# HYDROGEOLOGICAL SETTINGS AND ORIGIN OF GROUNDWATER COMPOSITION IN THE SOUTHERN PART OF THE GORCE MTS, KOWANIEC MAŁY CATCHMENT

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**Abstract:** The Gorce Mts of southern Poland occur in a, natural upland area that is viewed as valuable and is protected. It has an inadequate and irregular network of long-term monitoring points at the national level with regard to groundwater quality and vulnerability to contamination. The paper discusses the results of an investigation of groundwater in the Kowaniec Mały drainage basin, in the southern part of the Gorce Massif. It provides new hydrogeochemical data that shed light on the origin and evolution of groundwater chemistry in this region. On the basis of a hydrogeological survey of 33 natural springs, trends in the spatial and temporal variation of the physicochemical properties of the groundwater are presented. Three hydrochemical types of water were distinguished, namely $HCO_3$-Ca, $HCO_3$-Ca-Mg and $HCO_3$-$SO_4$-Ca. The detailed analysis of ionic ratios shows that the dissolution of carbonates (mainly calcite) and aluminosilicates (mainly albite) played a fundamental role in the formation of the chemical composition of the groundwater in the study area. These processes are responsible for the presence of the dominant ions, such as $HCO_3^-$ and $Ca^{2+}$, as well as $SiO_2$ and in part $Na^+$ and $K^+$. Chloride–sodium mineralization is connected first of all with recharge by rain water and the direct dissolution of halite, contained in the aquifer rocks or formed during the evaporation of the water. The most probable sources of dissolved $SO_4^{2-}$ are the atmospheric sulphates contained in recharge meteoric waters in the case of springs located at higher altitudes and the reduced inorganic sulphur compounds dispersed in fine-grained sedimentary rocks, mostly as pyrite, which undergoes oxidation during rock weathering. Ion exchange processes involving clay minerals also were present and affected mainly the concentrations of $Na^+ + K^+$ and $Ca^{2+}$.

**Key words:** Groundwater chemical composition, groundwater origin, ionic ratios, water-rock interaction, recognition of source rocks.

## INTRODUCTION

Geological and hydrogeological investigations in the West Beskids until now have been mainly connected with prospecting for hydrocarbon and mineral water as well as with geological cartography studies (Cieszkowski, 2006a). However, the hydrogeological settings in the southern part of the Gorce Massif have been the least recognized (Burtan *et al.*, 1978a; Chowaniec and Witek, 1997). A hydrogeological survey in this area recently was renewed owing to preparation of reports on the groundwater protection areas within Major Groundwater Reservoir No. 439 – the Magura Beds Basin – and the assessment of disposable groundwater resources of the Dunajec river catchment. There are only four country-level groundwater monitoring points in the entire area of the Gorce Massif, namely: 2332 (II/835/1) and 141 (II/770/1) at Poręba Wielka, 2006 (II/826/1) at Rabka-Zdrój, and 520 at Ochotnica Dolna (System, 2016a) (see Figs 1 and 4). All of them are located in the northern and eastern parts of the Gorce Massif. The well at Ochotnica Dolna is the only one that monitors the chemical composition of fresh groundwater within Major Groundwater Reservoir No. 439. There are no groundwater monitoring points in the central and southern parts of the Gorce Massif, where the study area is located. Owing to an insufficient number of groundwater monitoring points of the national monitoring network, the Gorce Massif area still remains the least known with regard to hydrogeological settings, groundwater chemical composition, its resources and vulnerability to contamination. Moreover, the hydrogeological conditions and groundwater resources are not monitored in either the Gorce National Park or the Special Conservation Area (PL H120018), 'Ostoja Gorczańska', designated under Nature 2000, with valuable natural ecosystems, directly dependent on groundwater and its quality (Schutten *et al.*, 2011; Marsland *et al.*, 2015).
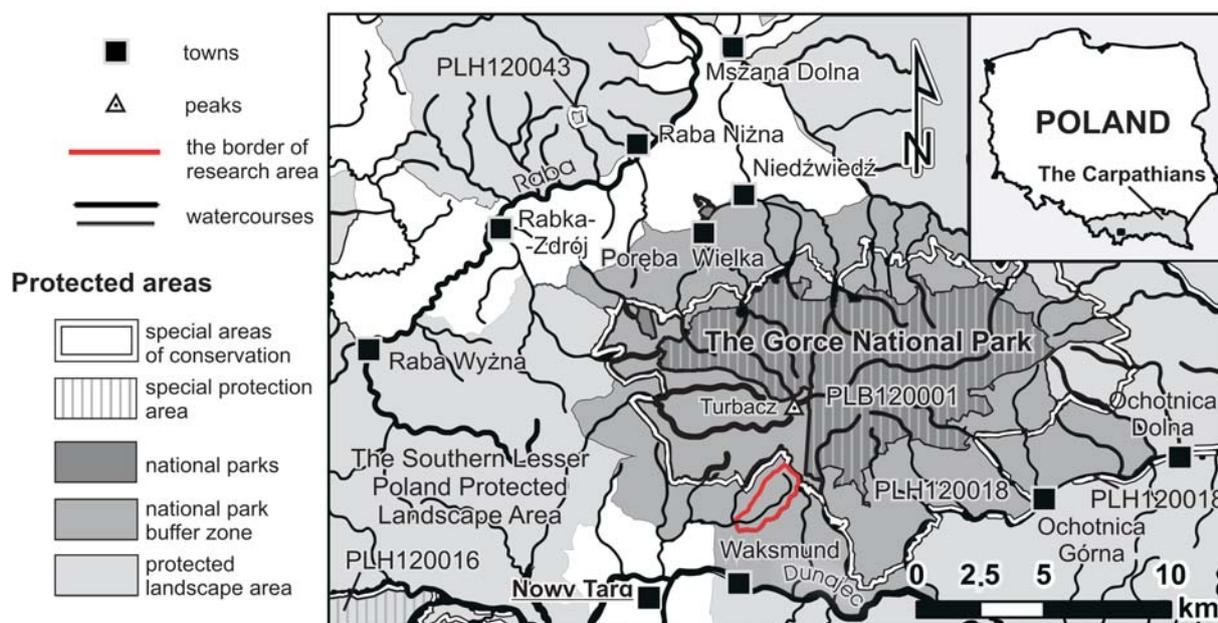
**Fig. 1.** Position of the Kowaniec Mały drainage basin and the borders of the nearby nature protection zones (after Dostęp, 2013).

This paper is focused on the analysis of hydrogeological settings and the occurrence of groundwater in the southern part of the Gorce Massif., where long-term groundwater monitoring has not been performed to date. On the basis of a hydrogeological survey of 33 natural springs within the Kowaniec Mały catchment, the trends in spatial and temporal variation of groundwater physicochemical properties are presented. A detailed analysis of groundwater chemical composition and calculated ionic ratios was carried out to determine the origin of the major chemical compounds dissolved in the water. An attempt was made to identify the main geochemical processes that gave rise to the chemical composition of the groundwater in this part of the Gorce Massif. A comparative analysis of groundwater chemical composition from different parts of the Gorce Massif was performed to emphasize the appropriateness of extending the national network of groundwater monitoring stations into the study area.

## LOCATION OF THE STUDY AREA

In terms of administrative divisions, the study area is situated in Małopolska Region, Nowotarski District, rural commune of Nowy Targ, southern Poland. The study area covers more than 3 km² and includes the catchment of the Kowaniec Mały Stream. The entire area is located within the Gorce National Park buffer zone and belongs to the Southern Małopolska Landscape Area (Fig. 1; Kondracki, 2009; Dostęp, 2013).

In the north-east, the catchment area terminates at the dome-shaped Bukowina Waksmundzka peak of 1103 m a.s.l. height (Cieszkowski, 2006a), from which water flows down to the south-west, to the Kowaniec Mały Stream. The maximum difference in altitude is 400 m. The land surface slopes vary from 1 to 33°: on the south side of the stream, values between 15° and 30° predominate, whereas on the

north side, values between 5° and 20° are most frequently encountered.

The Kowaniec Mały drainage basin is located in the Carpathian Climate Region (Wiszniewski and Chełchowski, 1987). The air temperature and the amount of precipitation to a large extent depend on the land relief . In the Gorce Massif, the coldest months of the year are January and February, with mean monthly temperatures from –4.4 to –4.2 °C. The warmest months are July (+15.3 °C) and August (+14.6 °C) (Stacja, 2016). The total annual precipitation ranges from 700 to 900 mm at the foot of the Gorce Massif and exceeds 1200 mm in the highest parts (e.g., in 2012; an annual precipitation of 927 mm was recorded in Rabka and 1195 mm on Mt. Turbacz). About 65% of the total annual precipitation falls in the spring and summer seasons (from April to September), with a maximum intensity in June and July; the lowest rainfalls are recorded in October (Miczyński, 2006). The snow depth recorded in 2012 and 2013 reached 116 cm (Fig. 2).

## GEOLOGICAL SETTINGS

The Gorce Massif belongs to the Polish Outer Carpathians (Stupnicka, 1997). Palaeogene formations in the study area belong to the Krynica Subunit of the Magura Nappe.

According to the official detailed geological maps at a scale of 1:50 000, provided by the Polish Geological Institute (Burtan et al., 1978a, b), the geological units of the study area are the Paleocene and Middle Eocene Turbacz Beds, the Middle and Upper Eocene Kowaniec Beds, and Upper Eocene conglomerate sandstones and conglomerates (Burtan et al., 1978a; Żelaźniewicz et al., 2011) The youngest Quaternary deposits of the Vistulian Glaciation occur along the southern part of the Kowaniec Mały Stream in the form of a small terrace composed of gravel, sand and glacial till (Fig. 3). However, it should be stressed that during the

last 38 years, there have been considerable developments in the understanding and description of the geological settings of the Gorce Massif, including the southern part of the massif. Thus the lithostratigraphic units of the Magura Nappe are divided into formations (basic lithostratigraphic units), related to the lithological and facies diversity of the Palaeogene rocks (Watycha, 1963; Cieszkowski and Olszewska, 1986; Birkenmajer and Oszczypko, 1989; Cieszkowski, 2006b; Oszczypko *et al.*, 2008). According to the findings of Birkenmajer and Oszczypko (1989), as well as Cieszkowski and Olszewska (1986), the Paleocene to Oligocene rocks of the Gorce Massif that belong to the Krynica Subunit of the Magura Nappe are represented by the Szczawnica Fm (Paleocene/Lower Eocene), the Zarzecze Fm (Lower Eocene) and the Magura Fm (Lower/Middle Eocene to Oligocene). The youngest lithostratigraphic unit of the Krynica ineSubunit, in the Gorce area, in the vicinity of Nowy Targ (at the southern foot of the Gorce Massif), is the Malcov Formation (Upper Eocene/Oligocene). The Magura Fm is made up of three members, namely: the Piwniczna Sandstone Member of the Turbacz Beds (Lower–Middle Eocene), the Kowaniec Beds (Middle–Upper Eocene) and the Poprad Sandstone Member, the Upper Eocene conglomeratic sandstones and conglomerates (Upper Eocene–Oligocene) (Cieszkowski, 2006b)

The oldest Turbacz Beds, composed of shales, sandstones and conglomerates, cover a small area (0.3 % of the entire catchment) and make up Bukowina Waksmundzka. About 88% of the study area is covered by the Kowaniec Beds, composed of sandstones intercalated with shale, marls
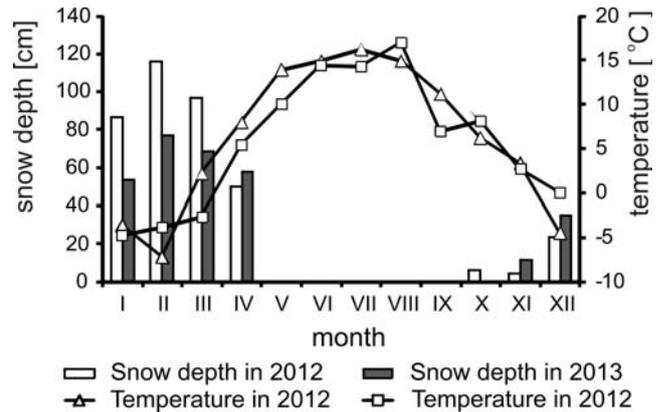


**Fig. 2.**    Mean monthly values of air temperature and snow depth recorded in the period 2012–2013 at the Turbacz weather station.

and conglomerates. A relatively small area is covered by conglomeratic sandstones and conglomerates (approx. 10.9%), which occur along the eastern border of the drainage basin (Burtan *et al.*, 1978a, b).

The grains of sandstones and conglomerates of the Turbacz Beds are cemented by calcite and clay minerals. Quartz, together with granite, gneiss and shist fragments, predominate in the mineral content of the beds. In the composition of sedimentary rocks, quartzitic sandstones, limestones and dolomites are dominant. Hornstones, lydites and marls are more rare. The sandstone-shale and shale-sandstone beds contain also grains of ferrous minerals.
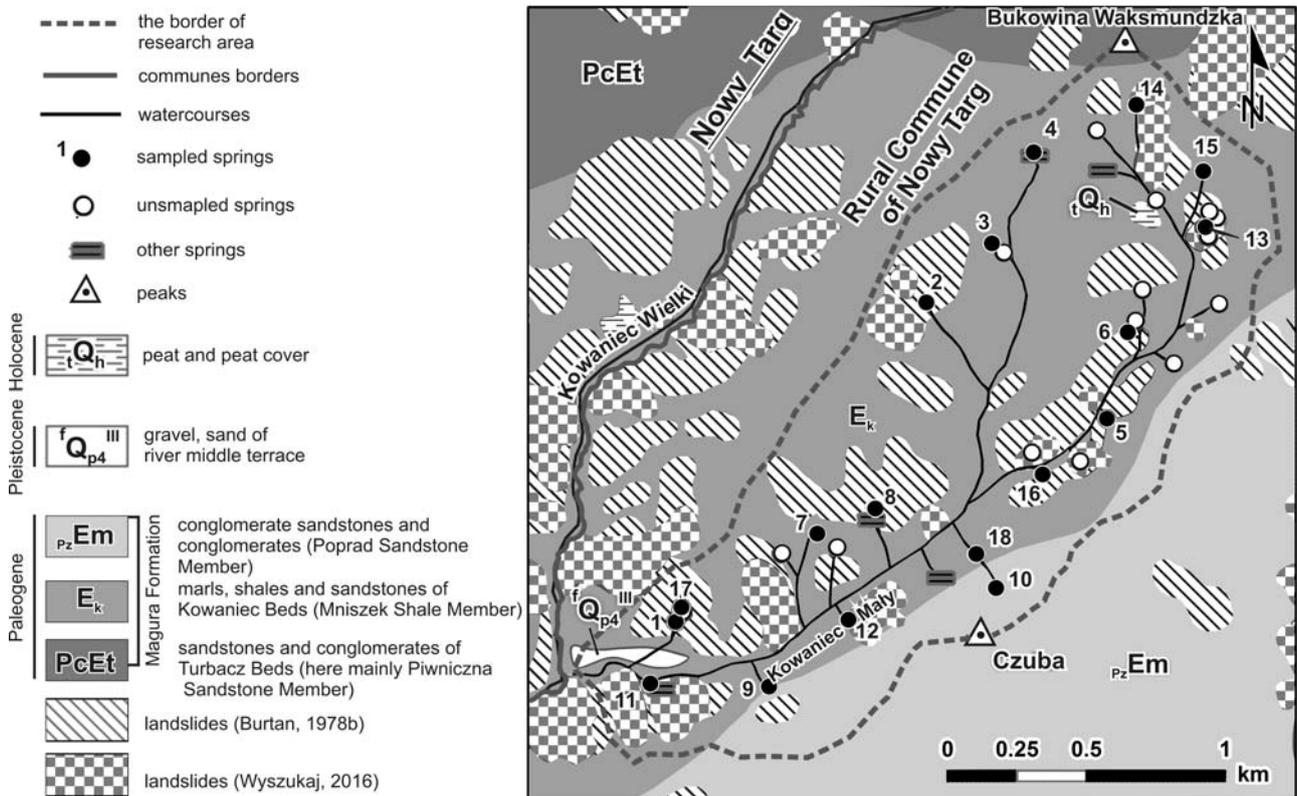


**Fig. 3.**    Generalized geological settings in the study area (after Burtan *et al.*, 1978b with some changes after Birkenmajer and Oszczypko, 1989; Cieszkowski 2006; location of new landslides after Wyszukaj, 2016).
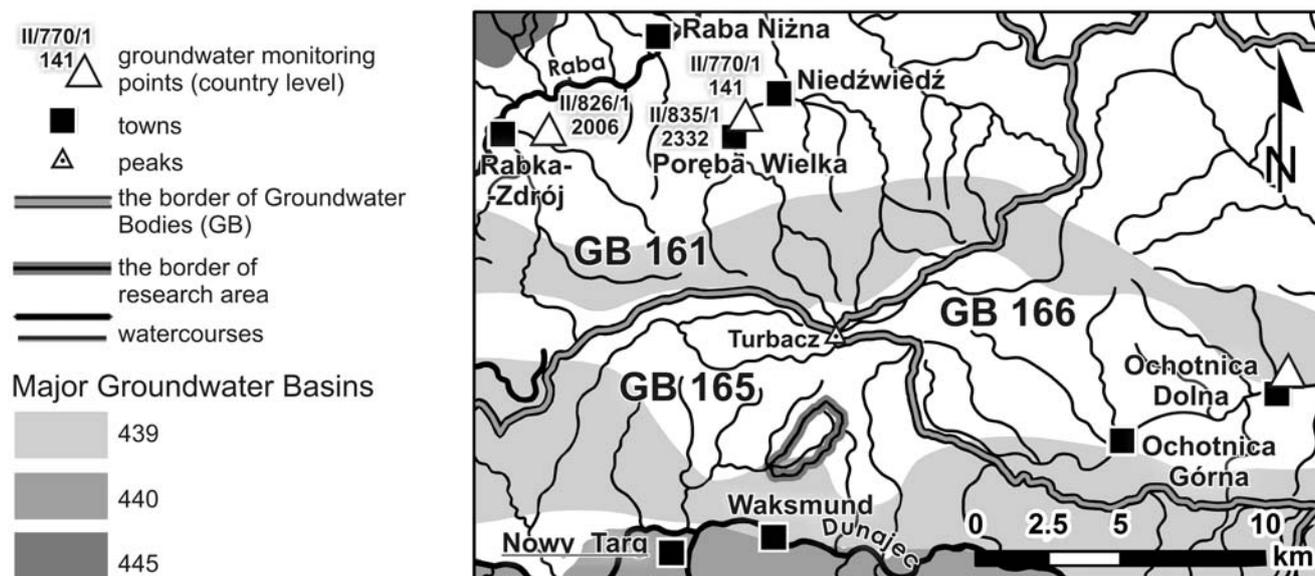
**Fig. 4.**     The position of the study area and country level groundwater monitoring points on the background of hydrogeological units of the Gorce Massif (compiled after Kleczkowski, 1990; Nowicki *et al.*, 2009;  System, 2016a).

The Kowaniec Beds, mainly sandstones interbedded with shales, contain significant concentrations of iron compounds and plant detritus. Sandstones grains are cemented with calcite and silica. Their brown colour is evidence of iron and manganese oxidation reactions. The lowest part of the Kowaniec Beds is composed of quartz (80–90%); with fragments of limestones, dolomites, hornstones, marls, quartzitic sandstones, chlorite and sericitic shales, granites, pyrite and iron compounds occurring in smaller amounts.

Conglomeratic sandstones and conglomerates mostly consist of quartz grains. Fragments of feldspars, crystalline rocks (with chlorite, muscovite, biotite and graphite), shales, quartzites, limestones and dolomites, as well as pyrite grains and dark iron compounds that are observed less frequently. The largest amounts of biotite and muscovite are characteristic for the uppermost part of the conglomerate beds (Burtan *et al.*, 1978a).

Landslides, especially consequent ones, are characteristic phenomena in the study area  developed in the Kowaniec Beds; they are mainly connected with the presence of thin beds of fine-grained sandstone interbedded with shales and bentonite. According to the Detailed Geological Map of Poland at a scale of 1:50 000, approximately 25% of the area of the Kowaniec Mały drainage basin is occupied by landslides. In contrast, the findings of the SOPO Project (The Anti-Landslide Protection System) of the Polish Geological Institute-National Research Institute, which document mass movement, show that the area concealed by landslides is significantly smaller (Fig. 3). The smaller extent of the landslides, documented by the SOPO Project, stems from lack of recognition of part of the mass movements that previously had been studied as landslides (Rubinkiewicz, 2012). Moreover, it should be emphasized that the SOPO Project is in progress, and the landslides database is constantly being updated (System, 2016b; Wyszukaj, 2016). Comparison of geological settings (Fig. 3) with the distribution of slopes (Fig. 5) demonstrates that the northern part of the study area

is strongly affected by denudation and thus characterized by an increased frequency of landslides. In the study area, landslides play an important role in the development and occurrence of natural springs and seepages and exert an influence on hydrogeological conditions in the shallow zone.

## HYDROGEOLOGICAL CONDITIONS

With regard to hydrogeological conditions, the study area is situated in the Outer Carpathian subregion (Paczyński, 2007). Three groundwater bodies have been distinguished in the Gorce Massif, namely No. 161, No. 165 and No. 166; the Kowaniec Mały catchment belongs to Groundwater Body Number 165 (Nowicki *et al.*, 2009). Documented groundwater resources of good quality and economically significant quantities occur in the Gorce Massif only within Major Groundwater Basin (MBR) No. 439, the Magura Beds Basin (Gorce) shown in Figure 4. The most southerly part of the Kowaniec Mały catchment (mainly the estuary part of the stream) belongs to this basin. According to Kleczkowski (1990), available groundwater resources of the whole basin are estimated as being about 23 000 $m^3$/d and the available groundwater coefficient is about 0.59 l/s/$km^2$. It is necessary to emphasize that the delineation of the borders of the Major Groundwater Basin (MBR) No. 439 in the Palaeogene flysch rocks is a huge generalization; therefore it is crucial to refer to more detailed studies on the hydrogeology of the Flysch Carpathians.

Generally, the occurrence of freshwater in the Outer Carpathians region is connected with the sand-gravel cover, glacial till-debris and fissured flysch sediments. The water-bearing capacity of the Cretaceous and Palaeogene flysch depends more on the degree of fissure and fracture development than on the porosity of the rock matrix (e.g., Bober and Oszczypko, 1964; Oszczypko, 1966a; Małecka and Murzynowski, 1978). The dominating relationship be-

tween the degree of fissure development (i.e. weathering and tectonic fractures) and the water-bearing capacity of the Magura Sandstones in the vicinity of Śnieżnica Massif (Beskid Wyspowy Mts) was confirmed by Bober and Oszczypko (1964). On the basis of a study of the Szaflary Beds at Szaflary, it was determined that groundwater flow is linked significantly more with fracture width than with microfractures. The hydraulic conductivity of the Szaflary Beds was estimated to be from $10^{-8}$ to $10^{-7}$ m/s. – the fracture width typical for these rocks is 20 µm – to $10^{-6}$ m/s, where the fracture width is 40 µm. The role of intergranular porosity and microporosity in rock permeability is negligible (Oszczypko, 1966a). Owing to the complex geometry, diversified density and length of a fracture network, there is no typical, continuous groundwater horizon. There is also an observed lack of correlation between lithological and facies characteristics on the one hand and water-bearing horizons on the other.

Groundwater recharge in the Outer Carpathians occurs via infiltration of precipitation through a discontinuous soil layer and a cover of weathered rocks ca. 1–3 m thick, as well as a near-surface network of fractures that originated from weathering and the strain relaxation process (Kleczkowski, 1979; Chowaniec, 2009).

The depth to the groundwater table ranges from few metres in the valley bottoms to 15–30 m in the watershed zones of mountainsides (Chowaniec, 1991). The volume of water infiltration and the water circulation depth depend on the slope, lithology and the landslide occurrence at the land surface. The majority of recharge water enters the rock formations at higher elevations (Chowaniec, 1991; Chowaniec and Witek, 1997).

Studies on the water-storage capacity of flysch rocks show that, depending on the area, the water-storage capacity starts decreasing form 15–30 m bgl (below ground level) on a mountainside and from 15 m bgl in the valley bottom (Niedzielski, 1974). The depth to the impermeable zone ($k \approx 10^{-7}$ m/s) falls within the range of 45–95 m bgl. The detailed studies of Oszczypko *et al.* (1981), dedicated to the water-bearing properties especially of the Magura Sandstone of the Krynica and Bystrica subunits in the Beskid Sądecki and the Beskid Niski mts, show a decrease of water-storage capacity values from 30–40 m bgl. The depth to the impermeable zone ($k \approx 10^{-7}$ m/s) ranged from 80–90 m bgl. The zone between 40 and 80–90 m bgl is characterized by hydraulic conductivity (k) values of more than $10^{-6}$ and lower than $10^{-5}$ m/s. The water-storage capacity of the Magura Sandstone exceeds the average water-storage capacities of flysch rocks. The maximum groundwater discharge rates reach 6–50 m³/h (mean 12 m³/h), which is considerably more than had been estimated by Michalik (1965) and Oszczypko (1966b), i.e. 9 m³/h (in the vicinity of Rabka, the Gorce Massif) and 24 m³/h (in the vicinity of Nowy Sącz, Beskid Sądecki Mts), respectively. A near-surface zone of up to 35–40 m bgl plays a key role in groundwater recharge.

The thickest water-bearing zones are located along the watershed boundary and in the valley bottom and therefore the occurrence of springs is usually related to the upper part of mountainside and valley bottom. Moreover, landslide development and mass movement cause a pronounced increase in water absorbability and a longer groundwater circulation time in an area of mountainsides and they significantly affect the location of spring discharge.

In the study area of the Kowaniec Mały catchment, there is a noticeable connection between the positions of landslides and the occurrences of springs (Fig. 3). Springs are often located below or within the limits of landslides. There is a lack of groundwater monitoring points in the southern part of the Gorce Massif. However, there are numerous natural groundwater manifestations in the form of springs. The spring density index in the Kowaniec Mały catchment equals 10.9 springs/km²; this is rather typical of the Outer Carpathians, where the spring density index is estimated as 5–15 springs/km² on average (Ziemońska, 1973; Chowaniec and Witek, 1997). For the Gorce Massif, this index varies considerably, from 4.2 springs/km² in the upper part of the Kamienica catchment to 29.8 springs/km² in the upper part of Poniczanka drainage basin within the Krynica and Bystrica subunits of the Magura Nappe (Langer, 1985; Satora *et al.*, 2010). In the study area, springs are usually covered by debris and/or weathered rocks. They are mostly rheocrene springs that drain well-oxygenated water, flowing down the slope of the terrain (gravity springs) and remove mud and silt particles to uncover a sandy or gravel bottom (Table 1).

In the study area, the spring discharge rates were generally one order of magnitude lower than those observed in the northern part of the Gorce Massif (Langer, 1985; Stępień and Stożek, 2013). They belong to Mainzer's discharge classes VIII and VII (Table 2). However, the greater rates of discharge (equal to Mainzer's class VI) were recorded in cased springs.

The majority of springs under study drain waters of the hypergene zone. Their discharge rates strongly depend on weather conditions; some of the springs dry out owing to prolonged drought periods and some of them can change the outflow position, as a result of major variation in the recharge volume (e.g., springs No. 6, 9, 10).

In the study area, the water flows towards the local

**Table 1**

The types of springs documented in the study area.
Unclassified – due to closed casing.

| Spring type | | Percentage [%] |
|---|---|---|
| Genesis and aquifer media character | Rock | 6 |
| | Debris | 9 |
| | Weathered cover | 33 |
| | Mixed | 40 |
| | Unclassified | 12 |
| The type of water overflow onto the land surface | Rheocrene | 61 |
| | Helocrene | 18 |
| | Limnocrene | 6 |
| | Unclassified | 15 |
| The nature of the hydraulic head in the aquifer at the point of discharge | Gravity | 79 |
| | Artesian | 5 |
| | Unclassified | 16 |

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**Table 2**

Physicochemical properties and chemical composition of groundwater in the Kowaniec Mały catchment, S Gorce Massif. The properties of groundwaters from National Environmental Monitoring Network are presented for comparison (Chemizm, 2016; Monitoring, 2016). TDS – total dissolved solids, Eh – redox potential, SC – specific conductance.

| Spring No | Sampling season | X | Y | Q | pH | Eh | SC | T | $SO_2$ | $O_2$ | TDS | $HCO_3^-$ | $SO_4^{2-}$ | $Cl^-$ | $Ca^{2+}$ | $Mg^{2+}$ | $Na^+$ | $K^+$ | Water type |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Poland CS92 | | [m³/d] | = | [mv] | [µS/cm] | [°C] | [mmol/dm³] | | [mg/dm³] | | | | | | | | |
| 1 | | 578333 | 182669 | 1.47 | 7.54 | 487 | 90.9 | 13.5 | 0.08 | 7.3 | 162.6 | 105.83 | 14 | 3.83 | 35.59 | 1.56 | 1.17 | 0.64 | HCO3-Ca |
| 2 | | 579236 | 183828 | 0.6 | 7.06 | 521 | 139.1 | 8.5 | 0.05 | 8.7 | 113.3 | 71.28 | 8 | 5.18 | 25.97 | 1.36 | 0.91 | 0.66 | HCO3-Ca |
| 3 | | 579472 | 184043 | 0.6 | 7.44 | 459 | 169.4 | 13.1 | 0.03 | 8.6 | 154.2 | 102.29 | 11 | 3.55 | 32.38 | 3.21 | 1.15 | 0.64 | HCO3-Ca |
| 4 | | 579622 | 184374 | 5.44 | 7.52 | 622 | 135.9 | 7.6 | 0.03 | 8.7 | 123.9 | 82.02 | 6 | 5.32 | 27.25 | 1.61 | 1.07 | 0.64 | HCO3-Ca |
| 5 | | 579886 | 183408 | 10.8 | 7.18 | 545 | 197.5 | 7.4 | 0.02 | 9.2 | 181.0 | 114.61 | 19 | 4.96 | 37.35 | 3.45 | 1.03 | 0.58 | HCO3-Ca |
| 6 | | 579962 | 183720 | 0.86 | 7.2 | 402 | 80.9 | 10.4 | 0.02 | 7.7 | 178.0 | 124.14 | 10 | 2.46 | 35.51 | 3.31 | 1.73 | 0.88 | HCO3-Ca |
| 7 | August 2012 | 578843 | 182990 | 0.69 | 7.28 | 514 | 308.7 | 9.5 | 0.02 | 8.8 | 282.8 | 194.08 | 18 | 5.53 | 57.23 | 4.86 | 2.06 | 1.06 | HCO3-Ca |
| 8 | | 579052 | 183081 | 0.6 | 7.94 | n/a | 241.4 | 7.3 | 0.08 | 8.9 | 213.1 | 148.06 | 12 | 2.88 | 44.49 | 3.26 | 1.59 | 0.84 | HCO3-Ca |
| 9 | | 578669 | 182434 | 0.26 | 6.58 | n/a | 90.8 | 9.2 | 0.11 | 6.4 | 90.7 | 52.85 | 12 | 3.03 | 19.96 | 0.63 | 1.14 | 1.04 | HCO3-SO4-Ca |
| 10 | | 579487 | 182792 | 0.17 | 6.94 | n/a | 66.1 | 14 | 0.08 | n/a | 88.1 | 50.04 | 14 | 2.18 | 19.32 | 1.17 | 0.85 | 0.49 | HCO3-SO4-Ca |
| 11 | | 578242 | 182445 | 6.13 | 7.29 | n/a | 241.7 | 7 | 0.07 | 7.2 | 196.9 | 120.72 | 23 | 6.52 | 38.48 | 6.18 | 1.31 | 0.72 | HCO3-Ca-Mg |
| 12 | | 578955 | 182677 | 0.43 | 7.37 | n/a | 243.8 | 11.1 | 0.04 | 9.4 | 216.9 | 138.78 | 19 | 5.88 | 47.37 | 3.36 | 1.29 | 1.19 | HCO3-Ca |
| 13 | | 580242 | 184102 | 0.43 | 6.91 | n/a | 168.7 | 13.4 | 0.02 | n/a | 166.5 | 120.96 | 2 | 3.47 | 35.11 | 3.6 | 1.02 | 0.37 | HCO3-Ca |
| 14 | | 579993 | 184547 | 0.17 | 7.04 | 425 | 188.4 | 8.2 | 0.03 | n/a | 173.1 | 118.03 | 10 | 4.47 | 34.31 | 4.23 | 1.3 | 0.72 | HCO3-Ca |
| 15 | | 580234 | 184305 | 1.47 | 6.94 | n/a | 232.5 | 9.9 | 0.00 | 8.0 | 201.8 | 143.56 | 9 | 1.46 | 39.52 | 6.42 | 1.09 | 0.77 | HCO3-Ca-Mg |
| 2 | | 579236 | 183828 | 0.86 | 7.04 | n/a | n/a | 4.8 | 0.02 | n/a | 173.2 | 116.89 | 11 | 2.05 | 39.76 | 1.5 | 1.31 | 0.65 | HCO3-Ca |
| 5 | | 579886 | 183408 | 4.32 | 7.51 | 449 | 228.6 | 4.8 | 0.02 | 9.7 | 138.4 | 81.44 | 23 | 1.32 | 25.49 | 4.83 | 1.71 | 0.64 | HCO3-SO4-Ca |
| 6 | | 579962 | 183720 | 0.86 | 6.97 | 510 | 84.0 | 4.9 | 0.01 | 10.2 | 84.9 | 48.82 | 9 | 4.96 | 18.44 | 1.71 | 1.67 | 0.33 | HCO3-Ca |
| 7 | | 578843 | 182990 | 2.16 | 7.62 | n/a | 290.0 | 5.4 | 0.02 | n/a | 242.9 | 158.31 | 19 | 4.4 | 50.98 | 7.14 | 2.19 | 0.87 | HCO3-Ca |
| 8 | | 579052 | 183081 | 0.86 | 7.53 | n/a | 223.0 | 5.7 | 0.02 | 10.3 | 203.5 | 131.95 | 14 | 10.35 | 38.96 | 5.47 | 1.94 | 0.83 | HCO3-Ca |
| 9 | February 2013 | 578669 | 182434 | 3.02 | 7.61 | n/a | n/a | n/a | 0.02 | 5.2 | 176.2 | 102.53 | 23 | 4.47 | 38.32 | 4.59 | 2.45 | 0.79 | HCO3-SO4-Ca |
| 10 | | 579487 | 182792 | 0.43 | 7.06 | 512 | 61.6 | 2.7 | 0.02 | 10.8 | 66.5 | 35.82 | 13 | 1.04 | 14.27 | 1.06 | 1 | 0.35 | HCO3-SO4-Ca |
| 11 | | 578242 | 182445 | 4.32 | 7.75 | 417 | 232.0 | 5.6 | 0.02 | 9.3 | 201.5 | 121.94 | 23 | 5.25 | 40.08 | 6.89 | 3.22 | 1.16 | HCO3-Ca-Mg |
| 14 | | 578955 | 182677 | n/a | 7.38 | 519 | 150.2 | 5.2 | 0.02 | 8.8 | 154.3 | 105.29 | 9 | 2.83 | 28.22 | 5.42 | 2.72 | 0.83 | HCO3-Ca-Mg |
| 15 | | 580234 | 184305 | 2.59 | 7.43 | 459 | 193.5 | 2.2 | 0.02 | 9.7 | 183.4 | 119.5 | 14 | 5.88 | 35.91 | 5.21 | 2.21 | 0.66 | HCO3-Ca |
| 16 | | 579655 | 183205 | 1.3 | 7.49 | 441 | 214.0 | 3.7 | 0.02 | 8.5 | 193.2 | 114.61 | 24 | 5.46 | 39.12 | 6.5 | 2.21 | 1.28 | HCO3-Ca-Mg |
| 17 | | 578354 | 182722 | 0.6 | 7.42 | 434 | 158.2 | 3.3 | 0.02 | 10.1 | 128.9 | 78.24 | 13 | 4.32 | 29.18 | 1.89 | 1.53 | 0.69 | HCO3-Ca |
| 18 | | 579416 | 182916 | 0.86 | 7.64 | 505 | 233.0 | 2.8 | 0.02 | 10.7 | 206.0 | 124.62 | 25.00 | 3.69 | 43.9 | 6.10 | 1.98 | 0.68 | HCO3-Ca |
| Monitoring network | | | | | | | | | | | | | | | | | | | |
| 141 (Poręba Wielka) | 2004-2005 | | | | 9.13 | n/a | 1746 | n/a | 0.14 | n/a | 534.4 | 326.5 | < 1 | 5.31 | 1.17 | 0.66 | 147.34 | 1.00 | HCO3-Na |
| 520 (Ochotnica Dolna) | 2004-2007, 2012 | | | | 7.54 | n/a | 1821 | 11.7 | 0.14 | 7.8 | 306.1 | 191.78 | 15.38 | 3.74 | 55.82 | 10.95 | 3.00 | 1.10 | HCO3-Ca |
| PL0550A (meteo station) | 2002-2014 | | | | 5.25 | n/a | 25.3 | n/a | n/a | n/a | 7.9 | 1.04 | 3.18 | 1.19 | 1.46 | 0.18 | 0.42 | 0.40 | SO4-Cl-Ca |

TDS – total dissolved solids, Eh – redox potential, SC – specific conductance, n/a – not analyzed. Position of springs: X – easting [m], and Y – northing [m], coordinate system Poland CS92

groundwater drainage base which is the Kowaniec Mały Stream, a 5th order watercourse. The drainage base for the area of south-west, southern and eastern parts of the Gorce Massif is the Dunajec river (Małecka *et al.*, 2007; Nowicki *et al.*, 2009). The area of the western, north-west and partly northern parts of the Gorce Massif is drained by the Raba's tributaries (Cieszkowski, 2006b).

## SAMPLING AND METHODS

The spring documentation and mapping were performed during field seasons in August 2012 and February 2013

with use of GPS receiver GARMIN 60CSX and Topographic Map of Poland on a scale of 1:10000 (Mapa, 2002). The data collected were processed using ArcGIS to prepare maps of spring location against the background of the surface geology (Fig. 3) and maps of groundwater TDS (total dissolved solids) distribution compared to land surface slopes (Fig. 5). Physicochemical parameters, such as specific conductance (SC), water temperature (T), pH, redox potential (ROP) and dissolved oxygen (DO), were measured in 33 springs (the total number of measurements in both research seasons was 46) by means of a CX-401 Elmetron multimeter with an oxygen sensor and electrodes attached. Spring discharge rates were estimated using a calibrated container and
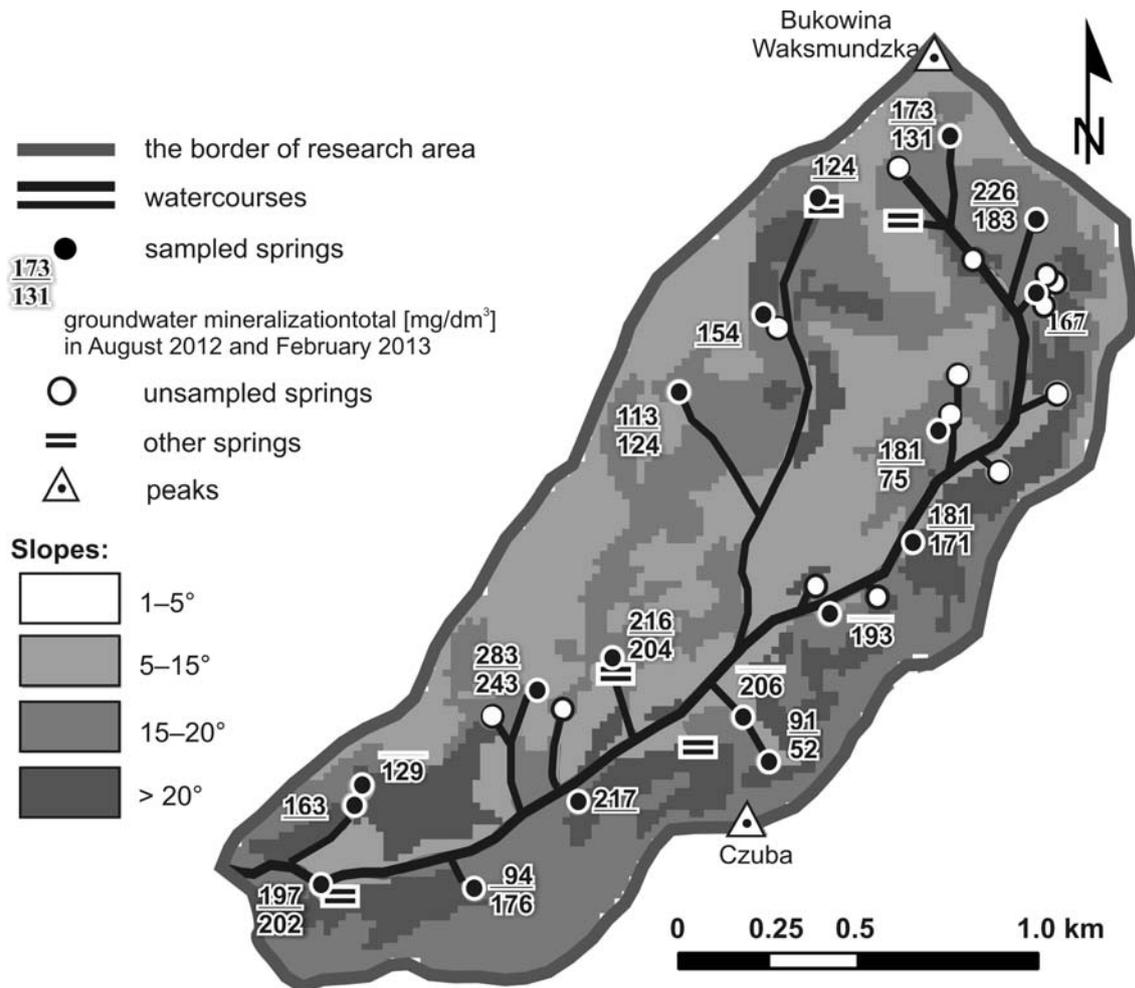
**Fig. 5.**     Spatial distribution of groundwater TDS (total dissolved solids) compared with the slopes of the land surface in the Kowaniec Mały catchment.

a stopwatch. On the basis of spring mapping, 18 representative springs were chosen for water sampling and chemical analyses. Water samples were collected in 0.7 L polyethylene bottles two times: in summer 15 samples and in winter 13 samples; 10 springs were sampled twice. The chemical analyses were carried out in the Laboratory of Hydro-geochemistry and the Laboratory of Water, Soil and Rocks Chemistry at the Faculty of Geology University of Warsaw, Warsaw, Poland. The content of $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, and $HCO_3^-$ ions were determined by titration methods. The concentrations of $SO_4^{2-}$ and $NO_3^-$ anions were measured using the DR-2000 HACH spectrophotometer. The content of $Na^+$ and $K^+$ cations and elemental Si were determined by means of the ICP-FAAS (Inductively Coupled Plasma – Flame Atomic Absorption Spectrometry) method.

## RESULTS AND DISCUSSION

### Field measurements and groundwater chemistry

The physicochemical properties and chemical composition of the water collected from 18 springs are presented in Table 2.

One of the most variable parameters of the groundwaters studied was temperature, which revealed considerable seasonal variation in the range of +1.4 to +11.3 °C (Tab. 2). Such variations in groundwater temperature indicate a strong connection with local rainfall events or snow thawing and a shallow circulation depth. Moreover, it was clearly observed that springs located at greater altitudes had lower temperatures of the discharged water.

The pH values of the water examined are typical for fresh groundwater of the Gorce Massif, falling within the range of 6.4–8.3 (Satora and Tylek, 1992; Satora *et al.*, 2010). The values of Eh from 400 to 622 mV are characteristic for groundwater directly recharged by fresh, oxygenated meteoric water (Macioszczyk and Dobrzyński, 2007). The dominant concentrations of dissolved oxygen were found to be around 8 mg/dm³ (85% of the measurements).

The TDS (total dissolved solids) values were between 66.5 mg/dm³ and 282.8 mg/dm³ (Tab. 2, Fig. 5). The lowest TDS value was measured in groundwater from spring number 10, located in conglomeratic sandstones and conglomerates of the Upper Eocene (Fig. 3). The highest TDS value was found in water from spring number 7, situated below an extensive landslide developed in the Kowaniec Beds, where
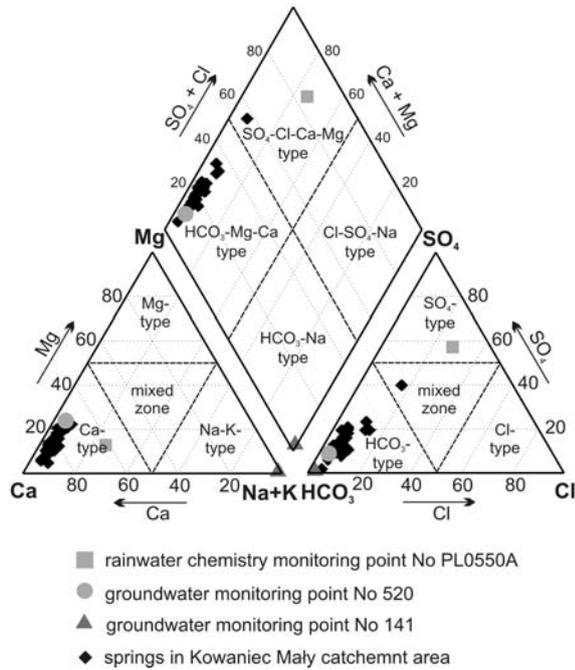
Fig. 6.    Piper diagram for the chemical composition of groundwater in the Kowaniec Mały catchment, SE Gorce Massif. Rainwater and groundwater monitored at the National Environmental Monitoring Network are shown for reference.
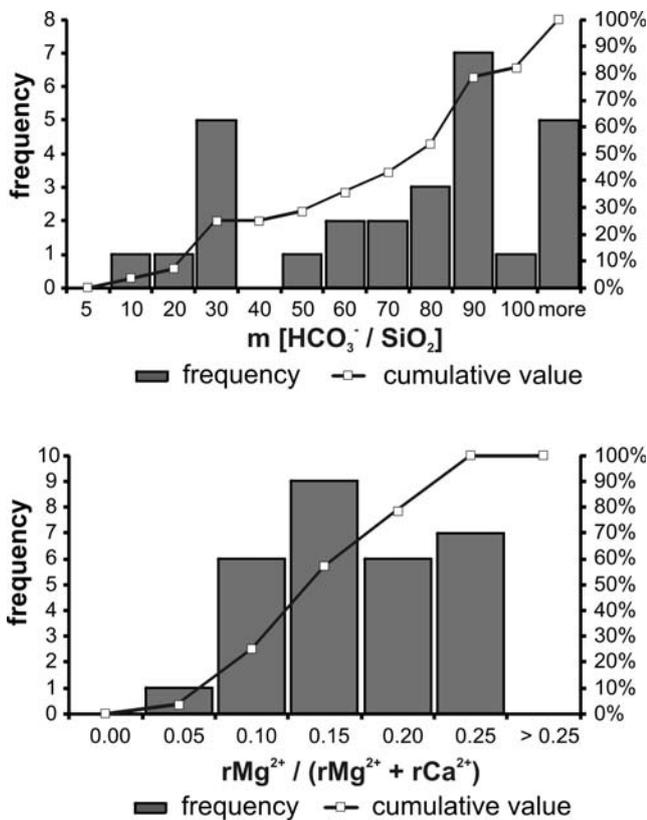


Fig. 7.    Frequency distribution of m[HCO$_3^-$/SiO$_2$] and r[Mg$^{2+}$/ (Ca$^{2+}$+Mg$^{2+}$)] ratios in groundwater of the Kowaniec Mały catchment; m – concentration in mmol/dm$^3$, r – concentration in meq/dm$^3$.

land surface slopes are between 10–15 (Figs 3, 5). There is a clear dependence between groundwater TDS and the altitude of the spring occurrence: groundwater with lower TDS values are found in springs located at higher altitudes; for example: springs 4, 2 and 14 are located higher and reveal lower groundwater TDS than springs 11, 12 and 18 (see Figs 3, 5). By comparison, the TDS values of groundwater drained by springs occurring in the Krosno Beds, the Hieroglyphic Beds and the Palaeogene Łącko Beds in the upper part of Mszanka drainage basin (northern part of the Gorce Massif) are within the range of 173–303 mg/dm$^3$ (Satora and Tylek, 1992).

However, the TDS values for groundwater monitored at intakes of National Environmental Monitoring Network are much higher, e.g. (Monitoring, 2016): monitoring point number 141 (well), TDS = 524.75–561.16 mg/dm$^3$; and monitoring point number 520 (spring), TDS = 255.83–298.16 mg/dm$^3$.

Such a difference may be connected first of all with the positions of the monitoring points. The springs within the Kowaniec Mały catchment generally are located at higher altitudes (i.e. 730–1049 m a.s.l.) than the groundwater monitoring points of national network; point number 141 is located at 510 m a.s.l., and point number 520 at 600 m a.s.l. (System, 2016a). The positions of the monitoring points at lower altitudes are related to longer distances of groundwater discharge from the recharge zone, higher infiltration depths and longer times of the water residence in the geologic environment. All of these factors have an influence on the increase of groundwater TDS in the discharge zone. The positive relationship between groundwater TDS and circulation depth is also noticeable in the case of the monitoring point at Poręba Wielka, where acratopegae were found in a confined aquifer at a depth of 30 m.

Groundwaters in the Kowaniec Mały catchment belong to three hydrochemical types, namely: (i) HCO$_3$-Ca , (ii) HCO$_3$-Ca-Mg and (iii) HCO$_3$-SO$_4$-Ca (Tab. 2, Fig. 6). Such a chemical composition is typical of shallow groundwater in the Polish Outer Carpathians (Chowaniec, 2009). Rainwater monitored at the meteorological station in Turbacz belongs to the SO$_4$-Cl-Ca-Mg type. Within the study area, groundwater of the HCO$_3$-Ca type predominates and any variations in major ion content usually indicate differences in aquifer lithology, circulation paths or local geochemical conditions. Waters of the HCO$_3$-SO$_4$-Ca type collected from springs 9 and 10 are the least mineralized and well-oxygenated (max 10.8 mg/dm$^3$ of dissolved O$_2$). They represent shallow groundwaters of the near-surface zone, directly recharged by atmospheric precipitation or snow thawing in the area covered by conglomeratic sandstones and conglomerates of Upper Eocene age. Waters of the HCO$_3$-Ca-Mg type were found in springs 5, 11, 14, and 16. They also are connected with a shallow, near-surface circulation zone of landslides, developed in the Kowaniec Beds (Tab. 2, Fig. 3,).

On the other hand, the groundwater monitored at Ochotnica Dolna (spring, No. 520) and Poręba Wielka (well, No. 141) in the northern part of the Gorce Massif belongs to the HCO$_3$-Ca and HCO$_3$-Na types, respectively. They are connected with water-bearing horizons of the Eocene Turbacz Beds and the Oligocene Krosno Beds and are characterized by higher TDS values, presumably due to greater distances

Selected ionic ratios in groundwater of the Kowaniec Mały drainage basin; rain water and groundwater from National Environmental Monitoring points are presented for reference. Concentrations expressed in: meq/dm$^3$ – r, mmol/dm$^3$ – m.

| Spring nu,ber | Sampling season | $r\dfrac{Na^+ + K^+}{Cl^-}$ | $m\dfrac{HCO_3^-}{SiO_2}$ | $r\dfrac{Mg^{2+}}{Ca^{2+} + Mg^{2+}}$ | $m\dfrac{SiO_2}{Na^+ + K^+ - Cl^-}$ | $r\dfrac{Ca^{2+}}{SO_4^{2=}}$ | $r\dfrac{SO_4^{2-} \cdot 100}{Cl^-}$ |
|---|---|---|---|---|---|---|---|
| 1 | | 0.62 | 22.76 | 0.07 | < 0 | 6.08 | 270.4 |
| 2 | | 0.39 | 21.47 | 0.08 | < 0 | 7.76 | 114.4 |
| 3 | | 0.66 | 48.04 | 0.14 | < 0 | 7.06 | 229.0 |
| 4 | | 0.42 | 52.47 | 0.09 | < 0 | 10.88 | 83.3 |
| 5 | | 0.43 | 85.87 | 0.13 | < 0 | 4.71 | 282.9 |
| 6 | | 1.42 | 132.70 | 0.13 | 0.61 | 8.52 | 301.4 |
| 7 | | 0.75 | 146.28 | 0.12 | < 0 | 7.62 | 240.4 |
| 8 | August 2012 | 1.11 | 29.58 | 0.11 | 7.27 | 8.88 | 308.6 |
| 9 | | 0.91 | 7.94 | 0.05 | < 0 | 3.98 | 294.1 |
| 10 | | 0.82 | 10.40 | 0.09 | < 0 | 3.30 | 478.7 |
| 11 | | 0.41 | 27.78 | 0.21 | < 0 | 4.01 | 260.3 |
| 12 | | 0.52 | 57.19 | 0.11 | < 0 | 5.97 | 238.6 |
| 13 | | 0.54 | 86.76 | 0.15 | < 0 | 41.71 | 42.9 |
| 14 | | 0.60 | 74.27 | 0.17 | < 0 | 8.23 | 165.1 |
| 15 | | 1.63 | 261.11 | 0.21 | 0.3 | 10.49 | 458.5 |
| 2 | | 1.28 | 96.00 | 0.06 | 1.18 | 8.66 | 394.8 |
| 5 | | 2.43 | 66.5 | 0.24 | 0.43 | 2.66 | 1294.6 |
| 8 | | 0.58 | 80.00 | 0.13 | < 0 | 4.89 | 134.3 |
| 7 | | 0.94 | 108.66 | 0.19 | < 0 | 6.42 | 319.4 |
| 8 | | 0.36 | 86.97 | 0.19 | < 0 | 6.66 | 100.00 |
| 9 | | 1.01 | 73.82 | 0.16 | < 0 | 3.99 | 380.2 |
| 10 | February 2013 | 1.79 | 29.50 | 0.11 | < 0 | 2.63 | 934.5 |
| 11 | | 1.15 | 84.93 | 0.22 | 1.19 | 4.18 | 323.6 |
| 14 | | 1.74 | 86.50 | 0.24 | 0.33 | 7.49 | 235.0 |
| 15 | | 0.68 | 124.64 | 0.19 | < 0 | 6.14 | 175.9 |
| 16 | | 0.84 | 81.52 | 0.22 | < 0 | 3.90 | 324.7 |
| 17 | | 0.70 | 67.30 | 0.10 | < 0 | 5.37 | 222.1 |
| 18 | | 0.99 | 86.72 | 0.19 | 7.14 | 4.21 | 501.0 |
| 141 | 2004–2005 | 1.50 | 38.50 | 0.48 | 0.04 | 8.71 | 304.8 |
| 520 | 2004–2007, 2012 | 42.90 | 21.75 | 0.24 | 7.92 | 2.76 | 14.0 |
| Rain | 2002–2014 | 0.85 | – | 0.13 | – | 1.11 | 194.1 |

from the recharge zones and deeper circulation pathways.

The chemical composition of groundwater is a consequence of the wide range of variable geochemical processes occurring within the geological environment, e.g. water–rock interactions, redox processes, hydrothermal reactions, and water mixing (Hounslow, 1995). The chemical composition of groundwater in the Kowaniec Mały catchment presumably is formed by dissolution/precipitation reactions during water interaction with the aquifer rocks. The ion exchange reactions and local variation in redox conditions also might have an influence on the final chemical composition of the groundwater studied. In the case of waters of a shallow circulation zone, the initial influence of rain water may be significant. The mixing of hypergene zone waters with groundwater of a deeper regional flow system is rather limited. The hydrogeological conditions in the study area are not favourable for very deep infiltration of atmospheric precipitation. There are no deep faults or fissures and all documented springs drain shallow groundwater systems.

**Formation of groundwater chemical composition**

A detailed analysis of the selected ionic ratios was performed in order to determine the origin of the chemical composition of the groundwater studied and to identify the source rocks of the major ions dissolved in the water. Interpretation of the ionic ratio is usually applied to the hydro-geochemical characterization of groundwater, to source rock identification or prospecting for mineral deposits (e.g., Macioszczyk, 1987; Hounslow, 1995; Porowski, 2001, 2006).

Table 3 shows the most important ionic ratios calculated and applied in this study.

The initial composition of shallow groundwater originates from rainfall. During surface runoff and underground
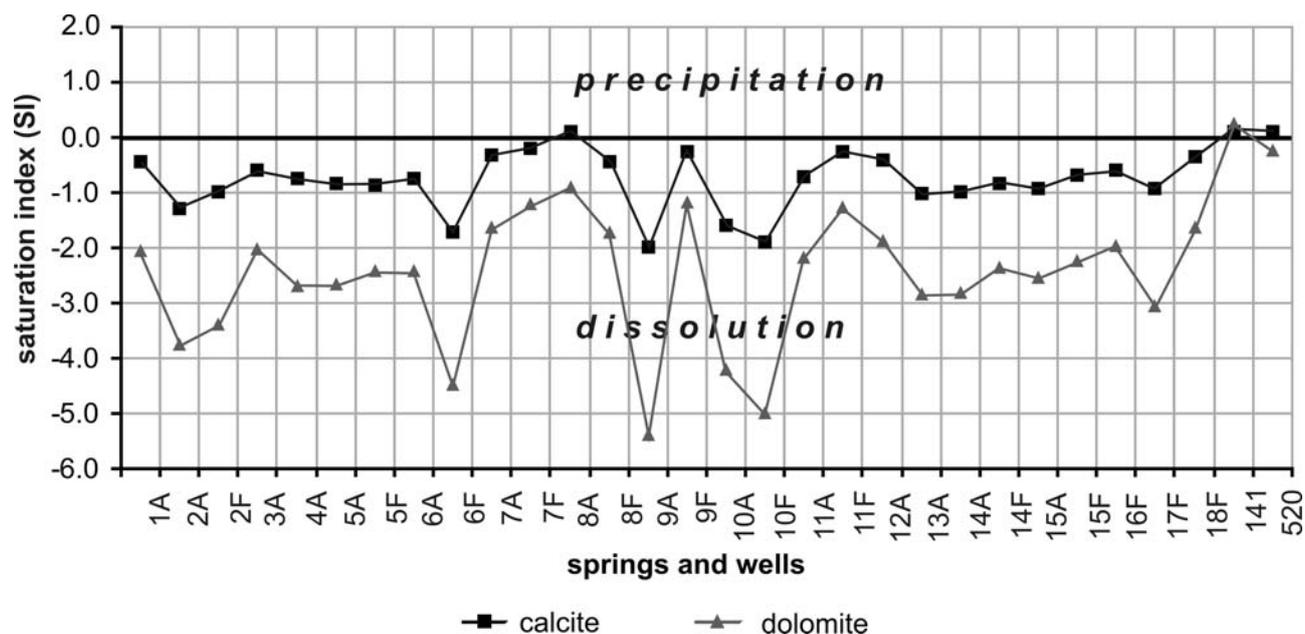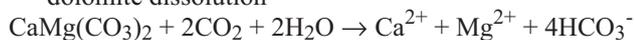
**Fig. 8.**    Saturation index (SI) for calcite and dolomite in groundwater of the Kowaniec Mały catchment. Monitoring points at Poręba Wielka (141) and Ochotnica Dolna (520) are presented for reference. A – August, F – February.

flow, water composition is altered mainly by evaporation, aeration and interaction with rocks (e.g., Hounslow, 1995). During rock weathering, $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$, $HCO_3^-$ and $SiO_2$ are added to the water. The amount of each ion depends on the rock mineralogy. In many cases, the minerals of the source rocks can be deduced from ionic ratios.

*Carbonate dissolution*

Bicarbonate and calcium ions predominate in the chemical composition of the groundwater of the Kowaniec Mały catchment. A simple bicarbonate – silica ratio $m[HCO_3^-/SiO_2]$ expressed in $mmol/dm^3$, can be used to distinguish between carbonate and silicate weathering (Hounslow, 1995). Bicarbonate is formed, when $CO_2$ and water react with various minerals in the process of acid hydrolysis. Carbonates dissolve without releasing silica, whereas the dissolution of silicates may release considerable amounts of silica, e.g. dissolution of albite. A $m[HCO_3^-/SiO_2]$ ratio greater than 10 is usually considered as the indicator of carbonate dissolution and less than 5 as the indicator of silicate dissolution; the ratio between 10 and 5 indicates an ambiguous situation. All groundwaters in the study area, except for spring No. 9, reveal a ratio greater than 10, namely from about 21 to 261 (Fig. 7, Tab. 3). The water form spring No. 9, taken in the summer period, shows a value of around 7.9. This strongly indicates that the dissolution of carbonates plays a crucial role in the formation of the chemical composition of groundwaters in the southern part of the Gorce Massif. Generally, in low-temperature systems carbonates, mainly calcite, are known to be the most liable to dissolution and subsequent recrystallization. Typical reactions of carbonate dissolution can be written as follows:

dolomite dissolution
$$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$$
calcite dissolution
$$2CaCO_3 + 2CO_2 + 2H_2O \rightarrow 2Ca^{2+} + 4HCO_3^-$$

The ratio $r[Mg^{2+}/(Ca^{2+}+Mg^{2+})]$, expressed in $meq/dm^3$, assists an understanding of which carbonate minerals undergo dissolution to a greater extent. When $m[HCO_3^-/SiO_2]$ > 10, as in the case of the groundwaters studied, the values of the $r[Mg^{2+}/(Ca^{2+}+Mg^{2+})]$ ratio of around 0.5 indicate dolomite weathering, below 0.5 limestone dissolution, and above 0.5 dolomite dissolution or calcite precipitation (Fig. 7).

The values of $r[Mg^{2+}/(Ca^{2+}+Mg^{2+})]$ ratio in the groundwaters of the Kowaniec Mały catchment are clearly below 0.5, indicating that the $Ca^{2+}$ concentration is much greater than that of $Mg^{2+}$. This strongly indicates that limestone dissolution is the main process of water-rock interaction responsible for $Ca^{2+}$ and $Mg^{2+}$ concentrations in the groundwaters studied. The water from monitoring point No.141 at Poręba Wielka, in the northern part of the Gorce Massif, reveals this ratio to be around 0.48, which shows that also dolomite weathering or calcite precipitation may occur when the water resides longer and infiltrates deeper in the geological environment. Favourable geochemical conditions for carbonate dissolution and/or precipitation are corroborated by the saturation index  (SI) values (Fig. 8).

The aquifer rocks in the study area are composed of limestone, dolomite and marl grains bounded by calcite or silica cement and are present in the Turbacz Beds, the Kowaniec Beds and conglomeratic sandstones and conglomerates of the Upper Eocene (Burtan *et al.*, 1978a).

*Halite dissolution and rainfall*

Chlorides are among the most conservative constituents of groundwater. The sources of chlorides are very limited in the geological environment and they behave conservatively in the majority of geochemical processes connected with water evaporation, dilution, diagenetic water-rock interaction reactions (Carpenter, 1978; Hem 1989; Hounslow, 1995; Appelo and Postma, 1996, Porowski, 2001). The primary source of chloride in shallow groundwater usually is

the dissolution of sodium chloride (NaCl). The process of NaCl salinity formation in groundwater can occur in two ways: (a) directly, through water contact with halite and dissolution of natural evaporite deposits, for example, in the present study, there may have been water contact with small amounts of evaporitic grains or chloride salts formed during subaerial evaporation of rain water; and (b) indirectly, when groundwater originates from the evaporation of ocean water via rainfall. The r[Na/Cl] ratio (r is expressed in meq/dm$^3$) can be used in the preliminary identification of the origin of chloride-sodium salinity in groundwater. The ratio that is typical of the average composition of the ocean water is around 0.87, with the assumption that $Na^+ = Na^+ + K^+$. This value remains constant during the simple dissolution of ocean water or its subaerial evaporation until halite starts to precipitate (Carpenter, 1978). The same value of this ratio is characteristic of meteoric water, originating mainly from seawater aerosols and evaporation over the oceans. The values of this ratio of close to 1.0 indicate that the chloride salinity originates from dissolution of chloride evaporites, mainly halite, which can be formed during various processes of evaporation of meteoric water or groundwater in the hydrological cycle (Fig. 9).

As can be seen in Fig. 9, about 50% of groundwaters in the Kowaniec Mały catchment reveal a r[Na$^+$/Cl$^-$)] ratio within the range of what is typical for ocean water and halite. This strongly indicates that the sodium – chloride mineralization comes form: (i) the variation in the Cl$^-$ content of rain water due to the varying degree of subaerial evaporation of rain water during rainfall and infiltration (i.e. the Na/Cl ratio typical for ocean water remains constant), and (ii) the direct dissolution of halite contained in the soil and aquifer rocks or formed during the subaerial evaporation of rain water on the ground surface (i.e. a Na/Cl ratio close to 1.0). On the other hand, the non-conservative behaviour of alkali metals (i.e. Na$^+$ and K$^+$) in the geological environment is responsible for values of this ratio that are less than 0.5 or much greater than 1.0. In the first case, depletion in Na$^+$ may be the result of ion exchange reactions and sodium removal from solution, e.g. reverse ion exchange reactions (for further explanation, see the next chapter). In the second case, the excess of Na$^+$ (together with K$^+$) in groundwater over the concentration compensated by halite chloride indicates the occurrence of so-called non-halite sodium, which is assumed to originate from aluminosilicate weathering (mainly albite) or ion exchange reactions, e.g. natural softening (for an explanation: see the next chapter).

### Silicates dissolution and ion exchange

Silica in shallow groundwater is usually derived from the weathering of aluminosilicates. The ionic ratio of m[SiO$_2$/(Na$^+$+K$^+$-Cl$^-$)], expressed in mmol/dm$^3$, is considered to reflect ion exchange between water and clay minerals or the hydrolysis of alkali feldspars, mainly albite (Hem, 1985; Hounslow, 1995). In principle, this index shows the ratio of the so-called non-halite sodium to SiO$_2$ and helps to identify the sources of silica and sodium dissolved in the groundwater. An excess of silica over non-halite sodium indicates the weathering of granite or basalt. Values of this ra-
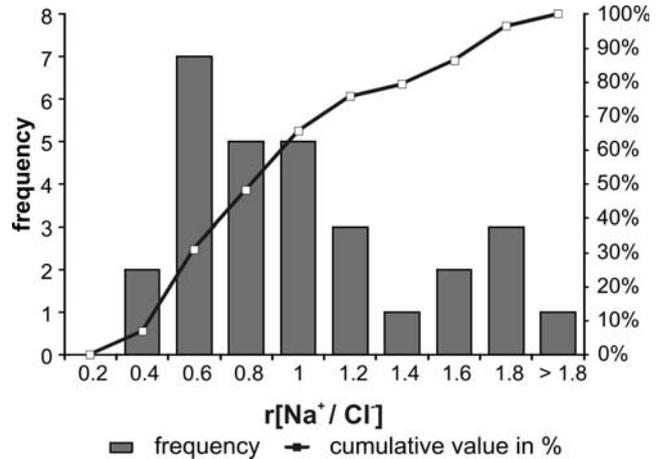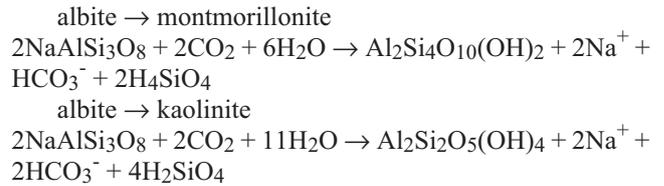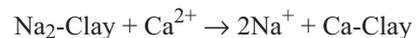


**Fig. 9.**  Frequency distribution of r[Na$^+$/Cl$^-$)] ratio in groundwater of the Kowaniec Mały catchment; here Na$^+$ = Na$^+$ + K$^+$, r – concentration in meq/dm$^3$.

tio between 1 and 2, i.e. SiO$_2$>(Na$^+$+K$^+$-Cl$^-$) and SiO$_2$<2 (Na$^+$+K$^+$-Cl$^-$), indicate that the hydrolysis of alkali feldspars may be the main process of incorporation of Na$^+$ ions into the solution. It is assumed that primarily albite is dissolved and the solid weathering product formed is either kaolinite or montmorillonite:

albite → montmorillonite
$2NaAlSi_3O_8 + 2CO_2 + 6H_2O → Al_2Si_4O_{10}(OH)_2 + 2Na^+ + HCO_3^- + 2H_4SiO_4$
albite → kaolinite
$2NaAlSi_3O_8 + 2CO_2 + 11H_2O → Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_2SiO_4$

Values of this ratio greater than 2 indicate considerable excess of silica over sodium plus potassium. Such a situation indicates that the rocks subjected to weathering contain a considerable quantity of sodium-poor ferromagnesian silicates, such as olivine, pyroxene or amphibole (Hounslow, 1995).

Where the SiO$_2$ concentration is less than that of non-halite Na, i.e. the ratio is below 1, cation exchange is probably the source of most of the excess sodium. In aquifers containing montmorillonitic clay, natural softening by ion exchange may occur, i.e. both Ca$^{2+}$ and Mg$^{2+}$ can be removed from water and replaced by Na$^+$ (Hounslow, 1995):

$Na_2$-Clay + Ca$^{2+}$ → 2Na$^+$ + Ca-Clay

Distribution of m[SiO$_2$/(Na$^+$+K$^+$-Cl)] ratio in groundwater studied is shown in Fig. 10.

Majority of waters studied (about 70% of water samples taken for analysis) reveal depletion in alkali metals, i.e. concentration of SiO$_2$ is greater than Na$^+$ and K$^+$ and a total concentration of alkali metals is less than Cl$^-$, and there is no sodium excess that could be considered as additional non-halite sodium. This chemical composition of the groundwaters studied indicates that they belong to a very shallow zone of active groundwater exchange and contain a considerable admixture of fast infiltrating rainwaters. The source
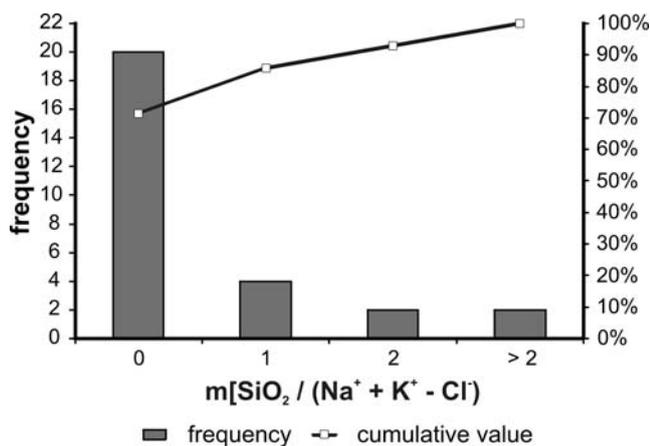
**Fig. 10.** Frequency distribution of m[SiO$_2$/(Na$^+$+K$^+$-Cl)] ratio in the groundwater of the Kowaniec Mały catchment; m – concentration in mmol/dm$^3$.

of SiO$_2$ in the groundwater studied is connected mainly with the weathering of granite, basalt and sodium-poor ferromagnesian silicates. On the other hand, the ion exchange processes may also be responsible for the removal of alkali metals from solution. Such processes are known as reverse ion exchange or reverse softening and require the presence of clay with exchangeable calcium (e.g. usually montmorillonite) and water higher in sodium than the clay-exchange equilibrium concentration (Hounslow, 1995). Reverse softening can be written as follows:

$$2Na^+ + Ca\text{-}Clay \rightarrow Na_2\text{-}Clay + Ca^{2+}$$

The remaining groundwaters (i.e. about 30%) have variable concentrations of SiO$_2$ and non-halite Na$^+$. In such a case, the m[SiO$_2$/(Na$^+$+K$^+$-Cl)] ratio shows a wide range of values from below 1 to above 2, which indicates also that aluminosilicate weathering is the main process responsible for the concentration of silica and alkali metals in the groundwaters.

### Pyrite oxidation and/or gypsum dissolution

Primary sources of sulphate (SO$_4^{2-}$) in groundwater are usually minerals such as pyrite (FeS$_2$), gypsum (CaSO$_4$ · 2H$_2$O) or anhydrite (CaSO$_4$), as well as organic sulphur compounds formed during the combustion of coal and petroleum and incorporated into groundwater via rainfall or snow melt (Hounslow, 1995; Appelo and Postma, 1996). The ratio r[Ca$^{2+}$/SO$_4^{2-}$], expressed in meq/dm$^3$, allows a distinction to be made between sulphates originating from direct dissolution of gypsum (and anhydrite) and the neutralization of acid waters by limestone or dolomite. In favorable hydrogeological conditions (e.g. the absence of intensive carbonate dissolution), gypsum dissolution is indicated by relatively equal concentrations of Ca$^{2+}$ and SO$_4^{2-}$ in water, which gives a value of r[Ca$^{2+}$/SO$_4^{2-}$] ratio around 1.0 (Fig. 11).

Where the Ca$^{2+}$ concentration is clearly lower than SO$_4^{2-}$ the ratio is less than 1.0, which usually indicates pyrite oxidation or Ca$^{2+}$ removal from solution in the process of calcite precipitation or ion exchange (i.e. natural soften-
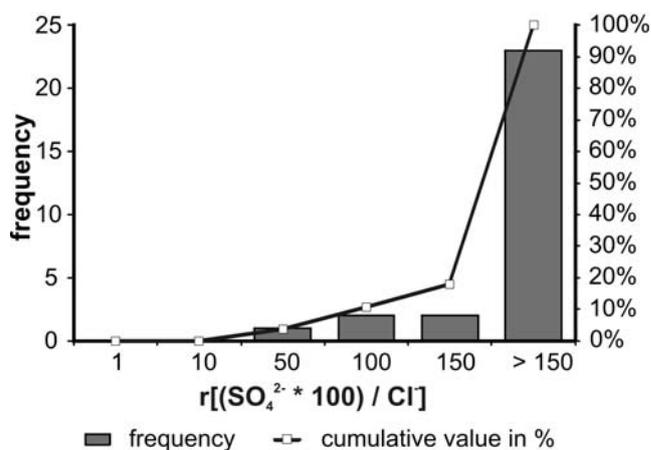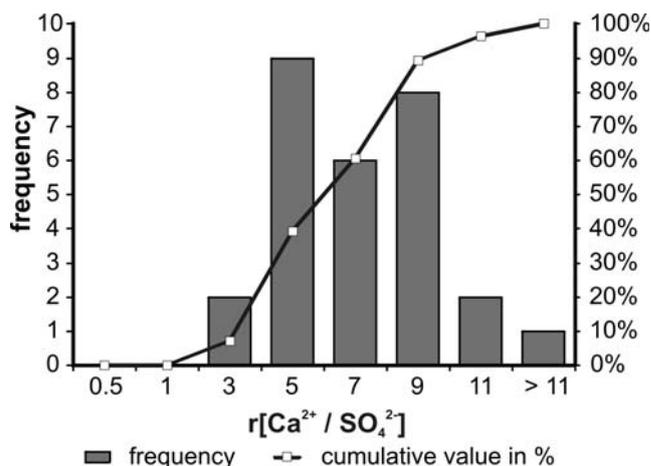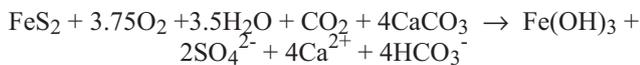




**Fig. 11.** Frequency distribution of r[Ca$^{2+}$/SO$_4^{2-}$] and r[(SO$_4^{2-}$ ×100)/Cl] ratios in groundwater of the Kowaniec Mały catchment; m – concentration in mmol/dm$^3$.

ing). However, all groundwaters in the Kowaniec Mały catchment have this ratio greater than 1.0 (i.e. Ca$^{2+}$ concentration exceeds considerably SO$_4^{2-}$ content; Fig. 11, Tab. 2), which indicates an excess of calcium ions and a Ca$^{2+}$ source other than gypsum, presumably calcite and/or silicates. In a geological environment where carbonates are present in aquifer rocks, which is the case of the Kowaniec Mały catchment, it is admittedly not possible to differentiate the sources of sulphates only on the basis of ionic ratios due to an excess of Ca$^{2+}$. In the present study, it is likely that the sulphates in the groundwater come from various sources. Because of the very low SO$_4^{2-}$ concentrations in the groundwater studied, ranging from 2 to 25 mg/dm$^3$, the most probable sources of sulphates are (i) atmospheric sulphates, namely, SO$_4^{2-}$ contained in recharge meteoric waters, i.e. snow and rainfall (Cook *et al.*, 2000), or (ii) reduced inorganic sulphur compounds dispersed in fine-grained sedimentary rocks, mostly in the form of pyrite, which undergoes oxidation during rock weathering, and finally (iii) gypsum, although its contribution may depend on the extent of local evaporation processes.

In the case of the springs located at higher altitudes in the Gorce Massif, the infiltration of meteoric water (rainfall, snow melt) seems to be the most important source of dis-

solved $SO_4^{2-}$. This is corroborated by the fact that sulphates are dominant in the chemical composition of rain water monitored at the meteorological station in Turbacz; its hydrochemical type is $SO_4$-Cl-Ca (Tab. 2). On the other hand, a clear relationship between the altitude of spring position and the $SO_4^{2-}$ content in water indicates the role of sulphide mineral oxidation. The groundwater from springs, located higher in the mountains (e.g., springs No. 4, 13, 14, 15, located in the vicinity of Bukowina Waksmundzka), have the lowest $SO_4^{2-}$ concentrations, whereas in the groundwater from the springs located closer to local drainage base, near Kowaniec Mały and its estuary, the sulphate content increases, undoubtedly owing to water-rock interaction processes that take place along the flow paths of the groundwater. The most probable reaction for pyrite oxidation in the presence of calcite can be written as follows (after Hounslow, 1995):

$$FeS_2 + 3.75O_2 + 3.5H_2O + CO_2 + 4CaCO_3 \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4Ca^{2+} + 4HCO_3^-$$

Pyrite oxidation will only occur in the presence of dissolved oxygen, which is the case for the groundwater in the Kowaniec Mały catchment (see Tab. 2). The process assumes the precipitation of insoluble ferric hydroxide. However, ferric iron will remain in solution at low pH values and may accumulate in solution as ferrous iron under anoxic conditions.

The $r[(SO_4^{2-} \times 100)/Cl^-]$, expressed in $meq/dm^3$, usually indicates the character of the geologic environment of groundwater occurrence (e.g., Macioszczyk, 1987; Razowska, 1999). Low values of this ratio, below $1.0 – 10.0$, indicate a strongly reducing environment. Values within the range of several tens and more are characteristic for shallow meteoric waters in the active exchange zone in an oxidizing environment (Tab. 3, Fig. 11). Groundwaters in the Kowaniec Mały catchment and the water monitored in Ochotnica Dolna have this ratio in the range from 42 to more than 1000 (i.e. 1294 for waters of spring No. 6), which indicates oxidizing conditions in the shallow zone of active groundwater exchange. This additionally is corroborated by the high content of dissolved $O_2$ and high positive Eh values from 400 to 622 mV (Tab. 2).

The oxidizing conditions in the groundwater horizons of the Kowaniec Mały drainage basin undoubtedly facilitate the oxidation of pyrite grains, existing in the mineralogical composition of Kowaniec Beds and conglomeratic sandstones and conglomerates of Upper Eocene age (Burtan *et al.*, 1978a). The lowest value of the $r[(SO_4^{2-} \cdot 100)/Cl^-]$ ratio of around 14 was found in groundwater from the well monitored at Poręba Wielka, where the concentration of $SO_4^{2-}$ was below 1 $mg/dm^3$ (Tab. 3). This indicates a much deeper zone of groundwater occurrence – the total depth of the well at Poręba Wielka is about 100 m – and a much more reducing environment, probably favorable for sulphate reduction processes.

A detailed analysis of the ionic ratios of the groundwater, drained by springs in the Kowaniec Mały catchment, revealed considerable similarities with the groundwater monitored in the Ochotnica Dolna spring (monitoring point No.
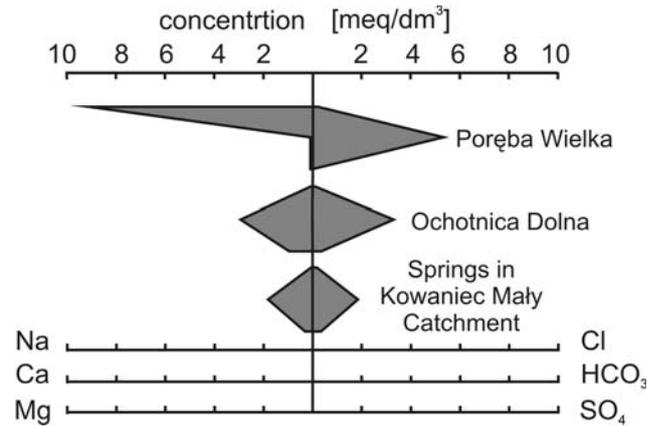


**Fig. 12.** Stiff diagrams for groundwater from the Kowaniec Mały drainage basin and northern parts of the Gorce Massif, based on monitoring points No. 520 (Ochotnica Dolna) and 141 (Poręba Wielka).

520), which belongs to the area of Kamienica catchment, in the north-eastern part of the Gorce Massif (Fig. 12).

On the other hand, the groundwater studied differs considerably in chemical composition, total dissolved solids content and dominant water-rock interaction processes from the groundwater monitored at Poręba Wielka (monitoring point No. 141; Fig. 12). The groundwater at Poręba Wielka is extracted from the well at a depth of about 100 m and is considered to be among the oldest fresh groundwater in the Outer Carpathians – similar to that found at Zawoja – observed in the National Environmental Monitoring Network (Chowaniec, 2009).

## CONCLUSIONS

Groundwaters in the Kowaniec Mały catchment, in the southern part of the Gorce Massif., belong to three hydrogeochemical types, namely $HCO_3$-Ca , $HCO_3$-Ca-Mg and $HCO_3$-$SO_4$-Ca. The physicochemical parameters of these waters – such as pH values that are close to the pH of rainwater, significant seasonal fluctuation in groundwater temperature, very low groundwater TDS (below 500 $mg/dm^3$), a redox potential typical of oxidizing conditions, and dissolved oxygen concentrations higher than 8 $mg/dm^3$ – all indicate their occurrence in the upper hydrogeochemical zone, at a shallow depth where active groundwater exchange occurs. The relatively rapid circulation and formation of the chemical composition are influenced mainly by surface relief, the occurrence of landslides and aquifer mineralogy.

The detailed analysis of ionic ratios shows that the dissolution of carbonates, mainly calcite, plays a crucial role in the formation of the chemical composition of groundwaters in the study area. This process is responsible for the acquisition of dominant ions, such as $HCO_3^-$ and $Ca^{2+}$. On the other hand, the hydrolysis of aluminosilicates is responsible for the occurrence of $SiO_2$ in solution and partly for the $Na^+$ and $K^+$ concentrations. Aluminosilicate hydrolysis occurs during the weathering of granitic or basaltic rock grains contained in the sandstones with a solid weathering product

formed as clay minerals (e.g. kaolinite or montmorillonite); additionally, ions of $HCO_3^-$ are incorporated into the aqueous phase. The main chloride – sodium mineralization of the groundwater studied, which is usually from 1.5 to 5 times greater than that observed in rain water at the nearest meteorological station (see Tab. 2), is presumably obtained owing to two processes: (i) the variation of $Cl^-$ content in rain water due to the varying degree of subaerial evaporation of rain water during rainfall and infiltration (i.e. the Na/Cl ratio typical of ocean water remains constant) and (ii) direct dissolution of halite contained in the soil, aquifer rocks or formed during the subaerial evaporation of rain water on the ground surface (i.e. Na/Cl ratio close to 1.0). The source of dissolved $SO_4^{2-}$ in the groundwaters studied can be variable, namely: (i) atmospheric sulphates, i.e. sulphates contained in meteoric recharge waters, and/or (ii) sulphide minerals dispersed in fine-grained sedimentary rocks, mostly pyrite, which undergo oxidation during rock weathering, or (iii) gypsum, the amount of which depends on the extent of local evaporation processes. Moreover, processes of ion exchange involving clay minerals are also present; they affect mainly the concentrations of $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$, e.g. natural softening ($Na^+$ is transferred into the solution). The localization of the Kowaniec Mały drainage basin within the range under nature conservation indicates that this area is not subjected to intensive human influences. However, the proximity of urban settlements (e.g. Nowy Targ), the local hydrogeological conditions, and most importantly the vulnerability of the groundwater to possible contamination, indicate the necessity for the establishment of stations for the monitoring of groundwater quality in this part of the Gorce Massif.

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