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## Critical loads of acidity to lakes in the Polish Tatra Mountains.

A study of the yearly  
variations in the  
precipitation and water  
chemistry



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P.O. Box 69, Korsvoll	Televeien 1	Rute 866	Thormøhlensgt 55	Søndre Tollbugate 3
N-0808 Oslo 8	N-4890 Grimstad	N-2312 Ottestad	N-5008 Bergen	N-9000 Tromsø
Norway	Norway	Norway	Norway	Norway
Phone (47) 22 18 51 00	Phone (47) 37 04 30 33	Phone (47) 62 57 64 00	Phone (47) 55 32 56 40	Phone (47) 77 68 52 80
Telefax (47) 22 18 52 00	Telefax (47) 37 04 45 13	Telefax (47) 62 57 66 53	Telefax (47) 55 32 88 33	Telefax (47) 77 68 05 09

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<b>Author(s):</b> Bente M. Wathne Wojciech A. Mill Marek Kot Dorota Rzychon Arne Henriksen Kjetil Tørseth	NIVA Inst. for Ecology of Industrial Areas Tatra Mountain National Park Inst. for Ecology of Industrial Areas NIVA NILU	<b>Topic group:</b> Acid Precipitation
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**Abstract:**

As part of the Agreement on Environmental Cooperation between Norway and Poland critical loads of acidity and their exceedance to two lakes in the Polish Tatra Mountains have been calculated after an extensive programme on water chemistry and precipitation. The critical load of acidity is exceeded in Dlugi Staw, one of the two lakes in the study. The main difference between the comparable areas is the great importance of nitrogen deposition in the Tatra Mountains. The nitrogen leaching of Dlugi Staw is about 90% of the incoming nitrogen, i.e. almost all incoming nitrogen is leaving the lake as nitrate, while Zielony Staw is retaining about 50% of the incoming nitrogen. The nitrate leaching in the two Tatra lakes is much higher than the nitrate leaching of high mountain lakes in Norway subjected to similar sulphur and nitrogen deposition. Here, we find maximum leaching values of less than 30% of the incoming nitrogen. We have no reasonable explanation for this at the present time. To be able to understand this differences, further studies are needed.

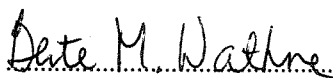
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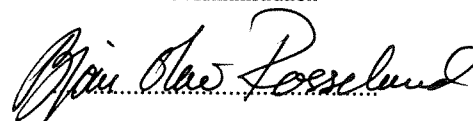
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Bente M. Wathne

For the Administration



Bjørn Olav Rosseland

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

**A study of the yearly variations in the precipitation and water chemistry**

Bente M. Wathne<sup>1</sup>  
Wojciech A. Mill<sup>2</sup>  
Marek Kot<sup>3</sup>  
Dorota Rzychon<sup>2</sup>  
Arne Henriksen<sup>1</sup>  
Kjetil Tørseth<sup>4</sup>

<sup>1</sup>Norwegian Institute for Water Research, Box 69, 0808 Oslo

<sup>2</sup>Institute for Ecology of Industrial Areas, ul. Kossutha 6, PL-40 832 Katowice

<sup>3</sup>Tatra Mountain National Park, ul. Chalubinskiego 42 a, PL-34 500, Zakopane

<sup>4</sup>Norwegian Institute for Air Research, Box 64, 2001 Lillestrøm

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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 Cooperative 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 from the first year of sampling were discussed under a Polish visit to Norway in November 1993, and will be reported here. The project activities for the Norwegian team has been financed by the Norwegian Ministry of Foreign Affairs.

## ABSTRACT

Critical loads of acidity to surface waters, is defined as *The highest load that will not lead in the long-term to harmful effects on biological systems, such as decline and disappearance of fish populations*. Critical loads have been most thoroughly studied with respect to sulphur, and critical loads for sulphur were exceeded long ago in large regions in Norway and in many other countries. The effect is manifested in the form of acidic fishless lakes. As part of the Agreement on Environmental Cooperation between Norway and Poland critical loads of acidity and their exceedance to two lakes in the Polish Tatra Mountains have been calculated after an extensive programme on water chemistry and precipitation. The Polish Tatra Mountains are situated on the boundary to Slovakia. This study concentrated on two acidification sensitive lakes, Dlugi Staw and Zielony Staw, located in the granitic area of the mountains, selected after an earlier investigation under the same agreement. Lake samples were collected biweekly from September 1992 to September 1993, and analysed at the Norwegian Institute for Water Research. Weekly precipitation samples were collected in the same period and sent to the Norwegian Institute for Air Research to be analysed. This study confirms the results from the earlier investigations, 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 Dlugi Staw, one of the two lakes in the study. The main difference between the comparable areas is the great importance of nitrogen deposition in the Tatra Mountains. The nitrogen leaching of Dlugi Staw is about 90% of the incoming nitrogen, i.e. almost all incoming nitrogen is leaving the lake as nitrate, while Zielony Staw is retaining about 50% of the incoming nitrogen. The nitrate leaching in the two Tatra lakes is much higher than the nitrate leaching of high mountain lakes in Norway subjected to similar sulphur and nitrogen deposition. Here, we find maximum leaching values of less than 30% of the incoming nitrogen. The nitrogen deposition in the Tatra is about the same as in southernmost Norway. Thus, it is surprising that the nitrate concentrations in the Tatra lakes are significantly higher than those in Norway, even for the alpine lakes in southern Norway. We have no reasonable explanation for this at the present time. To be able to understand this differences, further studies are needed. They should involve continuous measurements of water flow from the Zielony and Dlugi lakes and also measurements of dry deposition. The future activities should also include an extension to other potential sensitive areas in Poland. Further, steps should be taken to co-ordinate the acidification studies on the Slovakian side of the granitic Tatra Mountains.

## 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 exceedances 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 a 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.*, 1992). The following up of this first Cooperative work is 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 first year of this project will be reported here together with a discussion of future joint activities for the Polish and Norwegian groups.

## 2. DEFINITIONS

Critical loads for "unacceptable change" are set in relation to effects on terrestrial and aquatic organisms. Some useful definitions are given in the box.

### DEFINITIONS

**Critical load:** The highest load that will not lead in the long-term to harmful effects on biological systems, such as decline and disappearance of fish populations.

**Receptor:** An ecosystem which may potentially be affected by atmospheric inputs of sulphur and nitrogen (soil, ground water, surface water).

**Biological indicator:** selected organism(s) or populations which are sensitive to chemical changes as a result of atmospheric inputs of sulphur and nitrogen (forest, fish, invertebrates).

**Critical chemical value:** The value of a critical chemical component or combinations of components above or below no rise to a harmful response in a biological indicator is given (pH, ANC, Al/Ca ratio).

The *critical load* definition provides a framework for making numerical estimates of the loads at which adverse effects occur. Such estimates may be based upon a number of different methods and the selection of method depends to a large extent upon the *receptor* chosen and the availability of relevant data for the calculations. The effects on sensitive *biological indicators* are used to identify harm to freshwater systems. Organisms are often efficient "integrators" of the chemical conditions in their environment and may thus provide a convenient means of measuring effects. The methods for

calculating critical loads for acidity of freshwaters all use chemical data, often making assumptions regarding the water chemistry to acidification. The *critical chemical value* is based on our knowledge of the ecological tolerance of sensitive biological species to water chemistry.

### 3. CALCULATING CRITICAL LOADS OF ACIDITY TO FRESHWATERS

We have applied the Steady-State Water Chemistry method (Henriksen *et al.* 1990) to the data for the Tatra Mountain lakes. This method is described in the earlier mentioned manual for calculating critical loads and their exceedances compiled by The Task Force on Mapping.

#### THE STEADY-STATE WATER CHEMISTRY METHOD

Acid Neutralisation Capacity (ANC) is used as the chemical criterion for sensitive indicator organisms in surface waters. ANC is defined as the difference between non-marine base cations (BC)\* and strong acid anions (AN)\*:

$$[\text{ANC}] = [\text{BC}]^* - [\text{AN}]^* = [\text{HCO}_3^-] + [\text{A}^-] - [\text{H}^+] - [\text{Al}^{\text{n}+}] \quad (1)$$

where  $[\text{HCO}_3^-]$  is the bicarbonate concentration,  $[\text{A}^-]$  is the concentration of organic anions and  $[\text{Al}^{\text{n}+}]$  is the sum of all positively-charged aluminium species.

The critical load for a lake is defined as the original leaching of base cations from the catchment area. The critical load (CL) of acidity for a given indicator organism is given by :

$$\text{CL} = ([\text{BC}]^*_0 - [\text{ANC}_{\text{limit}}]) \cdot Q - \text{BC}^*_d \quad (2)$$

where  $\text{BC}^*_0$  is the preindustrial non-marine base cation concentration,  $\text{ANC}_{\text{limit}}$  is the critical ANC-concentration for the organism considered,  $Q$  is the mean annual runoff and  $\text{BC}^*_d$  is the non-marine base cation deposition. To compute the critical load, values for  $\text{BC}^*_0$  have to be estimated from present-day water chemistry data (see Henriksen *et al.* 1990).

The exceedance of the critical load for sulphur,  $\text{CL}_{\text{ex}}$ , is then calculated by comparing the critical load computed by Equation (2) with the present non-marine sulphate deposition,  $\text{SO}_4^*_d$ .

$$\text{CL}_{\text{ex}} = \text{CL} - \text{SO}_4^*_d \quad (3)$$

Note that this equation gives the critical load exceedance for sulphur, assuming that nitrogen does not contribute to the acidification.

Non-marine contributions are indicated by an asterisk (\*).

The method is only applicable to surface waters, and is a static method, i.e. the critical load is computed assuming a steady-state with respect to the inputs from the atmosphere. The method is applied in the same way as to the Scandinavian lakes. The Steady-State Water Chemistry method is shortly described in the box above. For further details see Henriksen *et al.* 1990.



## 4. THE TATRA MOUNTAINS

The Tatra Mountains (Tatra Mts) are situated on the border between Poland and Slovakia. It is a mountain ridge 53 kilometer 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, that 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 of air and precipitation levels of the highest in the country are characteristic for the Tatra Mts. Another distinctive features for that region are frequent, strong winds, transporting dusts and pollutants emitted into atmosphere. The diversity of flora in the Tatra Mts 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.

### 4.1 Localisation of the study area.

Figure 1 shows the location of the Tatra Mts in Poland as well as a detailed map of the study area. After preliminary research in an extensive territory, the study area has been reduced to the part of the Polish Tatra Mts. with cristalline core where the mineralization of surface waters is very weak, resulting in sensibility to acid deposition from the atmosphere. After thorough analysis of works already carried out within the described project, the lakes located in the area of Hala Gasienicowa were selected for further research. These lakes are: Staw Dlugi (TPO2), selected because of its significant degree of acidification and Zielony Staw (TP20), selected because of its rich biological life.

### 4.2 Localization of the precipitation station.

The sampling station for precipitation is situated in Hala Gasienicowa, in a station of the Institute of Meteorology and Water Management, near the lakes under investigation. The location of the meteorological station is presented in Figure 1. The station is located in the upper part of Sucha Woda Valley on the upper timberline (1520 m a.s.l.) in the northern slopes of the mountain ridge, with the south east exposition. The Sucha Woda Valley opens in the north east direction, and the prevailing wind circulation on the station is SW.

### 4.3 Hydrology.

The post-glacial lakes of the Tatra Mts are situated above the upper forest zone, on the level of mountain-pine and alps. 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 Mts Lakes are in most cases balanced, with differences amounting to several tens of centimetres. Maximal water level appears in the period of spring thaws as well as 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 are shown in Table 4.1

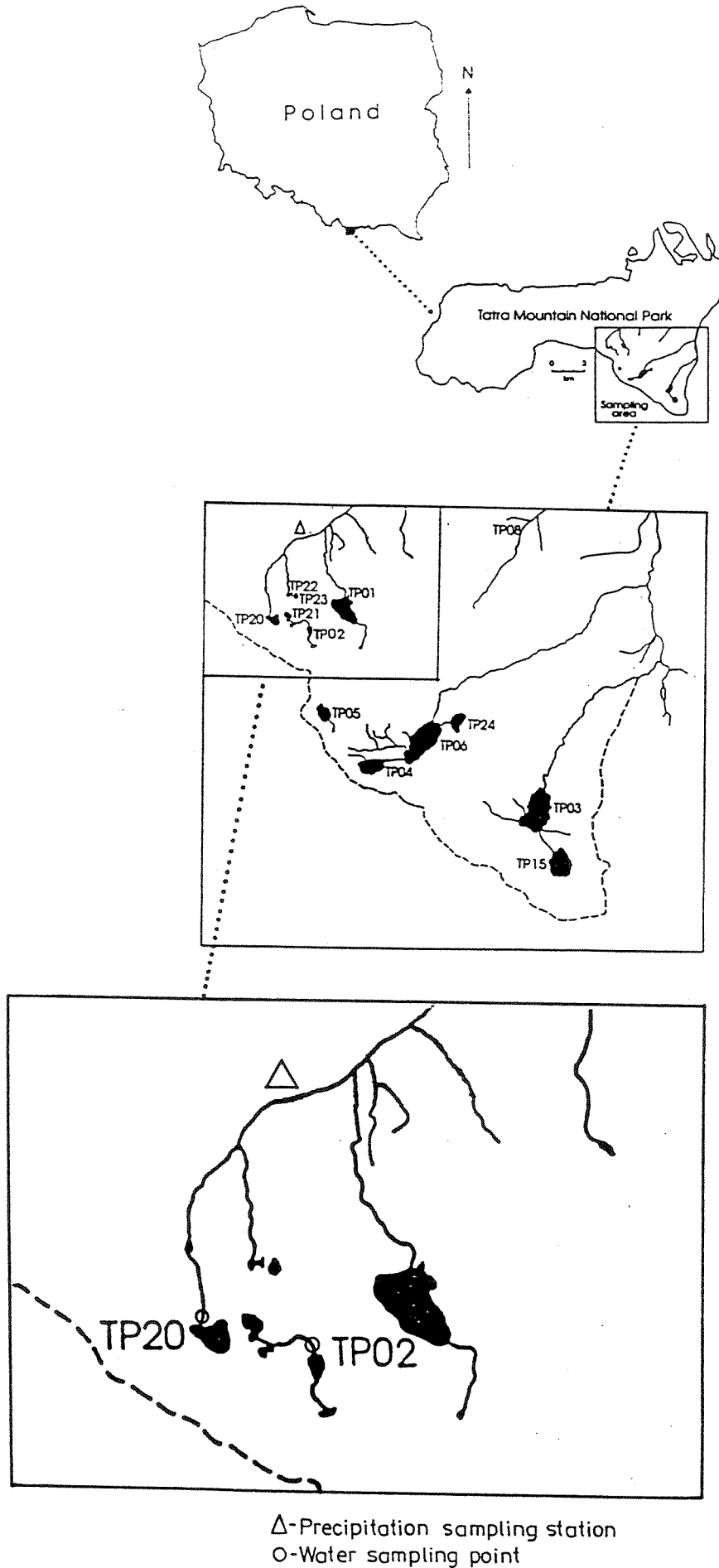


Figure 1. Location of the Tatra Mountain National Park and the study area.

Table.4.1. Morphological and hydrological parameters of studied lakes (Lajczak, 1980; Szafer et al., 1962).

Lake	Altitude a.s.l. (m)	Surface (ha)	Maximal depth (m)	Water volume in medium water level (mln m <sup>3</sup> )	Surface of catchment area of the lake (km <sup>2</sup> )
Zielony Staw Gasienicowy	1632	3.84	15.1	0.290	1.3
Dlugi Staw Gasienicowy	1784	1.59	10.6	0.081	-

Both lakes are supplied with waters from springs and episodic and seasonal creeks of different efficiency.

#### 4.4 Geology and soils.

Dlugi Staw and Zielony Staw are situated on the crystalline area of the High Tatras. Their location in concave forms created by glacial erosion is similar to other lakes in the Tatra Mts. The bottoms of the lakes and the rock steps confining them are cut in impermeable granite rocks surrounded by morainic covers and banks of different age. Moreover, in the surroundings of Zielony Staw a few inserts of carbonate rocks are observable on the western slopes of the valley (Kot, 1993).

Contemporarily, the morphology of the lakes neighbourhood is modelled by frost weathering, insolation weathering, vertical soil movements, needle-ice activity, rockfall, creep, gelifluction, snow avalanche activity, nivation around snow patches, deflation, surface and concentrated wash, piping (suffosion) and chemical denudation (Klapa, 1980). In the surroundings of both lakes barren soils and podzolic soils appear.

#### 4.5 Runoff.

The high mountain areas are situated within the masses of humid air, which characteristic feature is the variability of climatic conditions and various water-bearing capacity of rock formations, as well as rich water resources and complex water circulation both spatial and annual.

The mean value of runoff coefficient amounts to 0.83 for the Tatra Mts, and for crystalline Tatras 0.86 (Lajczak, 1988). This rather high value can be attributed to the rather low evaporation under the conditions of low temperature, increased air humidity, frequent precipitation as well as rapid water runoff in the crystalline rock zone.

Average annual, total unitary runoff, according to measurement data of 1961-1980, for the upper parts of Hala Gasienicowa amounts to 1 576 000 m<sup>3</sup> km<sup>-2</sup> yr<sup>-1</sup>, (Lajczak, 1988), and this value was used for calculations of the critical loads

The mean monthly runoff value was calculated using the data on precipitation values from the measurement station situated in Hala Gasienicowa. The monthly precipitation sums were increased with respect to the relation between precipitation amount and the elevation above sea level (separately for Dlugi Staw and Zielony Staw), the obtained values were then multiplied by the runoff quotient for the crystalline Tatras (Lajczak, 1988). Due to the fact that the deposited winter precipitation increase the runoff in the periode of spring thaws (May - end of July), they were added to the runoff calculated by the method presented above, according to the data on the ratio of snow cover decrease (Szafer et al., 1962).

#### 4.6 Climate and flora.

The climate of the Tatras represent features of high mountains, characteristic for the central European type of climate of the westerlies. High altitudes above s.l. as well as rich and deep relief are the cause of many climatic phenomena and differences. The main properties of the high mountain climate of the Tatras are: summer maximum and winter minimum in the annual course of the atmospheric pressure, prominent superiority of autumn temperature as compared with spring, smaller annual range of temperature on higher altitudes, abundance of winter inversions of temperature, increase of humidity and cloudiness in summer and their decrease in winter, equal proportions of summer and winter precipitation.

Among the peculiarities of the Tatras are to be noted frequent and strong winds and low values of relative humidity on peaks by air descending (Szafer *et al.* 1962).

Table.4.2. Vertical Climatic Zones after Hess, 1965.

Vertical climatic zone	Vegetation zone	Elevation a.s.l.	Mean temperature [°C]		
			Year	Jan.	Jul.
Cold	Alpine summit	2200-2663	-2.0	-12.0	4.0
Temperate cold	Alpine meadow	1850-2200	0.0	-10.0	6.0
Very cool	Dwarf pine	1550-1850	2.0	-8.5	8.2
Cool	Upper forest	1100-1550	4.0	-6.0	10.5
Temperate cool	Lower forest	700-1100	6.0	-5.5	13.0

In the Polish Tatras the average amounts of precipitation increase proportionally to the increase of altitude, from 1200-1300 mm in the marginal mountain area, to 2000 mm in the high mountain area. For the elevation above 2000 a.s.l. the precipitation inversion is observable (Lajczak, 1988). Mean annual sums of precipitation for Hala Gasienicowa for the period 1931-1960 amounted to 1678 mm. The average number of days with snow cover depends obviously on the elevation above s.l., and at the same time on temperature and contribution of snowfalls in the total sum of precipitation, which for Hala Gasienicowa is 193 days annually, for Kasprowy Wierch 230 days (Szafer *et al.* 1962). Particular climatic factors, related to annual mean temperature decreasing with elevation above s.l., develop climatic belts which coincide with the vegetation belts (Table 4.2.)

The location of the lakes meet the conditions of the very cool climatic zone. In the surroundings of Staw Długi the flora of screes poor in Oxysio-Safiragetium carpatince as well as flora of granite blocks - mostly lichens is observable.

In the surrounding of Zielony Staw secondary grass as well *Vaccinietum myrtylli*, *Empetro-Vaccinietum*, *Nardetalia* communities appear mostly in the mountain-pine zone and on the south-western side - the flora of moist grids and fixed granite screes - *Luzuletum Spadiceae*.

#### 4.7 Aquatic ecosystem

The waters of the Tatra lakes above timberline are ultraoligotrophic, inhabited with the phytoplankton dominated by smaller nannoplanktonic forms (*Mallomonas*, *Cryptomonas*). In the past in Tatra lakes there was a very high number of zooplanktonic species. Wierzejski (1882-1883), Litynski (1913) and Minkiewicz (1914) confirm the existence of 75 planktonic species belonging to the association *Calanoida* (*Daphnia pulicaria* Forbes, *Holopedium gibberum* Zaddach, *Polphemus pediculus* and *Heterocope saliens* Lill).

The fishless waters of Tatra mountains have been artificially stocked, since the end of nineteenth century to the fifties of twentieth century. The introduction of fish to the Tatra lakes caused extinction of the local population of shellfish zooplanktonic forms. Along with the disappearance of the *Calanoida* group, marked increase could be noticed in two cosmopolitan species of *Keratella quadrata* Ehrbs and *Polyartha dolichoptera* Idelson. (Gliwicz, 1985).

The lake Zielony Staw was fishless until 1948-49 when brook trout (*Salvelinus fontinalis*) was stocked into several small lakes in the Gasienicowa Valley. The successful stocking was the effect of the action from 21 October 1949 when the Polish Anglers Association put 6000 one year old brook trout into this lake (Paschalski in Kot, 1993). The population of brook trout increased and became overpopulated, but since 1965 overpopulation has been strongly controlled by parasitical fungus *Ichtiophonus intestinalis*. In spite of that, the brook trout population survived, controlled by parasites.

The fish population of Zielony Staw lake has an access to the Litworowy Staw located several hundred meters downstream, which is also one of the spawning places for all populations. At the same time as Zielony Staw some other small lakes in Gasienicowa Valley have been stocked. Dlugi Staw lake has also been populated by brook trout, but this population disappeared in the sixties.

Fish from Zielony Staw indicates the negative effect of the reduced pH and has a substantial increase in mucus secretion by brook trout. Apart from that, occasional fish death has been observed at the sites of thawing water entrance into the lake (May 1991), and also in case of the increase of water outflow resulting from intensive precipitation following the draught period (outflow from Litworowy Staw in Autumn 1990) (Byrcyn *et al.*, 1992).

## 5. HYDROCHEMICAL STUDIES IN THE POLISH TATRA MOUNTAINS

Extensive studies of the chemical properties of the Tatra lakes and streams were carried out in the 1950's and 1960's (Oleksynowa, Komornicki 1957-1969, 1979; Bombówna 1965, 1971; Paschalski, 1963). That research was aimed at finding the relation between the chemistry of surface waters and the geological factors. The studies showed that trace or low level of buffering (degrees II or III in I - X scale) and decreased mineralization values (dissolved salts; 28 - 63 mg/l) were characteristic for the crystalline Tatras waters.

In the 1980's, studies were undertaken on atmospheric pollution impact on the chemical composition of the Tatras surface waters, both in the Polish part (Malecka, 1989, 1991; Krywult, 1990, 1992; Wojtan, 1989; Polakiewicz, 1987; Kot, 1991, 1992, 1993) and in the Slovak part (Fott, 1982; Stuchlik, 1985; Fott, 1987).

All research proved a processing acidification of the crystalline Tatras surface waters. With respect to accumulation of analytic material, the research carried out can be divided into two groups:

- survey research, including single collecting of water samples from a significant number of lakes and streams (Oleksynowa and Komornicki 1957-1969, 1979; Stuchlik, 1985).
- research on the basis of single or several samples collected from waters of one or several lakes or catchment basins (Wojtan, 1989; Polakiewicz, 1987; Krywult, 1990, 1992; Malecka, 1985; Bombówna, 1965, 1968, 1969).

Waters of the lakes, being the subject of the current stage of research, have already been investigated many times. The survey of analyses research is presented in the Table 5.1.

Moreover, since 1987 the study of the changes of some physico-chemical parameters (temperature, pH, conductivity) of Zielony Staw Gasienicowy waters in annual cycle were carried out (Kot, 1991,1993). That research proved significant decrease of pH value, especially during spring thaws and after rainfalls occurring after long dry period.

Summarizing, it should be stated, that the results of the already performed research are incomparable due to the differences of sampling terms, range of performed analyses as well as differences in applied analytical methods.

The results of the research included in this work are the first attempt of global presentation of the problem of acid deposition impact on the Tatra Mountains lakes, with respect to changes of water chemistry and precipitation in annual cycle.

Table.5.1. Survey of selected chemical parameters concentrations in the waters of Dlugi Staw and Zielony Staw.

Lake	Year	pH	Ca	Mg	K	Na	N-NO <sub>3</sub>	N-NH <sub>4</sub>	SO <sub>4</sub>
Dlugi Staw	1935 <sup>1</sup>	6.25	6.0	-	-	-	-	-	-
	1960 <sup>2</sup>	5.8	2.4	0	-	-	-	-	4.3
	1966 <sup>3</sup>	6.2	2.5	0.6	0.07	0.20	0.330	0.08	1.5
Zielony Staw	1935 <sup>1</sup>	6.25	-	-	-	-	-	-	-
	1960 <sup>2</sup>	6.4	3.0	0.2	-	-	-	-	5.3
	1966 <sup>3</sup>	6.9	3.2	1.1	0.08	0.24	0.280	0.080	1.5

<sup>1</sup> Olszewski, 1939

<sup>2</sup> Oleksynowa, Komornicki, 1989

<sup>3</sup> Bombówna, 1971

## 6. DEPOSITION DATA

The studies on atmospheric precipitation chemistry carried out from July 1962 to December 1963 at Kasprowy Wierch and Lysa Polana, had already shown a very low pH of 4.1 (Orlicz and Vollova, 1974). The average level of sulphates recorded at that time was 10.23 mg/l and 7.05 mg/l while that of nitrates was 1.14 mg/l and 1.48 mg/l, for Kasprowy Wierch and Lysa Polana, respectively.

In the 1980s, studies on rainwater were carried out at ten sampling stations localised within the boundaries of the Tatra National Park (Malecka, 1989, 1991). The studies have shown that pH of rainfall, as noted in the years 1988 - 1990, ranged between 3.6 - 7.05. These low pH values have been also confirmed in the studies performed by Polakiewicz (1987), and Wojtan (1989). Both researchers reported the pH values within the range from 3.8 to 5.19.

From time to time, chemical analyses of wet precipitation were also carried out. For example, in July 1989, rainfall was being collected at Hala Gasienicowa, with sulphate concentration ranging between 2.1 and 11.1 mg/l (average: 5.1 mg/l) (Polakiewicz, 1989). According to Kasina (1989), average SO<sub>4</sub>-S wet precipitation in the Tatra Mountains amounts to 820 mg/m<sup>2</sup> year.

In June and July of 1986, Krywult studied the chemical composition of snow sampled from the High Tatra area. The following parameters were determined: pH of samples ranged between 5.0 - 5.6, the

average values were as follows: hardness was 41.9  $\mu\text{eq/l}$ , Cl content 1.0 mg/l,  $\text{SO}_4$  3.7 mg/l,  $\text{NO}_3\text{-N}$  0.1 mg/l. Apart from the above mentioned occasional studies, long term monitoring of the forest environment is carried out in Poland by the Institute of Forest Research. The monitoring covers determination of air pollutant concentrations ( $\text{SO}_2$ ,  $\text{NO}_x$ , and F) as well as measurements of dry deposition, with the application of the contact method using  $\text{K}_2\text{CO}_3$  as an absorbing agent. The dry deposition value determined with that method for the Tatra National Park area in the years 1988/89 amounted to 9.489 mg  $\text{SO}_2 \text{ m}^{-2} \text{ day}^{-1}$  and 0.163 mg  $\text{NO}_x \text{ m}^{-2} \text{ day}^{-1}$  (Wawrzoniak, 1989).

The nearest precipitation station included in the European Monitoring and Evaluation Programme (EMEP) is located at Chopok in Slovakia, at 2008 m a.s.l. (48°56' N and 19°35' E). In 1986 the annual precipitation was 1067 mm, the weighted yearly wet concentration of sulphur was 1.96 mg S/l and of nitrate 0.53 mg N/l. In 1992 the annual precipitation was 839 mm, the weighted yearly mean concentration of sulphate was 1.63 mg S/l, of nitrate 0.47 mg N/l and of ammonium 0.80 mg N/l. Due to the fact that the research results in Poland are fragmentary, and the results obtained from Chopok, because of noticeable participation of local emissions in air pollution, are not representative for Hala Gasienicowa, an annual series of precipitation quantity and quality research was performed in Hala Gasienicowa. Table 8.3. presents the results of the chemical analyses of precipitation in the years 1992/1993.

## 7. SAMPLING PROGRAMME

### 7.1. Sampling procedure for water chemistry.

In order to collect complex data on the Tatra Mts. waters chemistry, three research projects have been carried out. In the first stage samples from all major Tatras streams and lakes were collected and analysed. The second stage consisted in collecting samples only from those lakes, which the first stage proved to be sensitive to acid deposition (Henriksen *et al.*, 1992). The feature of investigated stream waters is high mineralization degree, that results from the calcareous-dolomitic substratum through which they flow, showing at the same time no sensitivity to acid deposition. In the third research project, that will be reported here, running from September 1992 to the end of August 1993, two of the most sensitive lakes were chosen for a more extensive sampling.

Every two weeks samples were taken from the two lakes: Dlugi Staw (TP02) and Zielony Staw (TP20). The sampling points were the outflow of the lakes. Bottles with samples were then mailed to NIVA, where they were analysed.

### 7.2. Sampling procedures for precipitation.

In order to collect data on pollution deposition from the atmosphere, a deposition station was installed in the area of the Institute of Meteorology and Water Management (IMWM) station, situated in the vicinity of the studied lakes, in Hala Gasienicowa. Precipitation as rain or snow was collected by use of the NILU precipitation sampler. The sampling equipment was operated by members from IMWM staff according to the provided instruction elaborated on the basis of description in Norwegian Standard 4864 - Air Research "Collection of samples of precipitation".

Weekly sums of precipitation were collected, then a representative part of the collected precipitation was taken out by the station keeper and sent to NILU for analysis of the main components in the precipitation.

## 8. RESULTS AND DISCUSSION

### 8.1 Precipitation results

In the year from 7th of September 1992 to 6th of September 1993 analysis of the precipitation samples showed mean values of sulphate (as sulphur), nitrate and ammonium (as nitrogen) of 1.12, 0.4 and 0.44 mg/l, respectively. The mean pH in precipitation was 4.38 with monthly values varying in the range 4.11 - 4.81. The monthly mean values are shown in Figure 8.1.

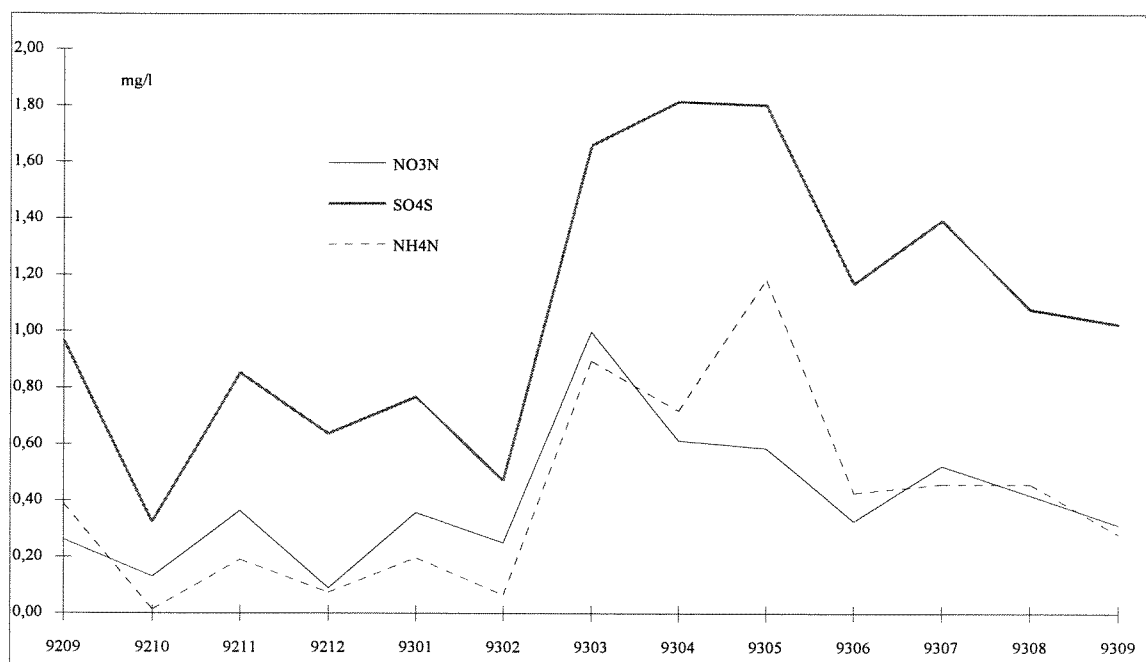


Figure 8.1. Monthly mean concentrations of NO<sub>3</sub>-N, SO<sub>4</sub>-S and NH<sub>4</sub>-N in precipitation samples from Hala Gasienicowa from September 1992 to September 1993.

The precipitation amount in the period was 1155 mm and resulted in a wet deposition of approx. 1.3 g SO<sub>4</sub>-S/m<sup>2</sup>, 0.46 g NO<sub>3</sub>-N/m<sup>2</sup> and 0.51 g NH<sub>4</sub>-N/m<sup>2</sup>. The monthly precipitation values are shown in Figure 8.2, and the monthly deposition values in Figure 8.3.

The highest monthly average concentrations of sulphate, nitrate and ammonia were measured in March, April and May. Due to the amount of precipitation, the largest monthly wet depositions was measured in May and June.

As mentioned, the nearest precipitation station included in the European Monitoring and Evaluation Programme (EMEP) is located at Chopok in Slovakia, location 48°56' N and 19°35' E at 2008 m above sea level. In Table 8.1, the 1992 annual precipitation and the weighted yearly mean concentrations of sulphate (SO<sub>4</sub>-S), nitrate (NO<sub>3</sub>-N) and of ammonium (NH<sub>4</sub>-N) are shown. The corresponding data for the EMEP-stations Birkenes and Skreådalen, the stations at Valle and Vatnedalen in the southernmost Norway, and the results for Hala Gasienicowa in the twelve months measured are also shown.

Southernmost Norway is the area most heavily exposed to acid rain in the country. Birkenes is situated not far from the coast, and the stations Valle, Skreådalen and Vatnedalen are situated in valleys at some distance from the coast



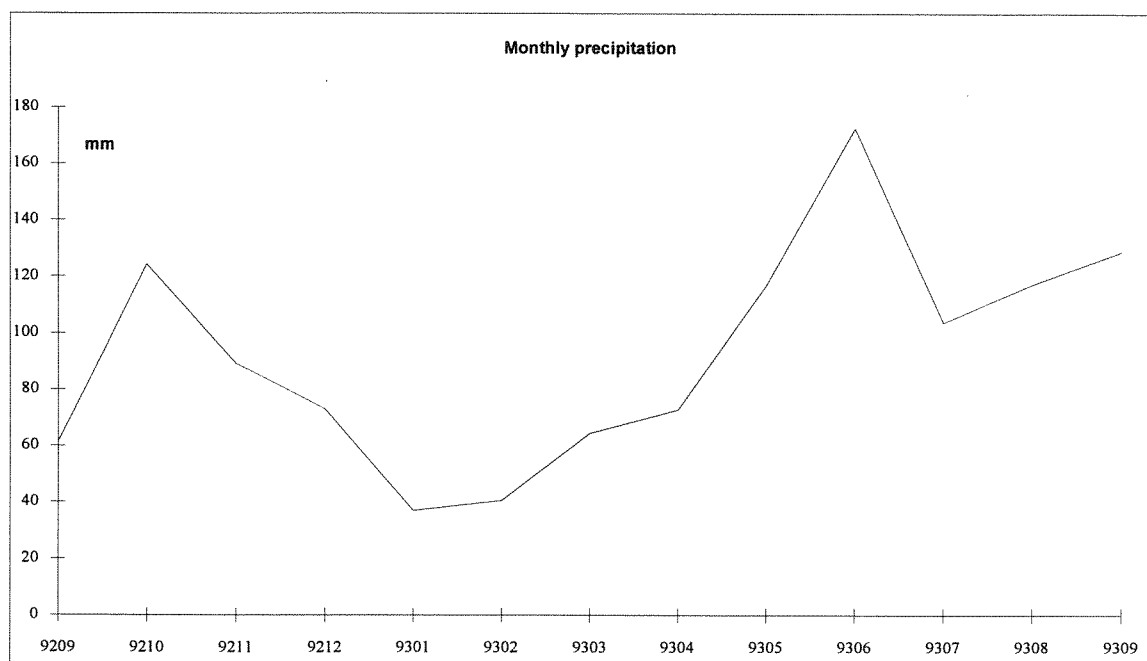


Figure 8.2. Monthly precipitation amount sampled at Hala Gasienicowa from September 1992 to September 1993.

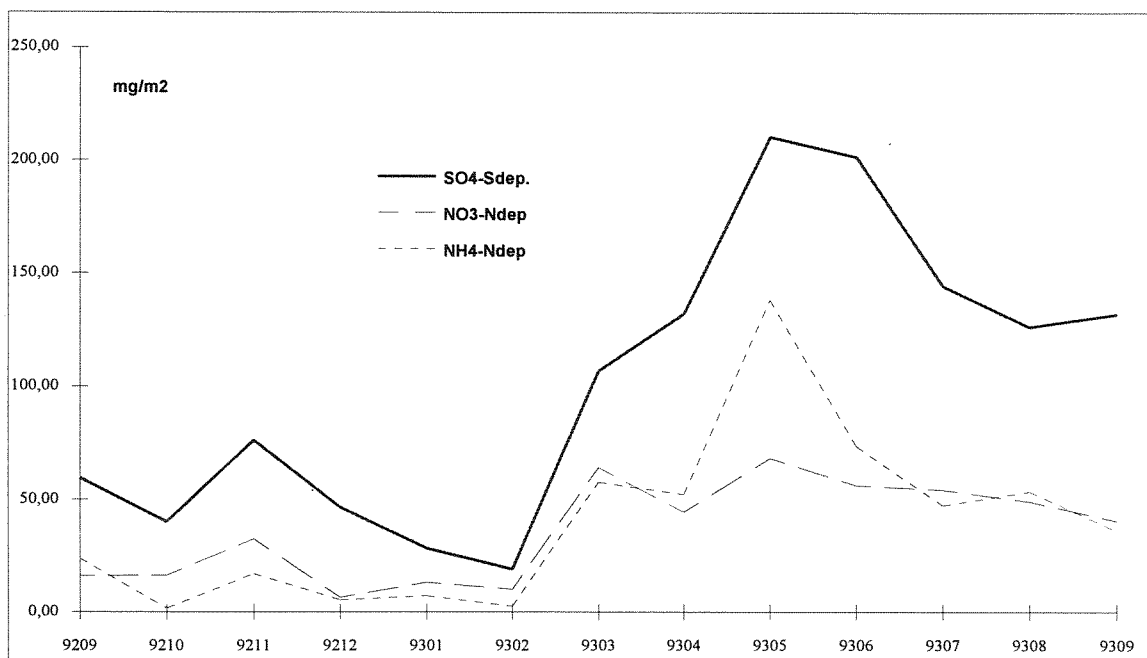


Figure 8.3. Monthly deposition values of NO<sub>3</sub>-N, SO<sub>4</sub>-S and NH<sub>4</sub>-N at Hala Gasienicowa from September 1992 to September 1993.

Table 8.1. Annual precipitation and weighted yearly mean concentrations of NO<sub>3</sub>-N, SO<sub>4</sub>-S and NH<sub>4</sub>-N, at the meteorological stations in Chopok (Slovakia) and Birkenes, Valle, Skreådalen and Vatnedalen (Norway) for 1992 and Hala Gasienicowa (Poland) for the periode September 1992 - September 1993.

Station	Year	h.a.s.l. (m)	mm	SO <sub>4</sub> -S (mgS/l)	Sum N (mgN/l)	NO <sub>3</sub> -N (mgN/l)	NH <sub>4</sub> -N (mgN/l)
Chopok	1992	2008	839	1,63	1,27	0,47	0,80
Birkenes	1992	190	1344	0,74*	0,96	0,52	0,44
Valle	1992	250	1120	0,46*	0,50	0,28	0,22
Skreådalen	1992	465	2728	0,37*	0,47	0,24	0,23
Vatnedalen	1992	800	1055	0,29*	0,28	0,17	0,11
Hala Gasienicowa	1992/93	1520	1202	1,12	0,84	0,40	0,44

\*= seasalt corrected value

Also the yearly deposition values for the stations and the relations between deposition of N and S are shown in table 8.2 for the stations Chopok, Birkenes, Valle, Skreådalen, and Vatnedalen for 1992 and Hala Gasienicowa for 1992/93.

The results from Hala Gasienicowa does not reflect the same time period as the results from the other stations. The one year values for concentrations in precipitation and for deposition should only be used for rough estimation, until better data are available.

Table 8.2. Yearly deposition values of NO<sub>3</sub>-N, SO<sub>4</sub>-S and NH<sub>4</sub>-N, at the meteorological stations in Chopok (Slovakia) and Birkenes, Valle, Skreådalen and Vatnedalen (Norway) for 1992 and Hala Gasienicowa (Poland) for the periode September 1992 - September 1993.

Station	Year	h.a.s.l. (m)	N/S	SO <sub>4</sub> -S (mgS/m <sup>2</sup> )	Sum N (mgN/m <sup>2</sup> )	NO <sub>3</sub> -N (mgN/m <sup>2</sup> )	NH <sub>4</sub> -N (mgN/m <sup>2</sup> )
Chopok	1992	2008	0,77	1368	1065	394	671
Birkenes	1992	190	1,30	991*	1292	703	589
Valle	1992	250	1,08	519*	560	318	242
Skreådalen	1992	465	1,25	1017*	1274	647	627
Vatnedalen	1992	800	0,95	301*	287	175	112
Hala Gasienicowa	1992/93	1520	0,75	1297	976	465	511

The SO<sub>4</sub>-S concentrations given for the Norwegian stations are seasalt corrected. Due to very low concentrations of marine components in the Tatras, corrections for marine sulphate has not been performed for the stations in Chopok and Hala Gasienicowa.

The data indicate that the concentrations of sulphur components in precipitation at Hala Gasienicowa are at a level in the middle between Chopok and Birkenes and higher than the valley stations in Norway. The nitrogen concentrations are in the same order of magnitude at Birkenes, Chopok, and Hala Gasienicowa, and higher than the Norwegian valley stations. The deposition of sulphur show the same pattern between the stations as the sulphur concentration, while nitrogen deposition at Birkenes, Skreådalen, Chopok, and Hala Gasienicowa, are in the same order of magnitude while the stations at Valle and Vatnedalen show lower deposition values. Estimated from these deposition data, the relative importance of N to acidification should not be less in Norway than in the Tatras.

The importance of the dry deposition in the Tatra region is not known. For the Norwegian stations we

know that the dry deposition normally is below 20 % of the total deposition. To attain more precise deposition values for the Tatra region, measurements giving the possibility to calculate the dry deposition are needed.

## 8.2. Water chemistry

### 8.2.1. Chemical composition

The concentrations of the major components are shown in Figure 8.2.1. The base cation concentrations are higher in Zielony Staw than in Dlugi Staw, and consequently the alkalinity is also higher. The sulphate concentrations are similar, indicating similar deposition of sulphate, while the nitrate concentration is significantly higher in Dlugi Staw than in Zielony Staw. The differences are largely due to the fact that Dlugi Staw is located at a higher altitude than Zielony Staw (Table 4.1). The concentration of base cations (calcium and magnesium) reflects normally the influence of the geology on lake water quality. Figure 8.2.2. compare lakes in the Tatra Mountains with lakes in southern Norway with similar concentrations of calcium and sulphate. The water chemistry of the selected lakes are very similar for the two countries, except for pH (5,49 and 6,62) and the concentrations of nitrate and alkalinity. The nitrate concentrations in the Tatra lakes are much higher

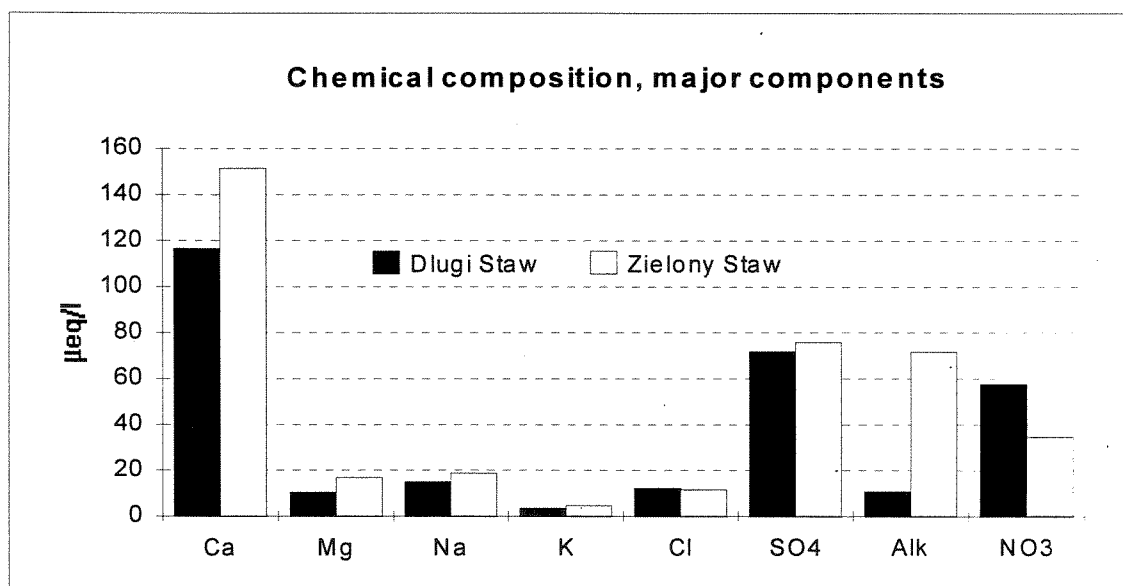


Figure 8.2.1. Mean concentrations (sept-92 to sept-93) of major components in the two Tatra lakes.

than in Norway, and the alkalinities are lower. As a consequence of the latter, the pH of the lakes are lower in the Tatra Mountain lakes. This indicate that the Tatra Lakes are more acidified than the Norwegian lakes. This difference is solely due to the higher nitrate concentrations. The differences in nitrate concentrations in the two sets of lakes are almost completely balanced by the differences in alkalinity. For example, for the second set of lakes the nitrate difference is 55 µeq/l, while the alkalinity difference is 45 µeq/l. Adding the difference in calcium concentration (10 µeq/l), the balance is complete. The Norwegian lakes are also alpine lakes located at 830 - 1150 m above sea level.

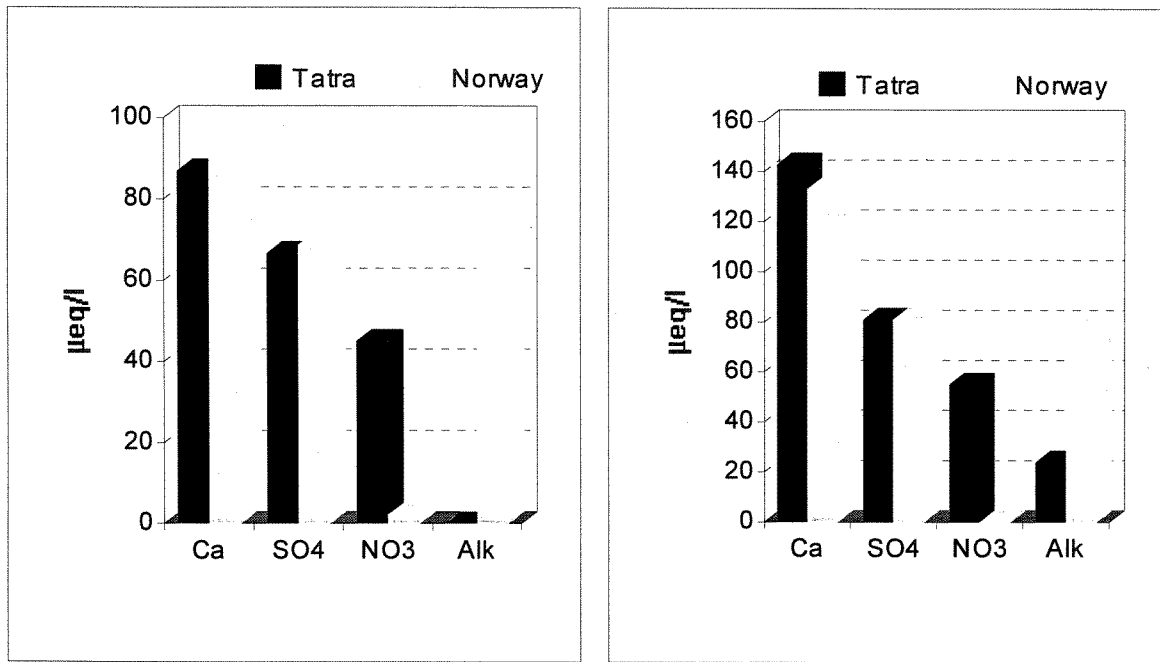


Figure 8.2.2. Comparison of water chemistry of lakes in the Polish Tatra Mountains and Norway in areas with similar geological settings.

### 8.2.2. Variations in concentrations

The Figures 8.2.3 to 8.2.6 show variations in pH and in concentrations of calcium, sulphate and nitrate in the two Tatra lakes for the period August 1992 to July 1993.

pH vary most in Dlugi Staw, with low values during fall and spring. This is clearly reflected in the dilution of calcium (Figure 8.2.4) during the same periods. The pH of Zielony Staw does not vary to the same extent, although a decline in pH is observed during the snow melt period in spring. Also, the calcium concentrations are rather stable during the observation period.

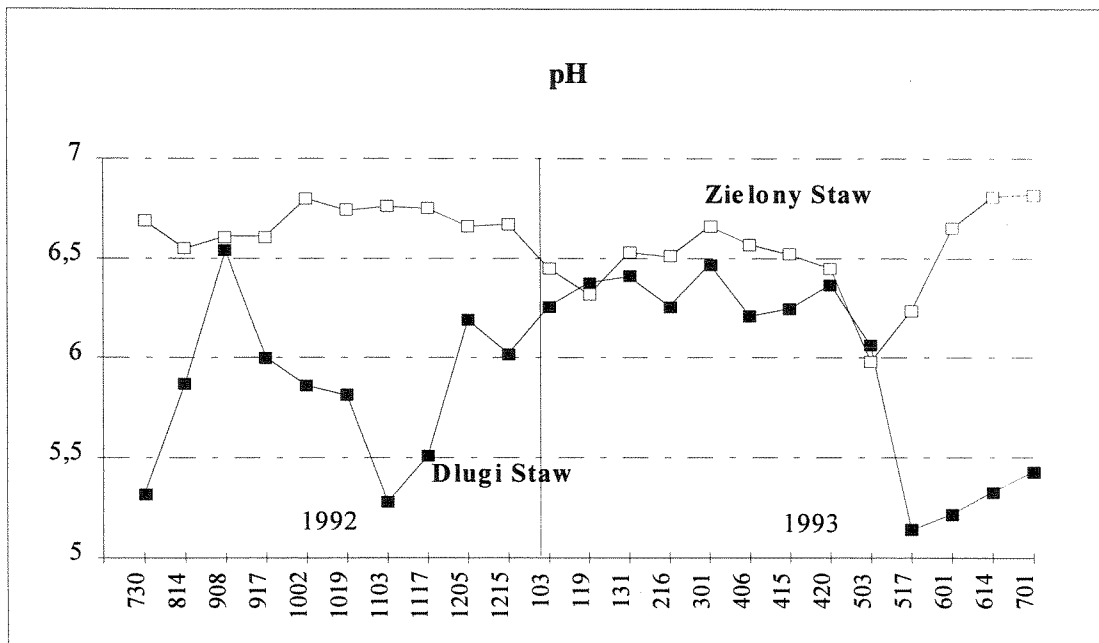


Figure 8.2.3. Variations in pH in two Tatra lakes.

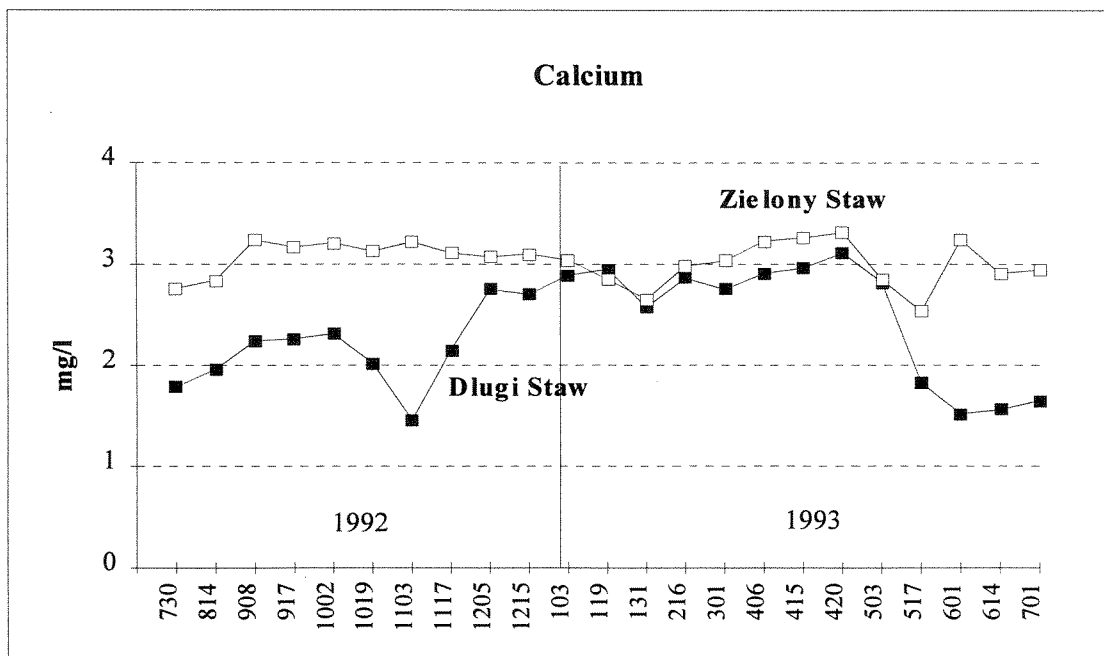


Figure 8.2.4. Variations in calcium in two Tatra lakes.

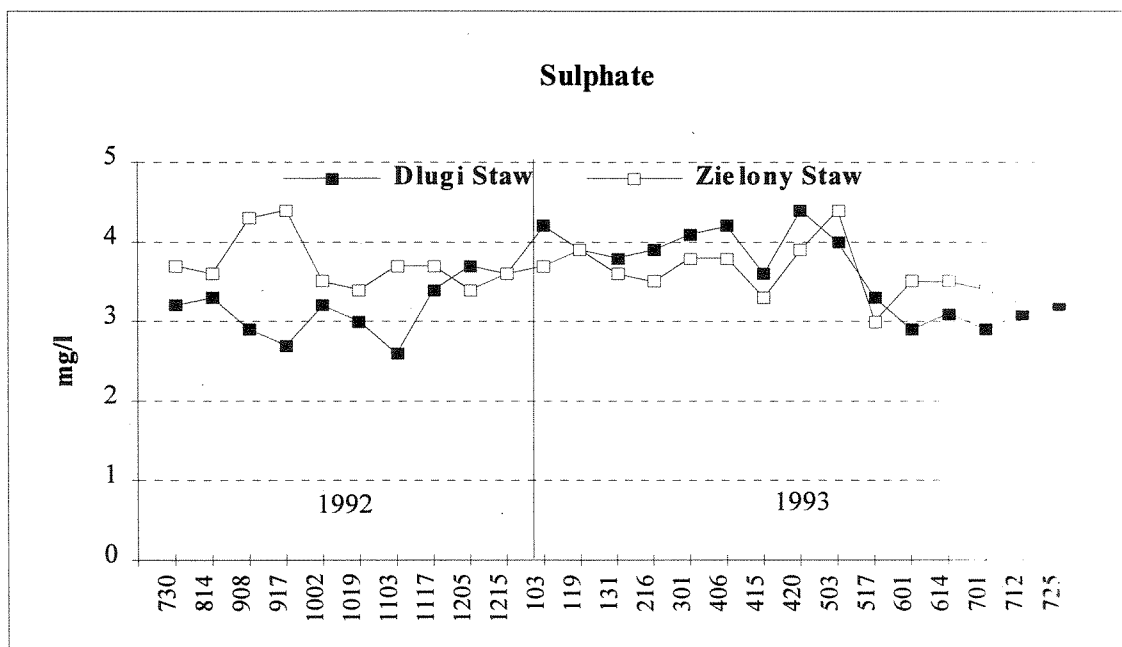


Figure 8.2.5. Variations in sulphate in two Tatra lakes.

The variations in sulphate (Figure 8.2.5) are not as seasonal as the variations in pH and calcium, although some dilution is observed for both lakes during the snowmelt period. The nitrate variations (Figure 8.2.6), however, are more systematic, with clear increase in concentrations from fall to snow melt for both lakes. Dlugi Staw also show a decrease in concentration in fall, due to the dilution effect shown in calcium (Figure 8.2.4).

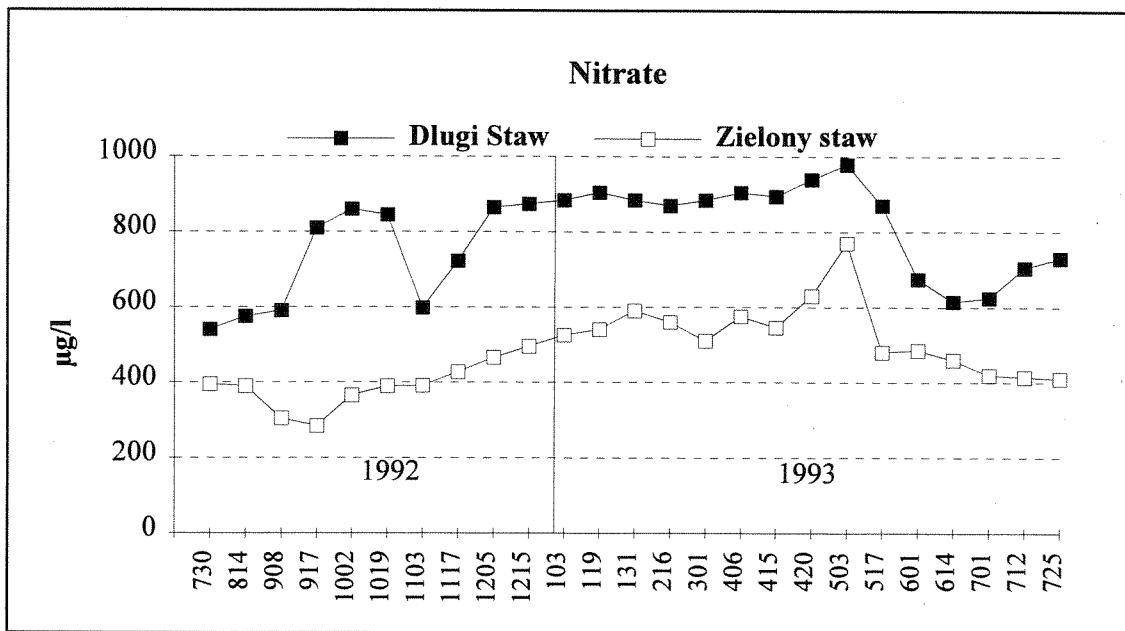


Figure 8.3.6. Variations in nitrate in two Tatra lakes.

### 8.2.3. Fluxes.

Based on the measurements at the meteorological station at Hala Gasienicowa, the deposition values are calculated for the period September 1992 to September 1993, altogether 12 months. The water fluxes for the two lakes have been estimated as described above, using the measured precipitation and assuming a 10% evapotranspiration. The fluxes for S and N have been calculated by multiplying the monthly water runoff by the average monthly concentrations for the two lakes for the period Sept. 92 to Sept. 93.

Table 8.2.1. Calculated fluxes of S and N from and estimated N-retention in two Tatra lakes for the period Sept. 1992 to Sept. 1993.

	Sulphur flux	Nitrogen flux	Assuming no S-retention		
			Corrected S-flux	Corrected N-flux	% N-leaching
Deposition	73125	64357			
<i>Dlugi</i>	63415	50112	73125	57875	<b>90</b>
<i>Zielony</i>	71691	31591	73125	32223	<b>50</b>

Table 8.2.1 indicate that there is not a complete balance between input and output of sulphur. In Norwegian catchments there is normally a balance between the input and output of sulphur (SFT 1993). The runoff values used for the calculations in Table 1 are based on precipitation amount at the deposition station, not on real measurements of flow, as it is for the Norwegian catchments. If we assume that the differences in sulphur fluxes are due to an underestimate of flow, and if we further assume that no sulphur is retained in the catchments of the lakes, we can correct the sulphur runoff values relative to the sulphur deposition (Table 8.2.1), and also correct the nitrogen runoff correspondingly. In this way it is possible to estimate the nitrogen leaching out of the two catchments (Table 8.2.1). The nitrogen leaching of Dlugi Staw is 90% of the incoming nitrogen, i.e. almost all incoming nitrogen is leaving the lake as nitrate, while Zielony Staw is retaining 50% of the incoming nitrogen. The difference in behaviour of the two lakes can be explained by their difference in altitude

and in vegetation cover of the catchments.

The nitrate leaching in the two Tatra lakes is much higher than the nitrate leaching of high mountain lakes in Norway subjected to similar sulphur and nitrogen deposition. Here, we find maximum leaching values of less than 30% of the incoming nitrogen.

It has been postulated that high nitrogen leaching from a catchment is due to increasing nitrogen saturation in the catchment. Nitrogen saturation has been defined as "the state at which the availability of ammonium and nitrate is in excess of the total combined plant and microbial nutritional demand, as manifested by leaching of significant amount of nitrate from the catchment" (Aberet *al.* 1989). It is, however, also possible that the contact time between the nitrogen compounds in the precipitation and the catchment is too short for the nitrogen to be assimilated by the plants and micro-organisms. Thus, most of the incoming nitrogen will leave as the mobile anion nitrate. The catchments in the Tatra mountains have a high precipitation rate, thin soil covers and short retention times, and thus most of the nitrate is leaving the catchment unaffected.

Figure 8.2.7. shows that the ratio of nitrogen to sulphur flux varies seasonally in Zielony Staw, and the ratio is lowest during the growing season, while Dlugi Staw shows virtually constant flux ratio during the year. Again, the differences in behaviour can be explained by the altitude and vegetation cover differences of the two lakes.

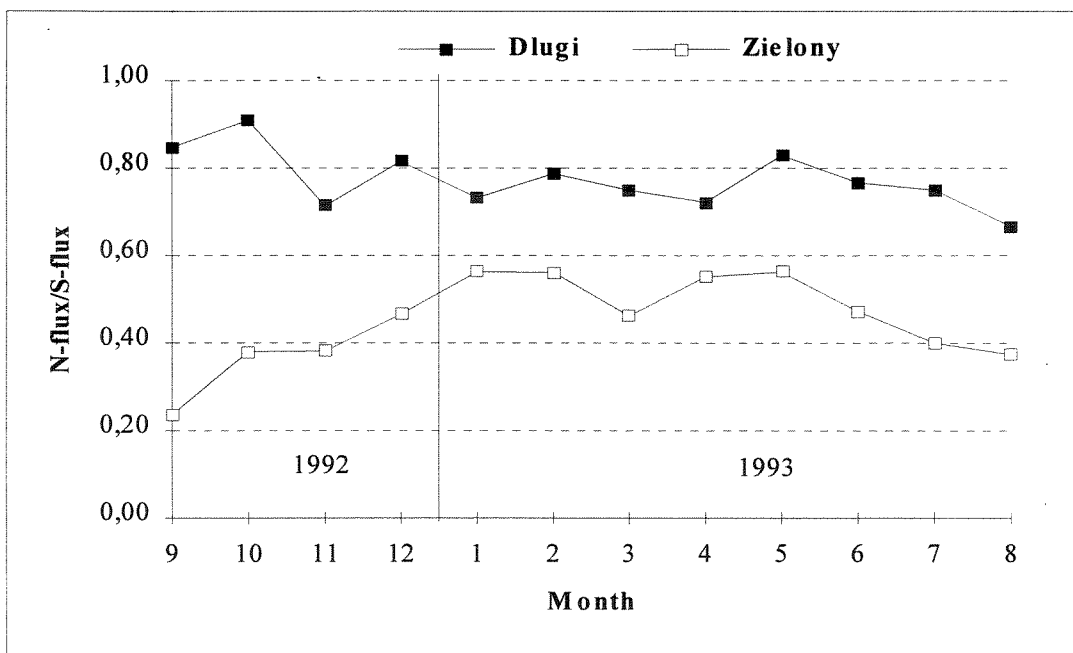


Figure 8.2.7. Monthly ratio of Nitrogen to Sulphur flux for two Tatra lakes.

The nitrogen deposition in the Tatra is about the same as in southernmost Norway (see table 8.2). Thus, it is surprising that the nitrate concentrations in the Tatra lakes are significantly higher than those in Norway, even for the alpine lakes in southern Norway. We have no reasonable explanation for this at the present time. As mentioned, there is a possibility that dry deposition is of greater importance in the Tatras than in Norway, but at the time being we have only wet deposition measurements from Hala Gasienicowa.

The calculations carried out above are approximate, because the runoff have been estimated from the precipitation station located some distance away. To obtain more precise runoff fluxes, continuous measurements of runoff from the lakes are required.

Also better possibilities for comparison between lakes in Norway and the Tatras will be achieved, when the results from the NIVA project "N from Mountain to Fjord" are available. Here an extensive water chemistry programme in five lakes will give new knowledge of the nitrogen concentrations in areas with thin soil cover.

The great importance of nitrogen in mountain areas in central Europe, are also seen in results from investigations in mountain areas in Norway compared with central Europe in other projects (Wathne *et al.*, 1990, Wathne and Patrick, 1994).

### 8.3 Critical load calculations

The method for calculating critical load (Chapter 3) is based on the yearly weighted concentrations of non-marine base cations and sulphate. From the data available we can estimate these concentrations for the period Aug. 1992 to Aug. 1993. The base cation deposition value of 17 keq/km<sup>2</sup>.yr, or 15 µeq/l was used for both lakes.

In order to determine a critical load, a critical chemical value for a biological indicator has to be set (see Chapter 2). For surface water this is done by setting a limit for ANC (ANC<sub>limit</sub>). The result of the calculations then depend largely on the value for ANC<sub>limit</sub> chosen. Data from Norway for water chemistry and general fish status has been used to assess a proper value for ANC<sub>limit</sub> for fish in Norway. A value of 20 µeq/l have been chosen (Henriksen *et al.*, 1992). We have calculated the critical loads for the two Tatra Mountain lakes using this ANC-value (table 8.4.1).

In order to calculate critical load exceedance for sulphur we have can either deduct the sulphur deposition to the lake catchment or use the sulphur runoff of the catchment. We know from Norwegian data that there is almost a one to one correlation between sulphur deposition and sulphur runoff in lakes located in granitic areas. Thus, we can use the sulphate concentration in the lake water to calculate the critical load exceedance for atmospheric sulphur (for details see Henriksen *et al.* 1990). There is at present no accepted method to assess the exceedance of both sulphur and nitrogen acidity to surface waters, but one suggestion is to use the present nitrate concentration in the lake water as a measure of the part of the nitrogen deposition that is acting like acid (Brydges and Summers 1989, Henriksen *et al.* 1993). This approach is based on the assumption that no significant leaching of nitrate is taking place under pristine conditions. We have calculated the critical load exceedance for total acidity (Table 8.4.1).

Table 8.4.1. Critical load and exceedance calculations (meq.m<sup>-2</sup>.yr<sup>-1</sup>)for two lakes in the Polish Tatra mountains.

	Yearly weighted mean concns. (µeq/l)				BC <sub>0</sub>	CL(A)	CL-ex(S+N)
	ECM*	SO <sub>4</sub>	NO <sub>3</sub>	BC <sub>dep</sub>			
Dlugi Staw	108	67	53	15	85	62	-28
Zielony Staw	163	76	34	15	135	112	38

BC<sub>0</sub> = "Original" base cation concentration.

CL(A) = Critical load of acidity.

CL-ex(S+N) = Critical load exceedance of sulphur and nitrogen.

In the earlier work in the Tatras (Henriksen *et al.*, 1992) the critical loads and critical loads exceedance for 13 lakes were calculated on the basis of a less extensive water sampling programme, and not including precipitation measurements. The results for Dlugi Staw and Zielony Staw are shown in Table 8.4.2.



Compared to the calculations on the basis of more accurate data, we can note that there are some changes, but the results are of the same order.

Table 8.4.2. Critical loads and critical load exceedances ( $\text{meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ ) for lakes in the Tatra Mountains based on averages from two sampling series.

Lake	CL(A)	CL-ex(S+N)
Dlugi Staw	44	- 48
Zielony Staw	115	55

CL(A) = Critical load of acidity.

CL-ex(S+N) = Critical load exceedance of sulphur and nitrogen.

The difference between the two lakes seems to be explained by the difference in altitude (see Table 4.1) and vegetation cover. The results indicate that the deposition values are the same for both lakes, as they also are situated close together in the same catchment. But the steeper surroundings and the lack of vegetation cover close to Dlugi Staw results in shorter contact time between the catchment and the precipitation before it reaches the lake. Shorter contact time gives less possibilities for nitrogen compounds to be assimilated by plants and micro-organisms, and of course reduced vegetation cover gives reduced possibilities for nitrogen assimilation.

## 9. CONCLUSIONS

The Cooperation and joint project between the two national groups are most beneficial to both parts. The Polish partners have the opportunity to work together with experienced people in the field of acidification, and through parallel analytical work between the two laboratories, to follow the development of their methods in this field. The Norwegian partners are gaining further insight in the regional extension of the acidification in Europe and increase the database of acid sensitive lakes in the world. We consider this very important, since acidification is an extensive international problem. Both parties consider it important and fruitful to extend the Cooperation further, also because it will, among many other things, promote exchange of scientific information and practice between our two countries.

The more intensive study reported here confirms the earlier work, and states 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 Dlugi Staw, one of the two lakes selected for this study.

The main difference between the comparable areas in Norwegian mountains and the Tatra Mountains, is the great importance of nitrogen deposition in the Tatras. The nitrogen leaching of Dlugi Staw is 90% of the incoming nitrogen, i.e. almost all incoming nitrogen is leaving the lake as nitrate, while Zielony Staw is retaining 50% of the incoming nitrogen. The nitrate leaching in the two Tatra lakes is much higher than the nitrate leaching of high mountain lakes in Norway subjected to similar sulphur and nitrogen deposition. Here, we find maximum leaching values of less than 30% of the incoming nitrogen. The nitrogen deposition in the Tatra is about the same as in southernmost Norway. Thus, it is surprising that the nitrate concentrations in the Tatra lakes are significantly higher than those in Norway, even for the alpine lakes in southern Norway. We have no reasonable explanation for this at the present time.

## 10. FUTURE AND FOLLOWING ACTIVITIES

The already completed project stages resulted in:

- a) thorough recognition of the effects of Tatra lakes acidification
- b) identification of the similarities and differences in the acidification mechanism for Norwegian mountains and Polish Tatras
- c) successful implementation of the Henriksen Model (Henriksen *et al.* 1990) to two reference lakes - Zielony Staw and Dlugi Staw, which resulted in satisfying estimates of critical loads for acidity and sulphur but not for nitrogen.

An accurate evaluation of critical loads for acidifying nitrogen should be based on a mass balance of nitrogen deposited from the air and nitrogen flowing out from the catchment. Therefore within the next project step in 1994 it is planned to carry out continuous measurements of water flow from the Zielony and Dlugi lakes. Also the wet deposition measurements already carried out at the Hala Gasienicowa station need to be continued and measurements of air concentrations should be added. The concentration measurements can be used for calculating the dry deposition in the area, which may be of greater importance in the Tatras than in Norwegian mountains, and explain some of the differences in nitrogen concentrations in the investigated lakes.

The future activities should also include an extension to other potential sensitive areas in Poland, such as the Silesian area. Here, a fruitful co-operation with the Czech Republic can probably be established. Further, steps should be taken to co-ordinate the acidification studies on the Slovakian side of the granitic Tatra Mountains.

## 11. REFERENCES

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## **Appendix A**

**Precipitation chemistry from Hala Gasienicowa September 1992 -  
September 1993.**

## POLEN.XLS

Date	mm	pH	COND µS/cm	Cl <sup>-</sup> mg/l	NO3N mg/l	SO4S mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	NH4N mg/l	SO4-Sdef mg/m <sup>2</sup>	NO3-Ndef mg/m <sup>2</sup>	NH4-Ndef mg/m <sup>2</sup>	H+def mg/m <sup>2</sup>	Ci:dep mg/m <sup>2</sup>	Nadep mg/m <sup>2</sup>	Kdep mg/m <sup>2</sup>	Cadep mg/m <sup>2</sup>	Mgdep mg/m <sup>2</sup>
92 9 7 714	2.9	4.40	42.8	1.47	0.72	2.34	0.30	1.43	1.16	0.12	0.68	6.8	2.1	2.0	1.15E-04	4.3	0.9	4.1	3.4	0.3
92 914 721	35.7	4.54	17.5	0.06	0.21	0.82	0.04	0.05	0.16	0.01	0.28	29.3	7.5	10.0	1.03E-03	2.1	1.4	1.8	5.7	0.2
92 921 728	1.6	4.32	50.7	0.51	1.31	2.73	0.29	0.36	1.16	0.22	1.47	4.4	4.1	2.4	7.64E-05	0.8	0.5	0.6	1.9	0.4
92 928 7 1	21.2	4.88	14.4	0.22	0.21	0.90	0.09	0.11	0.34	0.05	0.45	19.1	4.5	9.5	2.79E-04	4.7	1.9	2.3	7.2	1.1
9210 1 7 5	0.0											0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0
9210 5 712	0.0											0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0
921012 719	91.1	4.81	8.4	0.09	0.09	0.27	0.08	0.01	0.13	0.03	0.01	24.6	8.2	0.5	1.41E-03	8.2	7.3	0.5	11.8	2.7
921019 726	12.7	4.54	15.9	0.30	0.25	0.45	0.09	0.19	0.13	0.01	0.01	5.7	3.2	0.1	3.66E-04	3.8	1.1	2.4	1.7	0.1
921026 7 1	20.4	4.60	14.1	0.15	0.24	0.48	0.13	0.04	0.14	0.01	0.06	9.8	4.9	1.2	5.11E-04	3.1	2.7	0.8	2.9	0.1
9211 1 7 2	0.0											0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0
9211 2 7 9	21.0	4.12	44.5	0.73	0.50	1.59	0.39	0.09	0.34	0.06	0.43	33.4	10.5	9.0	1.59E-03	15.3	8.2	1.9	7.1	1.3
9211 9 716	5.1	4.21	35.2	0.38	0.67	0.88	0.20	0.07	0.17	0.01	0.30	4.5	3.4	1.5	3.14E-04	1.9	1.0	0.4	0.9	0.0
921116 723	46.0	4.49	16.8	0.17	0.21	0.48	0.11	0.03	0.06	0.01	0.04	22.1	9.7	1.8		7.8	5.1	1.4	2.8	0.2
921123 730	17.2	4.21	36.7	0.72	0.52	0.94	0.38	0.07	0.09	0.04	0.27	16.2	8.9	4.6	1.06E-03	12.4	6.5	1.2	1.5	0.7
9212 1 7 7	55.7	5.38	18.5	2.14	0.01	0.51	1.92	0.93	0.47	0.22	0.01	28.4	4.3	0.3	2.32E-04	119.2	106.9	51.8	26.2	12.3
9212 7 714	13.4	4.37	23.9	0.47	0.32	0.74	0.23	0.09	0.19	0.05	0.13	9.9	4.3	1.7	5.71E-04	6.3	3.1	1.2	2.5	0.7
921214 721	0.2		43.7									0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0
921221 728	3.8	4.06	59.1	1.96	0.52	2.18	0.33	1.50	0.28	0.06	0.89	8.3	2.0	3.4	3.30E-04	7.4	1.3	5.7	1.1	0.2
921228 7 1	0.0											0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0
93 1 1 7 4	0.0											0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0
93 1 4 711	19.3	4.51	16.5	0.38	0.24	0.55	0.15	0.05	0.13	0.02	0.05	10.6	4.6	1.0	5.95E-04	7.3	2.9	1.0	2.5	0.4
93 111 718	0.0											0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0
93 118 725	13.1	4.38	26.8	0.33	0.51	1.10	0.20	0.07	0.25	0.04	0.43	14.4	6.7	5.6	5.45E-04	4.3	2.6	0.9	3.3	0.5
93 125 7 1	4.5	4.60	20.2	0.64	0.41	0.74	0.28	0.17	0.44	0.06	0.14	3.3	1.8	0.6	1.13E-04	2.9	1.3	0.8	2.0	0.3
93 2 1 7 2	0.0											0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0
93 2 2 7 8	0.9	4.53	16.3									0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0
93 2 8 715	0.8	4.62	37.8									0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0
93 215 722	21.0	4.46	18.2	0.34	0.32	0.44	0.15	0.04	0.15	0.03	0.12	9.2	6.7	2.5	7.27E-04	7.1	3.2	0.8	3.2	0.6
93 222 728	17.8	4.37	31.7	0.73	0.19	0.55	0.13	0.45	0.13	0.01	0.01	9.8	3.4	0.1	7.58E-04	13.0	2.3	8.0	2.3	0.1
93 228 7 1	0.0											0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0
93 3 1 7 8	8.9	4.04	133.3	22.11	0.72	1.78	0.98	23.23	0.15	0.10	0.57	15.8	6.4	5.1	8.10E-04	196.8	8.7	208.7	1.3	0.9
93 3 8 715	3.8	3.53	181.7	1.74	3.51	5.47	0.30	0.66	0.41	0.04	3.19	20.8	13.3	12.1	1.12E-03	6.6	1.1	2.5	1.6	0.2
93 315 722	13.8	4.07	63.1	1.98	1.08	2.14	0.20	1.65	0.35	0.04	1.07	29.5	14.9	14.8	1.17E-03	27.3	2.8	22.8	4.8	0.6
93 322 729	33.1	4.31	35.7	0.91	0.82	1.14	0.39	0.07	0.36	0.08	0.76	37.7	27.1	25.2	1.62E-03	30.1	12.9	2.3	11.9	2.6
93 329 7 1	4.8	4.27	32.9	1.66	0.52	0.62	0.08	1.68	0.19	0.02	0.11	3.0	2.5	0.5	2.57E-04	8.0	0.4	8.1	0.9	0.1
93 4 1 7 5	5.1	4.32	26.3	0.18	0.25	1.02	0.06	0.10	0.15	0.01	0.30	5.2	1.3	1.5	2.44E-04	0.9	0.3	0.5	0.8	0.0
93 4 5 712	53.2	4.15	36.0	0.20	0.45	1.21	0.05	0.01	0.07	0.01	0.29	64.4	23.9	15.4	3.76E-03	10.6	2.7	0.3	3.7	0.3
93 412 719	9.6	4.18	57.8	0.69	1.02	3.44	0.21	0.32	0.93	0.10	2.07	33.0	9.8	19.9	6.33E-04	6.6	2.0	3.1	8.9	1.0
93 419 726	3.8	4.10	98.9	2.43	1.85	6.13	1.26	2.05	2.22	0.40	2.82	23.3	7.0	10.7	3.01E-04	9.2	4.8	7.8	8.4	1.5
93 426 7 1	1.0	6.42	89.6	1.68	2.51	6.06	1.26	1.01	5.81	0.48	4.77	6.1	2.5	4.8	3.79E-07	1.7	1.3	1.0	5.8	0.5
93 5 1 7	0.0											0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0
93 5 3 710	22.3	4.91	24.5	0.23	0.50	1.58	0.12	0.14	1.01	0.09	1.02	35.2	11.2	22.7	2.74E-04	5.1	2.7	3.1	22.5	2.0
93 510 717	41.4	4.28	44.3	0.33	0.78	2.27	0.09	0.11	0.74	0.08	1.56	94.0	32.3	64.6	2.17E-03	13.7	3.7	4.6	30.6	3.3
93 517 724	39.7	4.42	29.4	0.13	0.46	1.52	0.05	0.08	0.40	0.06	0.93	60.3	18.3	36.9	1.51E-03	5.2	2.0	3.2	15.9	2.4
93 524 731	13.4	4.69	26.9	0.18	0.50	1.57	0.10	0.13	0.72	0.09	1.05	21.0	6.7	14.1	2.73E-04	2.4	1.3	1.7	9.6	1.2
93 531 7 7	21.0	4.77	14.1	0.07	0.27	0.67	0.04	0.02	0.19	0.02	0.47	14.1	5.7	9.9	3.56E-04	1.5	0.8	0.4	4.0	0.4
93 6 7 714	17.8	4.34	28.9	0.13	0.41	1.48	0.07	0.09	0.53	0.10	0.60	26.3	7.3	10.7	8.12E-04	2.3	1.2	1.6	9.4	1.8
93 614 721	46.8	4.20	31.2	0.13	0.32	1.24	0.09	0.05	0.12	0.02	0.36	58.0	15.0	16.8	2.95E-03	6.1	4.2	2.3	5.6	0.9

POLEN.XLS

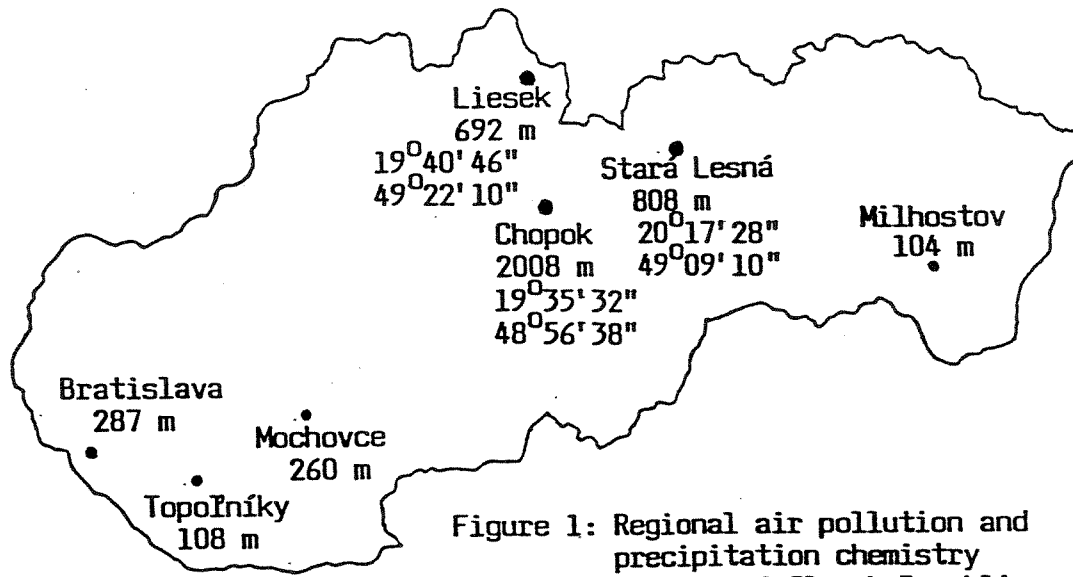
93 621 728	43.9	4.21	38.2	0.24	0.41	1.47	0.14	0.06	0.24	0.03	0.58	64.5	18.0	25.5	2.70E-03	10.5	26	10.5	1.3
93 628 711	43.0	4.27	26.8	0.13	0.24	0.90	0.04	0.01	0.07	0.01	0.25	38.7	10.3	10.8	2.31E-03	5.6	0.2	3.0	0.2
93 717 751	0.0											0.0	0.0	0.0		0.0	0.0	0.0	0.0
93 757 712	17.8	4.99	31.2	0.90	0.55	2.01	0.54	0.41	1.22	0.24	1.21	35.8	9.8	21.5	1.82E-04	16.0	9.6	7.3	4.3
93 712 719	13.9	4.15	38.9	0.47	0.56	1.47	0.23	0.24	0.18	0.03	0.58	20.4	7.8	8.1	9.82E-04	6.5	3.2	2.5	0.4
93 719 726	51.0	4.20	40.8	0.87	0.60	1.39	1.04	0.54	0.37	0.03	0.26	70.9	30.6	13.3	3.21E-03	44.4	53.0	27.5	1.5
93 726 711	21.0	4.53	20.9	0.31	0.29	0.83	0.28	0.25	0.22	0.03	0.22	17.4	6.1	4.6	6.19E-04	6.5	5.9	4.6	0.6
93 817 791	11.1	4.75	21.8	0.15	0.43	1.25	0.07	0.14	0.75	0.16	0.66	13.9	4.8	7.3	1.97E-04	1.7	0.8	1.6	1.8
93 897 716	14.0	4.26	34.0	0.30	0.49	1.47	0.11	0.08	0.44	0.11	0.41	20.6	6.9	5.7	7.68E-04	4.2	1.5	1.1	1.5
93 816 723	11.8	4.18	54.8	0.78	1.08	2.38	0.38	0.48	1.14	0.24	0.90	28.1	12.7	10.6	7.78E-04	9.2	4.5	5.7	1.5
93 823 730	66.9	4.58	19.2	0.11	0.30	0.78	0.04	0.02	0.21	0.04	0.38	52.2	20.1	25.4	1.76E-03	7.4	2.7	1.3	2.7
93 830 711	13.4	4.43	22.9	0.32	0.35	0.87	0.14	0.11	0.14	0.01	0.34	11.7	4.7	4.6	4.97E-04	4.3	1.9	1.5	0.1
93 917 761	82.2	4.18	37.2	0.25	0.40	1.28	0.03	0.01	0.05	0.01	0.37	105.2	32.9	30.4	5.42E-03	20.6	2.5	0.4	0.4
93 967 713	13.1	4.44	20.4	0.20	0.20	0.77	0.07	0.10	0.14	0.04	0.07	10.1	2.6	0.9	4.75E-04	2.6	0.9	1.3	1.8
93 913 720	16.9	5.30	7.6	0.25	0.03	0.44	0.15	0.02	0.34	0.07	0.01	7.4	0.5	0.1	8.45E-05	4.2	2.5	0.3	5.7
93 920 727	16.6	5.58	12.4	0.57	0.27	0.56	0.09	0.36	0.61	0.13	0.29	9.3	4.5	4.8	4.36E-05	9.5	1.5	6.0	10.1
93 927 711	0.0											0.0	0.0	0.0		0.0	0.0	0.0	0.0

	SO4-S	NO3-N	NH4-N	H+	Cl	Na	K	Ca	Mg
Approx one year:									
mm precipitation	1155								
Wet deposition	mg/m <sup>2</sup>	1297.0	464.5	511.3		703.00	306.46	417.40	344.99
Weighted mean concentration	mg/l	1.1	0.4	0.4		0.61	0.27	0.36	0.30
	pH			4.38					
Approx one year:									
mm precipitation	1155								
Wet deposition	mekv/m <sup>2</sup>	80.8	33.0	36.3		19.9	13.5	10.6	17.3
Weighted mean concentration	mekv/l	70.0	28.6	31.4		17.2	11.7	9.2	15.0
	mekv H+/l			41.60					



## **Appendix B**

**Regional air pollution and precipitation chemistry from network of Slovak Republic 1992.**



Mesiac	Zrazky mm	PH	Vodivost µS/cm	Na mg/l	K mg/l	Mg mg/l	Ca mg/l	Cl mg/l	NH4-N mg/l	NO3-N mg/l	SO4-S mg/l	Zn µg/l	Fe mg/l	Al mg/l	Mn µg/l	F µg/l	HCO3 mg/l	
I.	38.6	4.33	31.5	0.36	0.14	0.05	0.61	0.43	0.34	0.41	1.55	50	0.06	<0.10	8	20	<0.50	
II.	44.6	4.38	38.1	0.57	0.25	0.08	0.71	0.87	0.94	0.78	1.81	84	0.05	<0.10	45	20	<0.50	
III.	102.1	5.65	28.0	0.46	0.22	0.15	1.44	0.58	1.16	0.63	1.89	58	<0.05	<0.10	16	29	1.10	
IV.	72.0	5.33	29.9	0.44	0.16	0.22	1.67	0.70	1.14	0.75	2.20	154	<0.05	0.14	13	27	0.92	
V.	39.0	4.69	31.0	0.21	0.39	0.14	1.49	0.36	0.62	0.07	2.27	129	0.13	<0.10	19	28	1.22	
VI.	61.3	4.47	28.9	0.11	0.17	0.06	0.37	0.27	0.88	0.38	1.70	86	<0.05	<0.10	45	420	<0.50	
VII.	101.2	4.92	20.5	0.13	0.11	0.11	1.00	0.27	0.72	0.36	1.60	61	<0.05	<0.10	6	420	<0.50	
VIII.	24.6	6.11	40.1	0.34	0.46	0.21	2.59	0.52	1.91	0.89	2.77	305	<0.05	<0.10	16	29	3.97	
IX.	91.4	4.59	26.9	0.16	0.18	0.07	0.68	0.25	0.92	0.47	1.64	65	<0.05	<0.10	12	420	<0.50	
X.	139.8	5.06	17.2	0.30	0.17	0.09	0.66	0.45	0.50	0.32	1.06	54	<0.05	<0.10	45	420	<0.50	
XI.	51.1	4.42	34.4	0.62	0.25	0.11	0.71	1.02	0.59	0.60	1.65	90	<0.12	<0.10	6	420	<0.50	
XII.	73.5	4.67	19.6	0.38	0.24	0.05	0.25	0.46	0.48	0.28	0.99	63	<0.05	<0.10	45	420	<0.50	
Suma	839.2																	
Var.pr.		4.91	26.3	0.32	0.20	0.11	0.93	0.49	0.80	0.47	1.63	83	0.06	0.10	9	22	0.74	



## **Appendix C**

**Water chemistry from Hala Gasienicowa July 1992 - July 1993.**

**Dlugi Staw (02) and Zielony Staw (20)**

AR = 1992

Dataset: POLEN Lakes in the Tatra Mountains

LOK	AR	DATE	PH	K25	CA	MG	NA	K	CL	SULF	NO3N	NH4N	TOTN	TOC	ALK	RAL	ILAL	SI02
02	1992	0730	5.32	1.82	1.79	0.09	0.22	0.14	0.2	3.2	540		593	0.22	0.025	43	M 10	1.7
02	1992	0814	5.87	1.91	1.96	0.10	0.25	0.16	0.2	3.3	575		594	M 0.20	0.027	M 10	M 10	1.8
02	1992	0908	6.54	1.26	2.24	0.12	0.33	0.13	M 0.5	2.9	530		536	0.50	0.037	M 10	M 10	2.1
02	1992	0917	6.00	1.92	2.25	0.13	0.33	0.14	M 0.5	2.7	810		346	0.59	0.029	25	M 10	2.2
02	1992	1002	5.86	1.65	2.31	0.13	0.32	0.15	0.2	3.2	860	12	905	0.21	0.030	25	M 10	2.1
02	1992	1019	5.81	1.87	2.02	0.12	0.29	0.14	0.3	3.0	845	6	850	M 0.20	0.027	60	M 10	2.0
02	1992	1103	6.76	2.18	3.22	0.20	0.44	0.18	0.4	3.7	392		470	0.44	0.108	M 10	M 10	1.3
02	1992	1117	5.51	1.84	2.15	0.12	0.33	0.13	0.3	3.4	720		720	0.21	0.035	35	M 10	2.1
02	1992	1205	6.19	2.10	2.75	0.14	0.39	0.14	0.3	3.7	865		902	0.2	0.041	10	M 10	2.3
02	1992	1215	6.02	2.09	2.70	0.14	0.37	0.13	0.4	3.6	875		890	M 0.2	0.044	M 10	M 10	2.3
20	1992	0730	6.69	2.13	2.76	0.18	0.35	0.18	0.3	3.7	395		452	0.48		M 10	M 10	2.0
20	1992	0814	6.55	2.18	2.84	0.19	0.36	0.20	0.3	3.6	390		461	0.70		M 10	M 10	1.9
20	1992	0908	6.61	2.31	3.24	0.23	0.45	0.19	M 0.5	4.3	305		470	0.74	0.117	M 10	M 10	0.9
20	1992	0917	6.61	1.17	3.17	0.22	0.44	0.19	M 0.5	4.4	285		402	1.0	0.112	M 10	M 10	1.1
20	1992	1002	6.80	1.87	3.21	0.22	0.42	0.19	0.3	3.5	365	18	475	0.64	0.112	M 10	M 10	1.0
20	1992	1019	6.74	2.33	3.13	0.22	0.42	0.12	0.3	3.4	390	10	460	0.38	0.111	10	M 10	1.3
20	1992	1103	5.28	1.50	1.46	0.07	0.18	0.11	0.2	2.6	598		630	0.28	0.024	79	M 10	1.3
20	1992	1117	6.75	1.84	3.11	0.21	0.48	0.23	0.4	3.7	427		495	0.54	0.109	14	M 10	1.4
20	1992	1205	6.66	1.30	3.07	0.20	0.43	0.18	0.3	3.4	465		525	0.53		M 10	M 10	1.6
20	1992	1215	6.67	2.20	3.10	0.20	0.40	0.20	0.4	3.6	495		555	0.40	0.096	M 10	M 10	1.6

LOK	AR	DATE	PH	K25	CA	MG	NA	K	CL	SULF	NO3N	NH4N	TOTN	TOC	ALK	RAL	ILAL	SI02
02	1993	0103	6.26	2.26	2.89	0.15	0.44	0.11	0.4	4.2	885		910	M 0.2	0.050	M 10	M 10	2.3
02	1993	0119	6.38	2.17	2.95	0.20	0.46	0.13	0.3	3.9	580	1.3	640	M 0.2	0.083	M 10	M 10	2
02	1993	0131	6.41	2.24	2.57	0.16	0.47	0.14	0.3	3.3	885	M 5	900	M 0.2	0.051	M 10	M 10	2.7
02	1993	0216	6.26	2.2	2.86	0.16	0.43	0.15	0.3	3.9	370	3	885	M 0.2	0.045	M 10	M 10	2.5
02	1993	0301	6.47	2.34	2.75	0.14	0.46	0.17	0.4	4.1	885	3	925	M 0.20	0.056	M 10	M 10	2.6
02	1993	0406	6.21	2.31	2.91	0.16	0.46	0.13	0.3	4.2	905		970	0.55	0.054	M 10	M 10	2.5
02	1993	0415	6.25	2.25	2.96	0.16	0.47	0.15	0.3	3.5	895	5	930	M 0.2	0.052	M 10	M 10	2.6
02	1993	0420	6.37	2.46	3.11	0.15	0.49	0.14	0.5	4.4	940	8	965	M 0.2	0.050	M 10	M 10	2.6
02	1993	0503	6.06	2.35	2.82	0.14	0.33	0.14	0.3	4.0	980	13	1020	0.14	0.037	M 10	M 10	2.1
02	1993	0517	5.14	2.12	1.83	0.10	0.30	0.16	0.4	3.3	870		980	0.33	0.022	135	M 10	1.3
02	1993	0601	5.22	1.60	1.52	0.08	0.17	0.12	0.3	2.9	675	29	725	M 0.2	0.034	130	M 10	1.3
02	1993	0614	5.33	1.59	1.56	0.08	0.24	0.13	0.3	3.1	615	11	650	0.37	0.035	68	M 10	1.5
02	1993	0701	5.43	1.74	1.65	0.08	0.25	0.11	0.3	2.9	625	8	660	0.25	0.031	57	M 10	1.6
20	1993	0103	6.45	2.30	3.04	0.21	0.47	0.16	0.3	3.7	525		595	0.25	0.091	M 10	M 10	1.7
20	1993	0119	6.32	2.13	2.85	0.15	0.45	0.14	0.3	3.9	905	3	905	M 0.2	0.046	M 10	M 10	2.5
20	1993	0131	6.53	2.27	2.65	0.20	0.47	0.19	0.3	3.5	590	13	650	0.26	0.086	M 10	M 10	2.0
20	1993	0216	6.51	2.14	2.98	0.21	0.44	0.20	0.3	3.5	560	36	635	0.30	0.092	M 10	M 10	1.7
20	1993	0301	6.66	2.40	3.03	0.21	0.47	0.21	0.3	3.8	510	16	590	0.28	0.110	M 10	M 10	1.8
20	1993	0406	6.57	2.50	3.23	0.22	0.50	0.24	0.3	3.6	575		780	0.40	0.112	M 10	M 10	1.8
20	1993	0415	6.52	2.38	3.26	0.22	0.47	0.19	0.3	3.3	545	13	610	M 0.2	0.105	M 10	M 10	1.8
20	1993	0420	6.45	2.66	3.31	0.22	0.55	0.21	0.4	3.9	630	142	855	0.37	0.101	M 10	M 10	1.9
20	1993	0503	5.93	2.49	2.85	0.19	0.40	0.16	0.4	4.4	770	137	950	0.68	0.052	10	M 10	1.9
20	1993	0517	6.24	1.97	2.53	0.16	0.34	0.15	0.3	3.0	430		570	0.43	0.073	M 10	M 10	
20	1993	0601	6.65	2.26	3.24	0.21	0.37	0.17	0.3	3.5	465	5	535	0.36	0.115	M 10	M 10	1.9
20	1993	0614	6.81	2.22	2.91	0.19	0.43	0.17	0.3	3.5	460	16	515	0.38	0.108	10	M 10	1.9
20	1993	0701	6.82	2.22	2.94	0.19	0.41	0.15	0.3	3.4	420	10	500	0.25	0.110	10	M 10	1.9



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**Norwegian Institute for Water Research**

P.O.Box 173, Kjelsås N-0411 Oslo, Norway

Phone: + 47 22 18 51 00 Fax: + 47 22 18 52 00

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