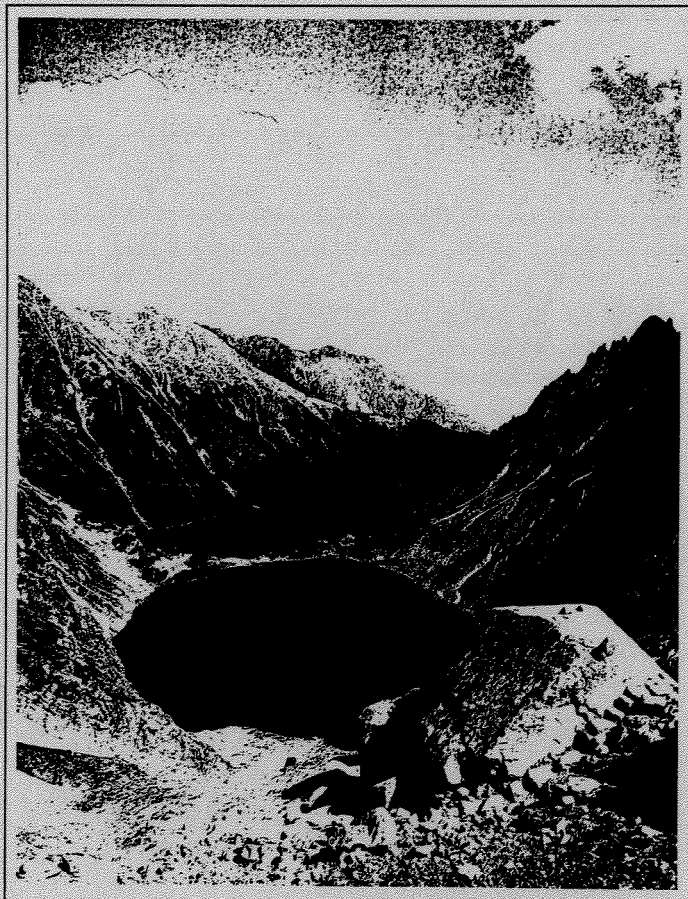



# Acid Rain Research

REPORT 29/1992

**Critical loads  
of acidity to  
surface waters**

A case study  
from  
the Polish Tatra  
Mountains



Norwegian Institute for Water Research  NIVA

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<b>Abstract:</b> As part of the Agreement on Environmental Cooperation between Norway and Poland critical loads of acidity and their exceedance to lakes in the granitic area of the Polish Tatra Mountains have been estimated. Lake samples were collected in summer and autumn 1991. The results indicate 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. Because of the serious acidification situation in the area, more intensive studies of deposition and yearly variations in water chemistry in several lakes should be carried out.. The future activities should also include an extension to other potential sensitive areas in Poland.
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Project leader

  
Arne Henriksen

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Bjørn Olav Rosseiland

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# **Critical loads of acidity to surface waters: A case study from the Polish Tatra Mountains**

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

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

<sup>2</sup>Institute of Environmental Protection, ul. Kossutha 6, PL-40 832 Katowice

<sup>3</sup>Tatra Mountain National Park, ul. Chalubinskiego 48, PL-34 500, Zakopane

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## PREFACE

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. During the work of this Task Force on Mapping, contact between Polen 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" has been established 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 Polish-Norwegian team collected water samples from the lakes in the period 6-9 October 1991. The Polish team spent four days in Norway from 20-24 February to complete the present report, which gives a description of the study area and present and discuss the results obtained from this joint study. The project activities for the Norwegian team has been financed by the Norwegian Ministry of Foreign Affairs.

## ABSTRACT

Critical load of acids 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 lakes in the Polish Tatra Mountains have been estimated. The Polish Tatra Mountains are situated on the boundary to Czechoslovakia. This study concentrated on lakes located in the granitic area of the mountains, where the acidification sensitive lakes were expected to be found. Lake samples were collected in summer and autumn 1991 and analyzed at the chemical laboratories of the Institute of Environmental Protection and the Norwegian Institute for Water Research. The results obtained were comparable, considering the differences in the applied analytical methods. This study indicates 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. Because of the serious acidification situation in the area, more thorough studies are needed. They should involve more intensive studies of deposition and yearly variations in water chemistry in several lakes. The future activities should also include an extension to other potential sensitive areas in Poland. Further, steps should be taken to coordinate the acidification studies on the Czechoslovakian 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 acidic compounds to an ecosystem. The ratio of sulphur to nitrogen can, therefore, vary without changing the critical load for acidic 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. The critical load for a particular receptor will vary from site to site, depending on its inherent sensitivity. At a given site the critical load for soils may differ from the critical load for a lake. In order to protect the whole environment the ultimate critical load should not exceed the lowest of these critical loads.

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" has been established. 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. This report will present and discuss the results in relation to surface water acidification in other countries, and to discuss future joint activities.

## 2. DEFINITIONS

Both sulphur and nitrogen contribute to the total input of acidic compounds to an ecosystem. The ratio of sulphur to nitrogen can, therefore, vary without changing the critical load for acidic compounds.

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

<b>DEFINITIONS</b>
<b>Critical load:</b> 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.
<b>Receptor:</b> An ecosystem which may potentially be affected by atmospheric inputs of sulphur and nitrogen (soil, groundwater, surface water).
<b>Biological indicator:</b> selected organism(s) or populations which are sensitive to chemical changes as a result of atmospheric inputs of sulphur and nitrogen (forest, fish, invertebrates).
<b>Critical chemical value:</b> 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

The Task Force on Mapping has compiled a manual for calculating critical loads and their exceedances, and describe three different methods for calculating critical loads for surface water, groundwater and soil:

1. The Steady-State Water chemistry Method
2. The Steady-State Mass Balance Method
3. The Dynamic Modelling Method

The first method is only applicable to surface waters, while methods 2 and 3 can be used for soil, groundwater and surface water. The first two methods are static, i.e. they compute the critical load assuming a steady-state with respect to the inputs from the atmosphere. The third method also takes into account time-dependent processes. We have applied the Steady-State Water Chemistry method to the data for the Tatra Mountain lakes in the same way as applied to the Scandinavian lakes. The method is shortly described in the box below. For further details see Henriksen *et al.* 1990.



### THE STEADY-STATE WATER CHEMISTRY METHOD

Acid Neutralization 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)\*:

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

where  $[\text{HCO}_3^-]$  is the bicarbonate concentration,  $[\text{A}^-]$  is the concentration of organic anions and  $[\text{Al}^{n+}]$  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 presentday 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,  $\text{SO}_4^*_d$ .

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

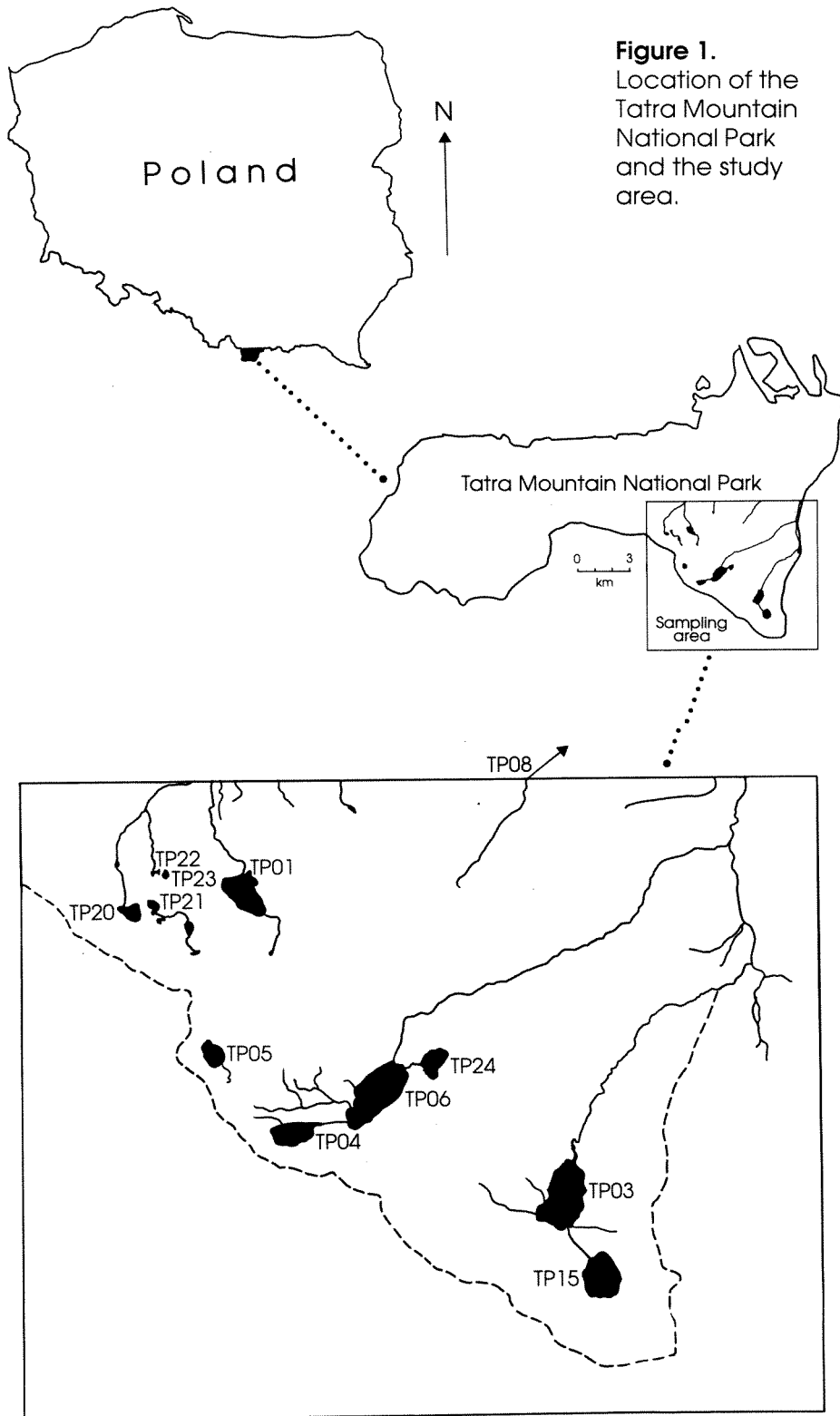
Note that this equation gives the critical load exceedance for sulphur, assuming that nitrogen does not contribute to the acidification.

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

## 4. THE TATRA MOUNTAINS

### 4.1 Localization of the study area

The Tatra Mountains, the highest part of the Carpathian arc, are situated on the border between Poland and Czechoslovakia. It is a mountain ridge 53 km long and 18 km wide, with the highest summit of 2663 m a.s.l. in Czechoslovakia and 2499 m in Poland. Figure 1 shows the location of the Tatra Mountains in Poland, and a detailed map of the study area. The lakes 01 to 15 was sampled on July 14, 1991 by the a Tatra Mountain National Park team. A separate set of bottles were submitted to NIVA shortly after sampling and analyzed according to the laboratorys routines. The second sampling trip was carried out on October 9, 1991 by a Polish and a Norwegian team, collecting samples from the locations 01, 02 and 20-23. The remaining samples were collected by the Polish team on October 16 from the locations 03-06, 16, and 24 and the bottles were mailed to NIVA where they were analyzed. The analytical results are shown in table 1. The locations 07 to 14 were omitted during the second sampling trip because they are rivers draining the calcareous rocks area of the Tatra Mountains.



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

Table1. Analytical results from lakes in the Tatra Mountain National Park  
(see Figure 1) sampled in July and October 1991.

Loca- tion	Year	Date	pH	COND mS/m	Ca	Mg	Na mg/l	K mg/l	Cl	SO <sub>4</sub>
01	1991	0714	6.52	2.42	2.86	0.16	0.38	0.16	0.4	3.9
01	1991	1009	6.59	2.37	2.84	0.16	0.40	0.18	0.2	4.0
02	1991	0714	5.49	1.76	1.74	0.11	0.25	0.14	0.1	3.2
02	1991	1009	5.79	2.06	2.21	0.13	0.35	0.18	M 0.2	3.7
03	1991	0714	6.79	2.94	4.24	0.19	0.39	0.13	0.3	4.1
03	1991	1016	6.98	3.21	4.56	0.21	0.45	0.16	0.3	4.9
04	1991	0714	6.67	2.10	2.70	0.15	0.34	0.11	0.3	3.2
04	1991	1016	6.56	2.10	2.67	0.14	0.36	0.13	MO.2	3.6
05	1991	0714	6.47	2.07	2.44	0.18	0.36	0.13	0.3	3.2
05	1991	1016	6.57	1.93	2.29	0.15	0.34	0.13	MO.2	3.9
06	1991	0714	6.71	2.33	3.11	0.17	0.38	0.12	0.3	3.3
06	1991	1016	6.64	2.13	2.68	0.16	0.39	0.14	MO.2	4.2
07	1991	0714	7.61	13.30	18.30	4.14	0.81	0.35	0.3	6.1
08	1991	0714	7.02	3.21	3.27	0.34	0.59	0.24	0.5	4.8
09	1991	0714	7.99	24.80	40.20	7.10	0.86	0.35	0.2	21.0
10	1991	0714	8.00	27.90	48.40	4.03	1.70	0.37	0.2	22.0
11	1991	0714	7.56	7.82	7.10	3.06	0.97	0.29	0.4	5.9
12	1991	0714	7.45	6.00	6.20	2.44	0.92	0.21	0.2	5.9
13	1991	0714	8.24	27.60	34.40	14.80	0.46	0.33	1.0	18.0
14	1991	0714	8.24	30.80	41.60	13.70	0.35	0.31	1.0	12.5
15	1991	0714	7.20	4.40	4.75	0.19	0.35	0.13	0.3	5.4
15	1991	1016	7.03	3.33	4.82	0.18	0.36	0.15	MO.2	5.1
20	1991	1009	6.85	2.48	3.12	0.22	0.43	0.20	M 0.2	3.7
21	1991	1009	6.52	2.20	2.57	0.18	0.41	0.17	M 0.2	3.9
22	1991	1009	6.13	2.05	2.25	0.16	0.39	0.18	0.2	3.9
23	1991	1009	5.68	2.00	2.01	0.15	0.35	0.18	M 0.2	3.9
24	1991	1016	7.20	3.80	5.84	0.14	0.48	0.14	0.2	4.4

Loca- tion	Year	Date	NO <sub>3</sub> µg N/l	Total N	Alk µeq/l	TOC mg C/l	Reactive Al	Non labile Al µg/l	Labile Al	SiO <sub>2</sub> mg/l
01	1991	0714	765	911	24.0	1.01	14	M 10	4	
01	1991	1009	750	741	37.8	0.35	M 10	M 10	0	2.1
02	1991	0714	625	710	0.0	0.85	82	M 10	72	
02	1991	1009	750	801	5.3	0.38	28	M 10	18	2.0
03	1991	0714	575	704	103.4	1.38	10	M 10	0	
03	1991	1016	530	563	133.3	0.66	M10	M10	0	2.0
04	1991	0714	420	591	61.9	1.55	M 10	M 10	0	
04	1991	1016	395	437	61.9	0.72	M10	M10	0	1.7
05	1991	0714	675	762	32.5	0.99	M 10	M 10	0	
05	1991	1016	555	581	28.2	0.32	M10	M10	0	1.6
06	1991	0714	510	603	75.4	1.41	12	M 10	2	
06	1991	1016	455	503	52.5	0.84	13	M10	3	1.9
07	1991	0714	595	785	1116.4	1.47	19	M 10	9	
08	1991	0714	585	689	69.2	1.34	19	M 10	9	
09	1991	0714	605	765	2308.8	1.90	17	M 10	7	
10	1991	0714	705	893	2369.2	2.36	12	M 10	2	
11	1991	0714	400	552	503.3	1.16	10	M 10	0	
12	1991	0714	335	522	396.7	1.25	M 10	M 10	0	
13	1991	0714	1010	1270	2671.2	2.48	14	M 10	4	
14	1991	0714	1000	1300	2993.1	2.18	14	M 10	4	
15	1991	0714	695	845	117.8	1.50	12	M 10	2	
15	1991	1016	645	680	129.1	0.45	M10	M10	0	1.6
20	1991	1009	400	480	91.0	0.68	M 10	M 10	0	1.7
21	1991	1009	650	702	29.3	0.29	M 10	M 10	0	2.2
22	1991	1009	650	683	12.0	0.34	M 10	M 10	0	2.2
23	1991	1009	600	671	1.6	0.42	14	M 10	4	2.1
24	1991	1016	400	461	215.3	0.63	M10	M10	0	1.3

## 4.2. Subdivision and geology

The Tatra Mountains are built of crystalline core which is composed of a carbonic magmatic intrusion, metamorphic rocks and mesozoic sedimentary rocks (limestones, dolomites, shales, marls). The surrounding basins of Podhale, Liptów and Spisz are formed of flysch rocks.

The Tatra Mountains were folded during the alpine orogenesis, and strongly transformed during the pleistocene glaciation period by alpine type glaciers which disappeared ten thousand years ago.

Based on orography and geological structure, the Tatra Mountains can be subdivided into the following units (see Figure 1):

*the High Tatra* is built of granites and granodiorites; it is the highest part of the ridge.

*the Western Tatra* is built of metamorphic rocks, gneisses and metamorphic schists. They are lower than the High Tatra, with the highest altitude of 2250 m a.s.l. The northern slopes of this area are built of mesozoic sedimentary rocks (Mapa geologiczna Tatr Polskich, 1979).

## 4.3 Climate

The Tatra Mountains occupy a transitional location between the maritime influence of the Atlantic Ocean and Eastern Europe continental influence. Their climate is determined by the elevation above the sea level and the predominant influence of western circulation. About 65 % of the time they are affected by maritime polar air masses coming from the Atlantic Ocean (Orlicz, 1962).

Continental air masses have a low moisture content and low cloudiness. These masses cause major temperature inversions in the neighbouring intermountain basins during the autumn and winter seasons (Niedzwiedz, 1981).

Particular climatic factors related to annual mean temperature decreasing with elevation above the sea level, develop climatic belts which coincide with the vegetation belts (see Table 1).

Table 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

Precipitation totals in the Tatra increase from 1400 mm/year at the foot of the mountains up to 1625 mm/year at the summits. However, the highest precipitation totals on the northern slopes of the Tatras occur at the height of 1500-1900 m and reach the value of 1800 mm/year (Gieysztor, 1962 and Hess, 1965).

The number of days with snow cover averages 290 days in the uppermost parts of the mountains (Hess, 1965).

#### 4.4 Runoff

For each investigated pond and stream in the Tatra mountains, runoff was determined, basing on data reported by Lajczak (1988). For the Tatra streams, the runoff was calculated from average values of individual annual runoff totals ( $l \cdot s^{-1} \cdot km^{-2}$ ), as presented by Lajczak for each catchment area. In case of ponds, the methodology applied was based on multiplication of average annual precipitation values (different for individual pond groups) by the runoff coefficient (Chomicz, K. and Samaj, F., 1974). For the highest part of the Tatra, the so-called Taty Wysokie, the runoff coefficient amounts to 0.83 (Lajczak, 1988). This rather high value can be attributed to the low evaporation under the conditions of low temperature, increased air humidity, frequent precipitation as well as rapid water runoff in the crystalline rock zone. The runoff values for each of the studied Tatra ponds and streams are shown in Table 3.

Table 3. *Runoff Values for the Tatra Ponds and Streams.*

Number of sampling station	Name of lake or stream	Runoff $10^3 \text{ m}^3 \text{ km}^{-2} \text{ yr}^{-1}$
TP 01	Czarny Staw Gasienicowy	1336.3
TP 02	Długi Staw Gasienicowy	1336.3
TP 03	Staw Morskie Oko	1297.2
TP 04	Czarny Staw (Dolina Pieciu Stawów Polskich)	1336.3
TP 05	Zadni Staw (Dolina Pieciu Stawów Polskich)	1336.3
TP 06	Wielki Staw (Dolina Pieciu Stawów Polskich)	1336.3
TP 08	Potok Waksmundzki	1573.6
TP 15	Czarny Staw nad Morskim Okiem	1297.2
TP 20	Staw Zielony	1336.3
TP 21	Staw Kurtkowiec	1336.3
TP 22	Staw Dwoisty Zachodni	1336.3
TP 23	Staw Dwoisty Wschodni	1336.3
TP 24	Przedni Staw	1336.3

#### 4.5 The relief

Various rock resistance of the crystalline core granite rocks in the High Tatra and granitoid and metamorphic rocks in the Western Tatra, causes the height difference of about 400 m. The High Tatra have a narrow to knife-edged ridge crest, steep rockwalls and rocky slopes. This part of the mountains had been much more diverted during the pleistocene period which resulted in U-shaped valleys, big glacial cirques now mainly replaced by lakes, large morains systems and thick fluvioglacial covers in the lower parts of valleys.

In the Western Tatra, rounded ridge crests dominate. The glacial forms are not so well developed as in the High Tatra. In the mesozoic rock part of this area, the system of fluvial denudational forms dominates. The slopes are steep or fairly steep and more mantled with covers of periglacial origin. On the limestones, the karstic forms and processes occur (Kotarba *et. al.*1987).

#### 4.6 Soils

On the crystalline rocks, the soil development processes have taken the podzolic direction. The mother rock is acidic and carbonate-free, covered with acidophilic and acidifying

vegetation, whereas frequent precipitation enhances the dislocation processes and low temperatures inhibit the organic matter decomposition.

On the crystalline rocks, in the climatic belts above timber line, polygonal soils and podzol rankers exist. Within the forest belts, humus iron podzol and iron humus occur. On the calcareous rocks above the timber line initial rendzinas, row humus rendzinas and humic rendzinas occur. In the forest belts brown rendzinas, typical brown soils and leached brown soils are present (Skiba, 1977).

#### 4.7 Vegetation

On the crystalline rocks in the zone of alpine summits, bare rocks or open pioner vegetation of association *Distichetum subnivale* exist. In the alpine meadow zone, grassland association *Trifido-Distichetum* is present. In the zone of dwarf pine, an *Mughetum carpathicum silicolum* association dominates. The upper forest zone is formed mainly of *Piceetum tatricum*.

On calcareous rocks, in the alpine meadow zone, *Caricetum firmae* prevails, and in the dwarf pine zone *Mughetum carpathicum calcicolum* dominates. In the upper forest zone *Piceetum tatricum* also exists. However in the lower forest zone, *Fagetum carpathicum Luzulo-Fagetum* dominates (Pawlowska, 1962).

#### 4.8 Aquatic ecosystem

The Tatra waters are populated with very few fish species, among which the brown trout, *Salmo trutta fario* dominates. In bigger streams, the greyling, *Thymallus Thymallus* can be also found, and in the past, *Salmo trutta m.trutta* used to live in such streams during the spawning season. Among the Tatra ponds, only Morskie Oko in Poland and Popradzki Staw in Czechoslovakia have been naturally stocked. Morskie Oko has always had its own population of the brown trout, also *Thymallus Thymallus* and *Salmo trutta m. trutta* have been often found in the lake.

As early as in 1881, the Tatra Mountains Society, along with the Fishing Society, undertook the initiative aimed at introducing the fry of three fish species into the waters of Morskie Oko and Stawy Gasienicowe, namely : *Salmo trutta lacustris*, *Salvelinus fontinalis* and *Coregonus lavaretus*. During the following years, the stocking procedure with the above mentioned species was several times repeated, with the fry of *Salvelinus alpinus* and *Salvelinus gairdneri* additionally introduced. All the species were imported from Salzburg (Austria).

About 1910, an attempt was undertaken aimed at stocking Wielki Staw situated in the valley of Dolina Pieciu Stawów Polskich with the stream trout and some other species. The stocking procedure in the valley was being performed repeatedly in the years 1950-1960, with introduction of two other trout species.

In Dolina Gasienicowa, the stocking with the spring trout was reiterated in 1948 for Zielony Staw Gasienicowy, and in the years 1950-1960 for the remaining ponds. In Zielony Staw Gasienicowy and Litworowy Staw Gasienicowy, after very intensive development of the brook trout population, a clear degeneration process had been observed since 1960, which

finished in 1965 with numerous fish deaths caused by parasitical fungus, *Ichtiophonus intestinalis*. In spite of that, the brook trout population has survived till now in Zielony and Litworowy Staw Gasienicowy, where the brown trout and the lake trout also live. In Dolina Pieciu Stawów Polskich, particularly in the ponds called Przedni, Wielki and Czarny, the brook trout occurs, while in Morskie Oko, the autochthonous population of the brown trout can be found (Podobinski 1982, Zarnecki 1955, Jara *et al.* 1972, Gliwicz 1985).

The ultraoligotrophic waters of the Tatra ponds exhibit the phytoplankton domination by smaller nannoplanktonic forms, with the predominance of such species as *Mallomonas* and *Cryptomonas*. Only in Morskie Oko, which is situated much lower than other lakes, some types of algae occur, including such species as *Gymnodinium tatricum* Wolosz. and *Asterionella formosa* Hass.

In most Tatra lakes, the contemporary zooplankton resources are extremely poor. It is mainly restricted to *Cyclops abyssorum tatricus* Kozm. and two cosmopolitan species of *Keratella quadrata* Ehrbs. and *Polyarthra dolichoptera* Idelson.

The scarcity of zooplankton species, however, was not characteristic for the Tatra ponds in the past. The plankton composition recorded by Wierzejski in the years 1882-1883, as well as by Litynski in 1913 and by Minkiewicz in 1914, confirms that during the recent years all species belonging to the association *Calanoida*, including *Daphnia pulex* Forbes, *Holopedium gibberum* Zaddach, *Polphemus pediculus* and *Heterocope saliens* Lill. Along with the disappearance of the *Calanoida* group, marked increase could be noticed in *Keratella quadrata* and *Polyarthra dolichoptera*.

It can be undoubtedly stated that the extinction of local populations of the shellfish zooplanktonic forms, was either directly or indirectly caused by introduction of fish into the Tatra ponds, which particularly relates to the brook trout. That kind of trout prefers the shellfish plankton much more than other species (Gliwicz, 1985).

On the other hand, the absence (extinction?) of a unique shellfish species, *Branchinecta paludosa* is a very negative phenomenon related to water acidification.

Another indicator of the negative effect of the reduced pH in the Tatra waters is the marked enhancement of mucus secretion by fish. Apart from that, occasional fish deaths have been observed early in the thawing season at the sites of the water entrance into the ponds (Zielony Staw Gasienicowy - spring, 1991) as well as in case of the increased water flow resulting from intensive precipitation following the draughts period (outflow from Litworowy Staw Gasienicowy - autumn of 1990) (Byrcyn *et al.*, 1992).

## 5. HYDROCHEMICAL STUDIES IN THE POLISH TATRA MOUNTAINS

Extensive studies on the chemical properties of the Tatra ponds and streams were carried out in the 1950's and 1960's (Oleksynowa, Komornicki, 1956, 1957, 1958, 1960, 1961, 1964, 1969, 1970; Bombówna, 1971; Paschalski, 1963). The studies showed that the waters of the crystalline Tatra displayed low buffer capacity and decreased mineralization values (dissolved salts) (28-63 mg/l ). In the 1980's, studies were undertaken on the atmospheric pollution impact on the chemical composition of the Tatra surface waters (Malecka, 1989, 1991; Krywult, 1990; Kot, 1991, Wojtan, unpublished data; Polakiewicz, Dobosz, unpublished data). Certain difficulties in comparing the current and historical analytical data can be



attributed to different range of the performed chemical determinations, as well as to divergence of the analytical methods applied. Due to the scarcity of the collected research data, it is impossible to determine trends within the water chemistry during the past thirty years, using statistical methods.

Due to the lack of coordination between the studies referred to above, their incompleteness can be clearly seen, particularly for determining the acidic deposition impact on the quality of the surface waters located in the examined area. Thus, there was an urgent need of a study specially designed for assessing acidification.

## 6. DEPOSITION DATA

Due to incompleteness of the available experimental data, it was difficult to assess deposition values related to acidic pollutants and base cations. The studies on atmospheric precipitation chemistry carried out from July 1962 to December 1963, among others, at Kasprowy Wierch and Lysa Polana, had already shown a very low pH of 4.1 (Orlicz M., Volfova E., 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 1980's, studies on rainwater were carried out at ten sampling stations localized within the boundaries of the Tatra National Park (Malecka, D., 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 (average: 5.1 mg/l) (Polakiewicz, Dobosz, 1990, unpublished data). 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 the samples ranged between 5.0-5.6, average hardness was 41.9 meq/l, Cl content - 1.0 mg/l, SO<sub>4</sub> - 3.7 mg/l and NO<sub>3</sub>-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 (SO<sub>2</sub>, NO<sub>x</sub> and F) as well as measurements of dry deposition, with the application of the contact method using K<sub>2</sub>CO<sub>3</sub> 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 SO<sub>2</sub>.m<sup>-2</sup> day<sup>-1</sup> and 0.163 mgNO<sub>x</sub>.m<sup>-2</sup> day<sup>-1</sup> (Wawrzoniak, 1989). The Institute of Forest Research is also involved in dust measurements using the sedimentation method. The average dustfall noted in the years 1988/89 amounted to 1.81 g m<sup>-2</sup> month<sup>-1</sup>. During the years 1986-1987, the Research Society at the Wroclaw Technical University, under the leadership of J. Dobosz (unpublished data), performed studies on the composition of dust pollutants at several locations in the Tatra Mountains. The data on the amount and concentration of pollutants differed very much, depending on the location of individual sampling stations. The following alkaline metal content values were found at the pond of Morskie Oko : Mg - 7.8 mg/g, Na - 12 mg/g, K - 7.1 mg/g, and Na - 29.3 mg/g.

On the basis of the above results, an attempt has been undertaken aimed at estimation of the total average deposition of base cations and sulphates at the area of the Tatra National Park. The following values have been calculated:

### Total deposition of sulphates

- wet deposition (according to Kasina) - 51 keq.km<sup>-2</sup>.year<sup>-1</sup>
- dry deposition (Inst.of Forest Res.) - 110 keq.km<sup>-2</sup>.year<sup>-1</sup>
- total deposition of sulphates - 161 keq.km<sup>-2</sup>.year<sup>-1</sup>

### Deposition of base cations

- dustfall - 21.6 tonnes.km<sup>-2</sup>.year<sup>-1</sup>
- base cation concentration in dust  
(above Morskie Oko) - 2.8 eq/kg
- base cation deposition - 60.4 keq.km<sup>-2</sup>.year<sup>-1</sup>

For the sake of comparison, the deposition of base cations and sulphate were calculated on the basis of measurements of snow chemical composition. Accepting the value of 1.720.000 m<sup>3</sup>.km<sup>-2</sup>.year<sup>-1</sup> as the average yearly precipitation level, the following results have been obtained :

- base cation deposition : 72 keq.km<sup>-2</sup>.year<sup>-1</sup>
- sulphate deposition : 132.4 keq.km<sup>-2</sup>.year<sup>-1</sup>

Considering the incompleteness and deficiency of the data used for calculations, the convergence of the results obtained can be treated as satisfactory. Thus, the below stated deposition values were applied for calculations performed within the Project:

<b>sulphate deposition</b>	<b>160 keq .km<sup>-2</sup> year<sup>-1</sup></b>
<b>base cation deposition</b>	<b>60 keq .km<sup>-2</sup> year<sup>-1</sup>.</b>

The weighted yearly average sulphate concentration in precipitation will then be 94 µeq/l, or, 1.5 mgS/l, and the corresponding value for base cations will be 35 µeq/l. Reliable data for nitrate and ammonium in the deposition in the Polish Tatra Mountains are not available.

The nearest precipitation station included in the Co-operative Programme for Monitoring and Evaluation of the Long range Transmission of Air Pollutants in Europe (EMEP) is located at Chopok in Checkoslovakia, location 48° 56' N and 19° 35' E, at 2008 m above sea level. In 1986 the annual precipitation was 1067 mm, the weighted yearly wet concentration of sulphur was 1.96 mgS/l and of nitrate 0.53 mgN/l. Data for base cations and ammonia are not available, but from the isopleth map prepared for Europe in 1986 the ammonia concentration can be inferred to be ca. 1.1 mgN/l. The corresponding data for the same year at the EMEP-station at Birkenes in southernmost Norway was 1613 mm, 1.01 mgS/l, 0.60 mgNO<sub>3</sub>-N/l and 0.69 mgNH<sub>4</sub>-N/l. The concentrations at the Czechoslovakian station are about twice as high as those at the station in Norway. The concentrations of sulphur in the precipitation in the Tatra is rather close to the concentration at the Checkoslovakian station, so we may assume the nitrogen concentrations in the deposition to be fairly similar. At least these values can be used for rough estimations, until better data will be made available.

## 7. CHEMICAL METHODS

The analytical methods used are somewhat different between the two laboratories.

### Norwegian Institute for Water Research

Parameter	Unit of measurement	Method of analysis
pH		Orion Model 801-A pH-meter with Radiometer combination electrode
Conductivity	mS/m 25 <sup>0</sup>	Philips PW 9509 digital meter
Ca	mg/l	Flame atomic absorption Perkin Elmer 560
Mg	mg/l	"
Na	mg/l	"
K	mg/l	"
SO <sub>4</sub>	mg/l	Waters ILC-1 ion chromatograph
Cl	mg/l	"
NO <sub>3</sub>	µgN/l	AutoAnalyzer, Cd-reduction method
Alkalinity	µeq/l	Acid titration to pH 4.5 with correction to equivalent alkalinity
Total organic carbon (TOC)	mgC/l	ASTRO model 2850 TOC/TC Analyzer
Reactive aluminium	µg/l	AutoAnalyzer with pyrocatechol violet
Non-labile aluminium		AutoAnalyzer after ion exchange
Total Nitrogen	µgN/l	Digestion with persulphate, NO <sub>3</sub> -method

### Institute of Environmental Protection

Parameter	Unit of measurement	Method of analysis
pH		Radelkis Model OP-208/1 pH-meter
Ca	mg/l	Flame atomic absorption Varian Techtron AA-6DA
Mg	mg/l	Nitrous oxide - acetylene
Na	mg/l	Air - acetylene
K	mg/l	Air - acetylene
Sulphate	mg/l	Technicon AutoAnalyzer BaSO <sub>4</sub> -precipitation
Chloride	mg/l	Hydrazine sulphate reduction
Nitrate	µgN/l	Mercury rhodanate method

## 8. RESULTS AND DISCUSSION

### 8.1 Analytical Methods

The two boxes on the previous side show that the analytical methods differ to some extent between the two laboratories, especially for the anions. The intention of our study was not, however, to do an intercalibration study between the two laboratories. Table 4 shows the average values for samples collected in July 1991. Although there are some significant differences between the two sets of results we consider the results acceptable, and they should generally give similar results for the calculation of critical loads.

Table 4. Average chemical values for 8 lakes sampled on July 14, 1991 analyzed both at NIVA and IEP.

Parameter	NIVA	IEP
pH	6,60	6,09
Ca	3.14	2,63
Mg	0,19	0,21
Na	0,38	0,32
K	0,15	0,27
Cl	0,30	<1.0
SO <sub>4</sub>	3.89	3.86
NO <sub>3</sub>	606	575

### 8.2 Water Chemistry - comparison between Tatra Mountains and southern Norway.

The concentration of base cations (calcium and magnesium) reflects the influence of the geology on lakewater quality. We have selected lakes in the Tatra Mountains and in southern Norway with similar concentrations of calcium and sulphate and compared their general chemistry (Table 5).

Table 5. Comparison of water chemistry of lakes in the Polish Tatra mountains and Norway in areas with similar geological settings.

Lake	pH	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Cl mg/l	SO <sub>4</sub> mg/l	NO <sub>3</sub> μg/l	Alk μeq/l	TOC mgC/l
Polish	5.49	1.74	0.11	0.25	0.14	0.1	3.2	625	0	0.85
Norwegian	6.62	1.80	0.38	0.49	0.25	0.4	3.3	31	66	1.46
Polish	6.52	2.86	0.16	0.38	0.16	0.4	3.9	765	24	1.01
Norwegian	6.77	2.65	0.17	0.47	0.14	0.5	3.9	2	69	1.31
Polish	5,68	2,01	0,15	0,35	0,18	0,2	3,9	600	2	0,42
Norwegian	6.68	2.02	0.08	0.39	0.14	0.3	3.3	3	43	0.94

Table 5 shows that the water chemistry of the selected lakes are very similar for the two countries, except for pH and the concentrations of nitrate and alkalinity. The nitrate concentrations in the Tatra lakes are much higher 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 indicates 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  $55 \mu\text{eq/l}$ , while the alkalinity difference is  $45 \mu\text{eq/l}$ . Adding the difference in calcium concentration ( $10 \mu\text{eq/l}$ ), the balance is complete. The Norwegian lakes are also alpine lakes located 830 - 1150 m above sea level. The nitrate concentrations in deposition in the Tatra Mountains on the Czechoslovakian side is almost twice as high as in Norway. Whether this is the case on the Polish side we do not know. Thus, it is necessary to establish a precipitation station in the National park to obtain suitable data for a more proper evaluation of the acidification situation in the Park.

### 8.3 Critical load calculations

The method for calculating critical load (chapter 3) is based on the yearly weighted base cation concentration. The calcium concentrations are very stable during the period between the snowmelts in spring (Kot, 1992). During the melting period the calcium concentrations normally goes down due to dilution. Based on empirical data for the area, however, we conclude preliminary that the concentrations of base cations during the period July-October are representative for the yearly weighted average concentrations. Thus, we can use the measured concentrations of base cations and the yearly runoff values for the critical load calculations. For the further analyses we have used the data analyzed at NIVA, particularly because the analytical program carried out at NIVA is more extensive. A base cation deposition value of  $60 \text{ keq/km}^2\cdot\text{yr}$ , or  $35 \mu\text{eq/l}$  has been used for all 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 ( $\text{ANC}_{\text{limit}}$ ). The result of the calculations then depend largely on the value for  $\text{ANC}_{\text{limit}}$  chosen. Data from Norway for water chemistry and general fish status has been used to assess a proper value for  $\text{ANC}_{\text{limit}}$  for fish in Norway. A value of  $20 \mu\text{eq/l}$  have been chosen, but also a value of  $0 \mu\text{eq/l}$  has been considered. We have calculated the critical loads for the Tatra Mountain lakes for both limits (Table 6).

In order to calculate critical load exceedance for sulphur we have to deduct the sulphur deposition to the lake catchment. We do not, however, have too reliable deposition data. We know, however, 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). 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 both for sulphur acidity and for total acidity, and also for  $\text{ANC}_{\text{limits}}$  for both  $0$  and  $20 \mu\text{eq/l}$  (Table 6).

Table 6. *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 the two sampling series.*

Lake no.	CL <sub>0</sub>	CL <sub>20</sub>	EX <sub>S0</sub>	EX <sub>S20</sub>	EX <sub>SN0</sub>	EX <sub>SN20</sub>
01	122	95	90	64	18	- <u>6</u>
<u>02</u>	71	44	16	43	- <u>21</u>	- <u>48</u>
03	208	183	118	154	128	102
04	116	90	99	70	60	32
<u>05</u>	95	68	68	42	12	- <u>15</u>
06	127	100	102	75	55	30
<u>08</u>	165	133	106	74	40	- <u>2</u>
15	218	192	168	142	104	78
20	142	115	120	93	82	55
<u>21</u>	105	78	71	45	9	- <u>17</u>
<u>22</u>	85	58	48	21	- <u>14</u>	- <u>41</u>
<u>23</u>	71	43	31	4	- <u>27</u>	- <u>5</u>
24	315	288	303	276	264	238

CL<sub>0</sub> = Critical load for ANC<sub>limit</sub> = 0  $\mu\text{eq/l}$

CL<sub>20</sub> = Critical load for ANC<sub>limit</sub> = 20  $\mu\text{eq/l}$

EX<sub>S0</sub> = Critical load exceedance for sulphur (ANC<sub>limit</sub> = 0  $\mu\text{eq/l}$ ).

EX<sub>S20</sub> = Critical load exceedance for sulphur (ANC<sub>limit</sub> = 20  $\mu\text{eq/l}$ ).

EX<sub>SN0</sub> = Critical load exceedance for sulphur and nitrogen (ANC<sub>limit</sub> = 0  $\mu\text{eq/l}$ ).

EX<sub>SN20</sub> = Critical load exceedance for sulphur and nitrogen (ANC<sub>limit</sub> = 20  $\mu\text{eq/l}$ ).

Table 6 shows that the critical load for sulphur and nitrogen is exceeded for six of the lakes, when ANC<sub>limit</sub> = 20  $\mu\text{eq/l}$  is used. Using only sulphur, none of the lakes are exceeded according to the calculation methods used. Compared with lakes located in granitic areas in Scandinavia and North America nitrogen is of much greater importance in the Tatra Mountains than in the other areas. They are in fact critical. This indicates that it is of great importance to establish a deposition station in the Tatra mountains as soon as possible operated according to the EMEP-standards. Also, the need of more frequent observations from some of the sensitive lakes over the year is necessary in order to arrive at better estimates of critical loads and their exceedances.

## 9. CONCLUSIONS

The joint study of the acidification of the lakes in the granitic part of the Polish Tatra Mountains have been most beneficial to both of the parties involved. The Polish partners have had the opportunity to work together with experienced people in the field of acidification, and to be able to compare the analytical results between the two laboratories. The comparison is favourable considering the different levels of advancement of the two laboratories. The Norwegian partners have gained further insight in the regional extension of the acidification in Europe and have increased the database of acid sensitive lakes in the world. We consider this very important, since acidification is an extensive international problem.

This simple study indicate clearly 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 with the comparable areas is the great importance of nitrogen deposition in the Tatra Mountains. because of the serious acidification situation in the area, more thorough studies are needed. They should involve more intensive studies of deposition and yearly variations in water chemistry in several lakes. The future activities should also include an extension to other potential sensitive areas in Poland. Further, steps should be taken to coordinate the acidification studies on the Checkoslovakian side of the granitic Tatra Mountains.

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.

#### **10. FUTURE ACTIVITIES**

To summarize the future activities should include: (1), establishing a deposition station in the Tatra Mountains according to the EMEP standards, which preferably should be included in the EMEP program, (2), to start regular (weekly or biweekly?) sampling of some sensitive lakes in the Polish Tatra Mountains. These studies should go on for at least one year with a complete list of chemical components. Further, similar studies as the present one should be carried out in other areas of Poland potentially sensitive to acidification.

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## APPENDIX I

*Paper presented at a NIVA-seminar on February 20, 1992.*

*Presented by Dr. Marek Kot.*

### **The prognosis of Tatra National Park forest stand degradation under the influence of air pollution.**

Zbigniew Krzan and Pawel Skawinski  
Research Station of Tatra National Park  
Chalubinskiego 42a  
34-500 ZAKOPANE

Symptoms of forest stand degradation in the Tatra National park (TNP) have been observed as a result of the long-term influence of air pollution. Work has been undertaken to synthesize the negative influence of different pollutants in the Park area. Simultaneously, work was done to quantify the relative sensitivities of the TNP forest stands to air pollution. Comparing both threats and relative sensitivity of the stands to air pollution, a map has been prepared showing the prognosis of possible stand degradation. This map has given primary information to the Park's Forest Service Division so they could undertake activities for a better protection of the forest stands, and to minimize the negative results of oncoming degradation processes in the TNP forests.

The negative influences of air pollution have been calculated from measurements taken at 36 points spread over the area of the park. Four-year measurements of SO<sub>2</sub>, NO<sub>x</sub>, fluor and dust deposits as well as pH of rainwater gave a basis for calculation of indexes of the total nature damage by air pollution (Figure 1.). These maps show that, evidently, most of the pollution comes from the densely urbanized area of the Podhale region, and especially from the town of Zakopane. There are also long distance pollution influences on the park area (Krzan 1989).

The relative sensitivity of the forest stands has been calculated including: forest standbiotope, tree composition, vertical stand structure and stand age. Indexes have been calculated for all possible homogenous stands within the park for which a map of forest sensitivity could be created. (figure 2). Most of the forests show rather high sensitivity to air pollution, especially stands growing at higher altitudes, and those changed by human activity in the past.

A forest stand degradation prognosis map was made comparing threats and sensitivity (Figure 3). This map can indicate some possible future changes in the forests of Tatra National Park as a result of persistent air pollution. It is evident that forest degradation will most probably start in spruce stands growing higher in the mountains close to the tree line. Forests there are growing in very unsuitable climatic and soil conditions, which increases the likelihood of their destruction. The next phase of forest decline will most probably occur in the planted spruce stands of lower altitudes. The best chances of survival will most probably be in the forests growing in calcium rich soils of the lower mountain zone. These forests are predominantly mixed, with significant presence of broad-leaved forest species (beech).

The possibility of total forest destruction in the TNP is real. A precedent is the ecological disaster in the Karkonosze Mountains of southwest Poland (Boratynski, Konca, Zientarski

1990). Unless we gain more of an understanding of the global effects to European ecosystems due to air pollution (Chadwick and Kuylenstierna 1991), this possibility may become a reality.

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## APPENDIX II

*Paper presented at a NIVA-seminar on February 20, 1992.*

### **Recent changes of surface water chemistry in the granitic part of the Tatra National Park - Poland**

Marek Kot  
Research Station of Tatra National Park  
Chalubinskiego 42a  
34-500 Zakopane

The water chemistry of the granitic part of the Tatra Mountains varies strongly over time. Water properties depend on the proportions and sources of water alimentation and from the resulting water chemistry. The precipitation in the Tatra Mountains is strongly acidified (Figure 1). Some chemical properties of precipitation, snowmelt water and stream water are shown in Table 1.

Variations in pH and conductivity in the granitic catchments (Czarny Staw Gasienicowy) and granitic-mesozoic mixed catchments (Zielony Staw Gasienicowy) is shown in the Figures 2 and 3.

The annual variations of calcium, sulphate and total hardness corresponds to the variations of pH and conductivity (Figure 4).

It is possible to distinguish the periods when water of the same origin is flowing (Kot 1991)

It is of great concern that, every year, in the central part of the High Tatra Mountains minimum pH-values in surface water correspond to lower pH in precipitation.

The pH-values in four typical catchments of the High Tatra Mountains are compared (Table 2, Figure 5). For this comparison waters of the same origins and periods were chosen.

It is clear that the greatest change in water chemistry since the 1960's are in the central, granodioritic part of the massif, and in the lakes at the highest altitudes.

It is also notable that the changes of water pH are larger in the spring than in the summer.

Without doubt, the main source of acidification in the Tatra Mountains is the melting of polluted snow.

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Table 1. *Water characteristics in the studied catchments in the upper Sucha Woda Valley, Tatra National Park.*

Water type	pH	Conductivity $\mu\text{S/cm}$
Rainwater	3.35 - 4.85	12 - 170
Fresh snowmelt water	3.95 - 5.15	7 - 42
Older snowmelt water	4.70 - 5.75	4 - 9
Throughflow (runoff)	4.65 - 5.40	15 - 27

Table 2. Changes in water-pH during the last 60 years at upper Sucha Woda Valley (Hala Gasienicowa).

Sampling location	pH					
	July			August		
	1935 <sup>1</sup>	1958 <sup>2</sup>	1990 <sup>4</sup>	1936 <sup>1</sup>	1960 <sup>3</sup>	1990 <sup>4</sup>
Zadni Staw	6.25	6.40	5.30	6.25	6.20	5.50
Zmarzly Staw	6.00	6.40	5.25	6.25	6.20	5.60
Zielony Staw	6.75	6.75	6.50	6.25	6.40	6.40
Czarny Staw	6.25	6.40	6.05	6.25	6.40	6.10

<sup>1</sup>Olszewski 1939, <sup>2</sup>Paschalski 1963, <sup>3</sup>Oleksynowa and Komornicki 1989, <sup>4</sup>Kot 1990.

Figure 2. pH and conductivity of precipitation  
Hala Gasienicowa May 1988-November 1991

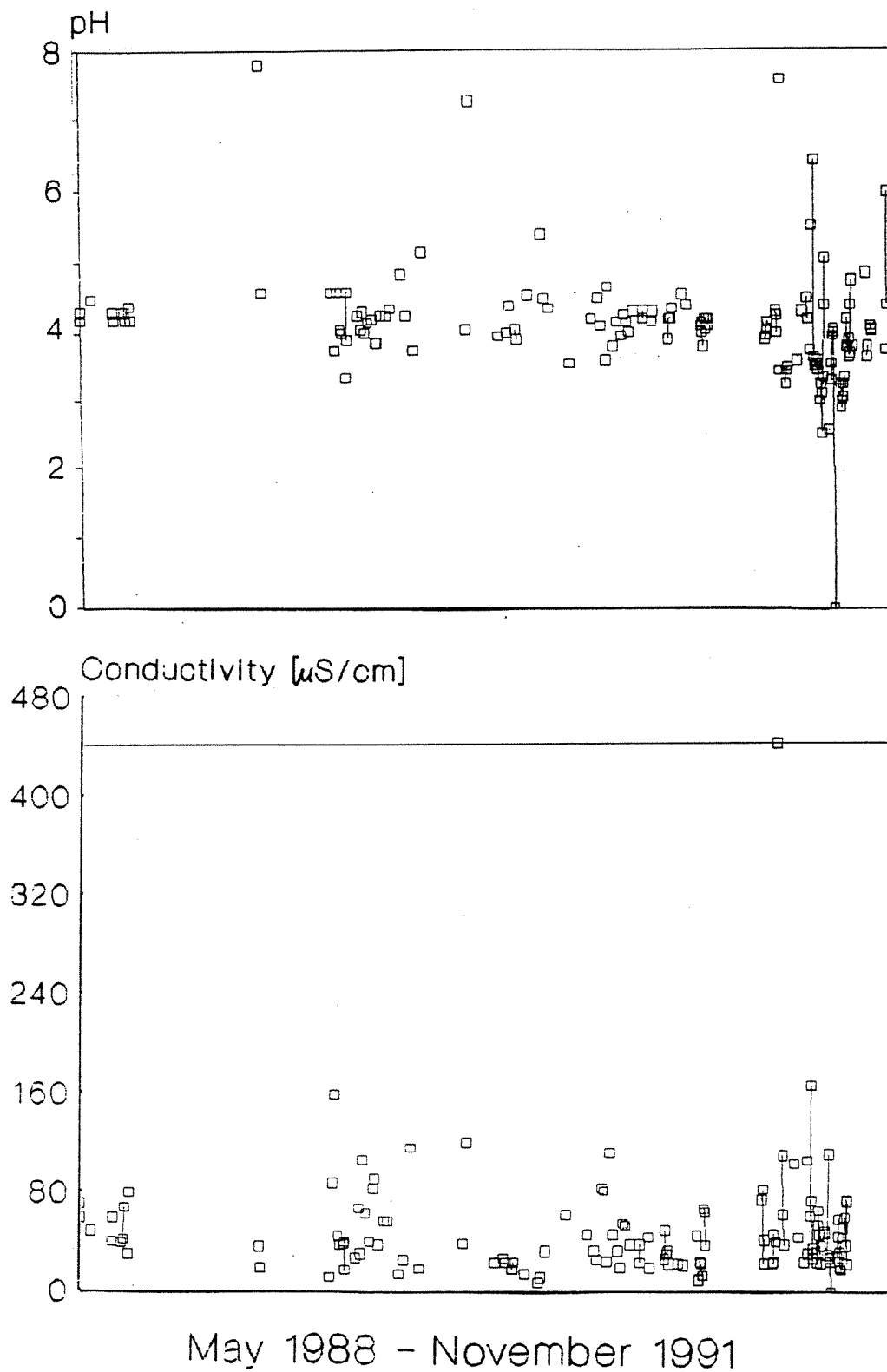
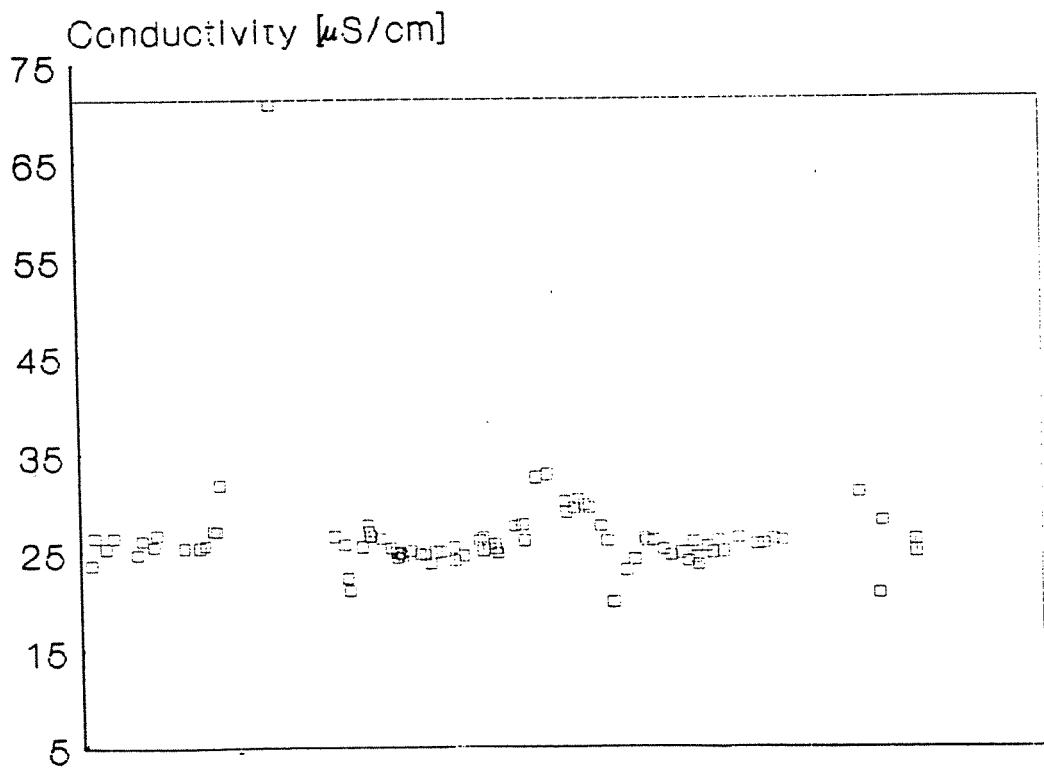
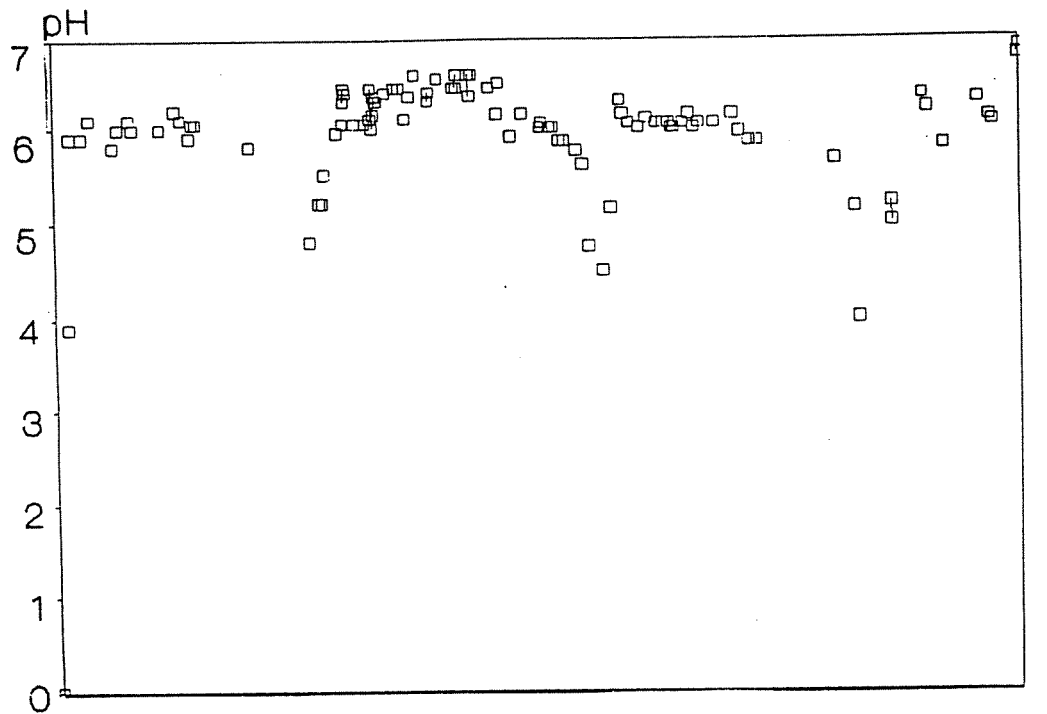


Figure 3. pH and conductivity of Czarny Staw Gasienicowy water 1988 - 1991



May 1988 - November 1991



Figure 4. pH and conductivity of Zielony Staw Gąsienicowy water 1988 - 1991

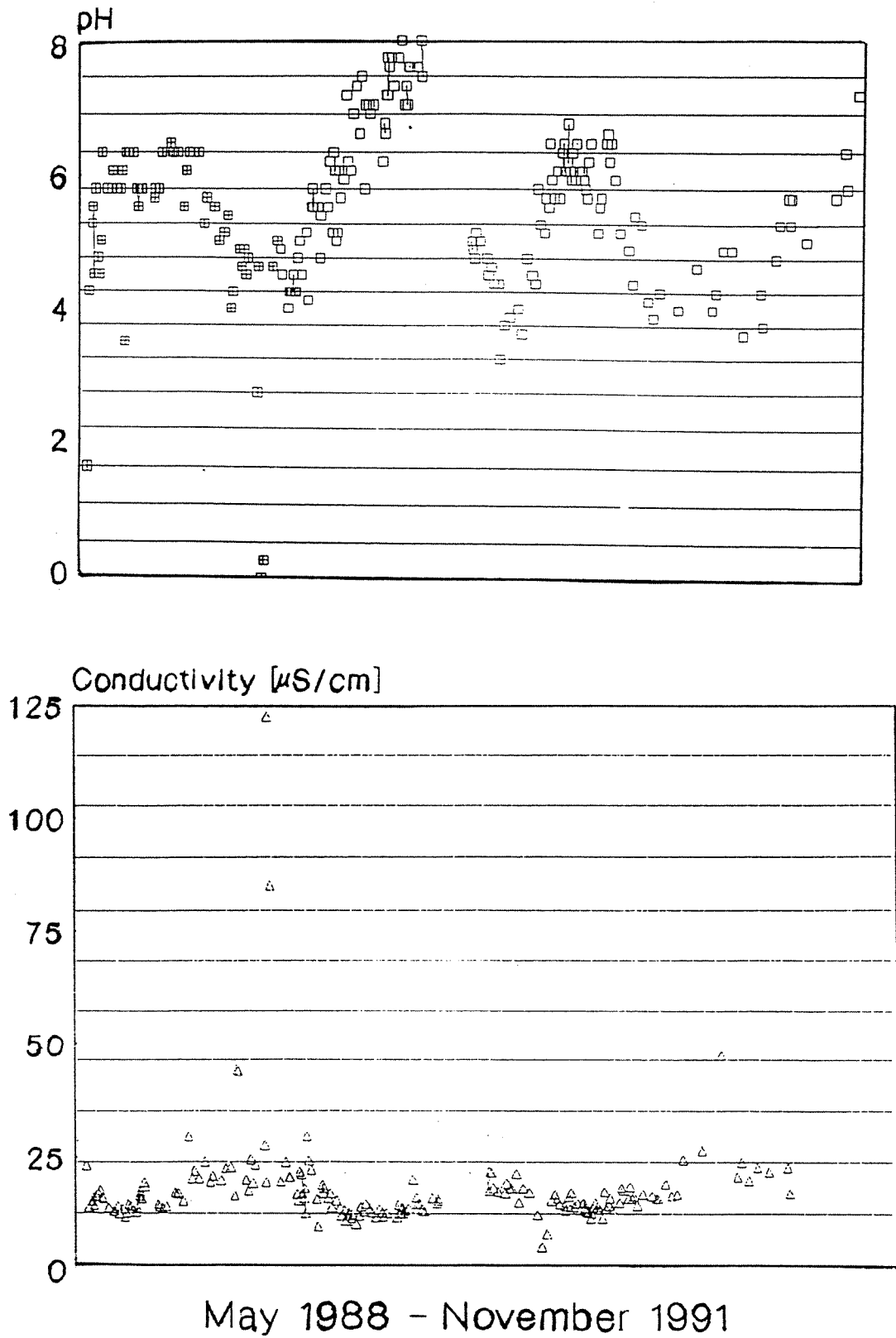


Figure 5. Calcium, sulphates and total hardness  
Zielony Staw Gas. 1990

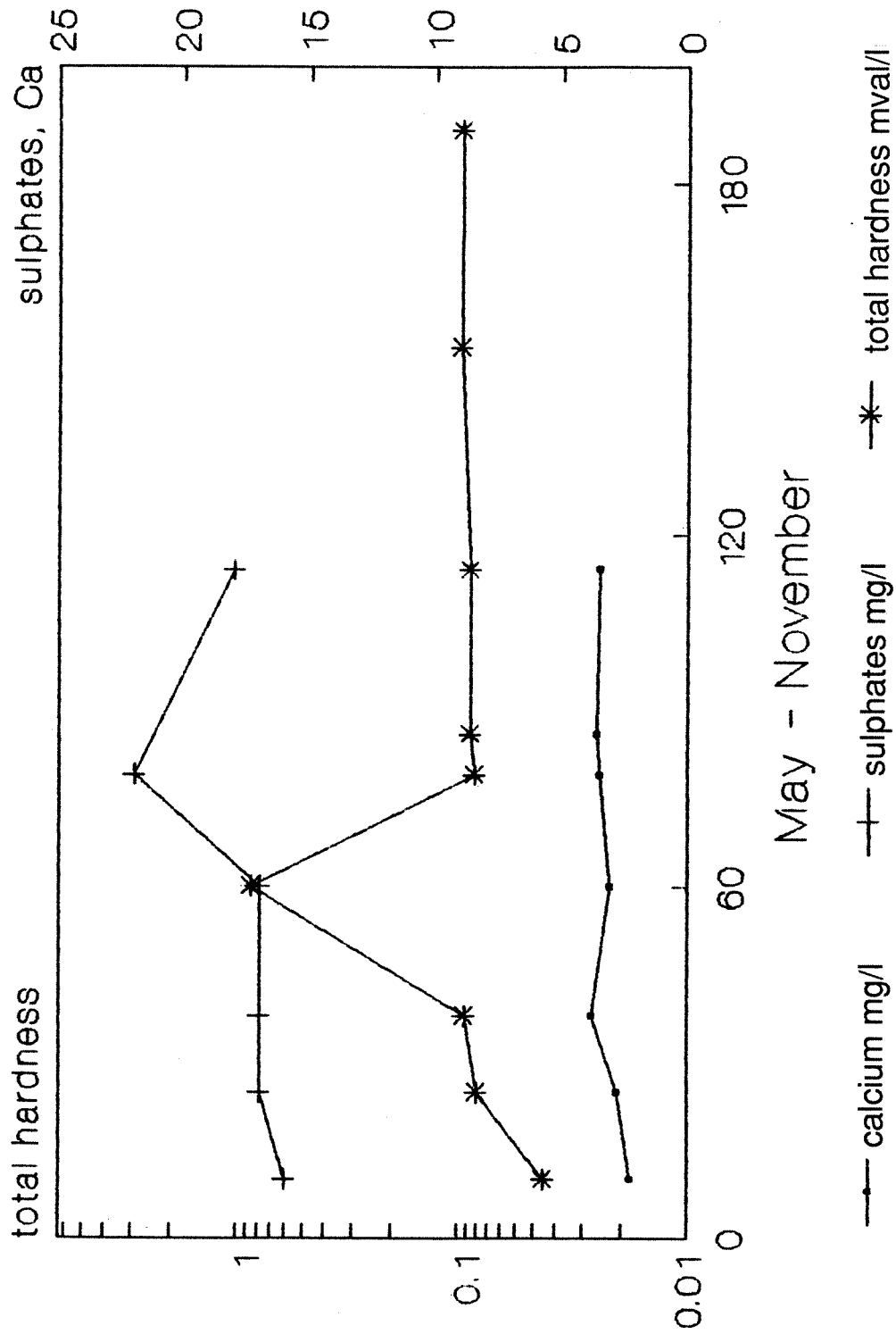
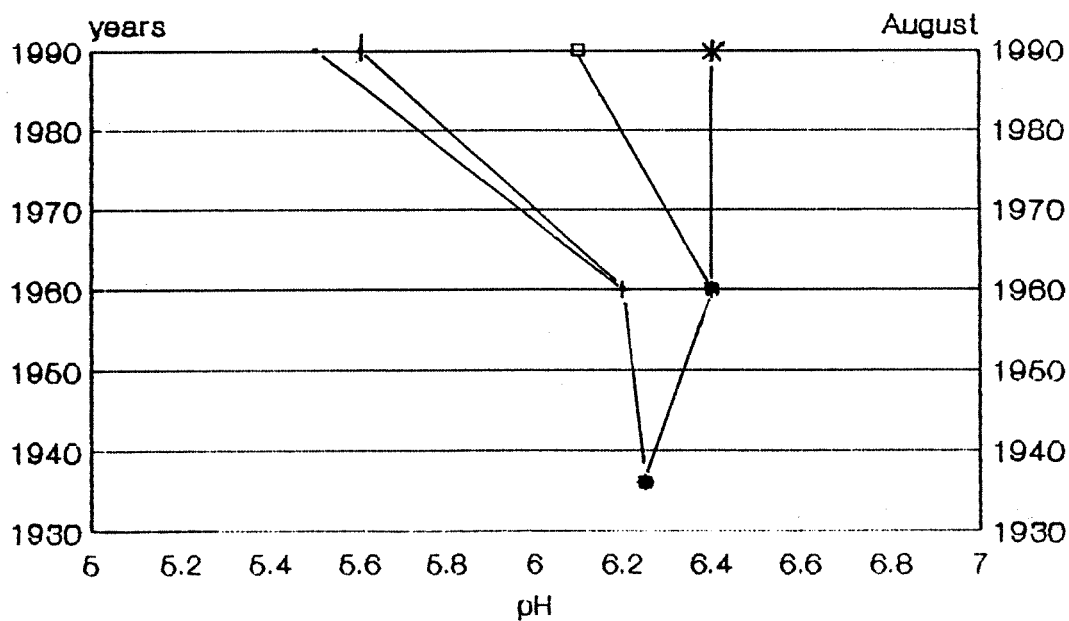
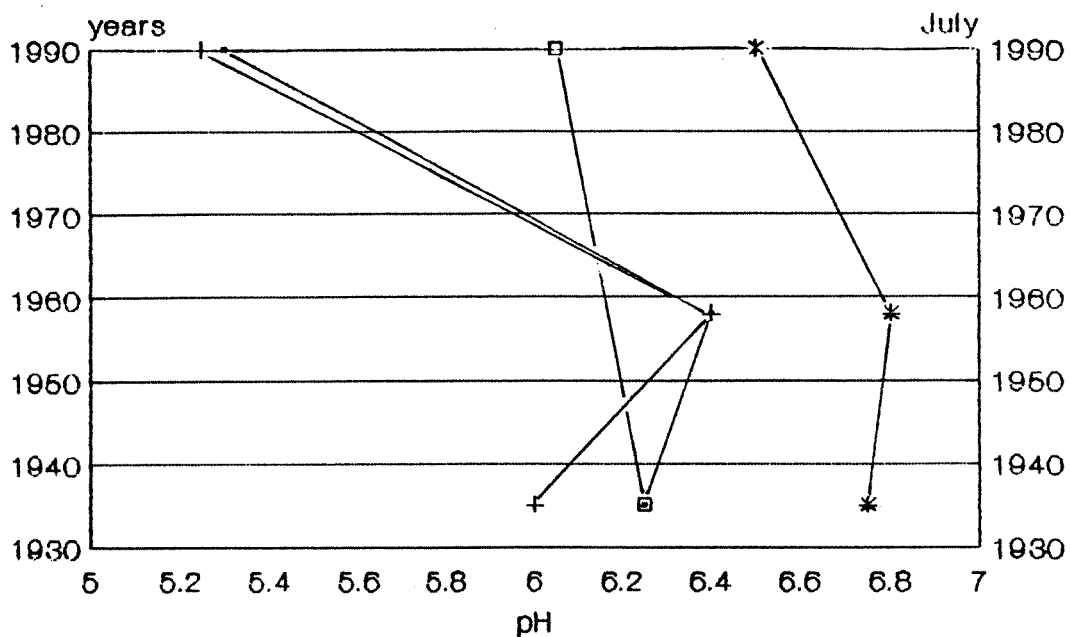


Figure 6. **Water pH changes, Sucha Woda Valley**  
1935 - 1958 - 1960 - 1990



• Zadni Gas.                      + Zmarzly Gas.  
\* Zielony Gas.                    ◻ Czarny Gas.

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Norsk institutt for vannforskning  NIVA

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