The Mofetta Tylicz – an example of carbonated water springs in the area of Tylicz (Beskid Sądecki, the Carpathians)

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Record

Chemical composition and its variability of the Mofetta Tylicz springs record unique conditions of their formation and stress that Mofetta Tylicz and similar springs in the Carpathians should be monitored, protected and also used as a touristic sites.

Abstract

The paper characterise the group of CO₂-rich (carbonated) water springs in the Carpathians, which are accompanied by exhalation of CO₂. These springs called the Mofetta Tylicz are the example of the environmental and touristic unique object. We present geological and hydrogeological background as well as chemical analysis of the springs composition. The springs are characterised by the variability of the chemical composition of analysed groundwater, which indicates the need to implement a systematic monitoring. The monitoring would assess the reasons for this variability and allow the effective protection of spring waters of this area in the future.

Keywords

carbonated groundwater • therapeutic water • CO₂ exhalation • Tylicz • the Carpathians

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1. Geological settings

The area of Tylicz, located in Poprad River Valley, is a part of the Polish Carpathians Massif (Beskidy Mts., Beskid Sądecki), a particularly interesting region as a place of therapeutic water drainage (mineral and containing CO₂) and the groundwater mining area with high touristic potential.

Geologically, this area is located in the south-west part of the Magura Nappe, on the border of the Bystrzyca and the Krynica subunits separated by an inverse fault plunged on NE (Krynica dislocation) (Oszczypko et al., 1999). The Bystrzyca subunit is composed of Łabowa, Beloveža, Żeleźnikowa and Magura formations. This subunit is described as broad zone secondarily pleated syncline (Oszczypko et al., 1999). The Łabowa Formation, with thickness of about 100 m, consists of red shales, thin-bedded flysch with interlocation of red shales. The Beloveža Formation is a complex of 300-m thick sediments, known as turbidites deposits with a predominance of argillaceous sediments. The Żeleźnikowa Formation (250 up to 350 m thick) consists of alternating grey-blueish calcareous sandstones, marls and marly shales (Oszczypko & Oszczypko-Clowes, 2010). The Maszkowice Sandstones, the Poprad Sandstones and the Mniszek Shales are components of the Magura Formation. The Maszkowice series represent a fractional layered sandstones (a part of turbidities deposits) that are intercalated with Łącko Marls – dark grey marls (0.5–3.5 m thick). The Mniszek Shales series are composed of variegated shales and thin-bedded flysch. The Poprad Sandstones Member is not mani-

fested on the surface and is known from deep drillings of several hundred metres depth. Thick-bedded sandstones of this unit mainly consist of medium-grained sands with intercalations of shales and mudstones (Oszczypko et al., 1999). The Krynica subunit consists of Szczawnica, Zarzecze and Magura formations and has a block fault nature (Oszczypko et al., 1999). The Szczawnica Formation is about 200 m of thin- to medium-bedded, fine- to medium-grained, calcareous sandstones (flysch). The Zarzecze Formation (which has thickness of up to 650 m near the estuaries of the Krynica and the Muszynka River) is composed of sandstones, mudstones and grey marble shales. The Magura Formation consists of Piwniczna Sandstones, characterised by the presence of conglomerates, thick-bedded sandstones and mudstones with intercalation of thin-bedded sandstones, mudstones and clay stones (Birkenmajer & Oszczypko, 1989; Oszczypko & Oszczypko-Clowes, 2010). In 2010 Oszczypko et al. established a new zone in the area of Tylicz, called Tylicz zone, which is located between the Bystrzyca and Krynica subunits. It contains the same formations as the Bystrzyca subunit.

2. Hydrogeological conditions

According to commonly used division by Paczyński (1995), the area of Tylicz is located in the Hydrogeological Carpathian Region (XIV) (Chowaniec, 2006) in the Major Groundwater Basin (MGB) no. 438 – Magura Nappe (Nowy Sącz) – a fissure-pore ba-

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Figure 1. Location of the Mofetta Tylicz on the geological background

sin, with an area of 250 sq km (Małecka et al., 2007). According to Kleczkowski (1990) and Skrzypczyk (2003), Tylicz is located in the Groundwater Body no. 154 (154 JCWPd). Groundwater of this area occurs in quaternary porous sands and gravels with a thickness of less than 10 m and Paleogene sandstones with a thickness of 10–20 m (Małecka et al., 2007). The hydraulic conductivity of the pore-fissured sediments ranges from $1.13 \cdot 10^{-4}$ to $1.25 \cdot 10^{-9}$ m/s (Nałęcki et al., 2004). Long-term investigations of the groundwater runoff in the region of Tylicz (Muszyńska catchment) brought varied results, from 0.50 to 13.11 L/s*sq km (on an average 6.90 L/s*sq km), depending on research methods (e.g. Ciężkowski et al., 1999; Guty, 2003; Duńczyk, 2004; Buczyński et al., 2007; Józefko et al., 2013). Significant or a significant form of groundwater drainage in the Tylicz area are springs (mineral, CO₂-rich and fresh groundwater), which were recorded in a number of 365. Average spring outflow ranges from 0.01 to 0.10 L/s. The spring density index for the Muszyńska River basin is 7.90. The

spring runoff, with 2.261 L/s*sq km, is also high (Ciężkowski et al., 1999; Buczyński et al., 2007; Józefko et al., 2013).

The presence of mineral and therapeutical groundwater (226 documented springs) containing CO₂ (carbonated water, CO₂-rich water) is characteristic for the Carpathians. The Poprad River Valley is famous for the most numerous springs called 'szczawa' with high content of free carbon dioxide (from 320 up to 2996 mg/L in Krynica-Zdrój where this gas is exploited on an industrial scale) (Ciężkowski et al., 2002). Węclawik (1991) proposed a division of mineral waters in the Carpathians into different zones. The central zone, also called zone A, corresponds to fresh carbonated groundwater occurring near the surface. Zone B, known as transition zone, is connected with mineral chloride CO₂-rich groundwater. Zone C, for which typical are brines and saline groundwater, occurs in deeper aquifers (Chowaniec, 2009). Chloride mineral and fresh CO₂-rich groundwater springs can be both found in the area of Tylicz (Świdziński, 1972). These springs

Figure 2. The view of the Mofetta Tylicz

Figure 3. Exhalation of CO₂ at the Mofetta Tylicz

have a great potential to be magnets for tourists as many of them were reconstructed and equipped with information boards and gazebos or benches. Educational nature trails, for example, 'Na Rakowcu' were established as well; however, there are still many springs that are difficult to reach and find.

The origins of the CO₂ in the Carpathian formation groundwater is not so easy to define. Results of research varies, what leads to the conclusion that there have to be more than one source of CO₂ (Ciężkowski et al., 2002). Lis and Hałas (1980) proved that the origin of CO₂ in the area of the Magura Nappe is related to the thermal decay of limestone of Mesozoic and Paleozoic platforms and clastic sediments from Paleogene and lower Miocene (Oszczypko, 1998; Ciężkowski et al., 2002). Studies of Oszczypko and Zuber (2002) suggest that the origin of chloride CO₂-rich groundwater is diagenetic as the result of the transition of smectite to illite, which takes place during the diagenesis of flysch sediments. The other metamorphic genesis theory of these water origin (based on the analysis of the isotopic composition) suggests that CO₂ arises in the Carpathians from an approximate depth of 15–20 km as a result of the dehydration and decarbonation of the bottom surface of the Carpathian flysch and base platform formations (Dowgiałło, 1980; Leśniak, 1980; Zuber & Grabczak, 1985; Zuber, 1987; Ciężkowski et al., 2002). Tectonics of the area seems to play a predominant role in the migration of the gaseous CO₂ in the Carpathian flysch (Ciężkowski et al., 2002). According to Ciężkowski et al. (2002), the metamorphic genesis of CO₂ cannot be postulated ruthlessly. There is also a possibility for magmatic and biogenetic genesis (Lis and Hałas, 1980; Ciężkowski et al., 2002) requiring precise research especially in the aspect of extraction of CO₂ in a bigger scale.

It is worth mentioning that in the Tylicz area, one of the most important regions of exploitation and bottling of therapeutic, mineral and fresh groundwater is located – the mining area TYLICZ I (31.93 sq km) where groundwater exploitation started in

the mid 1970s (Ciężkowski & Kapuściński, 2011; Porwisz et al., 1999; Kucharski & Sokołowski, 2007). Multivita company has been exploiting in Tylicz and Powroźnik and bottling water of a popular trade names 'Kropla Beskidu' and 'Kropla Mineralów'. Tylicz resources of mineral water are defined for 8.6 m³/h with a depression of 11.0–19.5m and are exploited from a depth of 32–160 m (Zarzecz Formation, layer of Łącko) (Poprawski et al., 1997; Kucharski & Sokołowski, 2007).).

3. Field description of the Mofetta Tylicz

The Mofetta Tylicz is a group of springs where the exhalation of CO₂ and outflow of carbonated water can be observed. Springs are located in the south-west part of the Tylicz village, exact location is to the right bank of the Muszynka River and the slope of the hill Szalone (828.8 m a.s.l.), between the river valleys Syhowny, from the south and Bradowiec, from the north. It belongs to the territory of the resort 'Domki w lesie' (Houses in the forest). The Mofetta is located at 582 m a.s.l. and its coordinates are longitude 21°00'72", latitude 49°39'07". From geological point of view, it is located in the Bystrzyca subunit near the border with the Krynica subunit in the buffer zone of the Poprad Landscape Park, on the Maszkowice Sandstone Member, which is a part of the Magura Formation (Figure 1).

In the 'Domki w lesie' resort, small signs show the way to the path through the petite forest leading to the springs, which makes it accessible only on foot. Mofetta springs, beleaguered by 11 concrete rings, are situated in low ground, surrounded by a wooden fence. The whole area is cleared of plants. Benches and a gazebo can be used to sit down, relax and watch the bubbling spring. The information board shows the location on a geological map and provides information about the spring like its history and the history of the Tylicz village (Figures 2 and 3).

Table 1. Main physical and chemical proprieties of the Mofetta Tylicz groundwater – data from 1963 to 2014

Date	Temperature [°C]	pH [-]	EC [mS/cm]	M _{tot} [mg/L]	Free CO ₂ [mg/L]	Data source
1963	12.0	-	-	-	940	cited by Porwisz et al. 1998
1975	-	5.80	-	238	-	cited by Porwisz et al. 1998
1994-04-20	12.0	-	-	861	940	Porwisz et al. 1995
1994-05-13	11.9	4.85	0.074	-	940	Porwisz et al. 1995
1998-06-25	10.0	-	0.330	-	2292	Porwisz et al. 1998
2006-06-01	9.5	4.19	0.080	101.1	1100	Staško et al. 2007
2006-09-14	10.4	5.28	0.445	443.5	1166	Staško et al. 2007
2014-11-26	8.8	5.57	0.478	250	796	this study

Table 2. Chemical composition of the Mofetta Tylicz groundwater – data from 2014

Compound	Unit	Concentration	Compound	Unit	Concentration
HCO ₃ ⁻	mg/L	195.3	Sr	µg/L	609.65
Cl ⁻		2.88	Al		148.83
SO ₄ ²⁺		1.64	Ba		51.83
NO ₃ ⁻		0.053	Li		6.42
NO ₂ ⁻		0.025	Ni		5.23
HPO ₄ ³⁻		<0.01	Cu		0.96
Na ⁺		8.51	Cd		0.21
K ⁺		0.63	Zn		0.18
Mg ²⁺		3.94	As		<1.0
Ca ²⁺		31.80	Co		<1.0
NH ₄ ⁺		<0.01	Cr		<1.0
Fe _{tot}		3.412	Pb		<1.0
Mn		0.694			

4. Chemical composition of the Mofetta Tylicz springs water

The Mofetta Tylicz as an important hydrogeological object was a subject of various research particularly in the context of hydrogeological evidence of the Poprad Valley aquifers. Hydrochemical aspects of these studies were limited mainly to determine the basic chemical parameters of groundwater and incomplete chemical analyses (Porwisz et al., 1995; Porwisz et al., 1998; Staško et al., 2007). Therefore, in November 2014, field works and laboratory analyses were made to allow full characteristic of carbonate groundwater of the Mofetta Tylicz springs.

Electrical conductivity (EC), pH and temperature were measured in the field, using multiparameter gauge Elmetron CX401. Concentration of free CO₂ was measured (also directly in the field) as acidity. A 100 mL of water sample was titrated with 0.05 M NaOH in the presence of phenolphthalein. The acidity was converted using the gram-equivalent of free CO₂. Concentration of HCO₃⁻

was measured as total alkalinity. A 100 mL of water sample was titrated using 0.05 M HCl in the presence of methyl orange. The alkalinity, in meq units, was recalculated using the gram-equivalent of HCO₃⁻. Analyses of cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) and anions (Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻, HPO₄³⁻) were carried out using Alliance Waters high-performance liquid chromatography (HPLC) 2695 with 432 Conductivity Detector and 2998 Photodiode Array Detector, an IC-Pak Anion HR column (glucuronate/borate eluent) and IC-Pak Cation M/D column (EDTA/HNO₃ eluent). Analyses of Fe, Mn, Sr, Al, Ba, Ni, Li, Cu, Cd, Zn, As, Co, Cr and Pb were obtained by flame atomic absorption spectrometry (F-AAS) and graphite furnace atomic absorption spectrometry methods (GF-AAS) using GBC Avanta atomic absorption spectrometer.

Actual and previous research showed that groundwater of the Mofetta Tylicz are fresh waters (total mineralisation < 1 g/L) (Table 1) with high content of free CO₂ and low pH value. Temperature of springs ranged from 8.8 to 12.0 °C, pH from 4.19 to 5.80, EC from 0.08 to 0.48 mS/cm and total mineralisation from 101 to

Figure 4. Piper diagram showing groundwater chemistry of the Mofetta Tylicz – data from 1975, 2006, 2014

$$CO_2^{0,8-2,29} M^{0,10-0,86} \frac{HCO_3^{83-97} SO_4^{1-15} Cl^{1-2}}{Ca^{52-79} Mg^{14-33} Na^{6-17} K^{1-5}} T^{9-12}$$

Figure 5. Kurlov's formula for data from 1963 to 2014; CO_2 in g/L, M in g/L, anions and cations in % meq/L, T in °C.

861 mg/L. The amount of free CO_2 ranged from 796 to 2292 mg/L (Table 1). All main chemical properties of water showed significant changes over the time, even during one year (2006) but still remained in a specified range (Figures 4 and 5; Table 1). At the same time, changes in chemical composition of main ions over the time were also observed. The groundwater studied in 2014 represented hydrogeochemical type HCO_3 -Ca; however, earlier studies showed the water type HCO_3 -Ca-Mg (2006) (Figures 4 and 5). This phenomena is typical for shallow CO_2 -rich groundwater of Carpathian zone A where shallow flow systems are highly sensitive to recharge and outflow changes, water mixing processes and anthropogenic influence. These processes often cause a change in hydrogeological and hydrogeochemical regime (Węclawik, 1991; Ciężkowski & Kapuściński, 2011; Rajchel, 2012). On the other hand, very low concentration of NO_3^- , NO_2^- , HPO_4^{3-} and NH_4^+ ions noted in water studied in 2014 (Table 2) suggest that the Mofetta Tylicz springs were not exposed to the direct influence of anthropogenic pollution (e.g. fertilization and sludge) (Witczak et al., 2013). Concentrations of almost all main

ions and metals analyzed in 2014 were below the Polish standards for water intended for human consumption (MH, 2010) and showed a good chemical status of groundwater (class I to III), according to the Regulation of the Minister of Environment (RME, 2008) (Table 2). Only iron (3.412 mg/L) and manganese (0.694 mg/L) concentrations were probably higher as a result of natural processes accompanying chemical reactions associated with the presence of acidic CO_2 in a flow system (Witczak et al., 2013).

5. Conclusion

The Carpathians, particularly the area of Tylicz, are well known for their therapeutic springs. Their specific properties (mineralisation, amount of free CO_2) make these waters ideal for geological field trips. A particular attention should be paid to springs with high free CO_2 content and CO_2 exhalation such as the Mofetta Tylicz. These studies showed that groundwater of the Mofetta Tylicz springs do not have a stable chemical composition and should be a subject of systematic chemical monitoring to indicate the reasons of the long-term groundwater's change over time. Also from the touristic point of view, many springs in the Tylicz area are not accessible or adopted for touristic visits and, therefore, are still not fully used. These unique natural wonders should be made available for visitors and tourists.

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