Vol. 9, No. 2, 2015 Chemical Technology

Kseniia Bystrevska[1], Valentina Pidlisnyuk[1] and Stefan Aschenbrenner[2]

RESEARCH OF THE RADIOACTIVE AND PHYSICO-CHEMICAL CHARACTERISTICS OF THERMAL GROUND WATERS IN THE SLOVAK REPUBLIC AND TRANSCARPATHIAN REGION, UKRAINE

[1]Department of the Environment, Faculty of Natural Resources, Matej Bel University in Banska Bystrica, 55, Tajovskeho str., 97401 Banska Bystrica, the Slovak Republic; valentina.pidlisnyuk@umb.sk
[2]Slovak Water Management Committee, branch in Banska Bystrica, 69, Partizanska cesta , 97498 Banska Bystrica, the Slovak Republic

Received: November 06, 2014 / Revised: November 17, 2014 / Accepted: February 20, 2015

Abstract. The thermal ground waters used for spa complexes in Zilinsky and Banskobystricky regions in the Slovak Republic and in Beregovo, Transcarpathian region, Western Ukraine, were analyzed for gamma-radiation level, content of selected radioactive elements and physico-chemical characteristics. Comparative analysis of the thermal ground waters showed that waters in Beregovo had the highest radiation level in terms of gamma spectrum, which was about two times higher than the limit; in contrast, radiation levels of research sites in the Slovak Republic were within Slovakian standard limits. The concentrations of radioactive elements Ra^{226} and U in the thermal ground waters in Beregovo, Ukraine and in Turčianske Teplice, the Slovak Republic were within the limit.

Researched thermal ground waters in the Slovak Republic and Ukraine had similarities in geomorphological characteristics and tectonic background. However, physico-chemical characteristics of waters were diverse: while SO_4^{2-} and HPO_4^{2-} concentrations were close for all research tests, waters in Beregovo showed highest levels of concentrations of Ca^{2+}, Na^{+}, Fe^{2+}, NH_4^{+}, and Cl^{-} ions concentrations. Recommendations on improvement of the environmental situation at the research sites and further use with respect to sustainability were developed.

Keywords*:* thermal ground waters, gamma-radiation level, radioactive element, physico-chemical characteristics.

1. Introduction

Thermal ground waters have global distribution in the crust, continuously receiving heat from the depths of the Earth, and occur in the areas of current and extinct volcanic activity in tectonically active mountain-fold areas and adjacent marginal troughs and intermountain basins [1]. Such areas are closely connected with ground water springs in the Slovak Republic and Western Carpathian, Ukraine [2]. Thermal ground waters, migrating from the depths of the Earth by tectonic disturbances, react with rocks and geological materials, become saturated with different chemicals, including radioactive isotopes. Such waters are usually sated with radioactive isotopes in places reaching the surface (spring or well) and often have increased gamma radiation. Due to prolonged spa use of ground waters gamma radiation background can rise [3].

Slovakian and Ukrainian thermal ground waters have many features in common: the nature of their origin, the geomorphological and hydrological structures, and climate conditions. Changes of natural conditions of ground waters in terms of radiation and physico-chemical characteristics were shown [5-8].

Nowadays, spa complexes located in Transcarpathian region, Ukraine and Zilinsky and Banskobystricky regions, the Slovak Republic are among the most intensive users of thermal groundwater resources. It may be assumed that such exploitation may negatively influence and alter the natural ground water systems. The main goal of the research was to explore the radioactive and physico-chemical characteristics of selected spa complexes located in the Slovak Republic and Western Ukraine and to provide a comparative analysis regarding impact of their exploitation to the state of thermal ground water and to develop recommendations for further use with respect to sustainability. In the Slovak Republic Sliac, Turčianske Teplice, and Rajecke Teplice were

explored, and in the Transcarpathian region, Western Ukraine, Beregovo was explored [4].

2. Experimental

In order to overview the main radioactive and physico-chemical characteristics of thermal ground waters at spa complexes in the Slovak Republic and Ukraine the sampling of groundwater and sludge were collected at the selected sites during January-March, 2014. Samplings were analyzed for content of the radioactive elements. At all selected sites the measurement of gamma-ray spectrum and exposure rate were accomplished, as well as determination of the total specific activity of radionuclides. The physico-chemical characteristics of selected ground waters were analyzed as well.

2.1. Determination of the Exposure Rate of Gamma Radiation

Estimation of gamma radiation exposure rate of groundwater samples and gamma-activity in soils located close to the thermal ground water sources were provided by use of devices radiometer RKS-20.03 “Pripyat” and dosimeter DBG-06T (0071). Radiometer RKS-20.03 “Pripyat” allows to detect radiation in general and quickly whereas dosimeter DBG-06T allows to measure radioactivity more precisely and for longer time. Combination of data received by using of both devices allows to receive the broad and sharp data; error of measuring (in %) by using RKS-20.03 “Pripyat” was ± 25 and by using DBG-06T ± 15.

Measurement of gamma-ray radiation was provided along profile lines, equally pointed in the researched areas. Such approach was proposed in accordance with Requirements for natural radioactivity in mineral resources during Geological Prospecting and Exploration [9-12]. Overall profile lines length was about 8000 m. Consequently, for four selected research sites 31 separated profile lines were set and drawn out, specifically, there were 7 profile lines in Beregovo, 7 profile lines in Sliač, 9 profile lines in Turčianske Teplice, and 8 profile lines in Rajecke Teplice.

Altogether 101 fixed points for measurement were made along all profile lines, specifically, there were 30 points in Beregovo, 25 points in Sliač, 26 points in Turčianske Teplice, and 20 points in Rajecke Teplice.

2.2. Methods of Sampling and Laboratory Analysis of Water Samples

Water samples and sludge were taken for two water sources, located close to spa facilities in Beregovo, Ukraine and Turčianske Teplice, the Slovak Republic.

1-liter glass bottles were used for sampling, preliminary treated by 50 ml of HNO_3. After collection of water samples bottles were tightly closed and kept at those conditions during transportation. Such approach ensures preservation of immutable quality of the water in accordance with Ukrainian standards.

Analysis of water samples and sludge was done at the certified laboratory of the State Enterprise "Ukrainian Geological Company", Kyiv, Ukraine, error of measurement for all tested samples was below 8 %.

Water samples taken from other water sources: Sliač and Rajecke Teplice were analyzed at Slovak Hydrometereological Institution in accordance with EU standard approach [13-16].

3. Results and Discussion

Results of gamma-radiation survey, accomplished along research profiles for four selected places are presented in Fig. 1 and Table 1, where surpassing of estimated gamma-radiation over standard one is shown. It may be seen that research points in Beregovo, Ukraine has rather high radiation level in terms of gamma spectrum, which is about two times higher than the limit. In contrast all research sites in the Slovak Republic in accordance to gamma-radiation survey are within Slovakian standard limits [10, 7]. However, in Turčianske Teplice the level of gamma radiation has a tendency to increase.

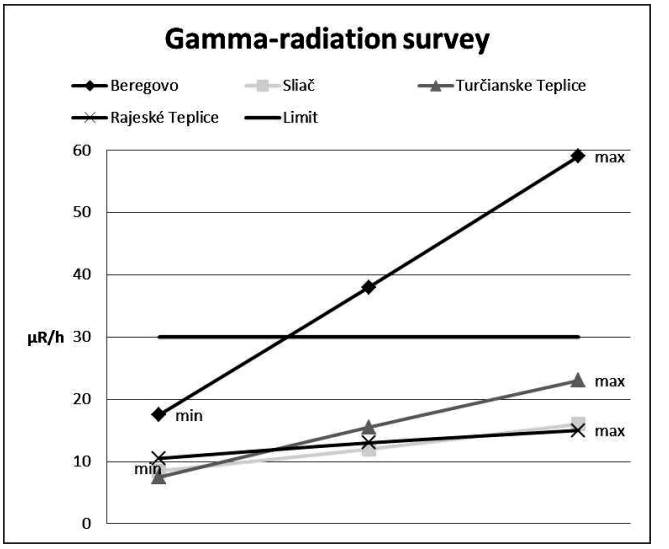

Fig. 1. Comparative analysis of gamma-radiation survey, μR/h

The estimated concentrations of radioactive elements Ra^{226} and U in the thermal ground waters for two research sites: Beregovo, Ukraine and Turčianske Teplice, the Slovak Republic, are presented in Table 2. The radioactive values are within the limits, however, in

terms of Slovakian categorization of radioactive risk (Table 3 [17], Beregovo site could be defined as B-category concerning the levels of Ra^{226}. That fact requires further research and analysis in order to explain the source of pollution.

Physico-chemical characteristics of all ground waters researched are summarized in Table 4. It may be concluded that despite ground waters similarities in terms of geomorphological characteristics, tectonic background and close location, physico-chemical characteristics for all waters are rather different.

Concerning the concentration of single elements it is seen that concentration of Ca^{2+} in Beregovo is the highest one. Concentrations of SO_4^{2-} and HPO_4^{2-} ions are rather close for all researched waters. Thermal ground waters in Beregovo show extremely high level of Na^+, Fe^{2+}, NH_4^+, and Cl^- ions concentrations as compared to other sites.

The data about changing of some physico-chemical characteristics (pH, concentration of CO_2 and anions SO_4^{2-}) of the thermal ground waters in Turčianske Teplice are shown in Figs. 2-4. It may be concluded that since 1968 till 2012 those characteristics changed greatly; in particular that effect is essential for concentration of CO_2, which may be connected with intensive use of the thermal ground waters.

The practical recommendations for mitigation of situation are about cleaning up the places of radioactive contamination in Beregovo, Ukraine and treating the wastewater and sludge before discharge. Another recommendation is about stabilization using of the thermal groundwater in Sliač, Turčianske Teplice, Rajecké Teplice, the Slovak Republic for prevention of further deterioration. Regular monitoring and control enforcing will assist positively as well.

Table 1

Comparative analysis of gamma-radiation survey, μR/h

Location	Min	Max	Average	Standard
Beregovo	17.5	59	38	30
Sliač	8.5	16	12	30
Turčianske Teplice	7.5	23	15.5	30
Rajecke Teplice	10.5	15	13	30

Table 2

Radioactive assessment of groundwater, Bq/l

Indicator/Location	Beregovo	Turčianske Teplice	Limit
Ra^{226}	0.137	0.036	1.9
U	0.035	0.037	12.1

Table 3

Categorization of radioactive risk for groundwater [17]

Indicator	Category A	Category B	Category C
Ra^{226}, Bq/l	0.05–0.1	0.1–0.5	0.5 and more

Table 4

Comparative analysis of physico-chemical assessment of groundwater

Indicators	Units	Beregovo	Sliač	Turčianske Teplice	Rajecke Teplice	Standard
Temperature	K	313.0–328.0	285.5–317.0	302.2–316.6	311.0	–
pH	pH	6.3–6.8	6.5	6.7–7.0	7.4	6.5–8.5
Ca^{2+}	Mg/l	180.0–270.0	722.2	256.9–258.1	119.0–120.6	> 30.0
Mg^{2+}	Mg/l	60.0–133.0	180.5	60.9–62.8	54.1–54.5	10.0(30.0)–125.0
Na^+	Mg/l	7306.0–9818.0	56.7	47.5	4.1–8.5	200.0
Fe^{2+}	Mg/l	0.3–1.0	< 0.01	0.014	< 0.005–0.006	0.2
NH_4^+	Mg/l	2.5–38.0	0.05	0.12	< 0.02–0.3	0.5
Cl^-	Mg/l	8686.0–13472.0	5.1	4.1	2.8–7.0	100.0–200.0
SO_4^{2-}	Mg/l	891.0–1484.0	1598.1	530.0–535.0	56.0–66.3	250.0
HPO_4^{2-}	Mg/l	0.03–0.05	< 0.03	0.02	0.02–0.05	3.5

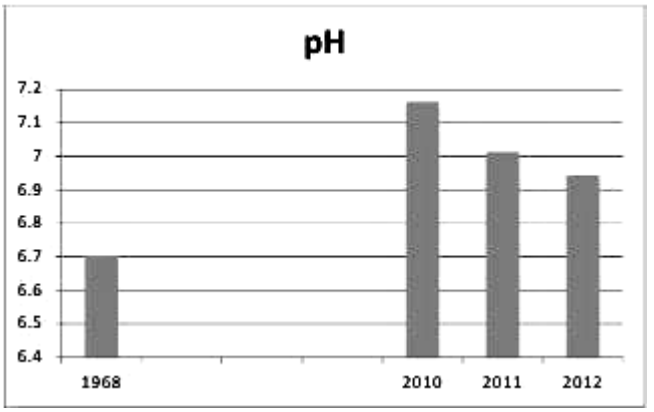

Fig. 2. pH changes, Turčianske Teplice, spring Modrý Bazén, well TM-19

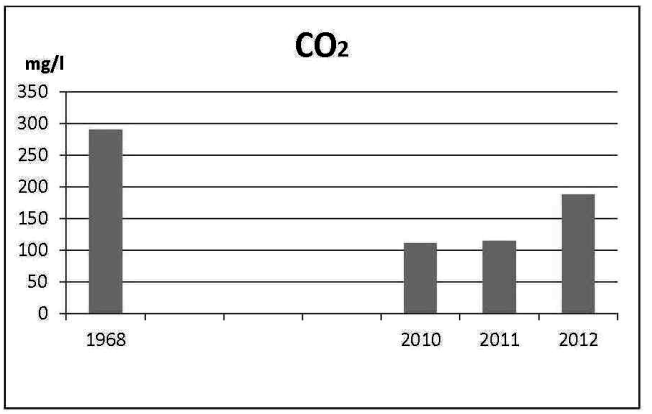

Fig. 3. Changes of CO_2 concentrations in Turčianske Teplice, spring Modrý Bazén, well TM-19

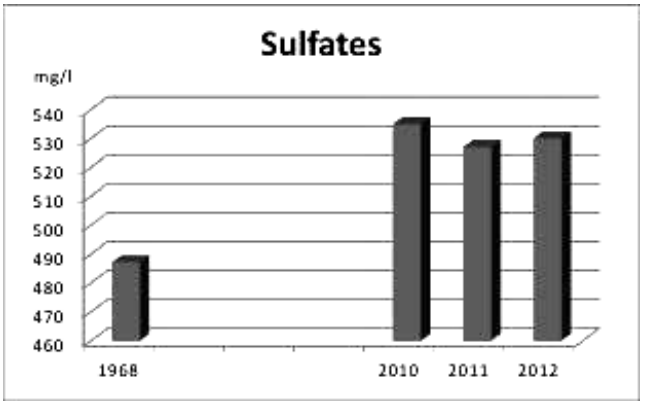

Fig. 4. Changes of sulfates concentrations, Turčianske Teplice, spring Modrý Bazén, well TM-19

4. Conclusions

The thermal ground waters used for spa complexes in Zilinsky and Banskobystricky regions in the Slovak Republic and in Beregovo, Transcarpathian region, Western Ukraine, were analyzed for gamma-radiation level, content of selected radioactive elements, and their physico-chemical characteristics. The possibility to implement the method of profiles for deep monitory of radioactive contamination of thermal ground waters in the Slovak Republic was confirmed.

It was established that Slovakian and Ukrainian thermal ground waters have features in common: the nature of their origin, the geomorphological and hydrological structures, and climate conditions. However, physico-chemical characteristics of waters were diverse: while SO_4^{2-} and HPO_4^{2-} concentrations were close for all research tests, waters in Beregovo showed the highest levels of Ca^{2+} , Na^{+}, Fe^{2+}, NH_4^{+}, and Cl^{-} ions concentrations. The high level of radiation in Beregovo, Ukraine, was detected at almost all research points, which was two times above the limit. For all research sites in the Slovak Republic the radiation level were lower than standard, however, in Turčianske Teplice the level of radiation has tendency to increase. It was established that state of thermal ground waters in Turčianske Teplice has deteriorated during the years of observation. The practical recommendations for improvement of the environmental situation at the research sites were developed, which are about cleaning up the places of radioactive contamination in Beregovo, Ukraine and treatment of wastewater and sludge before discharge. Another recommendation is about stabilization of using of thermal groundwater in Sliač, Turčianske Teplice, Rajecké Teplice, the Slovak Republic, for prevention of their observed deterioration. Regular monitoring and enforcing of the control of waters will assist positively as well.

The future research should focus on the monitoring of thermal groundwater in Turčianke Teplice, the Slovak Republic, where the effects of increasing gamma radiation and changes of physico-chemical characteristics were detected.

References

[1] Council Directive EC 83: 98: The Drinking Water Directive.
[2] Lamoreaux P. *et al.*: Springs and Bottled Waters of the World: Ancient History, Source, Occurrence, Quality and Use. Heiderberg, Springer 2001.
[3] Pidlisnyuk V. and Stefanovska T.: Integrated River Basin Management, 2007, **2**, 271.

[4] Cuka P. and Rachwal T.: Int. Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, 2013, **2**, 89.
[5] Cherepanya I. and Grechko V.: Otchet o Rezultatah Ecologo-Geohimicheskoy Siomky g.Beregovo za 1990-
1994. Kooperativ «Geolog», Beregovo 1996.
[6] Guidelines for drinking – water quality: WHO Recommendations. Edn. 4., Geneva 2011.
[7] Vestník MŽP SR: Odporučenie SKŽP na uplatňovanie ukazovateľov a Vyhláška MZ SR 528:2007 Podrobnosti o požiadavkách na obmedzenie ožiarenia z prírodného žiarenia.
[8] Predpis 538:2005: Z. z. Zákon o prírodných liečivých vodách.
[9] Smernica ES 60 : 2000 : Rámcová smernica o vode.
[10] Normy Radiaciynoi Bezpeky Ukrainy (NRBU-97). Kyiv 1996.
[11] Gupta M.: Radiation Measurements, 2013, **50**, 160.
[12] Vyhláška MZ SR 308: O požiadavkách na kvalitu vody, kontrolu kvality vody, 2012.
[13] Zákon 364 : 2004 : Z. z. o vodách.
[14] STN EN ISO 5667-3 : Kvalita vody, Odber vzoriek, Časť 3 : Pokyny na konzerváciu vzoriek vody a manipuláciu s nimi.
[15] Zbirnyk naukovyh prac / Institut geohimii navkolyshnioho seredovysha. Kyiv 2003.
[16] DSTU ISO 5667-11:2005. Yakist vody. Vidbyrannia prob. Chastyna 11. Nastanovy shodo vidbyrannia prob pidzemnyh vod (ISO 5667-11:1993, IDT). – K. : Derzspozivstandart Ukrainy, 2006. – 11 s.
[17] Vestník MŽP SR č 1, príloha 2: 1994: Odporučenie SKŽP na uplatňovanie ukazovateľov a normatívov pre asanáciu znečistených podzemných vôd a zemín.

ДОСЛІДЖЕННЯ РАДІОАКТИВНИХ ТА ФІЗИКО-ХІМІЧНИХ ХАРАКТЕРИСТИК ТЕРМАЛЬНИХ ГРУНТОВИХ ВОД У СЛОВАЧЧИНІ ТА ЗАКАРПАТСЬКІЙ ОБЛАСТІ УКРАЇНИ

Анотація. *Проведено аналіз термальних ґрунтових вод, які використовуються для спа-комплексів в Жилінському та Банскобистрицькому регіоні Словацької Республіки та в Берегово Закарпатської області (Західна Україна), щодо рівня гамма-випромінювання, вмісту окремих радіоактивних елементів і фізико-хімічних характеристик. Показано, що найвищий рівень радіації в межах спектру гамма-випромінювання мають води у Берегово, рівень яких приблизно в два рази вищий, ніж допустима межа; рівень радіації вод в Словаччині знаходяться в межах норми. Встановлено, що концентрації радіоактивних елементів Ra226 і U в ґрунтових водах в Берегово (Україна) і в Турчіанске Тепліце (Словаччина) знаходяться в межах норми.*

Показано, що досліджувані термальні ґрунтові води в Словаччині та Україні мають схожі геоморфологічні та тектонічні особливості, проте відрізняються за фізико-хімічними складом: при майже однакових концентраціях SO_4^{2-} і HPO_4^{2-} для всіх зразків, води у Берегові мають вищу концентрацію Ca^{2+}, Na^{+}, Fe^{2+}, $NH4^{+}$ і Cl^{-} йонів. Розроблено рекомендації щодо поліпшення екологічної ситуації та подальшого сталого розвитку досліджуваних територій.

Ключові слова: *термальні ґрунтові води, рівень гамма-випромінювання, радіоактивний елемент, фізико-хімічна характеристика.*