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SPRING CHEMOGRAPH ANALYSIS - THE INFLUENCE OF THAW EFFECT AND DISPERSED POLLUTION IMPULSES (CRACOW-CZESTOCHOWA UPLAND, POLAND)

ANALIZA KEMOGRAMOV IZVIROV - VPLIV EFEKTA TALJENJA SNEGA IN IMPULZOV RAZPRŠENEGA ONESNAŽEVANJA (KRAKOWSKO-CZESTOCHOWSKO VIŠAVJE, POLJSKA)

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Izvleček UDK 556.33/.34(438)

Andrzej Tyc: Analiza kemogramov izvirov - vpliv efekta taljenja snega in impulzov razpršenega onesnaževanja (Krakowsko-Czestochowsko višavje, Poljska)

Napajanje, tok in vskladiščenje podzemne vode so v karbonatnih vodonosnikih zelo spremenljivi. Skladno z različnimi stopnjami zakraselosti je napajanje v razponu od koncentriranega do razpršenega. Članek predstavlja rezultate proučevanja onesnaženja glede na različne načine napajanja v karbonatnih vodonosnikih, s pomočjo monitoringa temperature vode in koncentracij glavnih ionov. Na podlagi analize kemogramov kraških izvirov in ocene tradicionalnih modelov napajanja, avtor predlaga nov model. Taljenja snega se odraža v kemizmu voda (Ca^{2+}, SO_4^{2-} in NO_3^-, celokupna trdota, specifična električna prevodnost).

Ključne besede: hidrologija krasa, kraški izvir, kemograf, Poljska.

Abstract UDC 556.33/.34(438)

Andrzej Tyc: Spring chemograph analysis - the influence of thaw effect and dispersed pollution impulses (Cracow-Czestochowa Upland, Poland)

Groundwater recharge flow and subsurface water storage can be extremely variable in carbonate aquifers. Owing to different degrees of karstification, recharge can range from concentrated to dispersed. The paper outlines the results of an investigation of pollution in respect of different recharge situations in carbonate aquifers including of monitoring of water temperature and ion concentration. According to the chemograph analysis, the author suggests modifications to the traditional models. The thaw effect is demonstrated by water chemistry (Ca^{2+}, SO_4^{2-}, NO_3^-, total hardness, specific conductivity).

Key words: karst hydrology, karst spring, chemograph, Poland.

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INTRODUCTION

For several decades, karst hydrology has used different indirect methods to investigate groundwater systems in karst aquifers. These have included analysis of karst spring hydrographs and chemographs (Mangin 1975; Bakalowicz 1979; Bonacci 1987; Ford & Williams 1989; Bonacci 1993). The analysis of a spring runoff hydrograph during individual flushes has successfully been applied in hydrology, in respect that it enables us to classify karstic aquifers according to the degree of karstification they exhibit and to the state of development of the groundwater circulation system. With the general growth of hydrochemical investigations in karst areas, this kind of analysis has advanced to a stage where detailed spring chemographs have been drawn up for short spring flushes (Jakucs 1959; Bonacci 1987). Certainly, this method of indirect hydrological investigation has gained many advocates in recent times and its popularity is, no doubt, due to the increasing availability of automatic measuring stations in the field and the computer in the laboratory. Spring chemographs may be used in the cases of both a single flush and in the analysis of seasonal variability of spring hydrochemical conditions (see also, e.g. White & Stellmack 1968; Shuster & White 1971; Tyc 1992; Reeder & Day 1993; Tyc 1994; Lackey & Krothe 1996).

Research into changes of karstic water chemistry where influenced by anthropogenic pollution, which have been carried out in several karst areas, has provided much new data for the interpretation of spring chemographs. On the one hand, pollution represents a valuable chemical marker, whereas, on the other, it makes the evaluation of karst aquifer activity even more complicated than it usually is. In cold-temperate karst areas, where there is a regular annual snow cover, thaw flushes are an important factor in influencing the hydrological and hydrochemical regime of a karst aquifer.

With respect to the author's own observations carried out in the central part of the Cracow-Czestochowa Upland, and by analysing the results of the research from other areas (e.g. Reeder & Day, 1993; Lakey & Krothe, 1996), it became apparent that the generally accepted interpretation of karst spring chemographs should be modified for those areas where thaw flushes occur and where the groundwater environment is considerably polluted.

Classical chemograph analyses

Long-term research in different karst areas all over the World shows that there is a positive relationship between spring regimes, the types of circulation in the aquifer and the temporal variability of some physical features and chemical composition of spring water. The theoretical basis for the application of spring hydrographs analysis gave L. Jakucs (1959) (who investigated springs in Kolmos, Hungary); W.B. White & J.A. Stellmack (1968), W.B. White (1969), and E.T. Shuster & W.B. White (1971) (the Nittany Valley, Pennsylvania); R. Gospodarič & P. Habič (1976) (the Dynaric karst); S.R.H. Worthington (1991) (the Rocky Mountains of the U.S.A.) and, particularly, A. Mangin (1975), M. Bakalowicz (1979) and M. Bakalowicz & A. Mangin (1980) (the Aliou, Baget and Fontestorbes systems in the Pyrhenees, France). Recently, the latter investigation has been enlarged by A. Pulido-Bosch in the Torcal de Antequera System of Spain (e.g. Padilla *et al.* 1995). These authors all assume that karst aquifers are heterogeneous and represent all possible combinations and organisational stages of runoff which can range between the diffuse flow and conduit flow systems. The hydrological and hydrochemical regimes of springs (spring yields, temperature and specific conductivity and the temporal variability of the chemical properties of spring water) are in a direct relationship with the structure and condition of water circulation in the karst aquifer. This regime is modified by the limiting conditions of the aquifer. The variability of karst spring discharge relates to the variability of precipitation, the intensity of thawing and the volume of aquifer recharge by allochthonous surface streams. Therefore, the hydrological and hydrochemical regime of springs is mainly dependent on the recharge conditions. According to L. Jakucs (1959), it is important to recognise the relationship between the nature of the karst aquifer recharge and the spring response; springs of small variability are associated with autochthonous recharge (percolation and infiltration) whereas there is another type represented by springs of great variability, where, usually, allochthonous recharge by surface streams is a strong influence. According to S.R.H. Worthington (1991), the location of a spring at a particular altitude in relation to neighbouring springs which drain the same karst system, may also be an important factor in influencing variability of discharge.

From these considerations, it follows that any classification of springs in a karst area must contain the following: (1) full-flow springs, which drain the whole aquifer (2) underflow springs, which mainly drain basic underground runoff (3) overflow springs, which mainly drain flush runoff, and (4) underflow-overflow springs, which represent a transitional type. Springs which drain a whole aquifer are very rare in carbonate karst areas; they normally occur only in those areas where there are no overflow springs and the single spring is then situated at the lowest topographical point in the whole catchment. S.R.H. Worthington (1991) also assumed that each overflow spring must have a complementary underflow spring; however, in as much as these are seldom recorded in any survey of a karst area, they are often difficult to find. In such cases, the basal runoff goes beyond the aquifer, without surface discharge (therefore it is not possible to measure it). Thus, it is the overflow springs which tend to be the most frequently investigated (and, also, supposedly, the commonest) in carbonate karst terrains.

The best-known and commonly applied analysis of karst spring chemograph

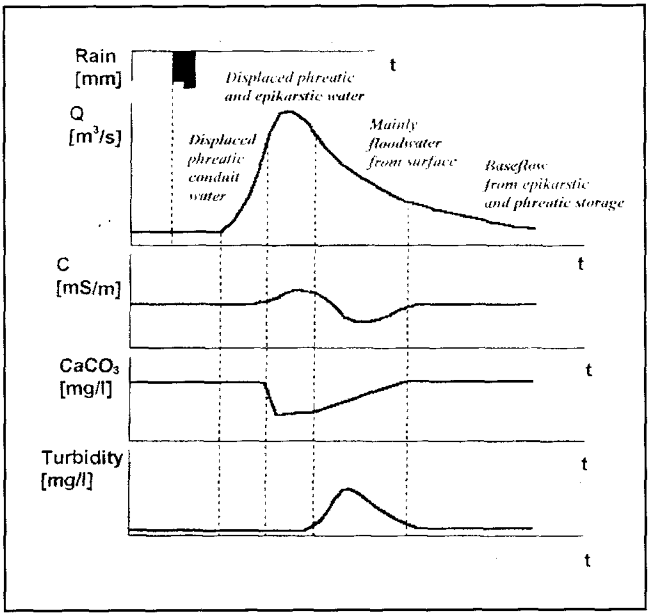

Fig. 1: Spring chemograph showing the origin of water discharging in spring during flood event in natural conditions without influence of thaw (after O. Bonacci, 1987 and D. Ford, P. Wiliams, 1989 - modified).

in the international literature assumes that, during a flush, the water comes from different parts of the aquifer and that its occurrence in discharge causes changes in the physical features (mainly the temperature, the specific conductivity and the amount of suspended matter and microorganisms) and chemical features such as total hardness, content of calcium or hydrocarbonates (Bonacci, 1987; Ford & Williams, 1989) (Fig. 1). This model further assumes that the maximal yield during a flush relates directly to a spring discharge which comes from the epikarst zone and karst conduits in the vadose zone. Later, during the flow recession, these coefficients increase slowly, eventually to revert to their original value. At this time, the base flow of the phreatic zone emerges as spring water discharge.

CASE STUDIES IN THE CRACOW-CZESTOCHOWA UPLAND

The results of investigations concerning the yield and physico-chemical properties of several springs in the central part of the Cracow-Czestochowa Upland now permit an evaluation of the hydrological regime and contemporary karst processes in the Upper Jurassic Aquifer. Special attention has been paid to the anthropogenic influences in the zone of spring recharge during the flush periods; the importance of these in the analysis of spring chemographs cannot be emphasised too much.

The area studied embraces the central part of the Upper Jurassic Aquifer between Olkusz and Zawiercie (Fig. 2). The aquifer is mostly unconfined and only a small area is overlain by Quaternary sediments and these are freely permeable. Cryogenic disturbance of the epikarst zone is very characteristic of

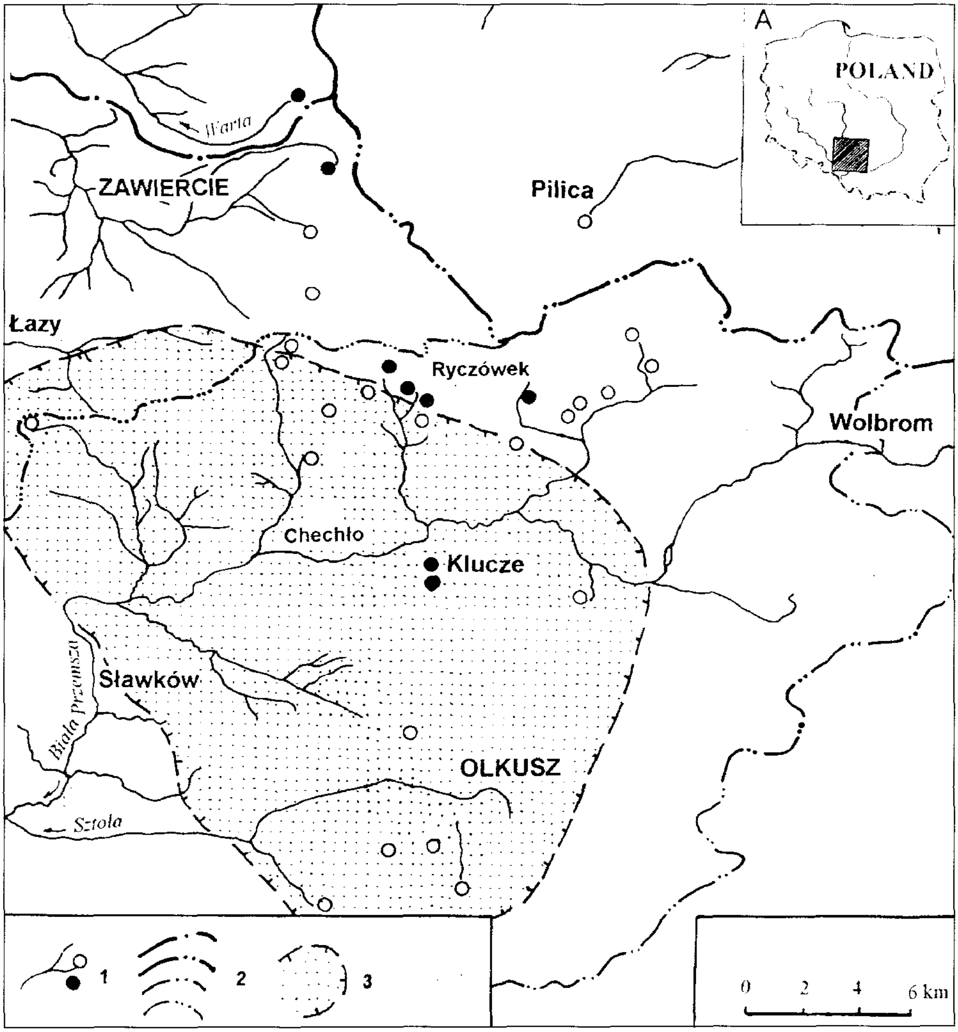

Fig. 2: Location and hydrographic network of the Olkusz-Zawiercie region (Cracow-Czestochowa Upland). 1-rivers and springs (filled circles show detail studied springs); 2-boundaries of topographic rivers basins: 1st, 2nd, 3rd and 4th order; 3-range of cone of hydraulic depression within Olkusz-Zawiercie Aquifer developed under artificial drainage.

the area (Tyc, 1996). The confining layer below is formed from Lower Oxfordian and Middle Jurassic clays. The Upper Jurassic limestone aquifer is variable in its lithology, comprising massive, platy and chalky types. Its thickness ranges from 50 to 400 m.

In the Cracow-Czestochowa Upland, the karst morphology and the groundwater drainage system are polygenetic. The karst drainage system takes two forms: (i) hydraulically inactive forms in the subsurface zone (including caves), and (ii) active forms in the deeper part of the aquifer (some of which may be sediment-filled). Recharge takes place over the entire outcrop, either directly or through the Quaternary cover. The mean annual precipitation in the area studied is 700 mm and 30% of this is snow-meltwater (Tyc, 1994)

Drainage from the aquifer takes place mainly from the springs but about 15% discharges north-eastwards through deep-level drainage below the Cretaceous cover into the Nida Basin. The hydrological regime of the springs in the area studied is thus a thaw-rain type (Tyc, 1994). The maximum yields usually occur during flushes, mostly in the period from February to April (the "flush maximum"). A second peak occurs in June or July (the "rain maximum"). Sometimes the peak yields are associated with excessive precipitation and may also occur in Autumn or even Winter, depending on the occurrence of unusual meteorological conditions. Normally, the precipitation maximum is two or three times lower than the maximal yields after thaws. Minimal spring discharges are normally in the winter months from October through to February or even March.

The temperatures of the spring water is another feature of the spring systems studied and normally, there are very few fluctuations, whether in the short- or the long-term. The water temperature is very closely related to the differences in spring-discharge during the year, especially so in the case of the Winter-Spring recharge periods. Intensive Winter recharge (e.g. during snow-free Winters) generally results in a decrease in the annual amplitude of fluctuation. By contrast, in the years when Spring-thaw is intensive, the annual amplitude of fluctuation increases markedly and minimal water temperatures occur one or two months later. At the end of the Summer, when cold water from thaw recharge runs off, the groundwater is recharged only by warm rainwater; this results in an increase of water temperature in the springs.

CHEMOGRAPH ANALYSIS OF SELECTED SPRINGS WHICH ARE INFLUENCED BY HUMAN IMPACT

A great deal of information may be obtained about the physical and chemical properties of water which circulates in the Upper Jurassic Aquifer by careful studies of the spring discharge. The Ryczowek II and Klucze I and II Springs, all located in the central part of the Cracow-Czestochowa Upland, are described here in order to illustrate the way a spring chemograph may be modified where there is a strong anthropogenic influence (Fig. 2). Figure 3 shows the seasonal variability of chemical properties and yields of the Ryczówek II Spring in the period 1989-90.

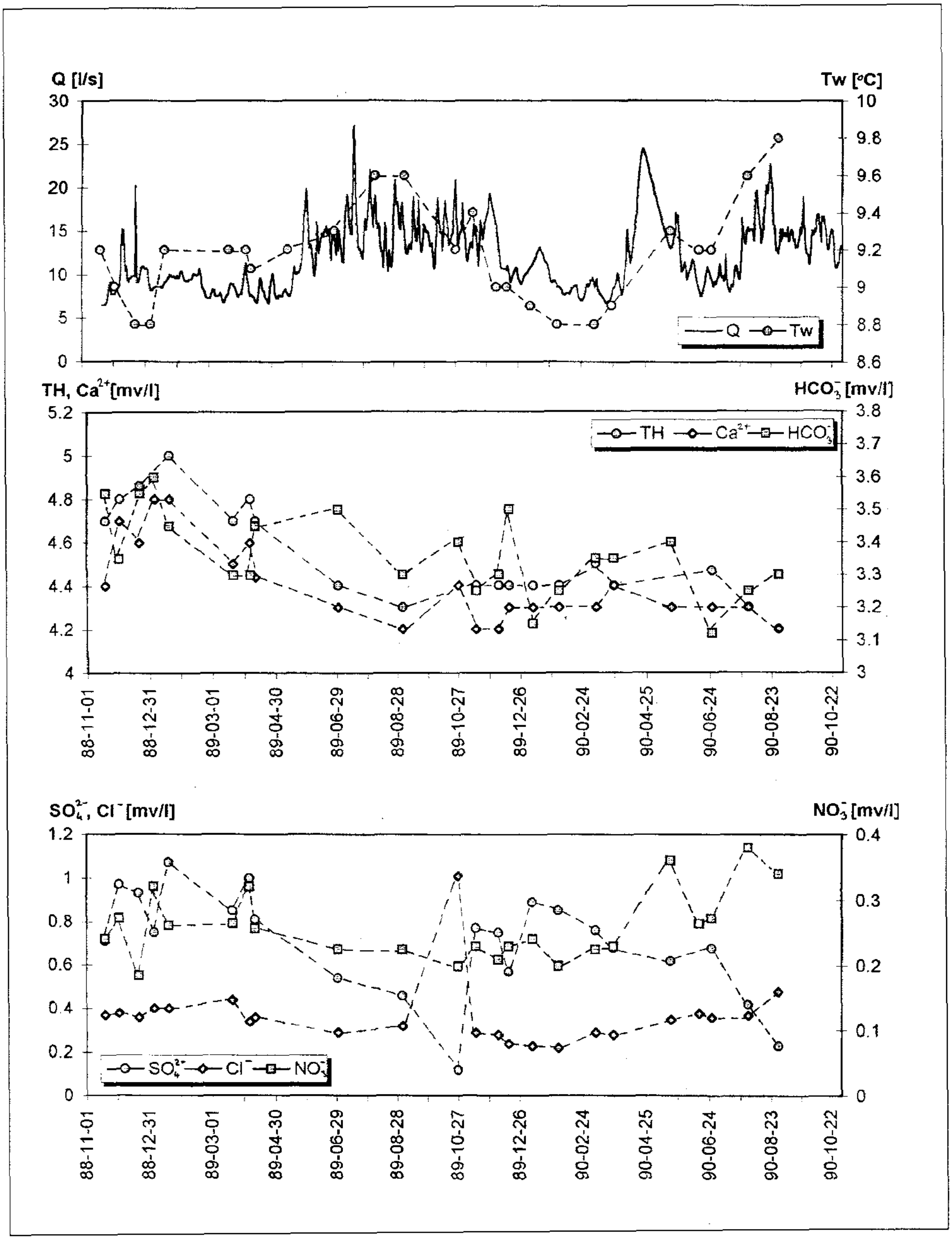

Fig. 3: Seasonal varibility of physical and chemical properties in spring water in Ryczowek II in the period of 1989-1990. Q-mean daily discharge, T_w-water temperature, TH-total hardness, Ca^{2+}-calcium, HCO_3^--bicarbonates, SO_4^{2-}-sulphates, Cl-chlorides, NO_3^--nitrates.

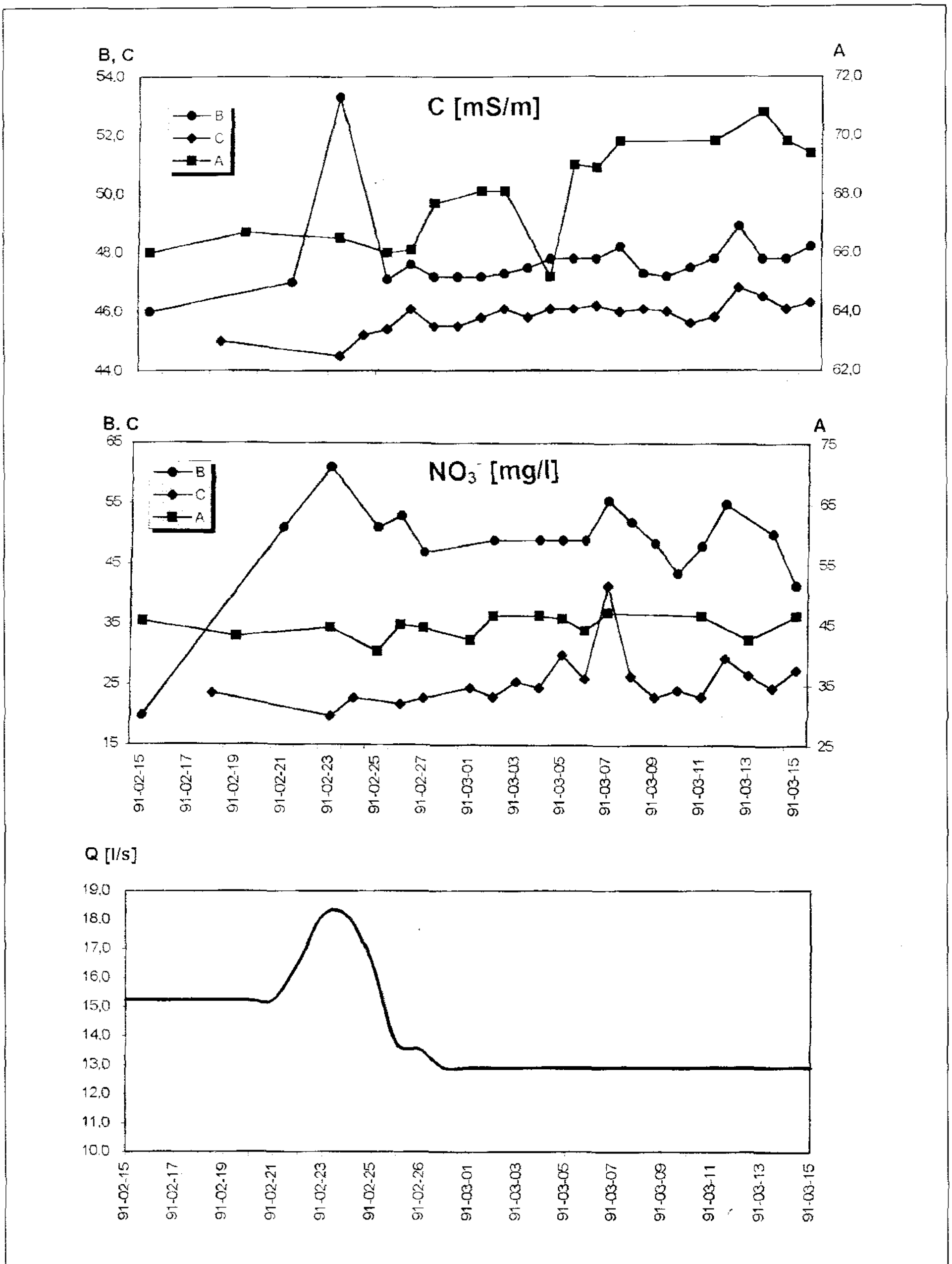

Fig. 4: Variability of specific conductivity (C mS/m) and nitrates (NO_3^- mg/l) in water of Klucze II (a), Klucze I (B) and Ryczowek II (C) springs during thaw season of 1991. Q-mean daily discharge in Ryczowek II.

In the karst areas which are not influenced by human activity, an increase in the yield is accompanied by a decrease of TH values and mineralisation. In the case of the Cracow-Czestochowa Upland, the spring chemographs are more complicated. Maximum discharge takes place during thaws and, at these times, there is an obvious increase in the values for specific conductivity, total hardness and ionic content which come mainly from pollutants. Detailed measurements during the thaw period were made at the Ryczówek II (a spring which has a fairly consistent flow), Klucze I (one with variable flows) and Klucze II (one which has consistent all-year-round flows) in the thaw period of 1991 (Fig. 4). This chemograph showed that the accepted view concerning changes of mineralisation and the amount of dissolved Ca^{2+} and Mg^{2+} salts during thaws is not wholly acceptable. The traditional view holds that, only in the case of Summer precipitation recharge does meteoric water infiltrate into the karst aquifer quickly. However, this does not adequately relate to the mineralisation and chemical composition of spring water which comes from thaw or thaw-rain recharge, which is an important element of spring discharges in such situations. This may be explained by considering in detail the relationship between the runoff hydrograph and the zones of the carbonate aquifer which are drained during the individual phases of a flush. During thaws, when a spring flush is preceded by the long contact of the water (i.e. that which comes from melting snow covers) and the ground, the increase of minerlaisation and total hardness is associated in the spring recharge with water from the the epikarst zone and the upper part of the vadose zone (this is the converse of previously accepted interpretation of spring chemograph). In the early phases of thawing (and also during winter thaws), water which migrates through the epikarst zone has a specific chemical properties, which, later, influences the "thaw effect" in water which discharges from the springs. This is well illustrated by the analyses of the soil water and water from weathered zone below soil cover at Książa Góra, in Ryczówek (456.2 m a.s.l.), which forms the recharge zone of the Ryczówek II Spring. The water sampled directly after the melting of an unusually thin snow cover here in February 1990 shows physical and chemical properties which are quite different from those exhibited by water which percolates through the soils and remains in the epikarst zone in a late spring (Tyc 1994, 1996) (Table 1). In case of the water sampled in Fubruary 1990, very large levels of Ca^{2+} (5.5 mv/l), total hardness (5.9 mv/l) and mineralisation (C = 69.1 mS/m) were recorded; these are all considerably larger than the maximal values noted during the whole study period at the Ryczówek Springs, whereas the content of hydrocarbonates in the water studied was small (0.4 mv/l) and the contents of other anions very large (SO_4^{2-}, 2-4 mv/l; NO_3^-, 1.1 mv/l). These are much larger than the values obtained from the Upper Jurassic Aquifer groundwater in other periods, whether before or after thaws. It is concluded, therefore, that Ca^{2+} content and total hardness of the epikarst water in these periods are more closely associa-

	C [mS/m]	TH [mg/l]	Ca^{2+} [mg/l]	Mg^{2+} [mg/l]	HCO_3^- [mg/l]	SO_4^{2-} [mg/l]	Cl^- [mg/l]	NO_3^- [mg/l]
THAWING SEASON								
Snow	5,3	8,0	8,0	0,0	17,1	11,0	2,5	3,2
Epikarstic zone *(dispersed flow)*	69,1	118,0	110,0	4,8	24,4	196,8	14,0	69,3
Spring water *(fed by dispersed flow)*	50,8	108,0	100,0	4,8	210,5	60,5	16,8	31,5
LATE SUMMER								
Rain water	6,0	8,4	6,8	1,0	3,1	10,1	3,5	5,7
Epikarstic zone *(dispersed flow)*	31,0	54,0	48,0	3,6	48,2	75,4	3,5	23,9
Spring water *(fed by dispersed flow)*	47,4	92,0	88,8	1,92	208,6	32,2	13,0	18,3

Table 1: Chemical comosition of water in recharge and discharge zones of Ryczowek II spring. Water samples represent thawing and late summer seasons of 1990 (after A. Tyc, 1996).

ted with sulphates and nitrates than with the $CaCO_3$ forthcoming from rock dissolution. This, in turn, shows that the spring water of a thaw flush maximum contains mainly Ca^{2+} and Mg^{2+} salts (probably sulphates and nitrates) which are associated with processes taking place in the soils and in the epikarst zone, and which are not the results of solution processes.

One result of the research described is the realisation that there is an artificial variability of the total hardness in the hydrological cycle. The natural changes in total hardness, which are influenced by environmental factors associated with solution of carbonates, overlap with the changes influenced by the cycles of pollution supplied to the aquifer. In a cold-temperate climatic zone, spring thaws play an important role. Fig. 5 shows the changes of total hardness values (TH) against a background of pH for the Ryczówek Spring.This shows that the pH-TH relationship takes two forms: (i) the pH and the TH both increase or decrease concomitantly, (ii) a pH decrease is accompanied by a TH increase. The first form is typical of groundwater in carbonate rocks. The reaction of the water reflects the level of saturation of dissolved carbonates; an increase of $CaCO_3$ reflects a more alkaline environment and *vice versa*. The second type of relationship shows that there are cases in the hydrological cycle when a decrease in the water reaction is demonstrably associated with an increase in the total hardness. This is probably caused by an increase in the amount of pollution in the groundwater and the content of calcium salts which come from outside the local $H_2O \rightarrow CO_2 \rightarrow CaCO_3$ system. This phenomenon

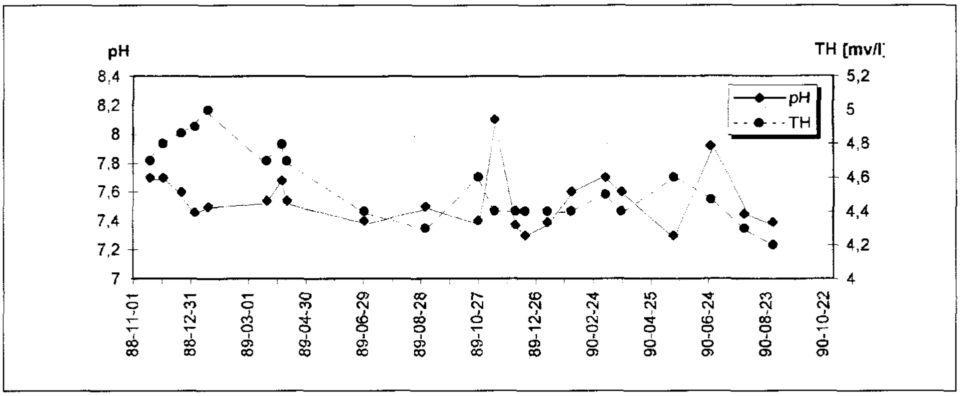

Fig. 5: Variability of pH and total hardness (TH) in water in Ryczowek II spring in the period of 1989-1990.

occurs during the runoff of the water from thaw recharge (and also during the Winters). This is also an element of the so-called "thaw effect" where human influence on the karst system is considerable.

This research suggests that the natural hydrochemical regime of the groundwater in the karst of the Cracow-Czestochowa Upland is influenced by human impact during periods of thaw and thaw-rain recharges in the epikarst zone and in associated soil covers (the "thaw effect"). This is illustrated in the chemograph of the thaw period for 1991 and the third week of December 1988, when a sudden thaw took place (thereby increasing the values of some chemical components in most of the springs studied (see Fig. 3).

CONCLUSIONS

The analysis of spring chemographs in the area of the Cracow-Czestochowa Upland shows that previously held views on changes of the dissolved calcium and magnesium salts during thaw discharges should be modified. This view seems also to be true in the case where spring recharge by summer rainwater takes place following meteoric water infiltrates relatively quickly into the karst aquifer and when the conduit system of water circulation predominates. However, it does not apply in the case where mineralisation and chemical composition of that spring water which comes from thaw or thaw-rain recharge takes place, i.e., normally in the Spring seasons of cold-temperate climates. It is emphasised here that, hitherto, classical elaborations of this problem concerned mainly the areas where rapid thaws have not occurred. Moreover, the karst in those areas was not significantly affected by human impact, a factor which appreciably affects the interpretation of karst aquifer behaviour. The monitoring of karst springs using automatic recording devices, which is being carried out in many parts of the World, should provide much new information about this problem. The springs of the Cracow-Czestochowa Upland are currently being monitored in this way.

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ANALIZA KEMOGRAMOV IZVIROV V PRIMERU VPLIVA EFEKTA TALJENJA SNEGA IN IMPULZOV RAZPRŠENEGA ONESNAŽENJA (NA PRIMERU IZVIROV V KRAKOWSKO-CZESTOCHOWSKEM VIŠAVJU)

Povzetek

Napajanje, tok in vskladiščenje podzemne vode so lahko v karbonatnih vodonosnikih ekstremno spremenljivi. Skladno z različnimi stopnjami zakraselosti je lahko napajanje v razponu od koncentriranega do razpršenega. Članek predstavlja rezultate proučevanja onesnaženja glede na različne načine napajanja v karbonatnih vodonosnikih. V ta namen je bil izpeljan monitoring temperature vode in koncentracij glavnih ionov v nekaterih izvirih višavja Krakow-Czestochowa v južni Poljski.

Analize kemogramov kraških izvirov, ki jih običajno srečujemo v mednarodni literaturi, so bile pregledane in ponovno ovrednotene. Tradicionalni modeli napajanja zaradi taljenja snega na kraških območjih zmernega podnebja in človeškega vpliva v zmerno-hladni klimi so bili ocenjeni in predlagane so bile nekatere spremembe. V predlaganem novem modelu se efekt taljenja snega in impulzi onesnaženja odražajo na kemizmu voda - značilna povečanja koncentracij Ca^{2+} , SO_4^{2-} in NO_3^-, celokupne trdote in specifične električne prevodnosti vode v tleh, epikraške vode in vode na izvirih - pri maksimalnih vrednostih napajanja zaradi taljenja snega. To spremlja še relativno nizka vsebnost bikarbonatov. Koncentracija kalcija in celokupna trdota v staljeni vodi sta bolj povezani s sulfati in nitrati iz onesnaženja kot pa z efektom raztapljanja v sistemu $CaCO_3$ - H_2O - CO_2.