CHEMISTRY OF CAVE WATER IN SMOCZA JAMA, CITY OF KRAKÓW, POLAND

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Abstract: The chemical composition of the water in Smocza Jama cave (city of Kraków, Kraków–Wieluń Upland) was studied. The cave is 276 m long and it was developed in the Upper Jurassic limestone. Nineteen water samples were collected between March 1995 and January 1998. The pool water and drip water were sampled. The former water samples represent Ca - Na - HCO$_3$ - SO$_4$ - Cl, while the latter ones SO$_4$ - Ca - Na type. In pool water the concentrations of Cl are higher than in drip water, while in drip water the SO$_4$ predominates. The chemical composition of the studied samples of both the pool and drip waters differs considerably from the composition typical of the limestone cave water. The studied water differs also in its chemical composition from the groundwater of the Kraków–Wieluń Upland. High concentrations of NO$_3$, SO$_4$, Cl, Na, K, and P suggest that the water in Smocza Jama is considerably affected by pollution. The chemical composition of the studied pool water can be the effect of mixing of, at least, two components. The water can: (i) filtrate from the Vistula river, (ii) percolate down from the surface of Wawel Hill, (iii) migrate from the nearby area, where the city centre is located, and (iv) ascend as artesian water from deeper confined aquifer. The former three of the four mentioned water sources may be strongly degraded due to long lasting human occupation of both Wawel Hill and the city centre, as well as pollution of the Vistula river. The high amount of SO$_4$ ions reaching 1439 mg/L in drip water results probably from leaching of litter and rubble poured over the cave in the 19th century.

Key words: cave water, chemistry, pollution, groundwater circulation, Kraków–Wieluń Upland.

Manuscript received 31 March 2005, accepted 16 August 2005

INTRODUCTION

The accessible caves give a unique opportunity to study chemical compositions and quality parameters of underground water. There has been a growing interest in chemical composition of cave waters in the recent years. They have been studied in terms of the velocity and time of water flow through the vadose zone in karstic aquifers. The transformation of chemistry of rain water during the contact with carbonate bedrock and the influence of deposition of speleothems have been studied as well. The other research has concerned the impact of pollution sources on quality of cave water. It is dripping water that has been most commonly studied since it offers a possibility to check chemical composition and transformation of water in the vadose zone. In contrast, the stagnant cave water pertaining to upper phreatic zone has been studied sporadically.

There are more than 1700 caves situated in the Kraków–Wieluń Upland (Gradziński & Szelerewicz, 2004).

The majority of caves are rather small, with their length not exceeding a few dozen metres and devoid of neither underground stream nor stagnant water. Only a few caves have small, perennial lakes. Smocza Jama (Dragon's Den) is one of the caves in question. A few small pools are located in this cave. The surface of the lakes is situated at the groundwater level. Water drips from cave ceilings in some places in the cave.

Although Smocza Jama has been known for a long time and it is situated in the region of recognized underground circulation (Kleczkowski, 1967, 1989; Kleczkowski *et al.*, 1994; Zuber *et al.*, 2004), the origin of water in the cave pools and factors governing the chemistry of this water have still been an open question. The purpose of this paper is to describe the chemistry of cave water and to explain its origin.

GEOLOGICAL SETTING

Smocza Jama cave is located in the southern part of the Kraków–Wieluń Upland within the city of Kraków (Figs 1, 2; Szelerewicz & Górny, 1986). It was developed in the Upper Jurassic microbial-spongy limestone of rocky type (sensu Dżułyński, 1952). The limestone builds up a small tectonic horst which is sourrounded by Miocene clay sediment filling the neighbouring grabens (Gradziński, 1972, p. 234). The horst is partly isolated, but its north-eastern part is attached to the other horst which is situated somehow lower. The royal castle Wawel is located on the former horst, while the historic city centre of Kraków on the latter one.

The cave is 276 m long (Gradziński & Szelerewicz, 2004). It consists of two parts linked by an artificial shaft mined in 1974 (Szelerewicz & Górny, 1986). The formerly known series of the cave is spacious and accessible for tourists. In contrast, the series discovered in the 70th of last century comprises some small chambers and extremely narrow squeezes, situated between them. The pools occur in these small chambers. They continue, as narrow fissures, down to the depth of about 4 m. The surface of the pools is located at the altitude about 199 m a.s.l., that is at the similar level as

the Vistula (Wisła) river, which flows in the proximity of about 50 m from the cave pools. Kleczkowski (1977) noted that water level in an artificial hole drilled in the old part of the cave in 1969 was located at the same level. Water level in the cave mirrors the changes of water level in the Vistula river (Kleczkowski, 1977). During the flood in 1997 when the water level in the river rose of about 5 m (R. Szczepanek – personal communication), the water filled the main chamber of the cave up to about 201.7 m a.s.l. (Wiśniewski, 1997).

MATERIALS AND METHODS

Nineteen water samples were collected between March 1995 and January 1998 (Table 1). Most of the samples (16) came from cave pools. Only three samples represented drip water. The sampling places are presented in the Fig. 3. In two pools some samples were collected from different depth (see Table 1). The pH was measured in the field. The total alkalinity (as bicarbonate HCO_3) was determined using 0.05 molar HCl acid by Gran titration. Chloride (Cl) contents were determined by the Mohr's method, using 0.01
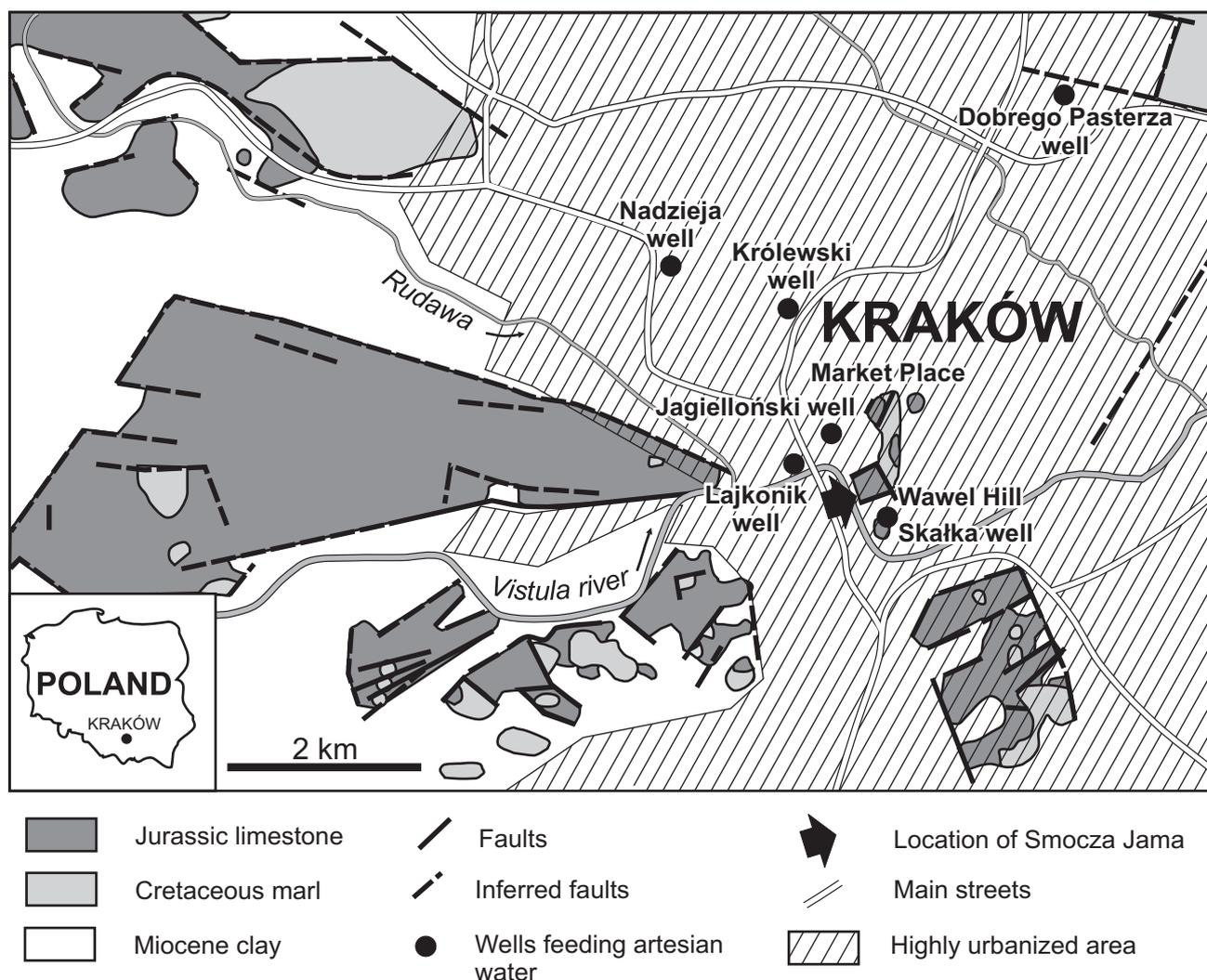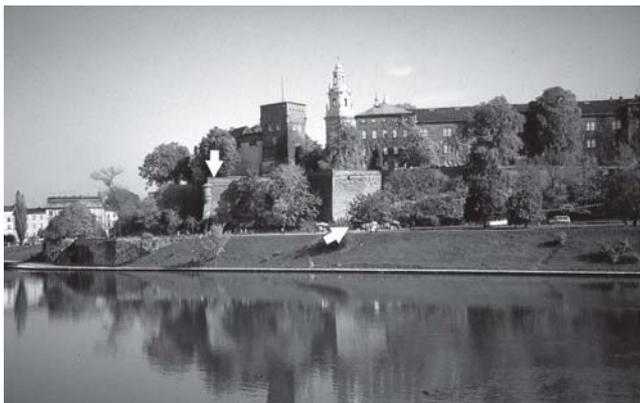

Fig. 1. Location of Smocza Jama cave, the geology after Gradziński (1972), location of artesian wells after Kleczkowski *et al.* (1994)

Fig. 2. Wawel Hill from the west, the entrances to the cave are marked with arrows, Vistula river in the foreground

molar $AgNO_3$. Both chloride and total alkalinity were measured within one day after sampling. Concentration of other components, that is calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), aluminium (Al), boron (B), barium (Ba), iron (Fe), lithium (Li), manganese (Mn), phosphorus (P), strontium (Sr), zinc (Zn) and total sulphur, calculated as sulphates (SO_4), was determined by the inductively coupled plasma-atomic emission spectroscopy (ICP AES) using Plasma a Perkin-Elmer product. Concentration of nitrates (NO_3) was determined using capillary elctrophoresis method by means of a 270 AH-T equipment, a Perkin-Elmer product. All laboratory analyses were done at the laboratory of Faculty of Geology, Geophysics and Environmental Protection, University of Science and Technology (AGH) in Kraków. The total dissolved solids (TDS) was calculated by summing concentrations of major ions.

RESULTS

All the studied water samples were of weakly alkaline type. Their pH index ranged between 7.27 and 8.67 (Table 1). As a rule, the TDS of pool waters was lower than that of drip waters. In the former case it ranged from 779.3 mg/L to 1013 mg/L while in the latter one from 1752 mg/L to 2841.7 mg/L.

The chemical composition of pool water samples is quite uniform. According to the system after Altovskij – Švec modified by Kleczkowski (1979, p. 50), the ions which showed concentration minimum 17% mval/L are included in identification of water type. This being taken into account, pool water samples are regarded as multiion type representing Ca - Na - HCO_3 - SO_4 - Cl type (Table 1). The pool water is dominated by HCO_3 anion, however the concentrations of SO_4 anion are only slightly lower (Fig. 4). The concentrations of SO_4 in drip water are about eight times greater than in pool water. Hence, in drip water samples molar part of SO_4 dominates over molar part of Ca, and in consequence the water is of SO_4 - Ca - Na type. Chlorium concentrations in the pool water sample range from 65.6 to 103.8 mg/L while in drip water samples are lower and they range between 10.58 and 39.49 mg/L. The concentrations of
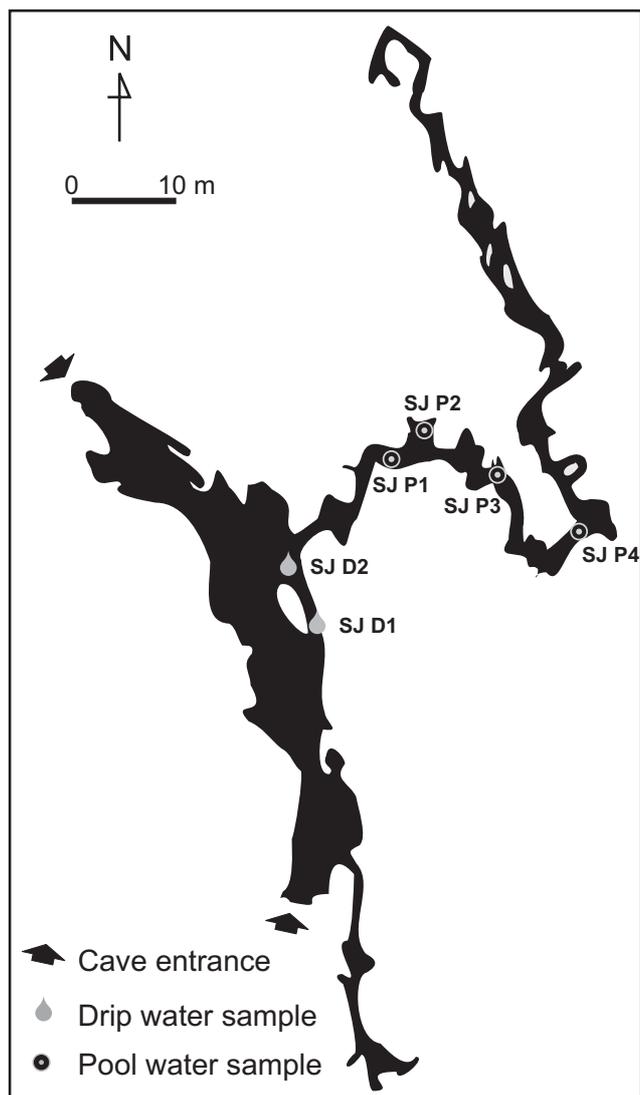
Fig. 3. Map of Smocza Jama cave (after Szelerewicz & Górny, 1986, supplemented) with sampling places

NO_3 in the studied samples are various. They fall into a range between 44.4 and 280.4 mg/L (Table 1).

Calcium is a dominant kation in every sample. The concentrations of K and Na are high. They vary from 44.24 to 130.2 mg/L and from 30.88 to 132.5 mg/L respectively. Thus, the Na/K ratio range from 0.74 to 1.98. The concentrations of the above elements in the drip water samples are significantly higher than in pool water. Both Na and K overrank Mg in abundance. Concentrations of SiO_2 in the studied samples fall into a range between 11.7 and 38.05 mg/L (Table 1).

Phosphorous is dominant microelement in the studied samples. Its concentrations in the pool water samples range between 1.05 and 1.64 mg/L while in drip water samples is lower than 0.6 mg/L. Apart from P, the studied samples comprise significant amount of B, Sr and Ba. Boron and Sr concentrations are higher in drip water than in pool water, while Ba content was uniform in both types of samples. Some samples comprise small amounts of Cu, Fe, Li, Mn, Zn and Al (Table 2).

Basic characteristics and major-ion concentrations in the studied samples from Smocza Jama cave;
P – pool water, D – drip water, all pool water taken from the pool surface but for samples marked with * – taken from the
depth of 1 m, and ** – taken from the depth of 2 m; n.c. – not calculated, n.m. – not measured

Sample number	Sampling date	pH	EC µS/cm	Temperature °C	TDS mg/L	HCO$_3$ mg/L	SO$_4$ mg/L	Cl mg/L	NO$_3$ mg/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	SiO$_2$ mg/L
SJ P1.1	03.10.1995	7.3	n.m.	13.0	997.8	275.1	225.7	95.58	105.4	164.1	20.64	61.35	49.91	22.5
SJ P1.2	31.03.1995	n.m.	n.m.	11.0	964.0	274.3	218.5	96	83.2	163	20.29	61.92	46.76	22.7
SJ P1.3	21.12.1995	n.m.	n.m.	11.4	794.0	282.1	157.8	65.6	55.8	133	15.96	45.47	38.24	20.8
SJ P1.4	10.06.1996	n.m.	n.m.	11.2	931.5	298.1	207.7	75.56	77.5	161.1	17.06	53.66	40.76	20.5
SJ P1.5	18.09.1996	8.0	1148	n.m.	917.6	267.3	206.7	72.63	84.9	177.6	18.56	51.9	37.97	n.o.
SJ P1.6	18.11.1997	8.7	1070	n.m.	954.2	267.1	222.6	72.13	113.2	154.4	21.7	55.34	47.7	27.6
SJ P1.6 **	18.11.1997	8.8	1139	n.m.	1009.6	288.6	235.9	74.58	116.1	162.2	22.8	60.39	49.05	27.9
SJ P2.2	31.03.1995	7.8	n.m.	11.2	989.7	293.6	223.9	96.71	74.2	165.1	20.87	65.56	49.73	22.8
SJ P2.2	21.12.1995	n.m.	n.m.	10.6	779.3	284.3	154.9	65.73	44.8	132.2	16.21	44.24	36.87	20.1
SJ P2.4	10.06.1996	7.7	1092	11.4	947.1	325.2	195.4	77.52	72.7	164.3	16.71	53.42	41.83	20.2
SJ P2.5	18.09.1996	8.0	n.m.	n.m.	885.7	277.3	182.5	70.95	80.6	157.5	18.58	49.29	48.94	n.a.
SJ P2.6	18.11.1997	8.5	935	n.m.	792.6	218.8	184.1	67.74	88.2	118.9	19.09	53.5	42.23	27.4
SJ P2.6 *	18.11.1997	8.6	1046	n.m.	941.5	288.6	211	66.45	100.4	148.5	23.05	55.38	48.14	30.3
SJ P2.6 **	18.11.1997	8.7	1091	n.m.	1013.0	307.4	231	75.1	104.6	161.1	24.3	60.26	49.25	29.3
SJ P3.2	31.03.1995	n.m.	n.m.	11.2	851.6	261.3	173.9	103.8	54.3	130.2	20.56	61.03	46.52	25.0
SJ P4.2	31.03.1995	n.m.	n.m.	11.2	780.1	270.6	143.8	70.4	67.1	132.5	16.21	48.57	30.88	24.7
pool sample mean value		n.c.	n.c.	n.c.	909.3	280.0	198.5	77.9	82.7	151.6	19.5	55.1	44.0	24.4
SJ D.1.2	14.01.1998	8.2	1931	n.m.	2841.7	229.6	1439	39.49	280.4	566.5	56.14	98.1	132.5	38.1
SJ D 2.1	31.03.1995	8.6	n.m.	n.m.	1845.8	197.8	1013.8	28.87	44.4	302.0	43.99	130.2	84.74	11.2
SJ D 2.2	14.01.1998	7.8	1270	n.m.	1752.9	239.8	906.3	10.58	53.2	348.2	10.36	86.34	98.1	24.8
drip sample mean value		n.c.	n.c.	n.c.	2146.8	222.4	1119.7	26.31	126.0	405.57	36.83	104.88	105.11	24.7

POLLUTION OF SMOCZA JAMA WATER

The chemical composition of the studied samples of both the pool and drip water are unusual and differ considerably from the composition typical of cave water. It is worth stressing that the studied samples from Smocza Jama are characterized by very high concentration of several ions. The content of major ions as SO$_4$, Cl, K, Na is several times greater than it has been reported from cave waters so far. For example, it overranks eight times the water from Green Lake in Carlsbad Caverns (Texas, USA) chemical composition of which is reported by (Hem, 1992, p. 99). Similarly, the concentration of Cl, Na, K ions in seepage water in Grotta di Ernesto (Italy) and Clamouse (France) caves given by Fairchild *et al.* (2000) are about 100 times lower than those in the studied samples, while the concentration of SO$_4$ and NO$_3$ is several dozen times lower. The concentration of these ions in water in Pettyjohns Cave (Georgia, USA; Mayer, 1999) and several Slovakian caves (J. Motyka *et al.* – unpublished data) are also lower than those detected in the studied samples. The microelements in drip water in the other caves have not been commonly studied so direct comparisons cannot be made.

High concentrations of NO$_3$, SO$_4$, Cl, Na, K, and P can suggest that the water in Smocza Jama is considerably affected by pollution (cf. Hem, 1992; Appelo & Postma, 1994; Lerner, 2002; Macioszczyk & Dobrzyński, 2002). It is also indicated by very low ratio Na/K in the studied samples.

Considering the cavern environment, similar and higher concentration of NO$_3$ and Cl is reported by Bolner and Tardy (1988) from the Budapest caves and is interpreted as an effect of fertilizer and sewage contamination as well as the inflow of salt used for deicing of streets. The percolation of polluted water with concentration of NO$_3$ and Cl reaching 180 and 60 mg/L respectively is described by Kogovšek (1997) from Postojnska jama cave (Slovenia). The elevated concentration of SO$_4$, Cl, NO$_3$, K, Na and P is also found in some caves of the Kraków–Wieluń Upland, where it is regarded as an effect of pollution, however it never reaches
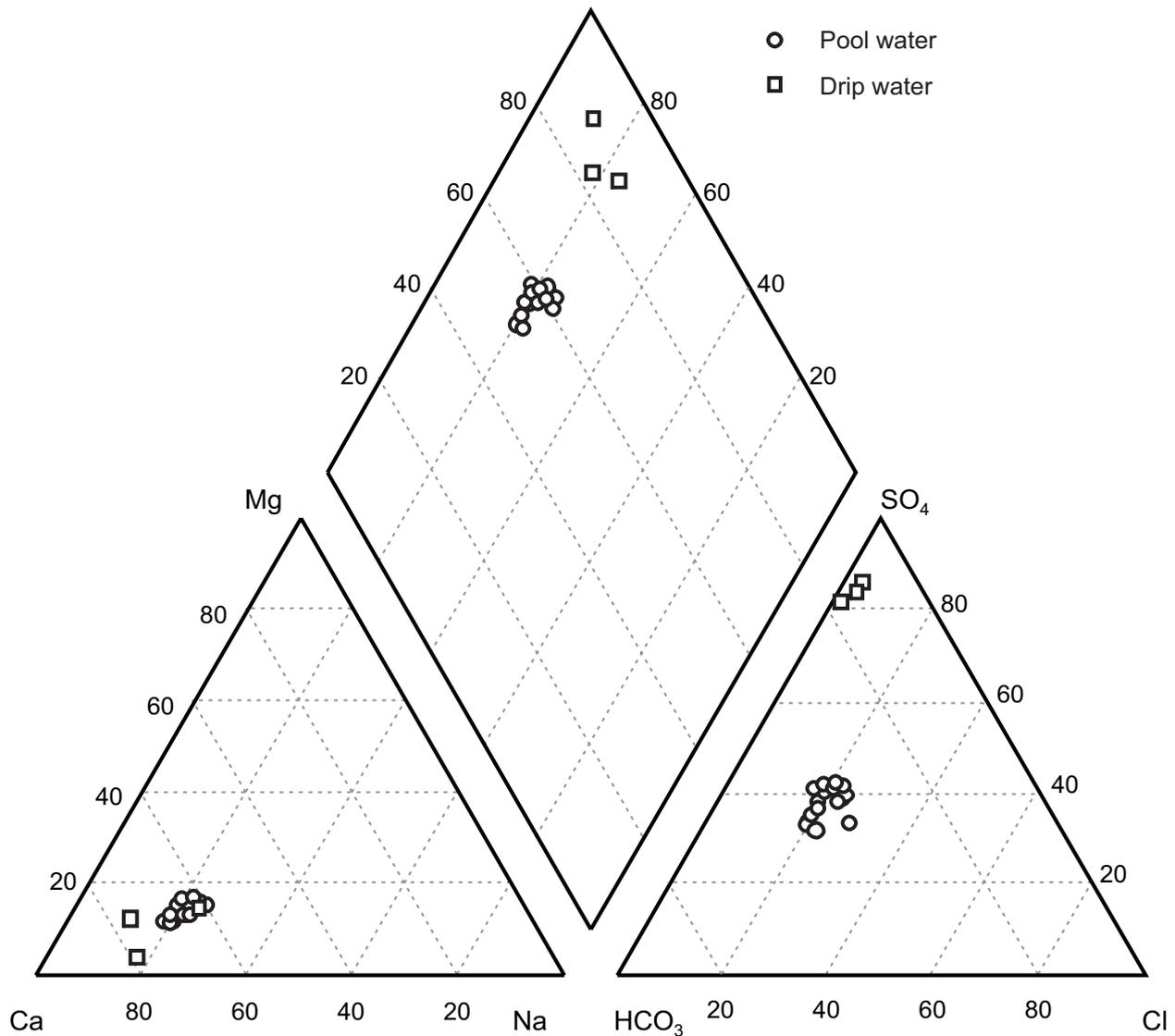
Fig. 4. Piper diagram showing the ionic composition of studied samples from Smocza Jama cave

such a high amount as in Smocza Jama (Klojzy-Karczmar-czyk *et al.*, 1999; Goc *et al.*, 2000; Górny *et al.*, 2001; Mo-tyka *et al.*, 2002). The water in Smocza Jama differs also in its chemical composition from groundwater typical of the Kraków–Wieluń Upland (cf. Różkowski, 1996). These facts leave room for a discussion on the possible origin of water in Smocza Jama. The discussion will centre on the possibility that there appear to be more that one source of water feeding the cave, since there is no correlation between several ions in the studied samples (Fig. 5).

SOURCES OF CAVE WATER MINERALIZATION

The atypical chemical composition of the studied pool water can be controlled by: (i) the lateral inflow of water from the Vistula river, (ii) the downward seepage of water, (iii) the lateral inflow of water from the nearby city centre, and (iv) the upward migration of ascending deep circulation water.

Lateral inflow of water from the Vistula river

The possible connection of pools in Smocza Jama with the Vistula river is postulated by Dumnicka and Wojtan (1990). They claim that chemical composition of water in the pools is an effect of mixing of groundwater with strongly polluted Vistula water. They also point out that small invertebrate benthic animals belonging to Ostracoda, Copepoda, Oligochaeta and Chironomideae can infiltrate into the cave from the river (see also Dumnicka, 2000). The above statement on influx of the river water into the cave and its mixing with cave water is based on the similarity of chemical composition of both waters.

The main factor controlling the chemical composition of the Vistula water is pollution. The Vistula water has been considerably degraded at least since the beginning of the 20th century. It is mainly due to the pumping of salt-water from coal mines located in the Upper Silesia region, that is in the upper part of the Vistula river catchment (Gajowiec & Różkowski, 1988). It causes that the river water is of Cl - Na type and contains also high amount of SO_4 ions (e.g., Mo-tyka & Postawa, 2004 and references quoted herein).

Microelement concentrations in the studied samples from Smocza Jama cave, molar ratios mMg/mCa and mSr/mCa are also given; P – pool water, D – drip water, all pool water taken from the pool surface but for samples marked with * – taken from the depth of 1 m, and ** – taken from the depth of 2 m; n.a. – not analyzed, n.c. – not calculated

| Sample number	B mg/L	Ba mg/L	Cu mg/L	Fe mg/L	Li mg/L	Mn mg/L	P mg/L	Sr mg/L	Zn mg/L	Al mg/L	mMg/ mCa	mSr/ mCa ‰
SJ P1.1	0.321	0.02	< 0.005	0.008	< 0.01	< 0.002	1.22	0.507	0.007	n.a.	0.207	1.41
SJ P1.2	0.32	0.026	< 0.005	0.025	0.02	0.004	1.25	0.49	0.004	n.a.	0.205	1.37
SJ P1.3	0.232	0.025	0.018	< 0.01	< 0.01	< 0.002	1.17	0.401	0.008	n.a.	0.198	1.38
SJ P1.4	0.22	0.014	< 0.005	0.055	0.02	< 0.002	1.42	0.34	< 0.002	0.061	0.175	0.97
SJ P1.5	0.33	0.03	< 0.005	0.033	0.015	0.017	1.32	0.501	0.007	0.18	0.172	1.29
SJ P1.6	0.353	0.035	< 0.005	0.14	< 0.01	< 0.002	1.5	0.613	< 0.002	0.146	0.232	1.82
SJ P1.6 **	0.481	0.045	< 0.005	0.022	< 0.01	< 0.002	1.41	0.69	0.009	< 0.06	0.231	1.95
SJ P2.2	0.32	0.022	< 0.005	0.007	0.023	0.002	1.11	0.477	0.005	< 0.06	0.208	1.32
SJ P2.2	0.242	0.021	0.02	< 0.01	0.017	< 0.002	1.22	0.39	< 0.002	< 0.06	0.202	1.35
SJ P2.4	0.24	0.013	< 0.005	< 0.01	0.02	< 0.002	1.51	0.331	< 0.002	0.062	0.168	0.92
SJ P2.5	0.32	0.031	< 0.005	< 0.01	0.016	0.011	1.05	0.48	0.003	0.1	0.194	1.39
SJ P2.6	0.324	0.04	< 0.005	< 0.01	0.022	< 0.002	1.48	0.513	< 0.002	< 0.06	0.265	1.97
SJ P2.6 *	0.342	0.034	< 0.005	0.195	0.021	< 0.002	1.74	0.612	< 0.002	0.16	0.256	1.89
SJ P2.6 **	0.341	0.032	< 0.005	0.276	< 0.01	< 0.002	1.64	0.661	< 0.002	0.162	0.249	1.88
SJ P3.2	0.298	0.016	< 0.005	0.007	< 0.01	0.003	1.11	0.521	0.004	< 0.06	0.260	1.83
SJ P4.2	0.284	0.018	< 0.005	0.006	0.02	0.003	1.28	0.388	0.005	< 0.06	0.202	1.34
pool sample mean value	0.311	0.026	n.c.	n.c.	n.c.	n.c.	1.34	0.494	n.c.	n.c.	n.c.	n.c.
SJ D.1.2	0.898	0.028	< 0.005	< 0.01	0.062	< 0.002	0.503	0.847	< 0.002	< 0.06	0.163	0.68
SJ D 2.1	0.474	0.029	< 0.005	0.008	0.034	0.002	< 0.1	0.59	0.006	< 0.06	0.240	0.89
SJ D 2.2	1.003	0.028	< 0.005	< 0.01	0.101	< 0.002	0.41	0.501	< 0.002	< 0.06	0.049	0.66
drip sample mean value	0.792	0.028	n.c.	n.c.	0.066	n.c.	0.457	0.646	n.c.	n.c.	n.c.	n.c.

Moreover, concentrations of amonium, nitrates, some metals and organic compounds prove that communal wastes (i.e., landfill lechate and human wastes) as well as pollutants connected with agricultural practices enter the river and cause the deterioration of water quality (Motyka & Postawa, 2004). The comparison of mean Vistula river composition with composition of pool water in Smocza Jama cave suggests that possible bank filtration can deliver some ions to the pool water. Sodium, Cl, SO_4, B and Sr ions detected in pool water can be of such origin. However, the concentrations of other ions, as K, Ba, NO_3 and P cannot be explained by the bank filtration of river water due to the fact that their concentrations in the river water are lower than that in pool water.

The seepage from the river to the aquifer is possible only in specific conditions. It can occur when water level in the river rises very rapidly but groundwater level does not. In such a situation the character of the river changes into that of loosing-type and the bank filtration can work efficiently. Taking into account the very close distance between the river and the cave, the above process seems possible.

However, during high water level the Vistula river is characterized by low concentrations of ions due to the dilution effects, which has been proved for Na and Cl ions contents (Krokowski *et al.*, 1994; Motyka & Postawa, 2004). For instance, during the high water level in March 1994 the concentration of Cl dropped below 200 mg/L (Krokowski *et al.*, 1994, rys. 6). Other ions react probably in a similar way (cf. Vadillo *et al.*, 1999). Thus, the migration of significant amounts of dissolved substances from the river to the cave pool seems to be of minor, if any, importance, however it cannot be excluded completely (cf. Kleczkowski, 1977).

Vertical seepage

Another factor which can control the chemistry of pool water is vertical seepage. The studied samples of drip water represent such type of inflow. Comparison of chemical composition of the pool water samples with the drip water ones points to the conclusion that several ions detected in the former water can be derived from the latter one. This conclusion relates specifically to SO_4, Cl, Ca, Mg, Na and K ions. It concerns also some microelements, such as B and
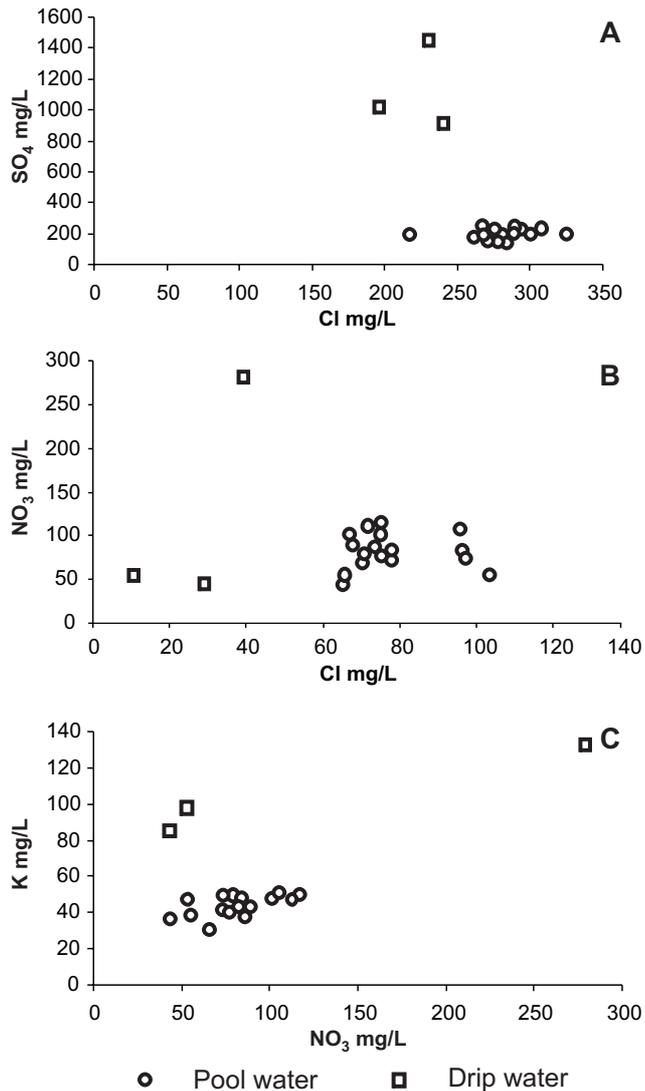
Fig. 5. Relationship between particular ions in the studied samples from Smocza Jama cave, **A** – SO_4, vs. Cl, **B** – NO_3 vs. Cl, **C** – K vs. NO_3

Sr. The drip water has higher concentrations of the above listed components than pool water has. The concentration of NO_3 in one sample of drip water, which equals 280 mg/L, suggests that also NO_3 in pool water can be supplied by vertical seepage. On the other hand, in two other samples of drip water the concentration of NO_3 is lower than the mean concentration of this ion in pool water, which gives the impression that there must be an alternative source of this ion for pool water. Also P comes from another source, since the concentration of this element in pool water is higher than in drip water.

The concentrations of several components such as SO_4, NO_3, Cl, Na, K, B, provide strong evidence that the drip water is considerably affected by pollution. It can be adequately explained by long lasting human occupation on Wawel Hill which has been settled continuously for more than ten centuries (Wyrozumski, 1992). In the 19th century the hill was densely populated (Estreicher, 1938, p. 171; Kleczkowski, 1977). The underground water was probably polluted already in the 19th century, which is suggested by

high concentration of nitrates in the artificial wells situated on the hill (Olszewski, 1871; Olszewski & Trochanowski, 1889; Bujwid, 1894; Lemberger, 1899; see also Kleczkowski, 1977). At present the hill has sewers installed and it is a paved and roofed area. The cave is isolated from the surface by concrete slabs, placed just under the pavement (Firlet, 1996, p. 86). The small amounts of water can, however, percolate due to sewers or gutter leakage and transport some pollutants down to the cave.

It is worth stressing that the mean concentration of SO_4 ions in drip water is very high and equals maximally 1119.7 mg/L It is almost twenty times greater than maximal concentration of this ion in the cave waters quoted by Picknett *et al.* (1976). Such high concentration has not been noticed even in polluted waters in limestone caves (cf. Kogovšek, 1997). It was, however, reported from gypsum caves (Klimchouk & Andrejchuk, 1997) and karst springs discharged gypsum-karst areas (Motyka & Witczak, 1992). There appear to be two possible explanations for such a concentration in the discussed case. Sulfate ions can have been leached from litter and rubble poured over the cave at the beginning, and heightened in the middle of the 19th century (Grabowski, 1909, p. 157; Firlet, 1996, p. 85). The thickness of the embankment over the limestone rock reaches 9 m (Heflik & Matl, 1991, fig. 6; Firlet, 1996, fig. 66). The gypsum filling some fractures in Jurassic limestone hosting the cave (Heflik & Matl, 1991) can serve as the other source of SO_4 ions.

Lateral inflow

Kleczkowski (1977) ascribed the origin of the groundwater within Wawel Hill to lateral inflow from the northeast, that is from the centre of the city of Kraków. The concentrations of several elements in the groundwater under the city centre (Kleczkowski, 2003) bear a strong resemblance to their concentration in the studied pool water. Of particular interest in this respect are Cl, SO_4, NO_3, Na nd P ions.

The city centre area, similarly to Wawel Hill, has been a human settlement for a long time (Wyrozumski, 1992). It caused the degradation of groundwater by landfill leachate and human wastes, which was noticed by Olszewski (1871), based on high concentration of NO_3 and NH_4 ions. The concentration of these ions decreased after installation of sewers in the city at the turn of the 19th and 20th century, but increased again in the second half of the 20th century (Kleczkowski, 2003). The groundwater in the central part of Kraków has also high concentrations of P and B, which is connected with human activities as well. Although the K ion concentrations have not been published, one can expect its higher values since K is a common component in polluted water (Lerner, 2002; Macioszczyk & Dobrzyński, 2002). The higher concentration of chlorides and sulfates under the city centre can be explained by the contact of the water with Miocene clays and enrichment by diffusion exchange or anthropogenic influence. Of these two possibilities Kleczkowski (2003) was inclined to favour the former one. Whatever the origin of groundwater mineralization in the city centre, the lateral migration of this water towards Wawel Hill can throw light on the unusual chemical composition of water in the studied cave pools.

Fig. 6. Lajkonik well providing an artesian water, Wawel Hill is visible in the background, photo taken in 2005

Inflow of ascending water

The Upper Jurassic limestone forms in the area of Kraków an aquifer confined by Miocen clays. It is documented by several wells providing artesian water (Fig. 6; Kleczkowski *et al.*, 1994). The highstanding fault-bounded horsts built of Upper Jurassic limestone and surrounded by impermeable clays, are the favourable places for a natural artesian outflow. In the 19th century the artesian spring fed by the water of Cl - Na type was known from the Market Place, which is located on such a horst bordered by NNE-SSW trending faults (Kleczkowski, 1967). Wawel Hill represents a limestone horst, hence one can expect the presence of ascending water within the hill. Moreover, the spatial arrangements and corrosional forms preserved in Smocza Jama prove that the cave was formed due to corrosion by artesian waters (Gradziński *et al.*, 1996).

Nevertheless, the comparison of chemical composition of the studied pool water with artesian water in the Kraków area does not clarify fully the above problem. The latter water is of multiion type and contains HCO_3, SO_4, Cl, Na and Mg ions. The proportions between these ions vary between particular outflows, but the concentrations of HCO_3, SO_4, Cl, Na, B and Sr ions in every outflow are higher than in the studied pools (cf. Kleczkowski *et al.*, 1994; Zuber *et al.*, 2004). It suggests that the addition of artesian water may influence the chemistry of the studied water. On the other hand, the artesian water is characterized by molar Sr/Ca ratio greater than 9‰, while this ratio for the pool water ranges between 0.9‰ and 2‰. Similarly, the molar mMg/mCa ratio of the studied water varies significantly from the ratio of the artesian one (Fig. 7).

The concentration of K is decidedly higher in the pool water than in the artesian water. It ranges from 30.8 mg/L to 49.91 mg/L in the former, while in the latter it varies between 5 and 11 mg/L and only exclusively equals 30.2 mg/L. Thus, the other factor than addition of ascending water governs the high concentration of K, and therefore affects the low Na/K ratio of the pool water. Moreover, the concentrations of NO_3 and P in the ascending water are decidedly lower than in the pool water. Both these elements,
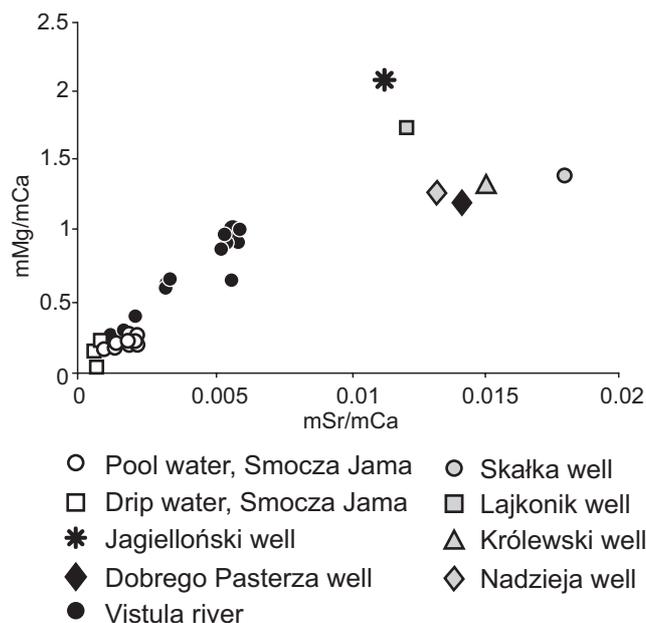
Fig. 7. Relationship between molar ratio mMg/mCa vs. mSr/mCa for the studied samples from Smocza Jama cave and for samples of ascending water in the Kraków region, the ratios of the latter were calculated based on data given by Zuber *et al.* (2004); the ratios for Vistula river water were calculated based on J. Motyka unpublished data

likewise K, are commonly connected with pollution. Hence, if the artesian water has any influence on the chemical composition of cave pools it must be mixed with the water degraded by human activity.

The additional argument for the influence of ascending water is the temperature of the pools, which ranges between 10.6 and 13 °C. It is higher than the temperature of the air in the caves of the Kraków–Wieluń Upland, which falls between 6 °C and 8 °C (Szelerewicz & Górny, 1986). In comparison the ascending water in the well outlets has the temperature between 10.6 °C and 12.7 °C (Kleczkowski *et al.*, 1994).

CONCLUSION

The collected data and arguments presented above point to the conclusion that there is no only one factor controlling the chemistry of Smocza Jama cave water. The water must have been the mixture of, at least, two components. One of them is strongly degraded by human activity, which is proved by high concentration of such ions as K, NO_3 and P. The water of downward seepage from the surface of Wawel Hill or lateral migration from the north-east can represent these components. The water of this kind probably mixes with the other one coming due to ascension from below or seeping from the Vistula river owing to bank filtration mechanism. However, the last possibility seems to be the least probable one.

REFERENCES

Appelo, C. A. J. & Postma, D., 1994. *Geochemistry, Groundwater and Pollution*. Balkema, Rotterdam, 535 pp.

Bolner, K. & Tardy, J., 1988. Bacteriological and chemical investigations of dripping waters in the caves of Budapest. In: *International Symposium on Physical, Chemical and Hydrological Research of Karst. Communications*. Slovenská speleologická sploćnosť, Liptovský Mikuláš, pp. 102–108.

Bujwid, O., 1894. Higieniczne badanie wód studziennych w Krakowie. (In Polish). *Przegląd Lekarski*, 34: 560–562.

Dumnicka, E., 2000. Studies on Oligochaeta taxocens in streams, interstitial and cave waters of southern Poland with remarks on Aphanoneura and Polychaeta distribution. *Acta Zoologica Cracoviensia*, 43: 339–392.

Dumnicka, E. & Wojtan, K., 1990. Differences between cave water ecological systems in the Kraków–Częstochowa Upland. *Stygologia*, 5: 241–247.

Dżułyński, S., 1952. The origin of the Upper Jurassic limestones in the Cracow area. (In Polish, English summary). *Rocznik Polskiego Towarzystwa Geologicznego*, 21: 125–180.

Estreicher, K., 1938. *Kraków. Przewodnik dla zwiedzających miasto i jego okolice*. (In Polish). Towarzystwo Miłośników Historii i Zabytków Miasta Krakowa, Kraków, 373 pp.

Fairchild, I. J., Borsato, A., Tooth, A. F., Frisia, S., Hawkesworth, Ch. J., Huang, Y., McDernmott, F. & Spiro, B., 2000. Controls on trace element (Sr-Mg) composition of carbonate cave waters: implications for speleothem climatic records. *Chemical Geology*, 166: 255–269.

Firlet, E. M., 1996. *Smocza Jama na Wawelu. Historia, legenda, smoki*. (In Polish). Universitas, Kraków, 160 pp.

Gajowiec, B. & Różkowski, J., 1988. Salinity of river waters within the upper Vistula drainage basin. (In Polish, English summary). *Kwartalnik Geologiczny*, 32: 715–728.

Goc, P., Górny, A., Klojzy-Karczmarczyk, B. & Motyka, J., 2000. Nitrates in cave waters of southern part of Cracow Upland. (In Polish, English summary). *Kras i Speleologia*, 10: 67–83.

Górny, A., Motyka, J., Partyka, J. & Różkowski, K., 2001. Jakość wód w strefie aeracji w wapieniach jurajskich w Ojcowskim Parku Narodowym. (In Polish). In: Partyka, J. (ed.), *Badania naukowe w południowej części Wyżyny Krakowsko-Częstochowskiej*. Ojcowski Park Narodowy, Ojców, pp. 35–39.

Grabowski, A., 1909. *Wspomnienia Ambrożego Grabowskiego. Tom II.* [wydał Stanisław Estreicher]. (In Polish). Towarzystwo Miłośników Historyi i Zabytków Krakowa, Kraków, 417 pp.

Gradziński, M., Górny, A. & Motyka, J., 1996. Wpływ ascencyjnych przepływów na powstanie jaskini Smocza Jama. (In Polish). In: Urban, J. (ed.), *Materiały Sympozjalne. XXX Sympozjum Sekcji Speleologicznej*. Polskie Towarzystwo Przyrodników, p. 16.

Gradziński, M. & Szelerewicz, M., 2004. Caves of the Kraków–Wieluń Upland – number and distribution. (In Polish, English summary). In: Partyka, J. (ed.), *Zróżnicowanie i przemiany środowiska przyrodniczo-kulturowego Wyżyny Krakowsko-Częstochowskiej. Tom 1. Przyroda*. Ojcowski Park Narodowy, Ojców, pp. 69–82.

Gradziński, R., 1972. *Przewodnik geologiczny po okolicach Krakowa*. (In Polish). Wydawnictwa Geologiczne, Warszawa, 235 pp.

Heflik, W. & Matl, K., 1991. Le characteristique géologique de la caverne Smocza Jama au Wawel. (In Polish, French summary). *Studia do Dziejów Wawelu*, 5: 29–53.

Hem, J. D., 1992. Study and Interpretation of the Chemical Characteristics of Natural Water. *United States Geological Survey, Water-Supply Paper*, 2254: 1–263.

Kleczkowski, A. S., 1967. Mineral waters in Cracow and their connection with geological structure. *Bulletin de l'Académie Polonaise des Sciences*, *Série des Sciences Géologiques et Géographiques*, 15: 139–159.

Kleczkowski, A. S., 1977. Hydrogeological conditions of the Wawel Hill in Cracow. (In Polish, English summary). *Biuletyn Geologiczny*, 21: 153–175.

Kleczkowski, A. S., 1979. *Hydrogeologia ziem wokół Polski*. (In Polish). Wydawnictwa Geologiczne, Warszawa, 184 pp.

Kleczkowski, A. S., 1989. An outline of hydrogeological problems of the Cracow region, south Poland. (In Polish, English summary). *Przegląd Geologiczny*, 37: 323–326.

Kleczkowski, A. S., 2003. *Kształtowanie chemizmu czwartorzędowych wód podziemnych Krakowa 1870-2002; tendencje dalszych zmian*. (In Polish). Akademia Górniczo-Hutnicza, Kraków, 131 pp.

Kleczkowski, A. S., Myszka, J., Solecki, T. & Stopa, J., 1994. *Krakowskie artezyjskie zdroje wód pitnych z wapieni jury*. (In Polish). Wydział Geologii, Geofizyki i Ochrony Środowiska AGH, Kraków, 61 pp.

Klimchouk, A. & Andrejchuk, V., 1997. Environmental problems in gypsum karst terrains. International Journal of Speleology, 25: 145–156.

Klojzy-Karczmarczyk, B., Krawczyk, M., Motyka, J. & Różkowski, K., 1999. Selected anion concentrations sampled from the Łokietek Cave water (Ojców National Park). (In Polish, English summary). *Współczesne Problemy Hydrogeologii*, 9: 439–442.

Kogovšek, J., 1997, Pollution transport in the vadose zone. An example from Postojnska Jama – Slovenia. In: Gunay, G. & Johnson. A. I., (eds), *Karst Waters & Environmental Impacts. Proceedings of the 5th International Symposium and Field Seminar on Karst Waters and Environmental Impacts. Antalya, Turkey, 10 – 20 Sept. 1995*. Balkema, Rotterdam, pp. 161–165.

Krokowski, J., Karnas, M., Opial-Gałuszka, U. & Zientarska, B., 1994. Pomiar zasolenia wody w rzece Wiśle w przekroju powyżej Krakowa. In: *Zasolenie rzeki Wisły. Materiały z Sympozjum, Kraków, 29 listopada 1994*. (In Polish). Sekcja Ochrony Jakości Wód Komitetu Gospodarki Wodnej Polskiej Akademii Nauk, Kraków, pp. 90–106.

Lemberger, I., 1899. Rozbiór chemiczno-bakteryologiczny wód studziennych miasta Krakowa. (In Polish). *Sprawozdanie Komisyi Fizyo- graficznej*, 34 [for 1898]: 101–135.

Lerner, D. N., 2002. Identyfying and quantifying urban recharge: a review. *Hydrogeology Journal*, 10: 143–152.

Macioszczyk, A. & Dobrzyński, D., 2002. *Hydrogeochemia. Strefy aktywnej wymiany wód podziemnych*. (In Polish). Wydawnictwo Naukowe PWN, Warszawa, 448 pp.

Mayer, J., 1999. Spatial and temporal variation of groundwater chemistry in Pettyjohns Cave, northwest Georgia, USA. *Journal of Cave and Karst Studies*, 61: 131–138.

Motyka, J. & Postawa, A., 2004. The groundwater of Zakrzówek horst. (In Polish, English summary). *Biuletyn Państwowego Instytutu Geologicznego*, 412: 71–130.

Motyka, J., Różkowski, K., Sikora, W. & Goc, J., 2002. Influence

of the unsaturated zone in Upper Jurassic limestones on the chemistry of groundwater (Ojców National Park, southern Poland). (In Polish, English abstract). *Biuletyn Państwowego Instytutu Geologicznego*, 404: 123–144.

Motyka, J. & Witczak, S., 1992. Groundwater chemistry in the vicinity of the Ouled Farès area, northern margin of the Cheliff Valley (N Algeria). *Annales Societatis Geologorum Poloniae*, 62: 317–338.

Olszewski, K., 1871. Rozbiór chemiczny wód studziennych i rzecznych krakowskich. (In Polish). *Sprawozdanie Komisyi Fizyograficznéj*, 5 [for 1870]: 131–162.

Olszewski, K. & Trochanowski, K., 1889. Chemiczny rozbiór wód studziennych miasta Krakowa. *Sprawozdanie Komisyi Fizyograficznej*, 23 [for 1888]: 56–97.

Picknett, R. G., Bray, L. G. & Stenner, R. D., 1976. The chemistry of cave waters. In; Ford, C. D. & Cullingford, C. H. D., (eds), *The Science of Speleology*, Academic Press, London, pp. 213–266.

Różkowski, J., 1996. Transformation in chemical composition of karst water in the southern part of the Cracow Upland (Rudawa and Prądnik drainage areas). (In Polish). *Kras i Speleologia, Numer Specjalny*, 1: 1–106.

Szelerewicz, M. & Górny, A., 1986. *Jaskinie Wyżyny Krakowsko-Wieluńskiej*. (In Polish), Wydawnictwo "Kraj", Kraków, 200 pp.

Vadillo, I., Carrasco, C., Andreo, B., García de Torres, A. & Bosch, C., 1999. Chemical composition of landfill leachate in a karst area with a Mediterranean climate (Marbella, southern Spain). *Environmental Geology*, 37: 326–332.

Wiśniewski, W. W., 1997. Powódź a Smocza Jama. (In Polish). *Jaskinie Wyżyny Informator*, 17: 1–2.

Wyrozumski, J., 1992. Dzieje Krakowa. Kraków do schyłku wieków srednich. Tom 1. (In Polish). Wydawnictwo Literackie, Kraków, 576 pp.

Zuber, A., Weise, S. M., Motyka, J., Osenbrück, K. & Różański, K., 2004. Age and flow pattern of groundwater in a Jurassic limestone aquifer and related Tertiary sands derived from combined isotope, noble gas and chemical data. *Journal of Hydrology*, 286: 87–112.

Streszczenie

CHEMIZM WÓD PODZIEMNYCH W SMOCZEJ JAMIE, KRAKÓW, POLSKA

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Jaskinia Smocza Jama jest usytuowana w centrum Krakowa, w południowej części Wyżyny Krakowsko-Wieluńskiej (Fig. 1, 2). Powstała ona w wapieniach jury górnej budujących niewielki zrąb otoczony głównie iłami mioceńskimi znajdującymi się w sąsiednich rowach tektonicznych. W jaskini występują jeziorka (Fig. 3); ich powierzchnia położona jest w przybliżeniu na poziomie wód Wisły, która płynie w odległości ok. 50 m od jaskini. Fluktuacje poziomu wody w jaskini nawiązują do zmian poziomu wody w Wiśle (Kleczkowski, 1977).

Badane było szesnaście próbek wody pobranych z jeziorek i trzy próbki wody kapiącej ze stropu jaskini (Fig. 3). Wszystkie próbki reprezentowały wody słabo alkaliczne. Mineralizacja ogólna wód z jeziorek była mniejsza niż wody kapiącej. W pierwszym przypadku wynosiła od 779,25 mg/L do 1013,01 mg/L podczas gdy w drugim od 1752 mg/L do 2841,73 mg/L (Tabela 1).

Wody z jeziorek należały do typu wód wielojonowych Ca - Na - HCO_3 - SO_4 - Cl, jednakże zawartość HCO_3 jedynie nieznacznie przewyższała w nich zawartość SO_4 (Fig. 4). Natomiast w wodach kapiących zawartość SO_4 była ponad ośmiokrotnie większa. Wody te należały do typu SO_4 - Ca - Na. Wody z jeziorek charakteryzowały się większą niż wody kapiące zawartością Cl. Zarówno wody z jeziorek jak i wody kapiące miały znaczną zawartość Na i K. Wartość proporcji Na/K waha się w nich od 0,74 do 1,98. Fosfor był dominującym mikroelementem w badanych próbkach, przy czym jego zawartość w jeziorkach była większa niż w wodzie kapiącej (Tabela 2).

Chemizm wód w Smoczej Jamie jest zdecydowanie odmienny od opisywanych dotychczas w literaturze wód jaskiniowych (por. Hem, 1992, p. 99; Mayer, 1999; Fairchild *et al.*, 2000). Stosunkowo duża zawartość takich jonów jak SO_4, Cl, NO_3, K i Na sugerują, że wody te zostały zanieczyszczone (por. Hem, 1992; Appelo & Postma, 1994; Lerner, 2002; Macioszczyk & Dobrzyński, 2002). Badane wody w jeziorkach są najprawdopodobniej efektem mieszania przynajmniej dwóch wód składowych o różnym pochodzeniu, co decyduje o ich składzie chemicznym. Dowodzi tego między innymi brak korelacji pomiędzy niektórymi głównymi jonami (Fig. 5). Jeziorka mogą być zasilane poprzez migracje wód wiślanych, które są zanieczyszczone związkami mineralnymi, na skutek zrzucania wód kopalnianych, oraz organicznymi. Porównanie składu chemicznego wód w Wiśle i w jeziorkach dowodzi jednak, że takie jony jak K, Ba, NO_3 i P pochodzą zapewne z innego źródła, gdyż ich koncentracja w Wiśle jest mniejsza niż w badanych próbkach. Co więcej, woda z Wisły może migrować do jaskini kiedy poziom wody w rzece podnosi się szybciej niż poziom wód gruntowych. Tymczasem, jak dowodzą badania chemizmu wód wiślanych, ich mineralizacja jest znacząco niższa podczas wysokich stanów (Krokowski *et al.*, 1994; Motyka & Postawa, 2004). Chemizm wód w jeziorkach może być kształtowany również poprzez pionową migracje wód perkolacyjnych w strefie aeracji z powierzchni Wzgórza Wawelskiego jak i poprzez napływ wód z północno-wschodu z rejonu śródmieścia Krakowa. Należy się spodziewać, że zarówno jedne jak i drugie wody są w znacznym stopniu zdegradowane na skutek wielowiekowego osadnictwa ludzkiego w obu tych obszarach (por. Kleczkowski, 2003). Znacznego zanieczyszczenia wód perkolacyjnych dowodzą badane próbki wody kapiącej, które charakteryzują się m.in. wysoką koncentracją jonu SO_4 (Tabela 1). Jest to związane najprawdopodobniej z wypłukiwaniem tego jonu z znajdujących się bezpośrednio nad Smoczą Jamą nasypów złożonych z gruzu i śmieci (por. Grabowski, 1909; Firlet, 1996), a usypanych tam podczas niwelacji terenu w XIX w, i/lub rozpuszczaniem gipsu stwierdzonego przez Heflika i Matla (1991) w spękaniach w obrębie wapieni jurajskich, w których jaskinia jest wykształcona. Nie można również wykluczyć wpływu ascenzji na chemizm wód w jeziorkach w Smoczej Jamie (por. Kleczkowski, 1977). Przemawia za tym lokalizacja jaskini w izolowanym zrębie zbudowanych z wapieni jury górnej, który może być naturalnym miejscem rozładowania ciśnień artezyjskich. Znane ze sztucznych wypływów (zdrojów; Fig. 1, 6) wody artezyjskie w Krakowie mają zbliżony do jeziorek skład chemiczny i mogły być źródłem takich jonów jak: Cl, SO_4, Na, B i Sr (por. Kleczkowski *et al.*, 1994; Zuber *et al.*, 2004). Jednakże wody artezyjskie charakteryzują się zdecydowanie wyższymi proporcjami molowymi mSr/mCa i mMg/mCa niż badane wody jeziorek (Fig. 7). Ponadto wody artezyjskie cechują się niższą niż badane wody koncentracją NO_3, K i P.