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The carbonate aggressiveness of water in the karst areas of the basin of the Chochołowski and Kościeliski streams (Western Tatra Mts.)

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ABSTRACT

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Changes of the carbonate aggressiveness of water in the karst areas of the basin of the Chochołowski and Kościeliski streams (Western Tatra Mts.) are presented. The saturation index SI_c is lowest for rainwater, higher for groundwater and highest for surface water. Most of the surface water flowing out of the West Tatra Mountains has the ability to dissolve carbonate rocks.

INTRODUCTION

The water which dissolves rocks plays a significant role in the process of chemical denudation. The ability to dissolve a specified amount of calcium or magnesium carbonates is defined as the carbonate aggressiveness of water.

Up to now, the problem of carbonate aggressiveness of water in the area of the Tatra has been mentioned only sporadically. OLEKSYNOWA (1970) tried to define a balance of the CO_2-H_2O-$CaCO_3$ system for the water of calcareous basins. For the samples taken only at the outflow of streams from the Tatra Mountains OLEKSYNOWA found that the water was almost saturated with calcite. In qualifying chemical denudation for the calcareous-dolomitic area of the West Tatra, KOTARBA (1972), who carried out his research in the Mała Łąka Valley, made some remarks regarding the aggressiveness of both rainwater on rock surface and the water of the Małołącki stream. In the first case the water was aggressive only to a small extent, while in the second case its

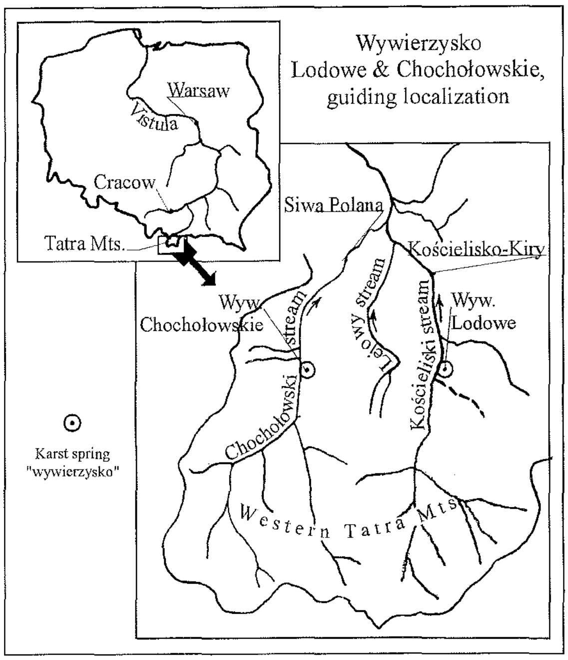

Fig. 1. Location of the studied karst springs in the Tatra Mountains

state lay between aggressiveness and saturation. The carbonate aggresiveness was also considered by PULINA (1975, 1992), and KRAWCZYK & OPOŁKA (1992), who specified the aggressiveness of the Kościeliski stream in the karst areas. This paper has been.written on the basis of the results obtained during the stationary field research (MAŁECKA 1984, 1996; BARCZYK 1994).

CALCULATIONS

The amount of dissolved carbonate mass is specified by the saturation limit of the solution, witch is dependent upon the content of aggressive CO_2 , the concentration of hydrogen ions (pH) and the solution temperature (PULINA 1992). The carbonate aggressiveness is measured by means of either direct or indirect – graphic methods (MARKOWICZ & PULINA 1979), or by using the Saturation Index (SI_c), which quantitatively defines the deviation of a particular type of water from the equilibrium state with calcite. In this work which concerns rain-, surface and karst-fissure water, the Saturation Index estimation method is used.

A general formula for the Saturation Index was given by WHITE (1988):

$$SI_c = \log \left(\frac{a_{Ca} \times a_{CO_3}}{K_c} \right) \quad [1]$$

where K_c – the equilibrium constant $[Ca^{2+}][CO_3^{2-}]$

The activities a_i given in the numerator can be calculated by the multiplication of the concentrations and activity coefficient of a particular ion:

$$a_i = \gamma_i \times C_i \quad [2]$$

where: γ_i – activity coefficient of a particular ion in a solution
C_i – content of a particular ion in the solution

The activity coefficients are calculated by means of the DEBYE-HÜCKEL (WHITE 1988) equation:

$$-\log\gamma_i = \left(\frac{A \times z_i^2 \times \sqrt{I}}{1 + \overset{0}{a}_i \times B \sqrt{I}} \right) \quad [3]$$

where: A, B – temperature-dependent constants (WHITE 1988)

z_i – charge of the ion

$\overset{0}{a}_i$ – the diameter of the ion

I – the ionic strength of the solution

For volume fractions (mval/dm^3), according to the composition of water, the ionic strength is formulated as:

$$I = 10^{-3}[C_{Ca}+C_{Mg}+C_{SO_4}+C_{CO_3}+0.5(C_{HCO_3}+C_{Cl}+C_{NO_3}+C_{Na}+C_K)] \quad [4]$$

After conversions, SI_c is given as (KRAWCZYK & OPOŁKA 1992):

$$SI_c = \log\gamma_{Ca} + \log(0.5 \times 10^{-3} \times C_{Ca}) + \log\gamma_{HCO_3} + \log(10^{-3}C_{HCO_3}) + pH + pK_c - pK_n \quad [5]$$

where:
C_{Ca}, C_{HCO_3} – content of calcium and hydrogen carbonates determined (mval/dm^3)
pH – water reaction measured in field conditions
pK_c, pK_n – equilibrium constants for carbonates
γ_{Ca}, γ_{HCO_3} – activity coefficients.

The values of the equilibrium constants for reaction of carbonates, and of the constants A and B specified for particular temperatures, that are necessary for the calculation of the carbonate aggressiveness, are given in Table 1.

t[^{0}C]	pK_n	pK_c	A	B
0	10.63	8.38	0.4883	0.3241×10^8
5	10.55	8.39	0.4921	0.3249×10^8
10	10.49	8.41	0.4960	0.3258×10^8
15	10.43	8.43	0.5000	0.3262×10^8
20	10.38	8.45	0.5042	0.3273×10^8
25	10.33	8.48	0.5085	0.3281×10^8

pK_n – negative logarithm of the equilibrium constant $[H^+][CO_3^{2-}]/[HCO_3^-]$
pK_c – negative logarithm of the equilibrium constant $[Ca^{2+}][CO_3^{2-}]$

Table 1. The equilibrium constants for reactions of carbonates used in the calculation of water aggresiveness (APPELO & POSTMA 1993) and the constants A and B for the Debye-Hückel equation (WHITE 1988)

It has generally been assumed that $SI_c = 0$ for the equilibrium of water with calcite. $SI_c < 0$ indicates the likelihood of water aggressiveness in relation to calcite, $SI_c > 0$ indicates the high likelihood that a mineral precipitates from a solution (MAŁECKI 1995). JENNE & BALL (1980) expanded the range of equilibrium towards a particular mineral to the value of Saturation Index SI_c in the range ±5% log K.

The values of the Saturation Index SI_c of the rainfall, surfacewater and groundwater of the karst areas of the Chochołowski and Kościeliski streams have been calculated using the above formula. Calculations of the SI_c index for the rainwater from the station in Polana Chochołowska were carried out as shown in the example below:

1. Calculations of the ionic strength of the solution I (equation [4]):

$$I = 10^{-3} \times [0.52+0.28+0.12+0.5 \times (0.58+0.16+0.04+0.01)]$$
$$I = 0.0013$$
$$\sqrt{I} = 0.036$$

2. Calculations of the activity coefficient for calcium ions γ_{Ca} (for a particular solution) (eq. [3]):

$$-\log\gamma_{Ca} = 4 \times 0.4921 \times 0.036/[1+(6 \times 10^{-8})\ (0.3249 \times 10^{8}) \times 0.036]$$
$$\log_{Ca} = -0.066$$
$$\gamma_{Ca} = 0.858$$

for the assumed temperature of 5°C the values **A** and **B** are 0.4921 and 0.324910^8, respectively.

$$\overset{0}{a}_{Ca} = 6 \times 10^{-8}$$

3. Calculations of the activity coefficient for hydrogen carbonate ions γ_{HCO3} (for a particular solution) (equation [3]):

$$-\log\gamma_{HCO_3} = 0.4921 \times 0.036/[1+(4 \times 10^{-8})\ (0.3249 \times 10^{8}) \times 0.036]$$
$$\log\gamma_{HCO_3} = -0.017$$
$$\gamma_{HCO_3} = 0.96$$

Values **A** and **B** are the same as in point 2

$$\overset{0}{a}_{HCO_3} = 4 \times 10^{-8}$$ (WHITE 1988).

4. Calculations of the saturation index SI_c (eq. [5]):

$$SI_c = -0.066+\log(0.5 \times 10^{-3} \times 0.52)-0.017+\log(10^{-3} \times 0.58)+4.5+8.39-10.55$$
$$SI_c = -4.56$$

measuring station	saturation index (SI_c)
polana Chochołowska	– 4.56
Hala Ornak	– 4.58
Kasprowy Wierch	– 4.66
Kościelisko-Kiry	– 4.95
average	– 4.69

Table 2. Saturation Index (SI_c) for the rainwater (using data from 1977-1991)

The calculations were based on the analysis of particular water samples. In the case of rainwater, estimated mean values of temperature and pH had to be assumed. A temperature of 5°C and pH value of 4.5 were used in the calculations (WELLBURN 1988, MASON 1991, MAŁECKA 1991, MIECHÓWKA 1993). If such assumptions are made, the values of SI_c at particular measuring points do not significantly differ: all are in the range from –4.56 to –4.95, and the mean value for the whole area equals –4.69 (Table 2).

Similarly, the distribution of the SI_c values for rainfall water over a period of one year does not show any significant differences (Table 3).

season	polana Chochołowska	Hala Ornak	Kasprowy Wierch	Kościelisko Kiry	average
spring	– 4.55	– 4.69	– 4.54	– 4.89	– 4.67
summer	– 4.71	– 4.65	– 4.92	– 5.03	– 4.83
autumn	– 4.67	– 4.71	– 4.51	lack of data	– 4.63
winter	– 4.65	– 4.71	– 4.55	lack of data	– 4.63

Table 3. Saturation Index SI_c for the rainwater in four seasons (using data from 1977-1991)

In almost all cases (except for the water from Hala Ornak), the summer rainfall has the highest values of SI_c.

DISCUSSION

The results obtained unequivocally indicate the well-marked aggressiveness of rain water in the

stream	saturation index SI_c	% fraction of crystalline rocks
Chochołowski	– 0.87	59
Lejowy	0.06	0
Kościeliski	– 0.32	45
Małołącki	– 0.61	12
Strążyski	– 0.09	0
Białego	0.03	0
Bystra	– 0.47	46
Olczyski	– 0.82	0
Filipka	– 0.55	0
Waksmundzki	– 1.89	76
Wołoszyński	– 3.45	38
Roztoka	– 4.48	94
Rybi	– 2.57	96

Table 4. Saturation Index SI_c for the surface water from the streams at their outflow from the Tatra Mts.

point	location	SI_c	Ca (% mval)
	Kościeliski Stream		
K1	above Hightatric Succescion	– 1.41	64.7
K2	above Wypływ spod Pisanej	– 0.92	69.5
K3	Wywierzysko Lodowe	– 0.79	67.0
K4	below Wywierzysko Lodowe	– 0.68	70.3
K5	Brama Kantaka	– 0.32	70.8
	Chochołowski Stream		
Ch1	above Hightatric Succession	– 1.89	46.5
Ch2	above Wyw. Chochołowskie	– 1.67	63.2
Ch3	below Wyw. Chochołowskie	– 1.00	82.0
Ch4	Siwa Polana	– 0.87	73.7

Table 5. Comparison of the variability of the saturation index SI_c and the content of Ca in the surface water of Kościeliski and Chochołowski streams (based on the mean values from 1977-1991)

whole area studied, as well as a lack of seasonal variability. The aggresiveness of ground water originates both from ground water that discharges into the streams and by contacts with bed rocks, in which a channel is incised. In the Tatra Mountains, the streams draining the crystalline core of the Western Tatra Mts. are characterised by the highest aggressiveness and, at the same time, by the lowest susceptibility of rocks to leaching. The values of the carbonate aggressiveness of the Tatra streams at the foot of the mountains are given for comparison in Table 4.

As the Chochołowski and Kościeliski streams (Text-fig. 1) flow along the valleys, crossing the diversified Tatra series in the boundary areas between rocks of the crystalline core of the Western Tatra Mts., Seisian sandstones and shales and carbonate rocks of a High Tatric Succession, rapid change of the susceptibility of formations to leaching takes place, despite the fact that the water has a constant aggressiveness. The changes of the SI_c values caused by a contact between water and rocks in the longitudinal profile of streams are shown schematically in Text-fig. 2.

In both cases, the SI_c index increases along the course of the stream, which means a gradual decrease in the aggressiveness of water. This is additionally illustrated by the data comparison in Table 5. The analysis of the SI_c values indirectly enables some conclusions to be drawn concerning hydrogeology. For instance, the high water aggressiveness of Wypływ spod Raptawickiej Turni (point D in Text-fig. 2) indicates a fast flux of water in the karst system and direct contact with rainfall water through open fractures.

In the investigated basins karst waters are represented mainly by vaucluse springs. The comparison of the SI_c values for water of Wywierzysko Chochołowskie (point A in Text-fig. 2) and Wywierzysko Lodowe (point F in Text-fig. 2) confirms the influence of the participation of surface water in the supplying of Wywierzysko Chochołowskie (SOLICKI & KOISAR 1973; BARCZYK 1994) and the exclusiveness of substratum discharge in the case of Wywierzysko Lodowe. In addition, the comparison indicates a long water residence in contact with the rock environment. In the case of Wywierzysko Chochołowskie (SI_c = –0.77), the duration of this contact is a little shorter than in the case of Wywierzysko Lodowe (SI_c = –0.69). The carbonate aggressiveness of both vaucluse springs is comparable with the values found for other springs in the Tatra (Table 6).

vaucluse spring	valley	saturation index SI_c
Chochołowskie	Chochołowska	– 0.77
Lodowe	Kościeliska	– 0.69
Bystre Górne	Bystra	– 1.28
Bystre Dolne	Bystra	– 0.67
Goryczkowe	Goryczkowa	– 0.68
Olczyskie	Olczyska	– 0.84

Table 6. Saturation Index SI_c in the water of the selected vaucluse springs in the Tatra Mts.

The analysis of the variability of the SI_c index in the studied areas enables us to assume two alternative scenarios for forming the final carbonate aggresiveness of surfacewater and groundwater. One possibility is the following chain: rainfall – a karst system – vaucluse springs; the water circulates long enough to cause a visible decline in the SI_c values. The other possibility is: surface water – a karst system – outflows, in which water residence time is much shorter. In addition, it is worth noticing the fact that in some cases both systems might be connected (Wypływ spod Pisanej, Wypływ spod Raptawickiej Turni). A persistence of this connection depends on

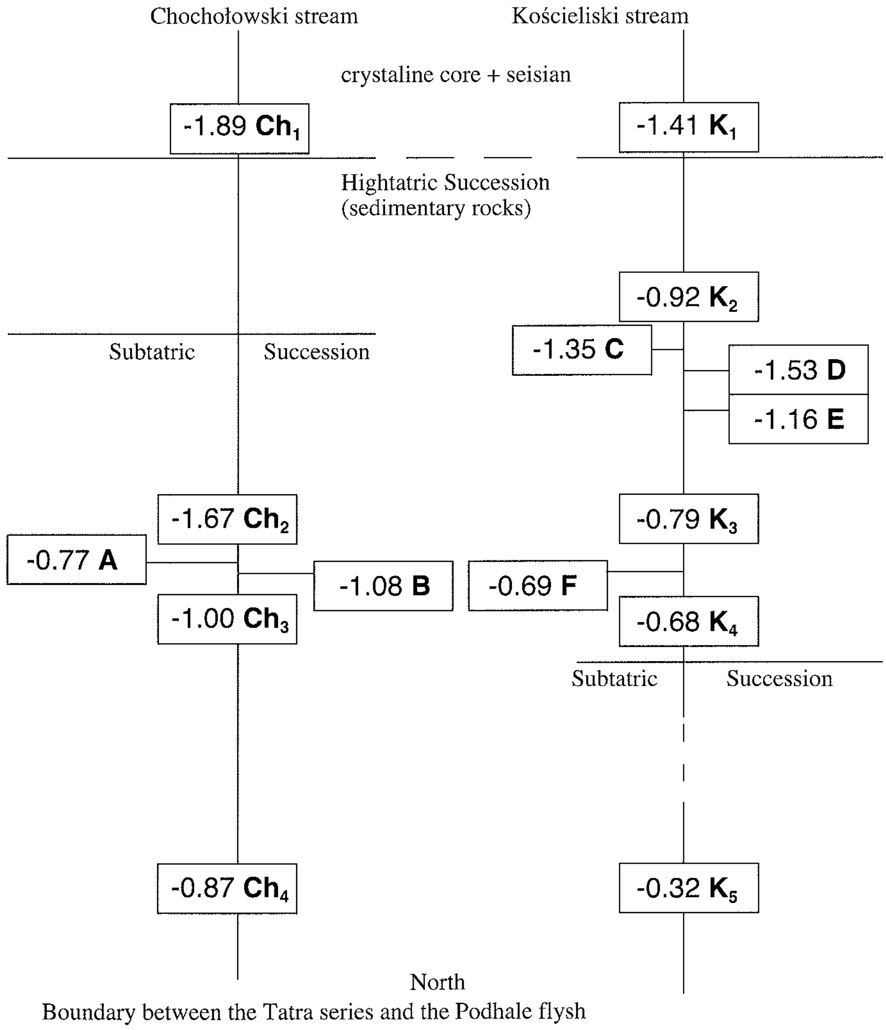

Fig. 2. The scheme of the variability of the saturation index Si_c along the course of the Chochołowski and Kościeliski streams; A – Wyw. Chochołowskie, B – Chochołowskie spring, C – Wypływ spod Pisanej, D – Wypływ spod Raptawickiej Turni, E - karst springs (Kościeliska valley), F – Wyw. Lodowe, K1, K2, K3, K4, K5 – sampling localites from the Kościeliski stream, Ch1, Ch2, Ch3, Ch4 - sampling localites from the Chochołowski stream (location see Text-fig. 1 and Table 5)

climatic conditions and, especially on the amount of rainfall, which influences the water table in streams and enables direct connections between a karst system and surface water to open, while the water level is high. It is reasonable to suppose that these scenarios can also be inferred in other karst areas of the Tatra Mountains.

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