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title: Groundwater chemistry in the area of the Ryjak Catchment (Magurski National Park, SE Poland)

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INTRODUCTION

Water chemistry in the Carpathian Mountains has been the subject of research since the 19th century. In the early years, researchers were mostly set on the discovery of mineral water aquifers. Although a great deal of groundwater research has been conducted in the Carpathians — especially in the last twenty years — still little is known about the groundwater chemistry of the eastern part of the Western Carpathians. The purpose of this paper is to present the spatial distribution of water outflows and their hydrochemical properties in the Ryjak catchment area, located in the southern part of Magurski National Park (SE Poland).

STUDY AREA

The research study was conducted in July and August of 2006, during a period of low precipitation (10 mm in July and 40 mm in August) in the catchment of Ryjak (45 km^2). It is situated, for the most part, within Magurski National Park, however, the upper part of the catchment consists of rural areas located in the park's outer fringe zone. Average elevation across the study area does not exceed 600 m. Its bedrock consists of Magura Nappe-type Carpathian flysch such as fine-grained sandstone and shale.

METHODS

Springs of interest were mapped and their discharge as well as basic physical and chemical properties (temperature, pH, SEC_{25}) measured *in situ*. The concentration of selected ions was analyzed using a Dionex ICS-2000 ion chromatography system. The following ions were analyzed: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, Li^{+}, HCO_3^{-}, SO_4^{2-}, Cl^{-}, NO_3^{-}, NO_2^{-}, PO_4^{3-}, F^{-}, Br^{-}. Aqueous Fe samples were acidified and analyzed using a Merck SQ 118 photometer. A cooled $CO_{2(aq)}$ sample was titrated within four hours of sample collection.

RESULTS

The total ion content of groundwater outflows was determined to be within 70–650 $mg \cdot dm^{-3}$. The chemical composition varied spatially, especially in the case of Na^{+}, K^{+}, SO_4^{2-}, and Cl^{-}. The carbon dioxide level detected in the springs of interest approached 80 $mg \cdot dm^{-3}$, which created favorable conditions for the precipitation of travertine as well as ferrous species. Most of the tested outflows (60%) were of a simple HCO_3–Ca type or an HCO_3–SO_4–Ca type (33%) based on the Szczukariew-Priklonski classification system. However, three outflows were discovered to have an atypical for this particular catchment, but already well known in the Carpathian Mountains (Rajchel 2002), type of water labeled HCO_3–Ca–Mg and HCO_3–Ca–Na (Fig. 1). The greatest degree of diversity in water chemistry was detected in springs located at the point of contact between variegated Eocene shale and shale with sandstone inserts in the northern part of the catchment. However, springs with the highest overall ion content were found in Oligocene sandstone, close to Dąb Mountain. The maximum discharge of the tested springs was found to be 1 $dm^3 \cdot s^{-1}$, however, most of the springs produced much smaller rates of discharge.

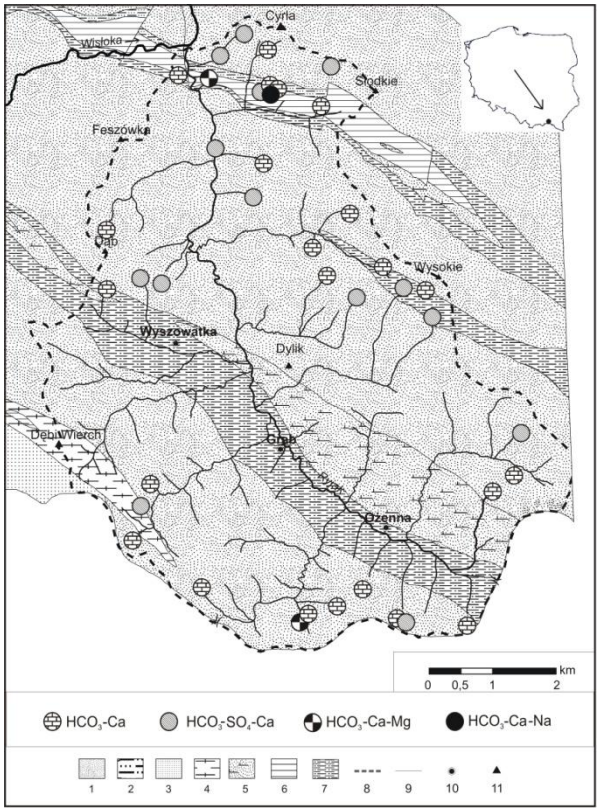

Figure 1. Hydrochemical classes of springs, based on on Szczukariew-Priklonski classification, in Ryjak catchment on geological map (self-processing based on A. Slaczka 1968): 1 — Oligocen thick-layered sandstone and shale (Magura beds); 2 — Eocene shale with sandstone insert (Magura beds); 3 — Eocene thick-layered sandstones (Magura beds); 4 — Eocene shale and thin-layered sandstones (Hieroglyphic and Magura beds); 5 — Eocene shale and thin-layered sandstones (Hieroglyphic and Beloweza beds); 6 — Eocene variegated shale; 7 — Eocene shale with sandstone-insert and shale with thin-layered sandstone (Magura and Hieroglyphic beds); 8 — Watershed; 9 — Streams; 10 — Villages; 11 — Main peaks.

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