

## Aquatic chemistry in correlation with water level in the Kasprowa Niznia Cave (Tatra Mts)\*

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**Abstract** – The values of conductivity, total hardness, alkalinity, total residue, total fixed residue, and calcium concentration measured at the times of low water level in the Kasprowa Niznia Cave were distinctly higher than those measured during high water level. Silicate values had the opposite pattern. Means of the above chemical factors were significantly different ( $p < 0.05$  or  $p < 0.005$ ). No dependence between the remaining parameters measured and water level in the studied cave was observed.

**Key words:** chemistry, cave waters, Tatra Mts.

**Zależność chemizmu wody od jej poziomu w Jaskini Kasprowa Niznia (Tatry).** Przy niskich stanach wody wartości przewodnictwa elektrolitycznego, twardości ogólnej i węglanowej oraz całkowitej suchej pozostałości i jej części mineralnej, a także koncentracja jonów Ca były wyraźnie wyższe, a koncentracja krzemionki — niższa. Różnice średnich były statystycznie istotne na poziomie  $p < 0.05$  lub  $p < 0.005$ . Pozostałe badane parametry nie wskazywały zróżnicowania zależnego od poziomu wody.

### 1. Introduction

The water chemistry of Tatra caves has not very often been studied (Chodorowska and Chodorowski 1959, Małecka 1993), sometimes being a part of biological investigations (Micherdziński 1956, Dumnicka and Wojtań 1989). Moreover, the samples were taken at times of low water level (winter, summer, or autumn when the precipitation was low). In most of the caves studied, access to the passages with permanent water bodies was then possible while in other seasons they were flooded and inaccessible.

The results obtained in previous studies showed comparatively great differences in water chemistry among the investigated caves. It depends on the character of the source and the depth of circulating water and also on the type of sampling site (Małecka 1993). It is assumed that stagnant waters, having longer contact with the surrounding rocks, contain more minerals than flowing ones.

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In the Tatra Mts there have been no special studies on changes in the water chemistry of cave water correlated to its level, only single data can be found in Chodorowska and Chodorowski (1959). During an investigation of the decomposition of organic matter in the water of the Kasprowa Niznia Cave (Dumnicka 1995, Galas et al. 1996) chemical analyses were also conducted. The water samples were taken at high and low water levels.

The aim of this study was to describe the changes in the chemical composition of the water during the year and to compare the water chemistry at different water levels.

## 2. Study area

The study was carried out in the Kasprowa Niznia Cave in the Kasprowa Valley, Tatra Mts (49°15'N, 19°58'E, the cave entrance at altitude 1228 m). The cave drains karstic (Jurassic limestone, Western Tatra Mts), and crystalline (High Tatra Mts) areas.

Samples were collected in various places in the cave — depending on the water level. At low water level it was possible to reach the permanent pool in the deepest part of the cave, about 150 m from the entrance (Station 1) (fig. 1). At high water level this place could not be reached, so the samples were taken nearer the entrance (Stations 2 and 3); once, when the cave was flooded, a sample was taken from the entrance (Station 4).

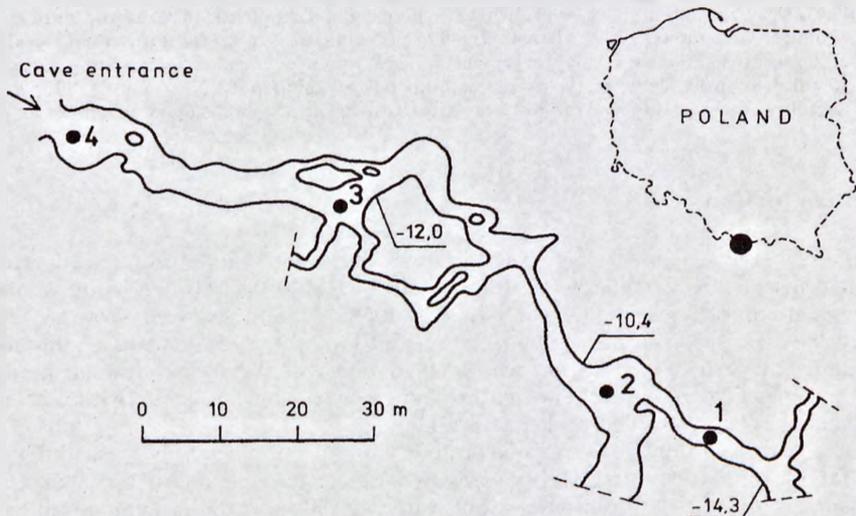


Fig. 1. Plan of the Kasprowa Niznia Cave with sampling stations (1-4).

### 3. Material and methods

The samples were taken on the following dates (month/day): 10/14 and 11/18 in 1992, 1/18, 3/9, 5/17, 6/6, 6/14, 6/29, 9/15, 9/27 and 11/30 in 1993, 1/31, 3/27, 6/29, and 7/11 in 1994. The intervals between samplings ranged from 8 days to 3 months.

Water for analysis was taken directly into polythene bottles; samples for oxygen content and BOD<sub>5</sub> were put in glass containers and fixed immediately. Water temperature, pH, and CO<sub>2</sub> content were measured in situ. Chemical analyses were made using commonly accepted methods (Hermanowicz et al. 1976, APHA 1992). The differences between mean values of parameters at low and high water level were tested using the t-test.

### 4. Results

In the period of the investigation the temperature of water in the cave was low, varying from 3.5 to 5.0 °C (mean 4.5 °C) (fig. 2). The pH was slightly alkaline, a higher value being found at low water level (range 7.4–8.2, mean 7.8), while at high water level the pH fell to 7.0 (range 7.0–8.1, mean 7.4).

The water of the Kasprowa Niżnia Cave is low in minerals (when compared with the water from other karstic terrains). The value of conductivity ranged from 106 to 221  $\mu\text{S cm}^{-1}$  (mean about 160  $\mu\text{S cm}^{-1}$ ). During the period of snow-melting and after heavy rains the value of conductivity decreased markedly when compared with the dry period of the year (i.e. autumn and winter) (fig. 2). The fluctuations of sulphate ion concentrations (4.9–12.8  $\text{mg dm}^{-3}$ ) were rapid and irregular (fig. 2). The highest values were noted at the beginning of the melting period in both the studied years (March 1993 and 1994), although a slightly higher mean value was observed at low water levels (Table I). The mean concentration of chloride was similar at high and low water levels (2.0 and 1.6  $\text{mg dm}^{-3}$  respectively). In the autumn and winter of the first year of investigation the chloride concentration was about 3  $\text{mg dm}^{-3}$ , decreasing to about 1.5  $\text{mg dm}^{-3}$  in spring of 1993 and remaining at this level to the end of study (fig. 2).

Total hardness was only slightly higher than carbonate hardness, except for one sampling date (14 October 1992), when the difference between these two parameters was above 2  $\text{mval dm}^{-3}$ . The highest and more constant values of total and carbonate hardness (2.0 and 1.9  $\text{mval dm}^{-3}$  respectively) were noted in dry periods (autumn and winter of both years). During the times of high water level, especially in the first studied year, the values of hardness and alkalinity were lower (1.4 and 1.3  $\text{mval dm}^{-3}$  respectively) and their fluctuations more intensive (fig. 2).

The changes in dominant cations in the cave water — calcium and magnesium — were prominent and varied from 13.2–40.0  $\text{mg dm}^{-3}$  for Ca and from 0.9–4.2  $\text{mg dm}^{-3}$  for Mg. The higher calcium values were observed at low water level (mean 35.5  $\text{mg dm}^{-3}$ ) compared with the value at high water level (mean 22.2  $\text{mg dm}^{-3}$ ) (fig. 2); these differences were statistically significant ( $p < 0.05$ ). Slightly lower magnesium values were noted at times of low water level when compared with high water level (Table I).

Greater fluctuations were found in the case of silicate values. An increased content at times of high water level was found (mean 4.5  $\text{mg dm}^{-3}$ ), a particularly high value being recorded at the time of snow-melting, in the second year of the

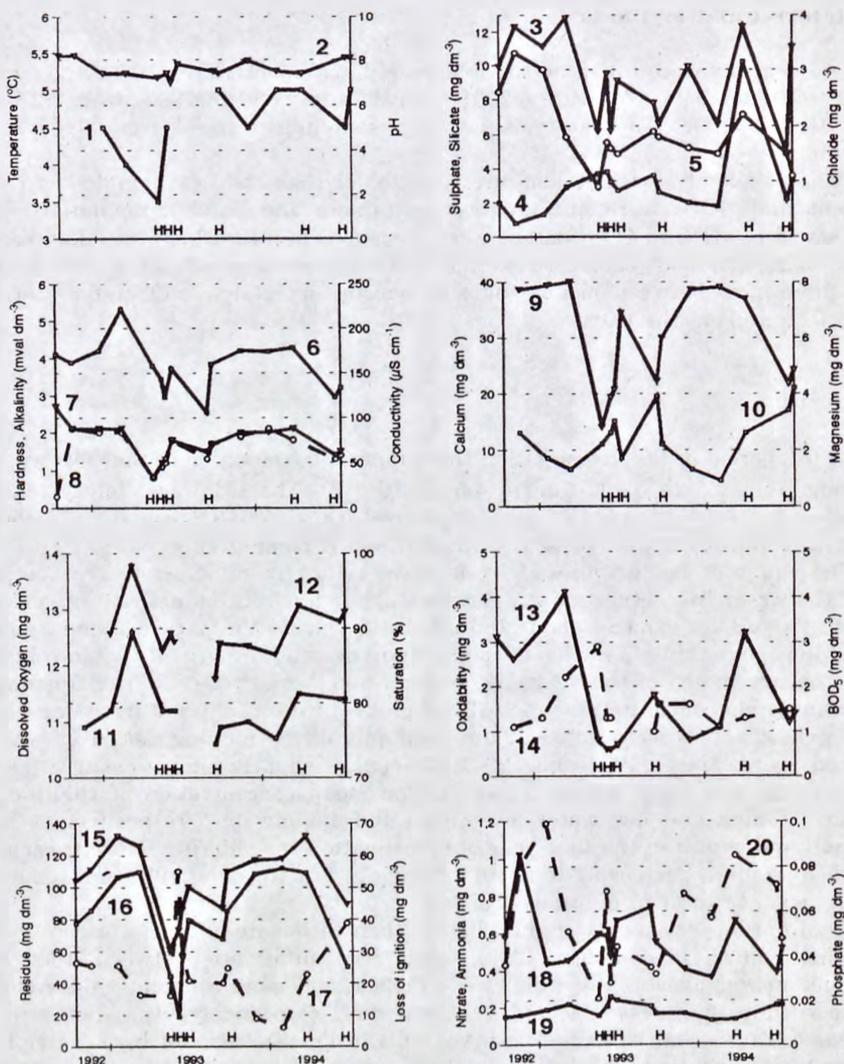


Fig 2. Changes in physico-chemical parameters in the water of the Kasprowa Niznia Cave from October 1992 to July 1994: 1 — temperature, 2 — pH, 3 — sulphate, 4 — silicate, 5 — chloride, 6 — conductivity, 7 — total hardness, 8 — alkalinity, 9 — calcium, 10 — magnesium, 11 — dissolved oxygen, 12 — oxygen saturation, 13 — oxidability, 14 — BOD<sub>5</sub>, 15 — total fixed residue, 16 — total residue, 17 — loss of ignition, 18 — nitrate, 19 — ammonium, 20 — phosphate.

study (fig. 2). At low water level the silicate concentration was only 2.2 mg dm<sup>-3</sup> (Table I). These differences were significant ( $p < 0.05$ ).

The content of dissolved oxygen and oxygen saturation was always high, the latter varying from 83% to 98.3%. The fluctuations in oxygen saturation were small and no correlation to water levels was found. Oxidability of the cave water, which

Table I. Average values of physico-chemical parameters of the water of the Kasprowa Niznia Cave from October 1992 to July 1994, and statistical significance of the differences between means for low and high water level.

Parameter	Unit	Mean	Water level		
			Low	High	p
pH		7.5	7.8	7.4	NS
Conductivity	$\mu\text{S cm}^{-1}$ (18 °C)	159.8	170.9	133.4	< 0.05
Total hardness	$\text{mval dm}^{-3}$	4.9	5.7	3.9	< 0.05
Alkalinity	$\text{mval dm}^{-3}$	1.7	1.9	1.3	< 0.005
Chloride	$\text{mg dm}^{-3}$	1.9	1.6	2.0	NS
Sulphate	$\text{mg dm}^{-3}$	9.1	9.9	7.8	NS
Silicate	$\text{mg dm}^{-3}$	3.1	2.2	4.5	< 0.05
Calcium	$\text{mg dm}^{-3}$	29.8	35.5	22.2	< 0.005
Magnesium	$\text{mg dm}^{-3}$	2.4	2.0	2.9	NS
Oxygen saturation	%	89.5	90.3	88.6	NS
Oxidability	$\text{mg O}_2 \text{dm}^{-3}$	1.8	2.1	1.4	NS
BOD <sub>5</sub>	$\text{mg O}_2 \text{dm}^{-3}$	1.5	1.5	1.6	NS

represents the amount of easily decomposed organic matter, was low. In the autumn and winter of the first year of study, the value of oxidability was about  $3 \text{ mg O}_2 \text{ dm}^{-3}$  (fig. 2), increasing to a value of  $4 \text{ mg O}_2 \text{ dm}^{-3}$  at the beginning of snow-melting time, to decline below the level of  $1 \text{ mg O}_2 \text{ dm}^{-3}$  when the cave was flooded. In the second year of study the oxidability values were lower, the autumn-winter rise was not recorded, only the repeated peak at the beginning of snow-melting being observed. Changes in BOD<sub>5</sub> values had a similar pattern to those of oxidability, but fluctuations in the former, were smaller and shifted for one sampling date (fig. 2). The mean values at the times of high and low water levels were almost identical (Table I).

The concentrations of total residue and its mineral part (total fixed residue) were distinctly higher at low water level, the differences between these two values at low and high water level being significant ( $p < 0.05$ ). The maximum value of loss of ignition was detected when the cave was completely flooded and water was flowing out of the cave entrance (June 1993) (fig. 2), while in the second year of the study at a time of high water level the maximum value of loss of ignition was slightly lower. The mean value of this parameter was higher at high water level ( $30.3 \text{ mg dm}^{-3}$ ) than at low water level ( $19.3 \text{ mg dm}^{-3}$ ), but this difference was not significant (Table I).

The mean nutrient concentrations (N-NH<sub>4</sub>, N-NO<sub>3</sub> and P-PO<sub>4</sub>) were similar at times of high and low water level (Table I). The concentration of N-NO<sub>3</sub> was above  $1 \text{ mg dm}^{-3}$  only on one sampling date, while the concentration of N-NH<sub>4</sub> was raised and almost constant throughout the study period (fig. 2). The maximum value of P-PO<sub>4</sub> was observed in the autumn and winter of the first year. Later on, these values decreased, and at high water level sharp fluctuations in the concentration of P-PO<sub>4</sub> were noted (fig. 2). The N-NO<sub>2</sub> concentrations were very low and less diversified throughout the study period (Table I).

The results of May and June 1993 samplings, obtained in a short period of time, showed that at high water level the changes in sulphates, silicate, calcium, conductivity, BOD<sub>5</sub>, total and mineral residue, and loss of ignition were greater and more rapid, while those of the remaining parameters were smaller (fig. 2).

## 5. Discussion

The waters of the Kasprowa Niznia Cave were studied in the early fifties by Chodorowska and Chodorowski (1959). Most of the chemical parameters investigated by them (pH, conductivity, total hardness, oxidability, and O<sub>2</sub> saturation) had similar values as the parameters found in the present study at times of low water level. Sulphate concentration (15.24 mg dm<sup>-3</sup>) measured once by them, was much higher than the maximum value in this study. Chodorowska and Chodorowski (1959) did not detect chloride ions in the water, while at the beginning of the nineties this anion was constantly present in low concentrations. A comparison of the oxidability and chloride concentrations, characteristic as an effect of human activity, indicates the slight human impact on the chemistry of the Kasprowa Niznia Cave water during the last 40 years. It seems that periodical functioning of the cave entrance as a resurgence leads to the removal of organic matter accumulated (naturally or introduced by speleologists) into the cave at low water level. The rapid water flow through the cave which occurred at least for some time during the year, had the effect of lowering the value of total and carbonate hardness and on the concentration of calcium, arising from processes of rock leaching. Because of this, the chemical composition of the water of the Kasprowa Niznia Cave is much more similar to that found in caves with running water (Wodna pod Pisana Cave, Dumnicka and Wojtan 1989; Bystra Cave, Malecka 1993), than to those with long-standing stagnant water (Bandzioch Kominiarski Cave, Malecka 1993). Chodorowska and Chodorowski (1959) also found lowered alkalinity when the water flow was greater. On the basis of underground water studies from different hydrochemical areas of the Tatra Mts Malecka (1991) assumed that in fissure and fissure-karstic waters of the Tatra Mts series (the cave water being part of it), the main parameter affecting the water chemistry is rock leaching, and the share of precipitation is 22–33%. In some seasons, especially during snow-melting time or after heavy rainfall, the chemical parameters in cave water are strongly modified by water filtrated to the cave centre. Then an increase in leached compounds from the soil, such as silicate, takes place. Similar changes were found in Hungarian cave waters (Cser et al. 1984). The chemistry of surface waters is also changeable during snow-melting time (Kot 1993).

The relatively small and less variable amount of nitrogen, phosphorus, and easily oxidated organic matter found in the water of the studied cave, is a consequence of an irregular water level. In stagnant waters, as a result of oxidation processes of nitrogen to nitrate and the lack of algae, concentrations of this biogen sometimes reach very high values, comparable to those found in very deep underground waters. Local accumulations of organic matter were found in the Zimna Cave, where a high value of oxidability (Chodorowska and Chodorowski 1959) and higher fauna density (Dumnicka 1981) were noted. On the other hand, small fauna densities found in the Kasprowa Niznia Cave (Dumnicka 1995) might result from the small amount of organic matter in the water.

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