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ISOTOPIC INVESTIGATION OF NITRATES IN HORYNIEC-ZDRÓJ WATERS

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ABSTRACT

In this work the isotopes of oxygen and nitrogen were determined in nitrates of water samples collected in Horyniec Zdrój and they allowed the preliminary indication of the source of NO_3^- ion. The obtained $\delta^{15}N$ and $\delta^{18}O$ values of nitrates dissolved in the Róża III therapeutic water are +2.1, +13.1 ‰, respectively. They indicate the origin of NO_3^- ion from bacterial decomposition of organic matter which is abundant in the aquifer.

Interpretation of the processes affecting the chemical and isotopic composition of investigated waters was possible by taking into account earlier isotopic analyses as well as chemical composition, geological structure and hydrogeological conditions prevailing in the aquifer. The results and discussion presented in this paper have excluded the possible influence of external contaminants in Horyniec-Zdrój waters used for therapeutic purposes.

Keywords: mineral and therapeutic waters, nitrate concentration, $\delta^{15}N$ and $\delta^{18}O$ in nitrates (NO_3^-), Horyniec-Zdrój

1. INTRODUCTION

Natural differences among stable isotope distribution in nature enable to use them as a source of information about processes occurring in the environment. Isotope ratio mass spectrometry (IR-MS) which is used for determination of stable isotopes in environmental samples allows to answer questions very precisely about the origin of the substance, the reasons for the increase or decrease of its concentration and the processes which modify its composition. In the Horyniec-Zdrój spa located on the edge of the Carpathian Foredeep, water from the Róża III intake (type HCO_3-SO_4, -Ca-Mg-Na, H_2S) is drawn from the Miocene formations for balneotherapy. Thanks to conducted therapies, diseases of the digestive system, rheumatism, musculoskeletal, cartilage and nerve pain are treated there. Horyniec-Zdrój is also famous for one of the largest peat deposits in Poland. Peat is an organic material, which is the product of decomposition of plants, and is characterized by high thermal capacity and low conductivity. These properties enable medicinal mud to treat inflammation of the affected tissues successfully.

Thanks to extensive determinations of isotopic ratios of $\delta^{18}O$, δD (in water) and $\delta^{34}S$ and $\delta^{18}O$ (in SO_4^{2-} ion) made so far (Baran & Hałas, 2010), the origin of Róża III water was recognized and the process of bacterial reduction of sulfate to hydrogen sulfide in the aquifer was indicated as a dominant factor influencing hydrogeochemistry of this water. According to Hałas et al. (2002) the genesis of hydrogen sulfide in the Horyniec area is associated with gypsum present in Miocene series of evaporates correlating chronologically with gypsum-anhydrite deposits in Kuczery village near Horyniec (Parafiniuk & Hałas, 1997; Bukowski & Szaran, 1997; Peryt et al., 1998; 2002).

Research conducted from 1995 to 2001 showed that the therapeutic waters from Horyniec do not contain tritium and ^{14}C determination suggested the age of the late Holocene (Ciężkowski et al., 2003). Assuming then, that the water from an adjacent hole S-II (located approximately 900 meters north of Róża III and IV wells) is recent, we concluded that the water exploited from the Róża III intake should be dated for the late Holocene, definitely for less than 3 thousand years, or rather in the range of 500–2,500 years (Baran & Hałas, 2010). Current measurements of ^{14}C, ^{4}He and the concentration of Ne, Ar, Kr, Xe provided additional information regarding the age and the inflow temperature of the water from Róża III intake (Palcsu et al., 2012). It turns out that these determinations rather confirm the mid-Holocene age of the investigated water ($^{14}C = 25.55$ pmc, estimated age ~ 6000 years). The calculated inflow temperature, which is approx. 7.3°C, corresponds to the average middle Holocene air temperatures in the study area.

During this work the colorimetric determinations of nitrate concentrations in the water sample from Róża III intake and surface water sample from the Radrużka river (flowing through Horyniec-Zdrój) were performed. In the same samples a double isotope marker which is $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- ion dissolved in water was determined. The goal of this research is to explain the origin of nitrates in water, which may deteriorate the therapeutic water quality. The isotopic composition of dissolved nitrate is modified by known processes of the nitrogen cycle in soil and groundwater such as: assimilation, mineralization, nitrification and denitrification. Other studies showed that the nitrates derived from the nitrogen of mineral compounds in the soil are isotopically different from nitrates derived from fertilizers (Aravena & Robertson, 1998; Kendall et al., 2007). This information allowed us to indicate the source of NO_3^- ion in the examined water samples.

2. GEOLOGICAL SETTING AND HYDROGEOLOGICAL CONDITIONS

Horyniec-Zdrój is located near the Polish border with Ukraine, near the Roztocze Rawskie chalk hills on the edge of the Carpathian Foredeep. The Roztocze anticline, uplifted in the course of tectonic movements during the Tertiary, was definitively developed during Quaternary. The area extending to the north of the Carpathian Foredeep where the Miocene sediments occur, forms a depression (Oszczypko, 1999). The geological profile of this depression shows a significant differentiation in both the vertical and horizontal directions. Their main rock complexes are chemical deposits represented by gypsum and salt evaporates, chloride facies of the deposits of rock salt (in the vicinity of the Carpathian Foredeep and partly beneath it, where the Miocene sediments are folded), whereas in their northern part, in the vicinity of Horyniec-Zdrój the sulfate facies with anhydrites occur (Dowgiałło, 1969; Oszczypko, 1981).

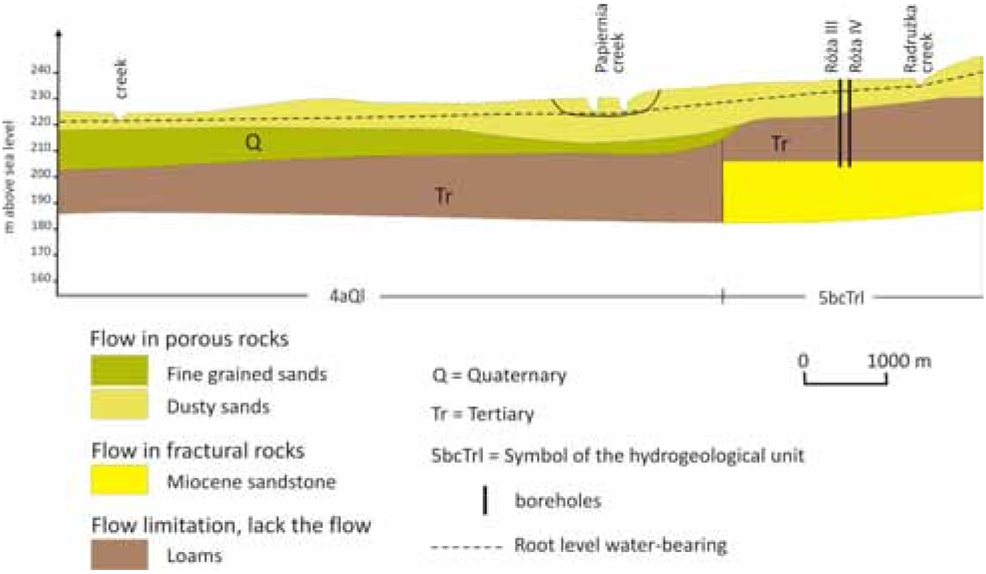

Figure 1: Geological cross-section of aquiferous layers of Roztocze Rawskie, (taken from Meszczyński & Dziewa, 2002, modified by the Authors).

Formation waters of sulfate-calcium, sulfide and calcium chlorine-anhydrite types, and specific poorly mineralized sulfide waters (Paczyński, Sadurski (ed.), 2007) are associated with these forms. Younger and more resilient Tertiary deposits, calcareous sandstones and limestones overlie older chalk forms, forming the framework of the whole Roztocze region. They are arranged as moraine clay lobes and sands of glacial origin.

Horyniec aquifer is associated primarily with limestone, sand and tertiary and Miocene sandstone (Fig. 1). Therapeutic water is drawn from the "Róża III" borehole with a depth of 29 m. Silty clays isolate this water which is present in fine-grained sands below, whereas at the bottom of this layer there is a layer (40 cm thick) of flint rubble. At a depth of 8–12 m some medium grained sands with fragments of limestone were found. The hydrogen sulfide in the examined therapeutic water is associated with the Horyniec sulfide post gypsum carbonates called "ratyńskie limestone". The spa area forms a shallow basin, which is filled with younger Neogene deposits, called "Krakowiec clays" and a thin layer of Quaternary deposits. These series are very resistant to erosion and contributed to mild geomorphological forms.

The hills and slopes are mostly covered by postglacial material like clays and sands, with dusty gritty loess. On the other hand, in the river valleys there are forms typical of river's accumulation: sands, gravels and silts. Marsh peats occur mostly in the wetlands. Neogene deposits are represented by the complex of lower Miocene limestone and gypsum, whilst the upper Miocene by the Krakowiec clays.

3. CHARACTERISTICS OF THE EXAMINED WATER

Chemical analysis of the therapeutic waters from Horyniec-Zdrój (Table 1) indicates that it is a 4-ions type HCO_3^--Ca^{2+}-Na^+-SO_4^{2-} water. Among the anions, HCO_3^- ion (396.5 mg/dm^3) and the cations, Ca^+ ion (92.8 – 105.5 mg/dm^3) are predominant. The concentration of $CaCO_3$ in the examined water is 296.5 mg /dm^3 and pH value varies in the range of 7.1 to 7.3. These values are indicative for slightly basic and medium hard waters. The sulfate content is from 96.7 to 124.8 mg/dm^3. The examined water shows high hydrogen sulfide concentration fluctuating from 12.2 to 44.9 mg H_2S/dm^3.

TABLE 1: Compiled chemical composition of the investigated water* (all values are given in mg/dm^3).

Well (analysis date)		TDS (mg/dm^3)	H_2S	HCO_3^-	Ca^{2+}	Na^+	Cl^-	Fe^{2+}	SO_4^{2-}	SiO_2	Mg^{2+}	K^+	F^-	Mn^{2+}
Róża III	III. 1960	573	17	n.m.	n.m.	n.m	27.0	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
	VII. 1989	548	44.9	n.m.	105.5	51.0	20.4	0.4	n.m.	n.m.	18.9	9.0	0.3	n.m.
	V. 2002	512	n.m.	396.5	92.8	53.0	14.7	0.02	124.8	45.0	15.4	9.7	0.25	0.01

*The results of chemical analyses of groundwater – archival materials – sources representative (PGI) Porwisz et al., 2002 (elaboration). Analyses performed by the laboratory of the Geological Enterprises Polgeol SA in Warsaw, TDS = total dissolved solids, n.m.= not measured.

Water from the Miocene aquifer is generally characterized by a high coloration caused by dissolved organic compounds produced in the coalification of organic matter. The total mineralization is higher than 500 mg/dm^3. The predominant chemical type of such water is HCO_3-Ca-Mg. However, such typical Miocene water is not classified as Horyniec-Zdrój water. Water from Róża III intake does not show elevated content of iron and manganese, and no water treatment is required.

4. MEASUREMENT METHODS OF ISOTOPIC COMPOSITION

In this study of $\delta^{15}N$ and $\delta^{18}O$ of the NO_3^- ion, the amount of water needed to be sampled for analysis depends on the concentration of nitrates. In order to determine the minimum amount of water sample for further studies and to select samples characterized by an increased amount of nitrate, concentration of NO_3^- was measured using a portable colorimeter. The minimum amount of nitrate for isotopic analysis is approximately 20 mg. In Radrużka creek the nitrate concentration was lower than 10 mg/dm^3, therefore the water samples were collected in larger volumes (5 liter bottles). Water samples with the highest concentration of nitrates from the Róża III intake and surface water from the Radrużka creek were collected for analyses and on the same day were transported to the laboratory.

Determination of the nitrate isotopic composition ($\delta^{15}N$ and $\delta^{18}O$) of the water samples was performed in the laboratory of the Department of Environmental Physics in the Faculty of Physics and Applied Computer Science in the AGH University of Science and Technology in Kraków.

Nitrates from water samples were extracted with anion exchange resins and converted to $AgNO_3$ by neutralization of the obtained HNO_3 with Ag_2O. Subsequently $AgNO_3$ was prepared chemically to obtain CO_2 and N_2 gases whose isotopic composition was measured using a mass spectrometer (Silva et al., 2000;

Chang et al., 2004; Chmura, 2008; Chmura et al., 2009). Determined $\delta^{15}N$ and $\delta^{18}O$ values were expressed relative to the isotopic composition of atmospheric nitrogen and to the international VSMOW standard, respectively. Standard uncertainties of the isotopic composition were ± 0.1‰ for both $\delta^{18}O$ and $\delta^{15}N$ (Baran & Hałas, 2011).

5. RESULTS AND DISCUSSION

Isotopic differentiation of nitrogen compounds is generally the result of the kinetic fractionation occurring as a consequence of bacterial processes (Kendall et al., 2007). A significant variation of nitrogen isotope composition is observed when various contaminants are introduced into soil. Most transformations of nitrogen compounds (mainly the biogenic processes of nitrification and denitrification) lead to an enrichment in heavy nitrogen isotope of substrates and depletion of the reaction products in this isotope. The nitrification is a two-step reaction: (1) the oxidation of NH_4^+ ions to NO_2^- by *Nitrosomonas*, which is relatively slow, and (2) a rapid oxidation of NO_2^- to NO_3^- by *Nitrobacter*. The slower process is mostly responsible for the magnitude of isotope fractionation. Therefore nitrates formed in the nitrification process are isotopically lighter than ammonium ions. Their $\delta^{15}N$ is shifted towards more negative values by -12 to -29‰ (Sheaer & Kohl, 1986). Oxygen isotopic composition of newly formed nitrate comes from water (2 molecules) and the dissolved oxygen gas O_2 (1 molecule). Therefore the nitrates produced in the soil by nitrification have $\delta^{18}O$ range from -10 to 10 ‰, taking into account the range of $\delta^{18}O$ values for water (-25 to + 4‰) and air (approximately + 23‰) (Figure 2) (Baran & Hałas, 2011).

The nitrate concentration and isotopic composition of NO_3^- ion, expressed as $\delta^{15}N$ and $\delta^{18}O$ in the two representative water samples from Horyniec-Zdrój are shown in Table 2.

TABLE 2: Nitrate concentration and isotopic composition of NO_3^- ion in waters collected in Horyniec-Zdrój.

Location	Date of collection	The results of measurements		
		Nitrate concentration [mg/dm^3]	$\delta^{15}N_{Air}$ [‰]	$\delta^{18}O_{VSMOW}$ [‰]
Róża III intake	14.12.2009	94	+2.1	+13.1
Radrużka creek	14.12.2009	10	+3.4	+7.1

In water sample from the Róża III intake we observe higher value of $\delta^{18}O$, which most likely indicate biogenic origin of the nitrate ion and a limited advancement of denitrification process. However, denitrification cannot be completely excluded. The temperature of water in Róża III intake was determined on the basis of noble gases isotopes is 7.3°C (Palscu et al., 2012). This temperature refers to the time of water infiltration to the aquifer, while the temperature which is recently measured in the well is approximately 11°C, which is different from optimal temperature (25°C) for the denitrification processes. In addition, it is noteworthy that if this process was advanced, then δ^{15}N in NO_3^- ion would be more positive than it is observed.

The isotopic composition of nitrates depends on their source and δ^{18}O of water in which the nitrates are formed. The results of the present study are located in the ranges of isotopic compositions characteristic of soil nitrogen. The above data support the concept that the Horyniec-Zdrój water has natural resistance to potential anthropogenic pollution and the nitrogen in dissolved nitrates is of natural origin.

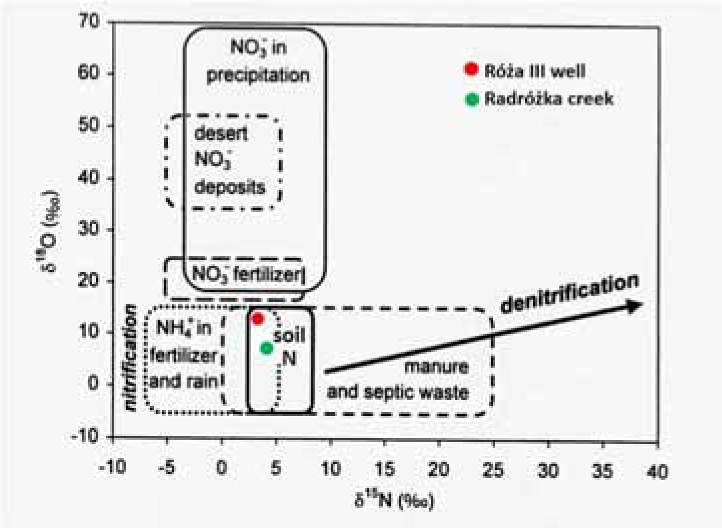

Figure 2: Oxygen δ^{18}O (NO_3^-) and nitrogen δ^{15}N (NO_3^-) in nitrate ion compared with typical ranges of variability of the isotope compositions of nitrates from various sources (Kendall, 1998).

It arises from the foregoing considerations that probably the most competitive process to denitrification in the Róża III water intake is bacterial sulfate reduction process occurring in this aquifer. In this environment the process undoubtedly is epigenetic, since sulfates are present in relatively high concentrations in these waters as a result of leaching of gypsum. Similar delta results of δ^{18}O and δ^{15}N were encountered for surface water of the Radrużka creek, for which it was expected that the nitrate ion is of soil origin due to very low pollution of this water.

6. CONCLUSION

The results of the previous studies on chemical and isotopic composition of sulfide waters from Róża III intake in Horyniec-Zdrój confirm that their therapeutic properties and quality are good and the water is of middle Holocene age. High concentration of nitrates in Horyniec-Zdrój water is a result of bacterial decomposition of organic matter. Nitrogen in the therapeutic water occurring as NO_3^- ion is derived from mineralization and nitrification of the organic matter during decomposition of plant material. The results of this study on the isotopic composition of oxygen $\delta^{18}O$ and nitrogen $\delta^{15}N$ in NO_3^- ion in water from the Róża III intake and the Radrużka creek surface water confirm this hypothesis. Therefore it may be excluded that the origin of nitrates in the examined water samples is anthropogenic (e.g. livestock effluent or nitrate fertilizers). Considering geology of the study area and stable isotope data, it can be concluded that Horyniec-Zdrój therapeutic water is well protected from anthropogenic pollution.

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