimum of nitrogen, i.e. retention and immobilisation of nitrogen, for these lakes: $2.7 \text{ meq m}^{-2} \text{ yr}^{-1}$. **b**: The sulphur level at which it is possible to obtain the critical load by a combined S/N reduction. The difference from this worst case scenario for the deposition of S and N at present and the situation in the lake today, is illustrated as the difference between the precipitation point (open circle) and the runoff point (filled circle).

According to the FAB-model calculations, annual weighted deposition of S and N at Zielony Staw is also higher than the CL for this lake (Figure 20), but as mentioned above the FAB-model expresses a worst case scenario at present deposition S and N. As illustrated in the figure, the chemistry in the lake water shows that the CL is still not exceeded. However, only minor reductions of either N- (10%) or S-inputs (8%) or both (different alternatives) are needed to obtain a deposition level lower than the CL-level for this lake.

3.5. Other Polish watersheds

During a visit to Poland in September 1995, another 9 watersheds from the Karkonosze Mountains were sampled. The intention of this survey was to give a first critical load calculation for this area. Unfortunately, we have no runoff data from these sites, which is necessary for critical load calculations. However, the water chemistry in this area reflects strong impact from atmospheric inputs of S- and N-compounds. Based on the September 1995 data, the pH of the different lakes varied from 4.77 to 5.94, which means that they are relatively acidic (See Table XII). The water chemistry in September 1995, seems to be slightly better than the corresponding survey conducted September 1994 (Rzychon et al., 1995). The primary cause of these differences is probably different hydrology or flow-regimes during the period of sampling, or simply analytical differences, because different laboratories have analysed the two sample sets.

As shown in Figure 21, all 9 waterbodies exhibit higher concentration of $\Sigma\text{SO}_4, \text{NO}_3$ and lower pH than both Dlugi and Zielony Staw, except for Maty Staw which had the same pH as Dlugi Staw. Furthermore, all have higher, several much higher, concentrations of labile Al in runoff compared with Dlugi and Zielony Staw (Figure 22). The concentration of SO_4^{2-} in runoff is extremely high at some sites, and all sites have much higher $[\text{SO}_4^{2-}]$ than Dlugi and Zielony Staw. Only two waterbodies had higher NO_3^- -concentration in runoff compared with Dlugi Staw, and only sites exhibited lower NO_3^- -concentration than Zielony Staw (Table XII). The concentration of Si in runoff was surprisingly higher in the 9 waterbodies compared with Dlugi and Zielony Staw (See Table A-6, in Appendix). Two localities have high TOC concentrations, which typically cause higher base cation concentrations in relation to $\Sigma\text{SO}_4, \text{NO}_3$ (Figure 21) and much higher ANC in relation to pH compared with the other sites (Figure 23).

Table XII. Concentration of chemical compounds in runoff from different watersheds sampled September 20-22, 1995. Data from Dlugi and Zielony Staw is from October 3, 1995. ^a: Lake; ^b: Stream. Plasawa 1,2,3 are different stations along the Plasawa stream.

Site	pH	Ca ²⁺ mg L ⁻¹	Mg ²⁺ mg L ⁻¹	Na ⁺ mg L ⁻¹	K ⁺ mg L ⁻¹	NH ₄ ⁺ -N μg N L ⁻¹	SO ₄ ²⁻ mg L ⁻¹	NO ₃ ⁻ -N μg N L ⁻¹	Cl ⁻ mg L ⁻¹	Alk μmol L ⁻¹
Kamieczyk ^b	5.11	2.76	0.53	2.32	0.38	5	11.3	490	0.9	8.1
Szklarka ^b	4.85	3.23	0.81	2.16	0.50	10	14.2	590	1.0	7.5
Tomniczka ^b	5.40	2.71	0.73	1.38	0.37	5	9.0	865	0.6	8.4
Maly Staw ^a	5.94	1.28	0.27	1.11	0.21	5	4.7	200	0.3	15.5
Wielki Staw ^a	4.94	1.13	0.18	0.81	0.24	10	5.0	360	0.4	3.9
Wrzosowka ^b	5.02	4.41	0.95	1.78	0.49	7	15.9	885	0.8	6.9
Plasawa 1 ^b	5.68	2.98	0.75	1.91	0.58	7	9.6	395	0.7	24.5
Plasawa 2 ^b	5.72	2.92	0.75	1.91	0.58	5	9.7	385	0.7	24.3
Plasawa 3 ^b	4.77	1.87	0.39	1.14	0.19	5	7.5	260	0.4	5.4
Dlugi Staw ^a	5.93	1.99	0.12	0.31	0.14	9	3.2	645	0.2	2.2
Zielony Staw ^a	6.79	2.86	0.21	0.34	0.19	45	3.1	300	0.2	122

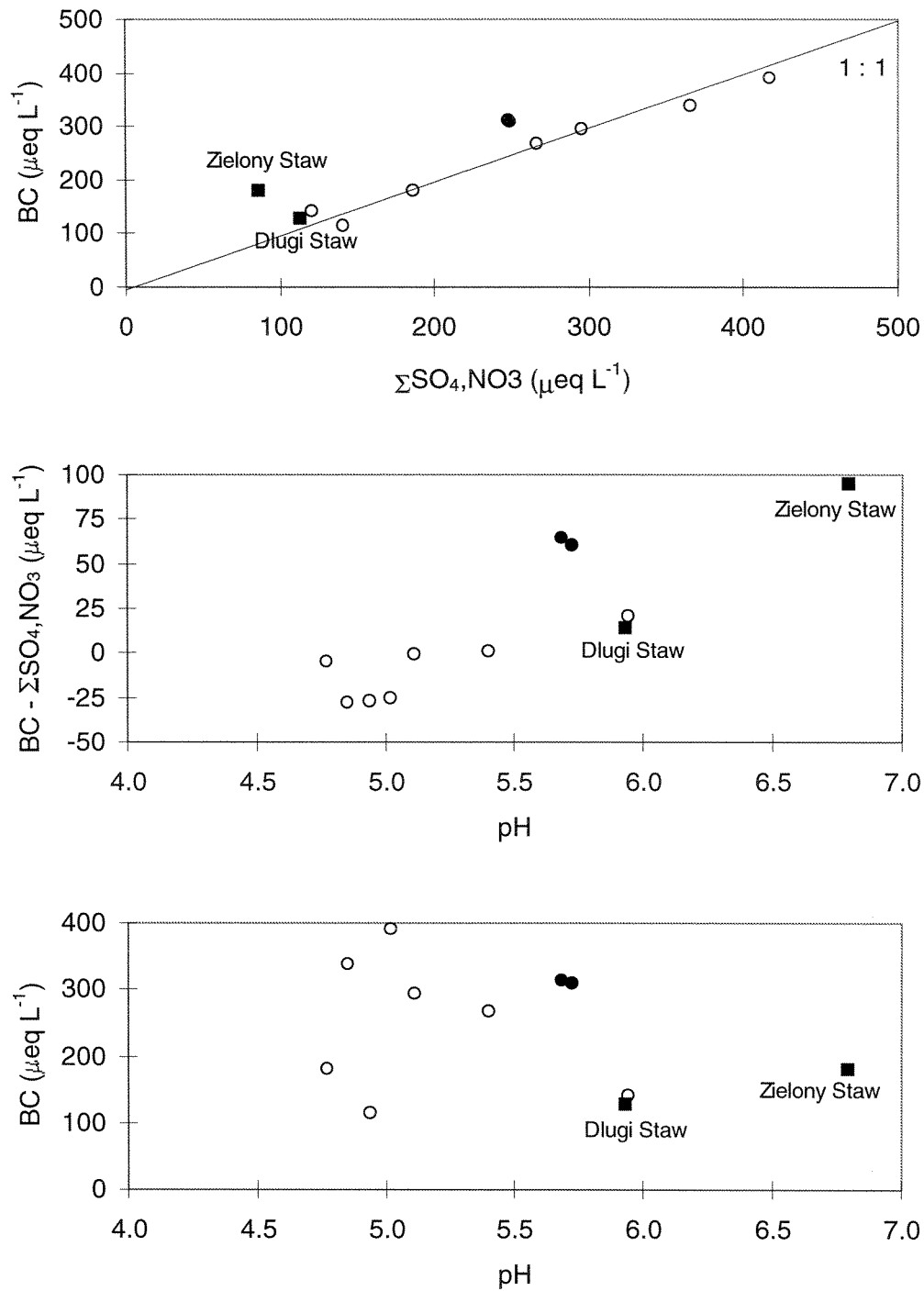


Figure 21. Relationships between $\Sigma\text{SO}_4, \text{NO}_3$ and ΣBase cations (BC), pH and $\Sigma\text{BC} - \Sigma\text{SO}_4, \text{NO}_3$ and pH and BC in 11 Polish waterbodies in the Tatra Mountains, sampled September 20-22, 1995. Data from Dlugi Staw and Zielony Staw are from October 3, 1995. ■ : Dlugi Staw and Zielony Staw •: Sites with high concentrations of total organic carbon, TOC.

In regional lake surveys covering different geology with respect to weatherability and mobilisation of base cations, a positive correlation normally exists between base cations and pH, i.e. high pH, high concentrations of base cations. In areas with more uniform geology, it is the other way around, i.e. negative correlation between pH (or high H^+ -concentration) and base cation concentration. A such tendency seems to be present for the lakes of this survey (Figure 21). This means that the catchments do "as best as they can" to prevent acidification by increasing dissolution of base cations through increased cation exchange and weathering. However, the acid neutralising capacity is not high enough, which means that water pH decreases and aluminium leaks out into surface waters (Figure 22) on chemical forms and at concentrations often harmful to aquatic organisms.

Based on this survey, it is easy to conclude that the critical loads are exceeded for all waterbodies. There are two localities with higher acid neutralising capacity (ANC) compared with the others, Plasawa 1 and 2. The major reason for this, is the high concentration of total organic carbon (TOC). A predominant part of TOC is weak organic acids with high pH-buffering capacity. It is well known that increased acidification of soil water causes increased mineral weathering. In addition natural organic acids do catalyse these processes (Inoue and Wada, 1971; Huang and Keller, 1972; Boyle *et al.*, 1974; Johnson *et al.*, 1981; Wilson, 1986; Lundström, 1990), as well as they play an important role in the acid/base chemistry of surface waters (Driscoll *et al.* 1989). To which extent the high TOC-concentrations in these lakes also reflect longer residence time of water within these catchments compared with the other watersheds is impossible to claim on the basis of this survey. However, if so, this also contributes to increased acid neutralising capacity, simply because of longer reaction-time between water and biogeochemical processes within the catchments.

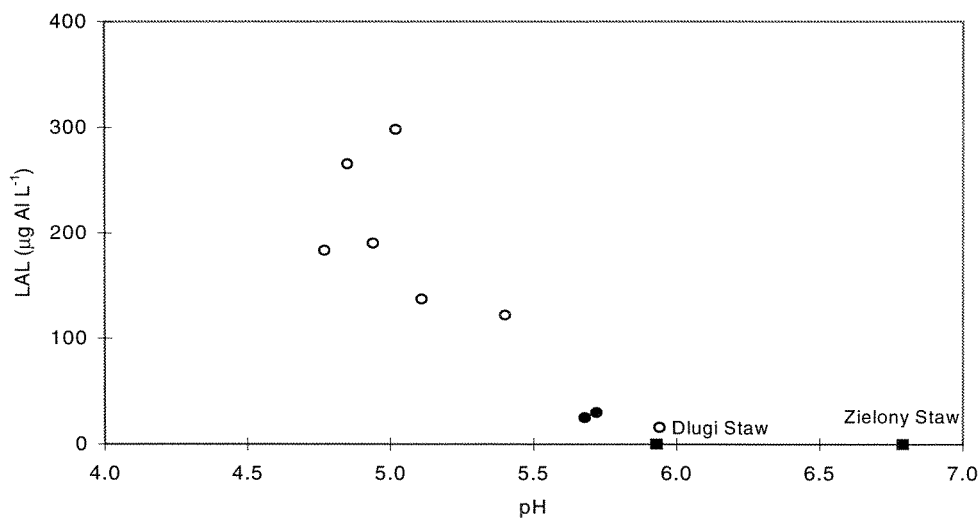


Figure 22. Relationships between pH and inorganic aluminium (LAL = labile Al) in 11 Polish watersheds in the Tatra Mountains, sampled September 20-22, 1995. Data from Dlugi Staw and Zielony Staw are from October 3, 1995. ■ : Dlugi Staw and Zielony Staw ●: Sites with high concentrations of total organic carbon, TOC.

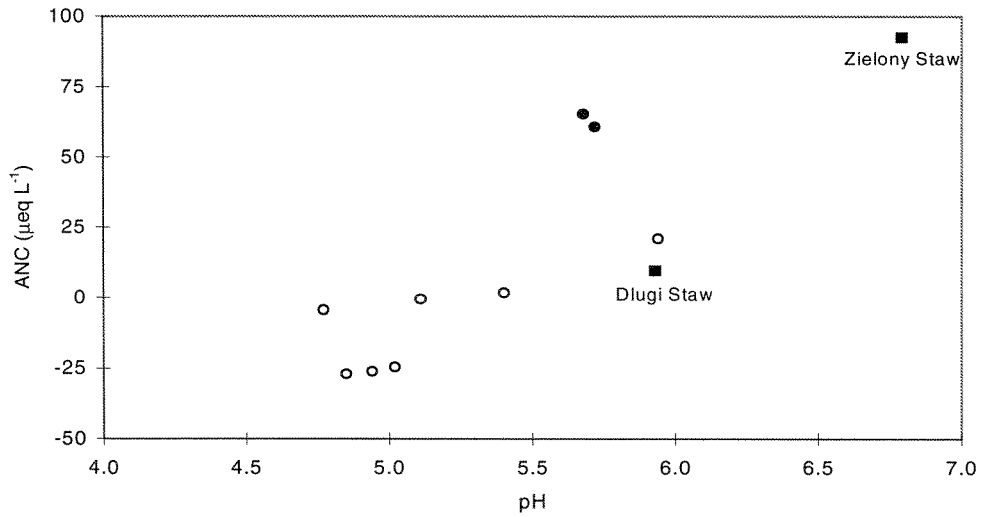


Figure 23. Relationships between pH and acid neutralising capacity (ANC) at 11 Polish waterbodies in the Tatra Mountains, sampled September 20-22, 1995. Data from Dlugi Staw and Zielony Staw are from October 3, 1995. ■ : Dlugi Staw and Zielony Staw ●: Sites with high concentrations of total organic carbon, TOC.

4. CONCLUSIONS

The two Polish lakes, Dlugi Staw and Zielony Staw, receive N and S-depositions in the same order of magnitude as parts of Southern Norway, i.e. $\geq 1 \text{ g N or S m}^{-2} \text{ yr}^{-1}$. The Polish lakes are located at high altitude, have minor vegetation cover and relatively steep catchment gradients. This means that the residence time of the water within the catchment is short and the biological needs of N-compounds small. These factors are most extreme at Dlugi Staw. This can be illustrated by the acid neutralising capacity (ANC) for the two lakes. While annual weighted ANC is $\approx 0 \text{ } \mu\text{eq L}^{-1}$ at Dlugi Staw, it is $\approx 70 \text{ } \mu\text{eq L}^{-1}$ at Zielony Staw.

The high inputs of N-compounds from the atmosphere may easily cause substantial N-leakage by runoff at both sites. Based on the nitrogen saturation classes given by Stoddard (1994), the watershed Dlugi Staw is close to the 3rd Stage and Zielony Staw in the 2nd Stage of N-saturation. This means that both watersheds are in chronic stages of N-saturation. As a consequence, biological demand exerts no control over winter and spring concentration of nitrogen, and the period of N-limitation during the growth season is much reduced. Excess of nitrogen may lead to build-up or accumulation of NH_4^+ in soil and nitrification may be stimulated. Nitrification is a strongly acidifying process. Since Dlugi Staw was classified in Stage 3 by Rzychon and Worsztynowicz (1995), it means that the watershed is a net source of N rather than a sink. Based on this survey, however, this is not fully true, since the total influx of nitrogen is still higher than the total efflux. However, the efflux of $\text{NO}_3^- > \text{influx of } \text{NO}_3^-$ at Dlugi Staw, which means that nitrification of NH_4^+ is of significant importance, besides mineralisation and high inputs of nitrogen. Thus, Dlugi Staw is most likely at the borderline between Stage 2 and 3.

According to the Steady-State Water Chemistry (SSWC) model for critical load (CL) calculations, at present none of the lakes are exceeded with respect to sulphur. However, by also accounting for nitrate leakage, the CL is exceeded at Dlugi Staw, while Zielony Staw still can tolerate further strong acid inputs. Based on the process-oriented First-Order Acidity Balance (FAB) model, CL is exceeded for both Dlugi Staw and Zielony Staw. However, while substantial reductions of S and/or N are needed to reach the CL-level at Dlugi Staw, only minor reductions are needed to obtain the CL-level at Zielony Staw. Since the FAB-model shows the worst case scenario when all inputs of N and S will be transformed to acidity, it is important to mention that the lake water chemistry in Zielony Staw at present is below the CL-level estimated by the FAB-model.

As long as the inputs of acid compounds are high, episodes particularly related to spring melt, may continue to cause water chemical conditions critical for aquatic life even in the well buffered Zielony Staw catchment, even though the lake water chemistry in Zielony Staw in 1995/96 shows that CL is still not exceeded with respect to inputs of N- and S-compounds. However, this chemically extreme melt water will be transported as an uppermost water layer through the lake. Accordingly, large parts of the lake will still have good water quality where organisms as fish can move into. On the other side, the outlet and inlet streams might be totally dominated by this melt water, which means that organisms living in streams have small changes to avoid extreme water quality episodes. Because of far higher acid neutralising capacity at Zielony Staw, such episodes are both more uncommon and less extreme at Zielony Staw compared with at Dlugi Staw.

The surface water survey implemented in the Karkonosze Mountains autumn 1995, documented strong impacts of atmospheric inputs of both S- and N-compounds. Thus, CL is exceeded at all investigated sites.

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APPENDIX

Table A-1. Monthly mean concentration of S- and N-compounds in dry deposition at Kasprowy Wierch. NO₂ was measured at Hala Gasienicowa.

Year	Mth	$\mu\text{g S m}^{-3}$ SO ₂	$\mu\text{g S m}^{-3}$ SO ₄	$\mu\text{g N m}^{-3}$ NO ₂	$\mu\text{g N m}^{-3}$ NO ₃	$\mu\text{g N m}^{-3}$ HNO ₃	$\mu\text{g N m}^{-3}$ NH ₃	$\mu\text{g N m}^{-3}$ NH ₄
1995	Jul	1.11	1.19	0.39	0.30	0.10	0.10	1.14
1995	Aug	1.08	1.13	0.45	0.32	0.11	0.11	1.28
1995	Sep	1.30	0.78	0.62	0.24	0.08	0.05	0.58
1995	Oct	0.49	0.74	0.50	0.21	0.07	0.06	0.63
1995	Nov	2.28	0.21	0.54	0.11	0.04	0.01	0.06
1995	Dec	1.45	0.16	0.90	0.08	0.03	0.01	0.06
1996	Jan	0.93	0.14	0.86	0.06	0.02	0.01	0.08
1996	Feb	3.72	0.45	0.86	0.11	0.04	0.02	0.19
1996	Mar	3.99	1.06	0.69	0.29	0.10	0.06	0.67
1996	Apr	2.06	1.11	0.60	0.52	0.17	0.10	1.14
1996	May	0.42	0.81	0.34	0.35	0.12	0.06	0.66
1996	Jun	1.14	1.24	0.34	0.29	0.10	0.09	0.99

Table A-2. Monthly precipitation of S- and N-compounds in dry deposition at Kasprowy Wierch. NO₂ was measured at Hala Gasienicowa.

Year	Mth	mg S m^2 SO ₂	mg S m^2 SO ₄	mg S m^2 NO ₂	mg S m^2 NO ₃	mg S m^2 HNO ₃	mg S m^2 NH ₃	mg S m^2 NH ₄
1995	Jul	10.12	9.08	3.01	3.25	13.56	11.58	9.92
1995	Aug	20.25	18.16	6.01	3.37	14.06	13.03	11.17
1995	Sep	23.59	12.13	8.01	2.49	10.37	5.72	4.90
1995	Oct	1.31	3.96	1.34	0.75	5.62	0.92	1.85
1995	Nov	5.91	1.09	1.40	0.36	2.72	0.09	0.18
1995	Dec	3.88	0.86	2.41	0.29	2.21	0.09	0.19
1996	Jan	2.49	0.75	2.31	0.21	1.61	0.12	0.24
1996	Feb	9.00	2.18	2.07	0.34	2.54	0.25	0.51
1996	Mar	10.69	5.68	1.85	1.04	7.83	0.98	1.96
1996	Apr	37.38	17.26	7.72	5.37	22.36	11.25	9.64
1996	May	7.87	13.02	4.49	3.70	15.40	6.75	5.79
1996	Jun	20.68	19.28	4.34	3.03	12.64	9.80	8.40

Table A-3. Monthly mean concentration of chemical compounds in wet-deposition at Hala Gasienicowa.

Year	Mth	Prec. mm	pH	Ca ²⁺ mg L ⁻¹	Mg ²⁺ mg L ⁻¹	Na ⁺ mg L ⁻¹	K ⁺ mg L ⁻¹	NH ₄ ⁺ mg N L ⁻¹	SO ₄ ²⁻ mg S L ⁻¹	NO ₃ ⁻ mg N L ⁻¹	Cl ⁻ mg L ⁻¹
1993	Jan	36.8	4.47	0.21	0.03	0.19	0.07	0.20	0.77	0.36	0.39
1993	Feb	40.6	4.42	0.14	0.02	0.14	0.23	0.07	0.49	0.26	0.52
1993	Mar	64.5	4.11	0.32	0.07	0.40	3.77	0.90	1.66	1.00	4.18
1993	Apr	72.6	4.17	0.38	0.04	0.15	0.17	0.72	1.81	0.61	0.40
1993	May	137.8	4.48	0.60	0.07	0.08	0.10	1.07	1.63	0.54	0.20
1993	Jun	169.1	4.24	0.22	0.03	0.10	0.05	0.45	1.23	0.35	0.16
1993	Jul	103.8	4.32	0.46	0.07	0.69	0.42	0.46	1.40	0.52	0.71
1993	Aug	117.2	4.47	0.38	0.07	0.10	0.09	0.46	1.08	0.42	0.23
1993	Sep	128.7	4.33	0.17	0.03	0.06	0.06	0.28	1.02	0.32	0.29
1993	Oct	29.9	5.29	0.63	0.09	0.16	0.06	0.27	0.63	0.13	0.26
1993	Nov	42.7	4.73	0.20	0.02	0.08	0.38	0.32	0.49	0.22	0.49
1993	Dec	29.7	4.58	0.29	0.05	0.35	0.54	0.19	0.60	0.37	0.88
1994	Jan	65.5	4.39	0.13	0.03	0.19	0.07	0.16	0.67	0.33	0.44
1994	Feb	11.1	4.05	0.47	0.05	0.16	0.08	0.56	1.78	0.60	0.43
1994	Mar	143.9	4.40	0.21	0.02	0.11	0.05	0.35	0.88	0.45	0.28
1994	Apr	162.9	4.59	0.71	0.06	0.22	0.14	0.36	1.00	0.36	0.34
1994	May	163.1	4.58	0.53	0.05	0.08	0.02	0.43	0.92	0.33	0.15
1994	Jun	204.8	4.41	0.26	0.03	0.22	0.18	0.64	1.30	0.38	0.31
1994	Jul	96.8	4.43	0.26	0.03	0.17	0.17	0.47	1.20	0.31	0.29
1994	Aug	138.9	4.91	0.28	0.08	0.08	0.20	0.47	0.69	0.26	0.28
1994	Sep	138.2	4.68	0.41	0.08	0.13	0.06	0.35	0.84	0.27	0.25
1994	Oct	127.7	4.61	0.18	0.03	0.10	0.08	0.23	0.56	0.21	0.21
1994	Nov	67.0	4.44	0.27	0.09	0.50	0.31	0.23	0.83	0.38	0.73
1994	Dec	49.4	4.36	0.22	0.03	0.22	0.30	0.15	0.71	0.34	0.60
1995	Jan	61.6	4.30	0.17	0.03	0.18	0.07	0.14	0.71	0.36	0.46
1995	Feb	39.5	4.43	0.29	0.05	0.48	0.31	0.46	0.95	0.49	0.79
1995	Mar	124.8	4.43	0.42	0.04	0.90	6.89	0.49	0.87	0.55	4.77
1995	Apr	139.2	4.56	0.35	0.05	0.48	0.48	0.45	0.93	0.33	0.94
1995	May	158.0	4.84	1.60	0.05	0.37	0.27	0.76	1.05	0.31	2.54
1995	Jun	200.7	4.64	0.26	0.04	0.03	0.14	0.37	0.72	0.20	0.12
1995	Jul	128.0	4.89	0.19	0.04	0.06	0.17	0.50	0.60	0.19	0.16
1995	Aug	155.7	4.66	0.42	0.10	0.11	0.17	0.51	1.00	0.34	0.30
1995	Sep	252.5	4.49	0.12	0.02	0.08	0.10	0.29	0.69	0.26	0.27
1995	Oct	15.0	4.19	0.31	0.09	0.12	1.02	0.49	1.41	0.50	0.45
1995	Nov	69.4	4.65	0.17	0.03	0.13	0.07	0.27	0.52	0.25	0.41
1995	Dec	23.1	4.49	0.43	0.03	0.15	1.12	0.22	1.00	0.36	0.57
1996	Jan	15.6	4.29	0.26	0.04	0.13	1.13	0.05	0.90	0.23	0.80
1996	Feb	6.4	4.61	0.62	0.04	0.06	0.04	0.33	0.83	0.30	0.73
1996	Mar	60.3	4.24	0.22	0.03	0.23	0.35	0.38	0.81	0.67	0.81
1996	Apr	62.2	4.42	0.68	0.07	0.10	0.40	0.94	1.59	0.60	0.60
1996	May	249.6	4.80	0.32	0.03	0.06	0.06	0.41	0.60	0.21	0.15
1996	Jun	238.9	4.43	0.18	0.03	0.06	0.17	0.52	1.02	0.33	0.29

Table A-3. Monthly mean concentration ($\mu\text{eq L}^{-1}$) of chemical compounds in wet-deposition at Hala Gasienicowa continues.

		H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	ΣCation	ΣAnion	Cat-An
		μeq L-1											
1993	Jan	33.9	10.5	2.5	8.3	3.7	14.3	48.1	25.7	11.0	73.0	73.8	-0.8
1993	Feb	38.0	7.0	1.6	6.1	12.0	5.0	30.6	18.6	14.7	69.8	49.2	20.6
1993	Mar	77.6	16.0	5.8	17.4	197.4	64.3	103.8	71.4	117.9	378.4	175.2	203.2
1993	Apr	67.6	19.0	3.3	6.5	8.9	51.4	113.1	43.6	11.3	156.7	156.7	0.0
1993	May	33.1	29.9	5.8	3.5	5.2	76.4	101.9	38.6	5.6	154.0	140.4	13.5
1993	Jun	57.5	11.0	2.5	4.3	2.6	32.1	76.9	25.0	4.5	110.1	101.9	8.2
1993	Jul	47.9	23.0	5.8	30.0	22.0	32.9	87.5	37.1	20.0	161.4	124.6	36.8
1993	Aug	33.9	19.0	5.8	4.3	4.7	32.9	67.5	30.0	6.5	100.5	97.5	3.0
1993	Sep	46.8	8.5	2.5	2.6	3.1	20.0	63.8	22.9	8.2	83.5	86.6	-3.1
1993	Oct	5.1	31.4	7.4	7.0	3.1	19.3	39.4	9.3	7.3	73.4	48.7	24.7
1993	Nov	18.6	10.0	1.6	3.5	19.9	22.9	30.6	15.7	13.8	76.5	46.3	30.1
1993	Dec	26.3	14.5	4.1	15.2	28.3	13.6	37.5	26.4	24.8	102.0	63.9	38.0
1994	Jan	40.7	6.5	2.5	8.3	3.7	11.4	41.9	23.6	12.4	73.1	65.4	7.6
1994	Feb	89.1	23.5	4.1	7.0	4.2	40.0	111.3	42.9	12.1	167.8	154.1	13.7
1994	Mar	39.8	10.5	1.6	4.8	2.6	25.0	55.0	32.1	7.9	84.3	87.1	-2.8
1994	Apr	25.7	35.4	4.9	9.6	7.3	25.7	62.5	25.7	9.6	108.7	88.2	20.5
1994	May	26.3	26.4	4.1	3.5	1.0	30.7	57.5	23.6	4.2	92.1	81.1	11.0
1994	Jun	38.9	13.0	2.5	9.6	9.4	45.7	81.3	27.1	8.7	119.1	108.4	10.7
1994	Jul	37.2	13.0	2.5	7.4	8.9	33.6	75.0	22.1	8.2	102.5	97.1	5.3
1994	Aug	12.3	14.0	6.6	3.5	10.5	33.6	43.1	18.6	7.9	80.4	61.7	18.7
1994	Sep	20.9	20.5	6.6	5.7	3.1	25.0	52.5	19.3	7.1	81.7	71.8	9.9
1994	Oct	24.5	9.0	2.5	4.3	4.2	16.4	35.0	15.0	5.9	61.0	50.0	11.0
1994	Nov	36.3	13.5	7.4	21.7	16.2	16.4	51.9	27.1	20.6	111.6	79.0	32.6
1994	Dec	43.7	11.0	2.5	9.6	15.7	10.7	44.4	24.3	16.9	93.1	68.7	24.4
1995	Jan	50.1	8.5	2.5	7.8	3.7	10.0	44.4	25.7	13.0	82.6	70.1	12.5
1995	Feb	37.2	14.5	4.1	20.9	16.2	32.9	59.4	35.0	22.3	125.7	94.4	31.3
1995	Mar	37.2	21.0	3.3	39.1	360.7	35.0	54.4	39.3	134.5	496.2	93.7	402.6
1995	Apr	27.5	17.5	4.1	20.9	25.1	32.1	58.1	23.6	26.5	127.3	81.7	45.6
1995	May	14.5	79.8	4.1	16.1	14.1	54.3	65.6	22.1	71.6	182.9	87.8	95.2
1995	Jun	22.9	13.0	3.3	1.3	7.3	26.4	45.0	14.3	3.4	74.2	59.3	15.0
1995	Jul	12.9	9.5	3.3	2.6	8.9	35.7	37.5	13.6	4.5	72.9	51.1	21.8
1995	Aug	21.9	21.0	8.2	4.8	8.9	36.4	62.5	24.3	8.5	101.2	86.8	14.4
1995	Sep	32.4	6.0	1.6	3.5	5.2	20.7	43.1	18.6	7.6	69.4	61.7	7.7
1995	Oct	64.6	15.5	7.4	5.2	53.4	35.0	88.1	35.7	12.7	181.1	123.8	57.2
1995	Nov	22.4	8.5	2.5	5.7	3.7	19.3	32.5	17.9	11.6	61.9	50.4	11.6
1995	Dec	32.4	21.5	2.5	6.5	58.6	15.7	62.5	25.7	16.1	137.2	88.2	48.9
1996	Jan	51.3	13.0	3.3	5.7	59.2	3.6	56.3	16.4	22.6	135.9	72.7	63.3
1996	Feb	24.5	30.9	3.3	2.6	2.1	23.6	51.9	21.4	20.6	87.1	73.3	13.7
1996	Mar	57.5	11.0	2.5	10.0	18.3	27.1	50.6	47.9	22.8	126.5	98.5	28.0
1996	Apr	38.0	33.9	5.8	4.3	20.9	67.1	99.4	42.9	16.9	170.1	142.2	27.9
1996	May	15.8	16.0	2.5	2.6	3.1	29.3	37.5	15.0	4.2	69.3	52.5	16.8
1996	Jun	37.2	9.0	2.5	2.6	8.9	37.1	63.8	23.6	8.2	97.3	87.3	9.9

Table A-4. Concentration of chemical compounds in runoff at Dlugi Staw.

Date	Runoff L m ⁻² d ⁻¹	pH	Ca ²⁺ mg L ⁻¹	Mg ²⁺ mg L ⁻¹	Na ⁺ mg L ⁻¹	K ⁺ mg L ⁻¹	NH ₄ ⁺ -N µg N L ⁻¹	SO ₄ ²⁻ mg L ⁻¹	NO ₃ ⁻ -N µg N L ⁻¹	Cl ⁻ mg L ⁻¹
01/01/94	0.24	6.26	2.92	0.15	0.48	0.13	5	4.2	850	0.2
17/01/94	0.24	6.39	2.91	0.16	0.45	0.13	5	4.1	835	0.2
04/02/94	0.24	6.63	2.87	0.16	0.50	0.14	5	4.1	855	0.2
15/02/94	0.24	6.40	2.92	0.16	0.45	0.14	5	4.2	860	0.2
28/02/94	0.24	6.17	2.88	0.15	0.44	0.12	5	4.6	845	0.3
14/03/94	0.24	6.16	2.84	0.14	0.47	0.14	5	4.1	865	0.2
29/03/94	0.24	6.17	2.87	0.16	0.49	0.13	5	4.1	925	0.2
19/04/94	0.24	6.18	3.17	0.17	0.49	0.14	6	4.0	910	0.3
04/05/94	1.09	5.96	2.93	0.16	0.42	0.13	5	3.8	960	0.3
17/05/94	4.77	5.67	2.04	0.12	0.34	0.12	36	3.0	670	0.3
22/05/94	14.16	5.36	1.47	0.10	0.26	0.14	45	2.9	625	0.3
31/05/94	10.45	5.32	1.46	0.10	0.26	0.13	21	2.9	590	0.2
20/06/94	7.72	5.27	1.54	0.06	0.26	0.11	15	2.9	545	0.2
04/07/94	7.72	5.63	1.50	0.05	0.30	0.12	9	2.8	490	0.2
18/07/94	7.72	5.54	1.42	0.04	0.25	0.10	10	2.7	470	0.2
25/07/94	3.30	5.91	1.97	0.11	0.35	0.12	5	3.9	535	0.2
16/08/94	2.67	5.95	1.93	0.11	0.41	0.23	15	3.3	560	0.3
29/08/94	3.30	5.86	1.83	0.09	0.26	0.16	16	3.2	595	0.2
19/09/94	4.00	5.91	1.92	0.11	0.40	0.15	22	3.2	715	0.3
02/10/94	2.09	5.99	2.08	0.12	0.47	0.22	21	3.4	705	0.2
18/10/94	2.67	5.94	2.16	0.12	0.33	0.13	14	3.4	715	0.1
01/11/94	2.09	5.73	2.25	0.13	0.39	0.16	8	3.5	725	0.2
15/11/94	2.09	6.05	2.31	0.13	0.32	0.13	5	3.5	780	0.2
30/11/94	1.57	6.09	2.44	0.14	0.36	0.11	5	3.6	775	0.3
23/12/94	1.09	6.25	2.52	0.13	0.45	0.11	5	3.9	775	0.3
14/02/95	1.57	6.26	2.82	0.17	0.41	0.15	5	4.3	995	0.3
14/03/95	2.09	5.96	2.18	0.12	0.28	0.12	5	3.8	730	0.3
18/04/95	0.24	6.42	2.71	0.15	0.38	0.13	5	4.4	835	0.2
02/05/95	7.72	5.29	1.88	0.12	0.30	0.14	48	3.5	875	0.4
16/05/95	7.72	5.16	1.88	0.12	0.29	0.13	29	3.5	890	0.4
30/05/95	1.57	6.18	2.85	0.16	0.36	0.15	5	4.1	1015	0.4
19/06/95	10.45	5.44	1.31	0.08	0.17	0.12	24	2.7	515	0.2
26/06/95	5.64	5.91	1.55	0.09	0.22	0.13	12	3.1	425	0.2
10/07/95	7.72	5.59	1.33	0.08	0.20	0.11	5	2.9	405	0.2
08/08/95	2.96	5.85	1.55	0.09	0.25	0.13	24	2.8	470	0.3
21/08/95	5.64	6.07	1.70	0.10	0.39	0.15	45	2.9	490	0.2
05/09/95	4.00	5.93	1.78	0.10	0.27	0.12	12	3.0	600	0.2
03/10/95	2.09	5.93	1.99	0.12	0.31	0.14	9	3.2	645	0.2
22/10/95	1.63	5.95	2.05	0.11	0.32	0.14	5	3.3	670	0.2
01/11/95	1.83	6.24	2.24	0.12	0.32	0.14	9	3.4	655	0.2
26/12/95	0.82	6.45	2.54	0.14	0.39	0.11	5	3.6	705	0.2
16/01/96	0.01	6.33	2.52	0.13	0.39	0.11	5	3.8	715	0.2
08/02/96	0.65	6.51	2.79	0.15	0.40	0.14	5	3.8	755	0.2
18/03/96	0.24	6.40	2.83	0.15	0.44	0.14	5	3.8	790	0.2
26/03/96	0.65	6.24	2.69	0.17	0.41	0.15	13	5.4	770	0.4
01/04/96	0.65	6.15	2.68	0.15	0.39	0.13	5	4.1	770	0.2
09/04/96	1.09	6.01	2.68	0.15	0.40	0.14	5	5.2	865	0.3
23/04/96	6.62	5.67	2.05	0.13	0.24	0.19	82	2.9	865	0.3
04/05/96	6.62	5.26	1.85	0.12	0.27	0.17	33	3.1	845	0.3
14/05/96	8.99	5.27	1.53	0.10	0.22	0.14	24	2.7	710	0.2
30/05/96	7.72	5.48	1.43	0.09	0.21	0.11	15	2.5	535	0.2
18/06/96	6.62	5.70	1.52	0.09	0.22	0.11	20	2.7	515	0.2
26/06/96	4.77	5.63	1.60	0.09	0.20	0.11	5	2.8	510	0.2
16/07/96	4.00	5.86	1.78	0.10	0.20	0.12	5	3.0	530	0.2
31/07/96	3.30	6.00	1.85	0.10	0.24	0.12	12	3.4	520	0.2

Table A-4. Concentration of chemical compounds in runoff at Dlugi Staw continues.

Date	K ₂₅ mS m ⁻¹	TOC mg L ⁻¹	RAI µg L ⁻¹	OAI µg L ⁻¹	LAI µg L ⁻¹	Tot- N µg L ⁻¹	Alk µmol L ⁻¹	Si mg SiO ₂ L ⁻¹
01/01/94	2.31	0.20	10	10	0	880	49	2.6
17/01/94	2.35	0.10	10	10	0	865	50	2.6
04/02/94	2.32	0.20	10	10	0	850	53	2.7
15/02/94	2.27	0.20	10	10	0	875	54	2.7
28/02/94	2.23	0.20	10	10	0	880	55	2.7
14/03/94	2.27	0.20	10	10	0	885	52	2.6
29/03/94	2.31	0.20	10	10	0	895	53	2.7
19/04/94	2.49	0.42	10	10	0	1040	60	2.7
04/05/94	2.34	0.20	10	10	0	995	45	2.4
17/05/94	1.84	0.44	16	10	6	730	35	1.8
22/05/94	1.61	0.35	87	10	77	695	32	1.1
31/05/94	1.56	0.20	92	10	82	650	33	1.3
20/06/94	1.63	0.20	74	10	64	600	33	1.5
04/07/94	1.51	0.20	41	10	31	555	37	1.5
18/07/94	1.41	0.20	25	10	15	510	34	1.5
25/07/94	1.70	0.20	10	10	0	595	41	2.0
16/08/94	1.77	0.20	10	10	0	655	42	2.1
29/08/94	1.59	0.20	23	10	13	655	42	2.0
19/09/94	1.62	0.20	20	10	10	725	40	1.9
02/10/94	1.78	0.26	19	10	9	830	42	2.2
18/10/94	1.78	0.29	13	10	3	735	41	2.1
01/11/94	1.79	0.25	13	10	3	745	43	2.2
15/11/94	1.82	0.20	10	10	0	770	45	2.2
30/11/94	1.84	0.26	10	10	0	755	47	2.3
23/12/94	1.95	0.20	10	10	0	775	47	2.4
14/02/95	2.14	0.20	10	10	0	985	46	2.3
14/03/95	1.74	0.57	10	10	0	765	40	2.2
18/04/95	2.09	0.20	10	10	0	820	54	2.6
02/05/95	1.90	0.38	109	10	99	935	30	1.5
16/05/95	1.93	0.52	127	10	117	915	28	1.5
30/05/95	2.23	0.51	10	10	0	1025	46	2.3
19/06/95	1.32	0.20	69	10	59	565	32	1.3
26/06/95	1.30	0.30	10	10	0	470	39	1.7
10/07/95	1.21	0.24	48	10	38	440	33	1.5
08/08/95	1.32	0.26	15	10	5	495	38	1.7
21/08/95	1.42	0.24	21	10	11	600	44	1.7
05/09/95	1.49	0.20	21	10	11	615	40	1.9
03/10/95	1.62	0.20	10	10	0	690	46	2.2
22/10/95	1.71	0.20	16	10	6	745	43	2.4
01/11/95	1.77	0.26	10	10	0	715	49	2.3
26/12/95	2.03	0.20	10	10	0	765	60	2.6
16/01/96	1.97	0.20	10	10	0	715	60	2.7
08/02/96	2.03	0.20	10	10	0	750	60	2.5
18/03/96	2.08	0.20	10	10	0	765	64	2.6
26/03/96	2.55	0.91	13	10	3	1005	62	2.5
01/04/96	2.11	0.20	10	10	0	765	62	2.5
09/04/96	2.17	0.20	10	10	0	850	54	2.4
23/04/96	1.84	0.33	13	10	3	950	44	1.6
04/05/96	2.07	0.53	76	10	66	910	36	1.6
14/05/96	1.59	0.20	82	10	72	745	26	1.4
30/05/96	1.40	0.20	45	10	35	650	31	1.5
18/06/96	1.42	0.20	34	10	24	585	32	1.6
26/06/96	1.39	0.38	38	10	28	545	34	1.8
16/07/96	1.47	0.32	19	10	9	575	37	1.9
31/07/96	1.50	0.24	16	10	6	585	40	2.0

Table A-5. Concentration of chemical compounds in runoff at Zielony Staw.

Date	Runoff L m ⁻² d ⁻¹	pH	Ca ²⁺ mg L ⁻¹	Mg ²⁺ mg L ⁻¹	Na ⁺ mg L ⁻¹	K ⁺ mg L ⁻¹	NH ₄ ⁺ -N µg N L ⁻¹	SO ₄ ²⁻ mg L ⁻¹	NO ₃ ⁻ -N µg N L ⁻¹	Cl ⁻ mg L ⁻¹
01/01/94	0.24	6.73	3.54	0.24	0.51	0.18	20	3.8	465	0.2
17/01/94	0.24	6.65	3.45	0.24	0.48	0.18	11	3.8	500	0.2
04/02/94	0.24	6.65	3.39	0.24	0.60	0.23	57	3.6	515	0.3
15/02/94	0.24	6.69	3.31	0.23	0.51	0.25	27	3.6	485	0.3
28/02/94	0.24	6.56	3.27	0.21	0.44	0.19	52	3.6	485	0.3
14/03/94	0.24	6.61	3.29	0.22	0.47	0.17	9	3.5	490	0.3
29/03/94	0.24	6.45	3.27	0.23	0.50	0.16	13	3.5	550	0.3
19/04/94	0.24	6.41	3.32	0.23	0.47	0.18	42	3.5	570	0.3
04/05/94	1.09	6.17	2.75	0.18	0.39	0.14	100	3.5	570	0.3
17/05/94	4.77	6.15	2.66	0.18	0.40	0.15	57	3.1	555	0.3
22/05/94	14.16	6.41	2.57	0.17	0.40	0.16	14	3.1	460	0.2
31/05/94	10.45	6.47	2.6	0.17	0.39	0.15	6	3.0	430	0.2
20/06/94	7.72	6.87	3.04	0.15	0.40	0.15	6	3.2	380	0.2
04/07/94	7.72	6.83	2.58	0.11	0.39	0.15	14	3.4	355	0.2
18/07/94	7.72	6.71	2.51	0.14	0.40	0.14	16	3.3	340	0.2
25/07/94	3.30	6.50	2.55	0.17	0.44	0.16	21	3.7	330	0.3
16/08/94	2.67	6.79	2.65	0.18	0.42	0.16	34	3.8	335	0.2
29/08/94	3.30	6.78	2.61	0.17	0.32	0.18	39	3.3	315	0.2
19/09/94	4.00	6.74	2.87	0.20	0.54	0.22	37	3.3	300	0.2
02/10/94	2.09	6.84	2.88	0.20	0.43	0.17	42	3.8	295	0.2
18/10/94	2.67	6.76	3.01	0.22	0.44	0.18	30	3.4	325	0.2
01/11/94	2.09	6.57	2.94	0.19	0.44	0.16	19	3.3	325	0.2
15/11/94	2.09	6.59	2.88	0.21	0.39	0.18	5	3.4	340	0.2
30/11/94	1.57	6.57	3.05	0.22	0.40	0.15	5	3.4	335	0.2
23/12/94	1.09	6.81	3.18	0.22	0.53	0.16	5	3.4	415	0.2
14/02/95	1.57	6.65	2.93	0.21	0.41	0.18	5	4.3	680	0.4
14/03/95	2.09	6.83	3.01	0.21	0.38	0.18	5	3.6	410	0.2
18/04/95	0.24	6.84	3.06	0.21	0.41	0.18	5	4.0	455	0.5
02/05/95	7.72	6.56	2.38	0.17	0.28	0.14	5	3.0	550	0.7
16/05/95	7.72	6.67	2.47	0.18	0.26	0.15	27	2.9	530	0.3
30/05/95	1.57	6.55	2.89	0.22	0.44	0.17	91	4.5	740	0.4
19/06/95	10.45	6.78	3.02	0.21	0.40	0.18	5	3.5	440	0.9
26/06/95	5.64	6.82	2.49	0.17	0.39	0.20	36	3.0	310	0.5
10/07/95	7.72	6.73	2.51	0.17	0.35	0.18	5	3.1	320	0.3
08/08/95	2.96	6.68	2.43	0.17	0.33	0.17	43	3.1	305	0.2
21/08/95	5.64	6.74	2.55	0.18	0.35	0.17	57	3.1	295	0.2
05/09/95	4.00	6.78	2.83	0.21	0.39	0.17	5	3.0	240	0.2
03/10/95	2.09	6.79	2.86	0.21	0.34	0.19	45	3.1	300	0.2
22/10/95	1.63	6.85	2.99	0.21	0.42	0.22	51	3.2	315	0.3
01/11/95	1.83	6.87	3.01	0.20	0.36	0.16	15	3.2	335	0.2
26/12/95	0.82	6.95	3.01	0.21	0.40	0.17	15	3.3	390	0.2
16/01/96	0.01	6.73	2.95	0.20	0.42	0.17	30	3.4	430	0.2
08/02/96	0.65	6.63	3.36	0.24	0.52	0.21	27	3.6	475	0.2
18/03/96	0.24	6.65	3.40	0.24	0.46	0.25	76	3.5	470	0.3
26/03/96	0.65	6.41	4.04	0.30	0.66	0.36	176	5.9	855	0.6
01/04/96	0.65	6.38	3.25	0.25	0.53	0.27	179	4.7	645	0.6
09/04/96	1.09	4.61	1.18	0.12	0.27	0.20	481	3.5	870	0.5
23/04/96	6.62	6.42	2.74	0.20	0.37	0.19	128	3.5	500	0.3
04/05/96	6.62	6.36	2.30	0.17	0.31	0.19	86	2.8	475	0.3
14/05/96	8.99	6.58	2.51	0.18	0.31	0.18	13	2.7	450	0.2
30/05/96	7.72	6.83	2.79	0.20	0.35	0.16	16	3.0	370	0.2
18/06/96	6.62	6.84	2.57	0.18	0.34	0.15	20	2.9	345	0.2
26/06/96	4.77	6.76	2.59	0.17	0.30	0.16	40	2.9	325	0.2
16/07/96	4.00	6.83	2.64	0.17	0.32	0.16	37	3.0	315	0.3
31/07/96	3.30	6.71	2.64	0.17	0.32	0.16	5	3.0	265	0.3

Table A-5. Concentration of chemical compounds in runoff at Zielony Staw continues.

Date	K ₂₅ mS m ⁻¹	TOC mg L ⁻¹	RAI µg L ⁻¹	OAI µg L ⁻¹	LAI µg L ⁻¹	Tot- N µg L ⁻¹	Alk µmol L ⁻¹	Si mg SiO ₂ L ⁻¹
01/01/94	2.52	0.42	10	10	0	560	122	1.4
17/01/94	2.49	0.41	10	10	0	570	117	1.5
04/02/94	2.63	0.37	10	10	0	745	120	1.6
15/02/94	2.53	0.23	10	10	0	600	119	1.5
28/02/94	2.45	0.34	10	10	0	655	120	1.5
14/03/94	2.42	0.39	10	10	0	560	118	1.5
29/03/94	2.45	0.51	10	10	0	610	113	1.7
19/04/94	2.54	0.30	10	10	0	715	106	1.7
04/05/94	2.26	0.44	12	10	2	720	82	1.8
17/05/94	2.17	0.55	10	10	0	645	74	1.8
22/05/94	1.98	0.27	12	10	2	515	93	1.9
31/05/94	1.97	0.23	10	10	0	460	100	1.9
20/06/94	2.16	0.25	10	10	0	420	114	1.9
04/07/94	2.05	0.33	10	10	0	405	99	1.9
18/07/94	1.97	0.39	10	10	0	405	94	1.8
25/07/94	1.96	0.52	10	10	0	435	92	1.9
16/08/94	2.03	0.47	10	10	0	450	100	1.7
29/08/94	1.87	0.47	10	10	0	415	106	1.4
19/09/94	2.02	0.66	10	10	0	440	121	1.0
02/10/94	2.03	0.49	10	10	0	435	120	0.9
18/10/94	2.09	0.48	10	10	0	410	121	1.0
01/11/94	2.01	0.56	10	10	0	395	116	1.1
15/11/94	2.07	0.49	10	10	0	400	116	1.2
30/11/94	2.05	0.53	10	10	0	380	114	1.3
23/12/94	2.08	0.41	10	10	0	460	108	1.5
14/02/95	2.19	0.37	10	10	0	695	78	1.9
14/03/95	2.12	0.24	10	10	0	440	108	1.1
18/04/95	2.17	0.42	10	10	0	485	106	1.8
02/05/95	1.77	0.29	10	10	0	565	78	1.8
16/05/95	1.83	0.23	10	10	0	565	83	1.8
30/05/95	2.28	0.46	10	10	0	860	73	1.8
19/06/95	2.12	0.26	10	10	0	460	113	2.0
26/06/95	1.83	0.32	10	10	0	415	100	1.8
10/07/95	1.81	0.50	10	10	0	380	97	1.8
08/08/95	1.78	0.45	10	10	0	375	95	1.7
21/08/95	1.82	0.52	10	10	0	405	104	1.6
05/09/95	1.93	0.97	10	10	0	355	124	1.1
03/10/95	2.02	0.68	10	10	0	430	122	1.2
22/10/95	2.16	0.38	10	10	0	455	124	1.3
01/11/95	2.09	0.43	10	10	0	390	118	1.4
26/12/95	2.22	0.42	10	10	0	475	116	1.6
16/01/96	2.19	0.33	10	10	0	510	116	1.7
08/02/96	2.35	0.43	10	10	0	535	122	1.7
18/03/96	2.40	0.43	10	10	0	636	128	1.7
26/03/96	3.32	0.64	10	10	0	1165	129	2.1
01/04/96	2.70	0.42	10	10	0	945	112	1.7
09/04/96	2.64	0.64	37	10	27	1450	15	0.4
23/04/96	2.25	0.50	10	10	0	910	107	1.6
04/05/96	2.00	0.47	16	10	6	625	97	1.7
14/05/96	1.85	0.27	13	10	3	450	94	1.9
30/05/96	1.65	0.28	10	10	0	430	117	1.7
18/06/96	1.92	0.33	10	10	0	415	102	1.6
26/06/96	1.86	0.35	10	10	0	410	102	1.7
16/07/96	1.87	0.42	10	10	0	400	104	1.4
31/07/96	1.85	0.96	10	10	0	365	102	1.1

Table A-6. Concentration of chemical compounds in runoff from different watersheds sampled September 20-22, 1995. Data from Długi and Zielony Staw is from October 3, 1995. ^a: Lake; ^b: Stream. Plasawa 1, 2, 3 are different stations along the Plasawa stream.

Site	pH	Ca ²⁺ mg L ⁻¹	Mg ²⁺ mg L ⁻¹	Na ⁺ mg L ⁻¹	K ⁺ mg L ⁻¹	NH ₄ ⁺ -N μg N L ⁻¹	SO ₄ ²⁻ mg L ⁻¹	NO ₃ ⁻ -N μg N L ⁻¹	Cl ⁻ mg L ⁻¹	Alk μmol L ⁻¹
Kamieczyk ^b	5.11	2.76	0.53	2.32	0.38	5	11.3	490	0.9	8.1
Szklarka ^b	4.85	3.23	0.81	2.16	0.50	10	14.2	590	1.0	7.5
Tomniczka ^b	5.40	2.71	0.73	1.38	0.37	5	9.0	865	0.6	8.4
Maly Staw ^a	5.94	1.28	0.27	1.11	0.21	5	4.7	200	0.3	15.5
Wielki Staw ^a	4.94	1.13	0.18	0.81	0.24	10	5.0	360	0.4	3.9
Wrzosowka ^b	5.02	4.41	0.95	1.78	0.49	7	15.9	885	0.8	6.9
Plasawa 1 ^b	5.68	2.98	0.75	1.91	0.58	7	9.6	395	0.7	24.5
Plasawa 2 ^b	5.72	2.92	0.75	1.91	0.58	5	9.7	385	0.7	24.3
Plasawa 3 ^b	4.77	1.87	0.39	1.14	0.19	5	7.5	260	0.4	5.4
Długi Staw ^a	5.93	1.99	0.12	0.31	0.14	9	3.2	645	0.2	2.2
Zielony Staw ^a	6.79	2.86	0.21	0.34	0.19	45	3.1	300	0.2	122

Table A-6. Concentration of chemical compounds in runoff from different watersheds sampled September 20-22, 1995 continues. Data from Długi and Zielony Staw is from October 3, 1995. ^a: Lake; ^b: Stream. Plasawa 1, 2, 3 are different stations along the Plasawa stream.

Site	K ₂₅ mS m ⁻¹	ANC μeq L ⁻¹	TOC mg L ⁻¹	RAI μg L ⁻¹	OAI μg L ⁻¹	LAI μg L ⁻¹	Tot- N μg L ⁻¹	Si mg SiO ₂ L ⁻¹
Kamieczyk ^b	3.90	-0.6	3.1	253	116	137	590	11.0
Szklarka ^b	4.79	-27.1	2.3	353	88	265	665	10.5
Tomniczka ^b	3.41	1.8	1.4	177	55	122	895	6.9
Maly Staw ^a	1.72	21.0	1.7	63	47	16	315	5.4
Wielki Staw ^a	2.03	-26.0	1.4	226	36	190	495	3.6
Wrzosowka ^b	5.22	-24.6	1.2	345	47	298	910	9.3
Plasawa 1 ^b	3.44	65.3	8.6	164	139	25	850	8.9
Plasawa 2 ^b	3.44	60.8	8.5	166	136	30	855	8.9
Plasawa 3 ^b	2.96	-4.4	6.4	405	222	183	435	6.7
Długi Staw ^a	1.62	9.6	0.20	10	10	0	690	2.2
Zielony Staw ^a	2.02	92.7	0.68	10	10	0	430	1.2



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