SPA ENVIRONMENTS IN CENTRAL SERBIA: GEOTHERMAL POTENTIAL, RADIOACTIVITY, HEAVY METALS AND PAHs

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Abstract

This study aims to estimate geothermal potential, radioactivity levels, and environmental pollution of six most popular spas in Central Serbia (Ovčar, Gornja Trepča, Vrnjačka, Mataruška, Bogutovačka and Sokobanja), as well as to evaluate potential exposure and health risks for living and visiting population. Thermal possibilities of the studied spas showed medium and low geothermal potential with total thermal power of 0.025 MW. Gamma dose rates in air varied from 63 to 178 nSv h^{-1}. Specific activities of natural radionuclides (^{226}Ra, ^{232}Th and ^{40}K) and ^{137}Cs in soil were measured; annual effective doses and excess lifetime cancer risk from radionuclides were calculated. Radon concentration in thermal-mineral waters from the spas ranged between 1.5 and 60.7 Bq L^{-1} (the highest values were measured in Sokobanja). The annual effective dose from

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radon due to water ingestion was calculated. The analyzed soils had a clay loam texture. The presence of As, Cr, Cu, Fe, Mn, Ni, Pb, Cd, Zn, and Hg in soil was investigated. The concentrations of As, Cr, Ni, and Hg exceeded the regulatory limits in many samples. Soil samples from Mataruška spa were generally the most contaminated with heavy metals, while the lowest heavy metal concentrations were observed in Sokobanja. Health effects of exposure to heavy metals in soil were estimated by non-carcinogenic risk and carcinogenic risk assessment. Total carcinogenic risk ranged between 6×10^{-4} and 137×10^{-4} for children and between 0.1×10^{-4} and 2.2×10^{-4} for adults. The sum of 16 PAHs analyzed in soil samples varied from 92 to 854 µg kg^{-1}.

Keywords: geothermal potential; radioactivity; heavy metals; PAHs; risk assessment

1. Introduction

Spa environments are areas of interest, particularly regarding their health-improving effects on human organism. In recent years, the various investigations have been conducted worldwide in order to promote spa tourism, and at the same time to cover important issues related to characterization of thermal-mineral waters and springs, their beneficial effects, and the utilization for balneology and medical treatments. The radiochemical properties of thermal-mineral waters are of great importance for balneotherapy of patients. Besides, monitoring of environmental radioactivity in spas is also important for assessing exposure of professional staff, maintenance workers, health tourists and the population that lives in the surrounding areas.

Some previous studies conducted in Serbian spas were limited to local priorities and promoted the development of tourism (Lukić et al., 2014; Valjarević et al., 2017) or included mineral water quality testing and their exploitation in spa tourism (Košić et al., 2011; Petrovic et al., 2010). Other studies considered geothermal potential and possibilities for sustainable development, as well as identification of the best solution for utilization (Dokmanović et al., 2012; Joksimović and Pavlović, 2014; Tulinius et al., 2015; Valjarević et al., 2018). Several studies have dealt with radon surveys in high natural radiation region of Niška Banja spa (Nikolov et al., 2014; Žunić et al., 2006), determination of radium ^{226}Ra in well and spring waters (Dragović et al., 2012; Joksić et al., 2007; Onishchenko et al., 2010), the analysis of hydrochemical and radiological data of spa waters (Tanasković et al., 2011; Tanasković et al., 2012).

Environmental background radiation mainly refers to terrestrial radiation, including both, natural and anthropogenic sources. It depends on geographical conditions, local geology and the distance from the possible releases of radioactivity. The preliminary data of environmental radioactivity could be given by measurements of gamma dose rates in air. Gama-spectrometry determination of soil radioactivity could be the meaningful indicator of radiological contamination, since soil is an essential medium for transfer of radionuclides to the biological systems. The analysis of radionuclides in water could also indicate exposure to radiation, particularly to radon and its highly radioactive progenies.

Terrestrial radiation is the main contributor to external exposure; about 98% of total radiation energy comes from gamma-emitting radionuclides present in trace amounts in the soil. Since they pose exposure risk to the population, a particular attention has been paid to low level doses that arise from terrestrial radiation. Local variations in low level exposure may differ by orders of magnitude (UNSCEAR, 2000).

Human activities also cause environmental contamination with heavy metals (Mehmood et al., 2019) and persistent organic pollutants (POPs) including polycyclic aromatic hydrocarbons (PAHs). PAHs are a group of stable organic substances predominantly produced during the processes of burning fossil fuels and other organic matters (Simoneit, 1977; Wakeham et al., 1980a,b). They induce carcinogenic, mutagenic and teratogenic effects (Grimmer, 1983; Hoffman and Wynder, 1971; Perera, 1997). Heavy metals produced during fossil fuel combustion, traffic, industrial and residential activities (Biasioli et al., 2006; Kong et al., 2011) can also pose a significant hazard to ecosystems and human health, due to their toxicity and persistence in nature. Heavy metals and POPs accumulate in soil and they can also be released back into the atmosphere.

Serbia is extremely rich with thermal and mineral springs and resources. It has more than 250 warm springs and more than 100 hydrothermal wells. This study investigates six Serbian spas which are the most popular, the most attractive, and the most visited by domestic and foreign tourists. According to the Census from 2011, 22123 inhabitants lived in these spa areas. However, the number of tourists visiting the spas each year is 10-15 times higher than that. In all these spas, water from mineral or thermal-mineral springs is used directly for drinking or taken to swimming pools and baths in the local hospitals and health resorts. Some of the local population also use this water for their households. One of the six spas (Sokobanja spa) is well-known by inhalation room with high levels of radon concentration used for therapeutic purposes.

Several aspects were considered in the study in order to explore the overall potential of these popular health resorts with regard to geothermal capacity and environment safety. The main aim was to provide information about radioactivity levels and environmental pollution in these spas as well as to assess potential health risk for the local population, visiting tourists and professional staff. Besides, the aim was to estimate the geothermal potential and possibilities of geothermal utilization of the spas.

2. Materials and methods

2.1. Study area

A study area occupies six spas in central part of Serbia (Figure1). In terms of regional overview, spas: Ovčar, GornjaTrepča, Vrnjačka, Mataruška and Bogutovačka are located in the southern part of Central Serbia, while Sokobanja is located in the central part of Eastern Serbia (Marković and Pavlović, 1995). Different mineralogical composition of the rocks and the existence of deep faults caused the occurrence of significant accumulations of mineral and thermal-mineral waters in the area of Central and Eastern Serbia. The occurrence of thermal waters is related to volcanic activity or post-volcanic phenomena. All the spas of Central Serbia are located in the wide river valley of the Western Morava and they are classified into the Western Morava spa zone, while Sokobanja is located in the Eastern Serbian spa zone according to the tourist-geographical aspect (Marković, 1987).

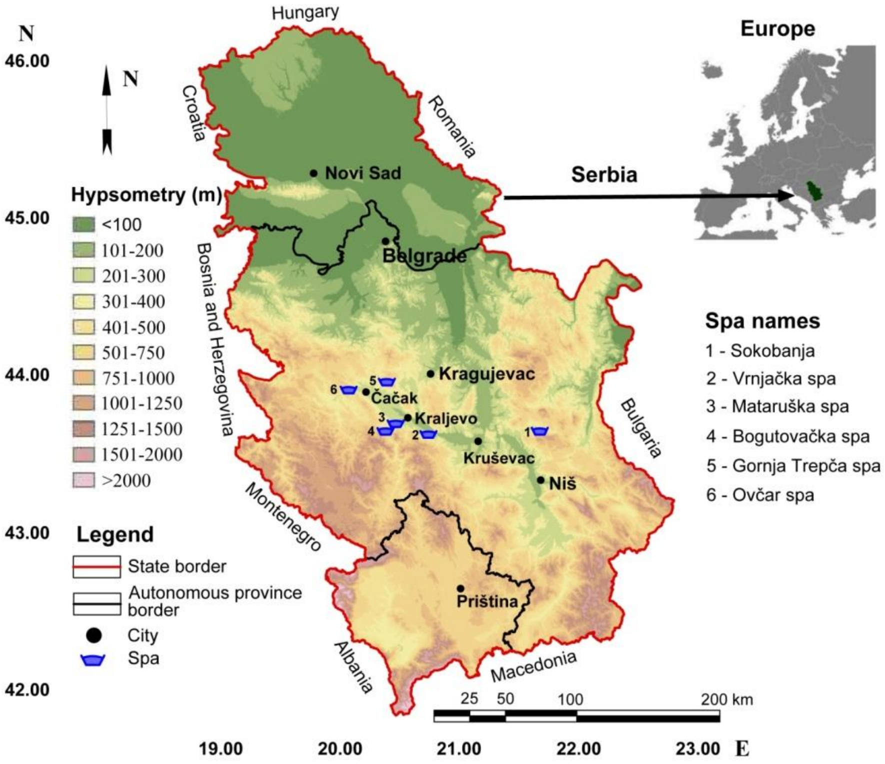

Fig. 1 Map of study area

2.1.1. Geological features

The geological structure of Central and Eastern Serbia is complex. There are magmatic, sedimentary and metamorphic rocks of different age of formations: from Paleozoic (crystalline schists) to Quaternary (alluvial deposits).

Vrnjačka Banja belongs to the geostructural unit which is basically built of crystalline schists from Paleozoic age and Cretaceous flysch. These are metamorphic rocks that form the northwest and central parts of Goč to Željin granitoids. Flysch rocks are situated eastern from this area. They are made of conglomerates and breccias, alevrolites, sandstones and clays created during the phase of Alpine orogenesis (Dimitrijević, 1997). The terrain around Sokobanja are formed from deposits of Mesozoic (Jurassic and Cretaceous) age, and predominantly of sedimentary origin and with the pronounced presence of volcanics. Cretaceous limestones occupied a large surrounding area of Sokobanja, as well as sedimentary schists and gneisses. During the lake phase of the Pannonian Sea evolution, Neogene and Quaternary sediments with limestones were deposited. This hydrogeological phenomenon (first discovered in the Sokobanja Basin) denotes a Karst terrain of a limited surface, completely surrounded by low-permeability rocks which interfere with groundwater flowing out from the Karst region (Filipović, 2003).

2.1.2. Thermal-mineral waters

The diverse geological structure, the existence of deep faults and the specific relationship among watertight and waterproof rocks, have allowed the existence of significant accumulations of mineral and thermal-mineral waters in the area of Central and Eastern Serbia. The occurrence of thermal waters is related to volcanic activity or post-volcanic phenomena. Thermal-mineral springs of Vrnjačka and Sokobanja spas reached the highest level of tourist valorization.

Mataruška, Ovčar and Bogutovačka spas also have significant natural potential, but it is poorly utilized.

2.2. Sampling and preparation

Soil was sampled nearby well-known mineral springs, including the old springs which are no longer in use. Samples were collected from 1 m^2 area and a depth of 0–15 cm, according to IAEA template method (IAEA, 2004). After oven drying (at 100 °C) to constant weight, pulverizing and sieving, samples were hermetically sealed in Marinelli beakers (450 mL) and left aside for a month prior to radioactivity measurements to ensure equilibrium between ^{226}Ra and its progeny.

Mineral waters were sampled from public springs and faucets located in spas' health resorts. Water was poured in the original RAD H_2O 250 mL sampling vials (Durridge Company Inc.) and immediately closed in order to avoid contact with air. Samples were transported to the laboratory and measured for radon content within the following 24 hours.

2.3. Geothermal potential

Spring waters' geothermal power (in MW) was calculated using the formula given in (Freeston, 1995):

$$Q = 4.184 \times 10^{-3} \times FR_{max} \times (T_{inlet} - T_{outlet}) \tag{1}$$

where: the first coefficient is related to heat capacity of thermal water under the normal adiabatic atmospheric pressure and normal coefficient of adhesion in lower layers, FRmax (kg s^{-1}) is maximal discharge, T_{inlet} and T_{outlet} are inlet and outlet water temperatures (°C), respectively. The conversion from power (in MW) to the energy (in TJy^{-1}) is done as follows: 1 MW = 31.5576 TJ y^{-1}.

2.4. *Determination of main physicochemical characteristics*

The pH value in a 1:5 (V/V) water suspension of soil and 1M KCl was measured by the ISO method 10390:1994, using glass electrode. The content of organic matter was determined by oxidation using the sulfochromic oxidation method ISO 14235:1998. The particle size distribution was estimated by the sieving and pipetting method. The size fractions were defined according to the ISSS soil texture classification. The cation exchange capacity (CEC) and the content of exchangeable cations (Ca, Mg, K, Na) in the soils were determined by ISO 11260: 1994.

2.5. *Radioactivity*

2.5.1. Ambient dose equivalent rate

Geiger counter Radex $RD1503^+$ was used to measure the level of environmental background in selected spas. This monitor is set to show ambient dose equivalent rate (ADER) in μSv h^{-1} (in the range from 0.05 to 9.99 μSv h^{-1}, with the uncertainty of ±15%), and it gives four values in each measuring circle which are averaged by counter itself. Calibration of the counter was done using ^{137}Cs at 5 μSv h^{-1} (CE certificated from Germany). The ADER measurements were conducted near springs at height of 1 m above ground and on the ground. There was no rainfall four days before the measurements, therefore the increase of dose due to short-lived radon progeny induced by precipitation was avoided (Melintescu et al., 2018; Mercier et al., 2009).

2.5.2. Gamma spectrometry analysis

Specific activities of radionuclides (^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs) in soil samples were measured using ORTEC GEM30-70 HPGe detector with relative efficiency of 30% and energy resolution (FWHM) of 1.65 keV at 1.33 MeV (^{60}Co) and 717 eV at 122 keV (^{57}Co). The background was reduced by shielding the detector with 10 cm thick lead. The calibration of the detector was performed using a mixed calibration source MBSS 2.

Gamma-activity of each sample and background were measured for 18000 s. Determination of specific activities of abovementioned radionuclides (more precisely their progenies) were done according to their gamma lines and intensities as described in Gulan et al. (2018).

2.5.3. Radon in water

Radon concentration measurements in water samples were performed by RAD7 device (Durridge Company Inc.) equipped with RAD H_2O water accessory. RAD7 instrument was factory-calibrated by the manufacturer and NRPI Inter-comparison was done in 2018 at SURO v.v.i. Institute, Prague, Czech Republic within the IAEA Technical Cooperation Projects RER/9/153. According to the user manual, the lower limit of detection (LLD) was less than 0.37 Bq L^{-1}. Before each measurement started, the device was purged until relative humidity dropped below 6%. WAT250 protocol was used and measurement lasted for 30 minutes for each sample. The measuring procedure included aeration process followed by four 5-minute counting cycles. Radon concentrations were obtained as a mean value of four 5-min measurements and the results were decay corrected to the sampling time.

2.6. Heavy metals

Total heavy metal concentrations in soil samples were determined by microwave assisted digestion in accordance to the USEPA Method 3051A using Milestone Ethos 1 microwave sample preparation system. Analysis was subsequently performed using ICP-OES (Varian Vista Pro-axial). Quality control was periodically carried out with IRMM BCR reference materials CRM-141R and CRM-142R. Recoveries were within ±10% of the certified values. Total mercury content using Direct Mercury Analyzer DMA 80 Milestone in accordance with USEPA Method 7473. The limit of detection for total mercury content was 0.0033 mg kg^{-1}. Quality control was periodically carried out with IRMM BCR reference materials 143R and deviations were within ±5 % of the certified values.Detailed description of the applied procedures was given by Stevanović et al. (2018).

2.7. Polycyclic aromatic hydrocarbons (PAHs)

The standard USEPA 3540C method was used for PAHs extraction from soil.The measurement was performed on a Agilent 6890 CG-5975MSD system equipped with a HP-5MS Capillary column. The 16 analyzed PAHs include naphtalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo[k]fluoranthene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, andindeno[1,2,3-cd]pyrene.A detailed procedure is described by Gulan et al. (2017).

3. Results and discussion

3.1. The possibilities of geothermal utilization

Composition and geothermal potential of some available thermal-mineral springs of the studied spas are presented in Table 1.The thermal possibilities of the studied spas showed medium and low potential. The main reason is insufficiently warm waters with medium discharge. The average discharge is 7.4 L s^{-1} with maximum of 14.5 L s^{-1}(Table 1). The maximum inlet temperature is 69°C, but outlet temperature is 45°C. It should be noted that the waters of Vrnjačka Spa are not thermal, but only mineral (springs with outlet temperatures beneath 20°C are classified in the group of *acratopegae* with no potential for geothermal utilization).

The total thermal power is estimated to be approximately 0.025 MW and appropriate energy was estimated to be 0.774 TJ y^{-1} (Table 1). This geothermal energy would be enough for heating some baths in the spa areas. This renewable energy may be used for heating of 10000 m^2, bathing and swimming and for curative purposes. Besides, a rise in water temperature by few degrees can also be used for agricultural drying, greenhouses, fish and other animal farming, industrial processes and others. In spite of significant advantages, most of this valuable and clean energy still disappears into rivers and streams or in closed areas of spas.

Total available thermal capacity of geothermal waters in this research (~0.025 MW) seems to be very small in comparison to some other spas and thermal springs in Serbia (Joksimović and Pavlović, 2014; Milenić et al., 2015; Valjarević et al., 2018). Nevertheless, geothermal energy may give sustainable development for all settlements and all citizens of these spas in the future. New investigation and geological research in the area would establish new boreholes with higher temperatures and better possibility for geothermal use.

3.2. Soil properties

Physicochemical properties of the analyzed soils are presented in Table 2. The soil pH measured in 1M KCl solution ranged from moderate acidity (5.43) to neutral (7.75). The $CaCO_3$ content showed high heterogeneity and ranged from 0.43 to 17.06%; organic matter content ranged from 0.75 to 5.89%. Clay content has shown the greatest variability (3.84 – 24.88%) relative to the particle size distribution. According to ISSS soil texture estimation, analyzed soils had a clay loam texture.

3.3. Radioactivity in spa environment

3.3.1. *Radioactivity in air*

Table 3 shows that ADER in the air varied from 103 to 178 nSv h^{-1}(with an average of 132.2 nSv h^{-1}) at the ground level, while the values at height of 1 m from the ground ranged from 63 to160 nSv h^{-1} (with an average of 116.8nSv h^{-1}) for all surveyed spas. These values are higher than the values at 1m height (77 to 100 nSv h^{-1}) reported by Serbian Radiation Protection and Nuclear Safety Agency (2018) for the territory of the Republic of Serbia from May to July 2017 (*i.e.* in the period when the survey was conducted). Higher ADER values were measured at ground level than at 1 m height. This was expected, since soil is permanent source of radiation, so noted differences in air can be influenced by diurnal changes (including meteorological parameters such as wind, temperature, humidity)which can yield ADER variation due to radon progenies for 6-17% (Lebedyte, 2003; Melintescu et al., 2018). Also, inhomogeneous distributions due to diverse chemical composition of soil should be taken into account.

3.3.2. Radioactivity in soil

Table 3 presents radioactivity in soil samples for each location. Descriptive statistics of specific activities of radionuclides in soil are presented in Table S1. The SPSS 20.0 software was used to perform Shapiro-Wilk's normality test which showed normal distribution of ^{232}Th activity concentrations. The mean values of specific activities obtained for ^{226}Ra, ^{232}Th and ^{40}K were comparable to worldwide average values: 32, 45 and 412 Bq kg^{-1}, respectively (UNSCEAR, 2008). A wide range of values (from 0.8 to111.9 Bqkg^{-1}) of specific activity of artificial radionuclide ^{137}Cs was measured.

The absorbed dose rates $\dot{D}$ (nGy h^{-1}) in the air (at 1 m above ground level) due to natural radionuclides and ^{137}Cs in the soil were calculated according the following formula (Kapdan et al., 2011; UNSCEAR, 2008):

$$\dot{D} = 0.462A_{Ra} + 0.604A_{Th} + 0.0417A_{K} + 0.1243A_{Cs} \qquad (2)$$

A_{Ra}, $A_{Th}A_{K}$, and A_{Cs} are specific activities of ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs in soil, respectively.

The absorbed dose rates, $\dot{D}$ (nGy h^{-1}), were converted to annual effective doses D_E (µSv) as follows:

$$D_E = DCF \times \dot{D} \times t \times p \qquad (3)$$

where DCF is the dose conversion factor (0.7 Sv Gy^{-1}); t is the annual exposure time (8760 h) and p = 0.2 is the outdoor occupancy factor. The annual effective doses ranged from 50.4 to 82.2 µSv (Table 3) with the average of 64.8 µSv. The contribution from ^{137}Cs varied between 0.1 and 17.1

μSv. Average annual effective dose from natural radionuclides (58.8 μSv) in soil was lower than the worldwide average (66 μSv) (UNSCEAR, 2008). The calculated annual effective dose was weakly correlated with ADER measured at 1 m above the ground(Spearman's rho=0.170). This can be explained by the fact that measured ambient dose rate has several components other than terrestrial gamma radiation, such as intrinsic background, airborne radionuclides, and secondary cosmic radiation.

Excess lifetime cancer risk (ELCR) outdoors was calculated as follows:

$$ELCR = D_E \times DL \times PC \tag{4}$$

where *DL* is average duration of life (70 y) and *PC* is the nominal probability coefficient for detriment-adjusted cancer risk of $5.5 \cdot 10^{-2}$ Sv^{-1} (ICRP, 2007). The values of *ELCR* ranged from $1.9 \cdot 10^{-4}$ to $3.2 \cdot 10^{-4}$ (Table 3); an average value of $2.5 \cdot 10^{-4}$ is the same as the worldwide average reported by UNSCEAR (2008).

3.3.3. Radon in water

The results of measuring radon concentration in water are presented in Table 3 (some values are missing due to the fact that some of the old springs were no longer available for sampling). The measured radon concentrations ranged between 1.5 and 60.7 Bq L^{-1}. Spearman correlation analysis indicated a weak correlation of radon in water with ^{226}Ra in surrounding soil (Spearman's rho = 0.167).

According to US Environmental Protection Agency regulation, the upper limit for radon in drinking water is 11.1 Bq L^{-1} (EPA, 1999). The last two water samples (Sokobanja 3 and 4) have been taken from two different locations but they came from the same spring. Both samples were taken from faucets; one of them was located inside the “Sokobanja” special hospital and the other one in the Turkish bath (“Hamam”) in which there is a radon inhalation room used for therapeutic purposes. Evidently, radon concentration in these samples exceed the recommended value, therefore this spring should not be used as a drinking water source.

The annual effective dose from radon due to water ingestion, E_{wing} (μSv y^{-1}), was calculated using the equation (UNSCEAR, 2000).

$$E_{wing} = C_{Rn} \times C_w \times EDC \tag{5}$$

where C_{Rn} (Bq L^{-1}) is radon concentration in water, C_w is the weighted estimate of annual water consumption and EDC is the effective dose coefficient for ingestion (3.5 nSv Bq^{-1}). Since radon is readily lost from water by heating or boiling, the value of 60 L y^{-1} has been proposed by UNSCEAR (2000) for the weighted direct consumption of tap water. The results are presented in the last column of Table 3.

3.4. Heavy metals in soil

Heavy metal concentrations in analyzed soils are presented in Table 4. Cadmium was below detection limit. According to Dutch standard for soil (VROM, 2000) and Serbian Soil Quality Regulation (Official Gazette 30/2018), regulatory limits for soil which indicate sustainable soil quality for Cr, Cu, Ni, Pb, Zn, Hg, As and Co are 100, 36, 35, 85, 140, 0.3, 29 and 9 mg kg^{-1}, respectively.

Exceeding regulatory limits indicates the level of contamination that distorts ecological balance and implies further investigations as well as limitations in the soil management (Official

Gazette 30/2018). All soils sampled in Mataruška, Vrnjačka, Bogutovačka and Gornja Trepča spas had elevated Ni and Cr concentrations and the origin of these metals in soils is natural since the soils in this area (Western Serbia) are formed on ultramafic rocks or sediments originating from the ultramafic rocks rich in heavy metals (Manojlović and Singh, 2012; Mrvić et al., 2009; Stajković-Srbinović et al., 2017). High positive correlation between Cr and Ni concentrations in analyzed soils (Spearman's rho =0.958) also indicate their natural origin (Ajmone -Marsan et al., 2008).

High concentration of lead was detected at one location at Ovčar spa (Ovčar 3). The concentration of 368.6 mg kg^{-1} was 2.5 times higher than the regulatory limit and the fact that it was measured in only one soil sample indicates anthropogenic origin of lead. The sampling location was approximately 50 m away from very traffic road (E 761) which is a part of the International E-road network thus it can be assumed that lead in nearby soil is originating from leaded gasoline used in previous decades.

High mercury concentrations were detected at sampling location Bogutovačka banja 2 and Gornja Trepča 1 (4.557 and 4.304 mg kg^{-1}, respectively). Samples from Mataruška spa were generally the most contaminated with heavy metals, while the lowest heavy metal concentrations were observed in Sokobanja.

Arsenic concentrations higher than regulatory limit were detected in 6 soil samples. Both samples from Mataruška Spa and sample Vrnjačka 1 had similar As content (35.41, 31.83 and 32.57 mg kg^{-1}, respectively) slightly higher than regulatory limit while soil samples from Ovčar 2, Bogutovačka 2 and Gornja Trepča 3 had much higher As concentrations. It cannot be stated with certainty whether these high levels of As are caused by anthropogenic activities, since significant amounts of arsenic can be naturally found in groundwaters specifically geothermal waters.

3.4.1. Health risk assessment from heavy metals

Health effects of exposure to heavy metals in soil were estimated through non-carcinogenic risk and carcinogenic risk assessment. US Environmental Protection Agency (USEPA, 2001) model was applied. Non-carcinogenic risk was estimated by calculating the total hazard index (THI). The population is commonly exposed to heavy metals through ingestion, air inhalation and dermal contact. The average daily doses (ADDs) were determined for adults and children, using the following equations (Chen et al., 2015):

$$ADD_{ing} = C \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \tag{6}$$

$$ADD_{inh} = C \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \tag{7}$$

$$ADD_{dermal} = C \times \frac{SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \tag{8}$$

where ADD_{ing}, ADD_{inh} and ADD_{dermal}(in mg kg^{-1} day^{-1}) represent the average daily intake from soil ingestion, inhalation and dermal absorption respectively; C is the concentration of metal in soil (mg kg^{-1}); $IngR$($IngR$= 100 mg d^{-1} for adults and $IngR$= 200mg d^{-1} for children) and $InhR$ (InhR = 20 m^3 d^{-1} for adults and $InhR$= 7.6m^3 d^{-1} for children) are the ingestion and inhalation rates, respectively; EF is the exposure frequency (EF = 350 d y^{-1}); ED is exposure duration (ED = 30 y for adults and ED = 6 y for children); BW is the body weight of exposed individual (BW = 70 kg for adults and BW = 15 kg for children); AT is the averaging time ($AT = 365 \times ED$ d); PEF is the emission factor ($PEF = 1.36 \times 10^9$ m^3 kg^{-1}); SA is the surface area of the exposed skin (SA = 1530 cm^2 for adults and SA = 860 cm^2 for children); AF is the adherence factor (AF = 0.07 mg cm^{-2} day^{-1} for adults and AF = 0.2 mg cm^{-2} day^{-1} for children); ABS is the dermal absorption factor (0.03, 0.04, 0.1, 0.35, 0.006, 0.02, and 0.05 for As, Cr, Cu, Ni, Pb, Zn, and Hg, respectively) (Chen et al., 2015; Health Canada, 2004).

Hazard quotients (HQ_{ing} for ingestion, HQ_{inh} for inhalation, and HQ_{der} for dermal exposure) were calculated for each metal by dividing average daily doses by the corresponding reference doses, *RfD* (presented in Table S2). Hazard index (*HI*) for each metal was then obtained by summing HQs related to different exposure pathways. Total hazard index (*THI*) presented in Table 4 was obtained as the sum of *HI*s of all measured metals. *THI* values were in the range of 0.53-10.27 for children and 0.06-1.21 for adults. Ingestion was generally the dominant exposure pathway. Cr and As made the greatest contribution to *THI*. The values of hazard index greater than 1 indicate that population may experience non-carcinogenic harmful effects due to long-term exposure to heavy metals in soil (USEPA, 2001).

Carcinogenic risk for each exposure pathway was obtained by multiplying average daily doses by the corresponding slope factor SF_i (Li et al., 2014). The average daily doses were calculated as previous (Eqs. 6-8), using $AT = 70\times365$ d. Carcinogenic slope factors are given in Table S2. The total carcinogenic risk (TCR) obtained by summing the contribution of As, Cr, Ni, and Pb (Table S1) ranged between 6×10^{-4} and 137×10^{-4} for children and between 0.1×10^{-4} to 2.2×10^{-4} for adults. The values of cancer risk above 10^{-4} indicate high risk for developing some type of cancer due to lifetime exposure to carcinogenic hazards (Wu et al., 2015).

3.5 PAH content in soil

The sum of 16 PAHs analyzed in soil samples varied from 92 to 854 μg kg^{-1} (Table S3) with an average value was 267.7 μg kg^{-1}. The presented results are in agreement with other data reported in the literature for the top layer of soils from nonindustrial areas in Europe. The average concentration of sum of PAHs in analyzed soils corresponds to average values reported by Maliszewska-Kordybach and Smreczak (1998) (105-290 μg kg^{-1}) and Oleszczuk and Pranagal (2007) (216 μg kg^{-1}) for soils in Poland and by Nam et al. (2008) (158 μg kg^{-1}) for the background soils in Norway.

Maliszewska-Kordybach (1996) classified soil according to total PAHs content: not contaminated (total PAHs < 200 μg kg^{-1}), weakly contaminated (total PAHs is 200-600 μg kg^{-1}), contaminated (total PAHs is 600-1000 μg kg^{-1}) and heavily contaminated (total PAHs is >1000 μg kg^{-1}). According to this classification, 10 analyzed soils samples could be considered not contaminated, 5 samples could be considered weakly contaminated (samples from Sokobanja and one sample from Vrnjačka spa) and 2 samples (Vrnjačka 3 and Ovčar 3) could be considered contaminated.

The PAHs that are present in the environment can also be divided into two groups depending on their origin, namely pyrogenic and petrogenic (Feng et al., 2009; Hylland, 2006; Lang et al., 1962). In general, pyrogenic PAHs are composed of larger ring systems (2-8 conjugated rings) than petrogenic PAHs thus pyrogenic/petrogenic origin of PAHs can be determined based on low molecular weight/high molecular weight PAH ratio (LMW/HMW). Low molecular weight PAHs are constituted from 2 or 3 rings, while high-molecular PAHs are composed of 4 and more rings.LMW/HMW PAH ratio in soil sampled at Vrnjačka spa (Vrnjačka 1) was higher than 1 indicating petrogenic origin of PAHs, probably due to oil spillage. In all other samples with PAH content higher than 200 μg kg^{-1} LMW/HMW ratio was below 1 (Table S3) indicating their pyrogenic origin due to the incomplete combustion of fossil fuels.

Of the 16 analyzed PAHs, seven are considered carcinogenic according to IARC (International Agency for Research on Cancer) classification. The sum of carcinogenic PAHs in analyzed soils ranged between detection limit and 484 µg kg^{-1} with the average value of 115 µg kg^{-1}.

There were no statistically significant correlations between the parameters describing soil physicochemical properties and the content of PAHs.

However, potential combined effects from concurrent exposure to radioactive or other dangerous chemical materials have not been the subject of this investigation, but synergistic effects should not be neglected. They might individually not be carcinogenic but may be capable to show carcinogenic interactions over a period of time. Health effects, such as cancer may not manifest for several years or decades after exposure.

4. Conclusion

Serbia is extremely rich with thermal and mineral resources which are not fully developed and efficiently utilized. The study was conducted in order to investigate the different environmental aspects (geothermal potential, radiological and chemical features) of six most popular spas in central Serbia (Ovčar, GornjaTrepča, Vrnjačka, Mataruška, Bogutovačka, and Sokobanja).

Thermal possibilities of the studied spas showed medium and low geothermal potential due to insufficiently warm waters with medium discharge. Total thermal power was 0.025 MW and the corresponding energy use was 0.774 TJ y^{-1}. However, new investigations and geological research might establish new boreholes with higher temperatures and better possibility for geothermal use in future.

Measured activity concentrations of natural radionuclides in soil were comparable to worldwide average values, while ^{137}Cs ranged from 0.8 to 111.9 Bqkg^{-1}. The annual effective doses ranged from 50.4 to 82.2 µSv (the contribution from ^{137}Cs varied between 0.1 and 17.1 µSv).

Ambient dose equivalent rate in air measured at the ground level and 1m above the ground varied from 63 to 178 nSv h^{-1}.

Radon concentration in spa waters ranged between 1.5 and 60.7 Bq L^{-1}. The highest radon values were measured in water samples from Sokobanja spa. This spa is well-known by promoting beneficial effects of radon inhalation on human health. However, according to US Environmental Protection Agency regulation, the water from Sokobanja spa resort should not be used for drinking. Termal/mineral waters from the rest of the spas under investigation can be considered safe with regard to radon content. No correlation was found between radon in water and ^{226}Ra in surrounding soil.

High concentrations of heavy metals in soil were detected. All soils sampled in Mataruška, Vrnjačka, Bogutovačka and GornjaTrepča spas had elevated Ni and Cr concentrations due to its natural origin from parental rocks. High concentration of lead was detected at one location at Ovčar spa and arsenic concentrations higher than the regulatory limit were detected in 6 soil samples. Some reported metals found in soils are probably of anthropogenic origin. Soil samples from Mataruška spa were generally the most contaminated with heavy metals, while the lowest heavy metal concentrations were observed in Sokobanja. Relatively high values of TCR (6×10^{-4}–137×10^{-4} for children and 0.1×10^{-4}– 2.2×10^{-4} for adults) were calculated indicating high risk for developing some type of cancer due to lifetime exposure. However, short-term exposure does not impose significant health risk to the tourists visiting these spas.

The sum of 16 PAHs analyzed in soil samples varied from 92 to 854 µg kg^{-1}. Five samples were weakly contaminated (samples from Sokobanja and one sample from Vrnjačka spa) and two samples collected from Vrnjačka and Ovčar spa could be considered contaminated. The sum of carcinogenic PAHs ranged from detection limit up to 484 µg kg^{-1}.

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Table 1. Composition and geothermal potential of thermal-mineral springs of studied spa

Spa	Type of thermal-mineral water	Discharge [L s^{-1}]	Temperature Inlet [$^{\circ}$C]	Temperature Outlet [$^{\circ}$C]	Thermal power [$\times 10^{-3}$MW]	Energy use [TJ y^{-1}]
Mataruška 1	$M_{1.39-1.48} = \frac{HCO_{87}^{3}Cl_{10}}{Na + K_{57}Mg_{26}Ca_{14}} Q > 10.0$	9.2	67	42.8	3.350	0.106
Ovčar 1	$M_{0.64} = \frac{HCO_{90}^{3}}{Ca_{60}Mg_{32}} Q > 30.0$	14.5	46	38	1.745	0.055
Ovčar 3	$M_{0.64} = \frac{HCO_{90}^{3}}{Ca_{60}Mg_{32}} Q > 30.0$	5.6	58	35	2.007	0.063
Bogutovačka 1	$M_{0.6} = \frac{HCO_{92}^{3}}{Mg_{43} + Ca_{29}Na + K_{28}} Q > 3.0$	13.5	49	25	4.875	0.154
GornjaTrepča 1	$M_{0.52} = \frac{HCO_{93}^{3}}{Mg_{74}Ca_{19}} Q > 20.0$	4.4	69	31	2.516	0.079
GornjaTrepča 3	$M_{0.52} = \frac{HCO_{93}^{3}}{Mg_{74}Ca_{19}} Q > 20.0$	8.2	54	29	3.085	0.097
Sokobanja 1	$M_{0.46} = \frac{HCO_{81}^{3}}{Ca_{66}Mg_{25}} Q > 10.0$	8.2	59	32	3.331	0.105
Sokobanja 2	$M_{0.54} = \frac{HCO_{80}^{3}}{Ca_{60}Mg_{32}} Q > 20.0$	1.3	55	31	0.469	0.015
Sokobanja 3	$M_{0.46} = \frac{HCO_{81}^{3}}{Ca_{66}Mg_{25}} Q > 10.0$	8.3	67	45	2.748	0.087
Sokobanja 4	$M_{0.46} = \frac{HCO_{81}^{3}}{Ca_{66}Mg_{25}} Q > 10.0$	1.1	67	43	0.397	0.013
Total					24.524	0.774

Table2. Physicochemical characteristics of soil

	Particle size distribution [%]				**pH**		**$CaCO_3$ %**	**Humus %**
	Sand 0.2-2 mm	Fine Sand 20-200 µm	Silt 2-20µm	Clay < 2µm	in KCl	in H_2O		
Mataruška 1	31.9	44.1	16.7	7.3	7.2	7.7	2.0	2.5
Mataruška 2	16.0	54.2	20.8	9.0	6.5	7.3	0.7	3.1
Ovčar1	39.4	44.2	12.6	3.8	7.4	7.8	7.2	2.3
Ovčar2	46.2	25.3	17.0	11.4	7.3	8.0	12.8	2.5
Ovčar3	36.8	44.1	14.4	4.7	7.7	8.1	12.4	2.0
Vrnjačka1	50.0	22.3	20.6	7.1	6.5	7.2	0.9	2.3
Vrnjačka 2	31.7	33.1	28.6	6.6	6.2	6.9	0.5	4.5
Vrnjačka 3	16.8	46.1	28.5	8.6	7.0	7.5	1.1	2.3
Bogutovačka1	12.8	50.6	23.0	13.5	7.2	7.9	1.8	1.4
Bogutovačka2	18.2	50.2	20.0	11.6	7.2	7.8	2.1	2.1
Gornja Trepča1	6.7	30.1	38.3	24.9	5.4	6.3	0.4	2.2
Gornja Trepča2	11.4	47.7	28.2	12.8	7.2	7.9	4.7	2.0
Gornja Trepča 3	51.8	3.3	20.9	24.0	5.6	6.2	0.5	5.9
Sokobanja 1	48.0	20.6	23.9	7.5	7.5	8.2	17.5	5.6
Sokobanja 2	22.0	45.8	17.9	14.4	7.7	8.7	12.4	0.8
Sokobanja 3	18.4	48.8	17.0	15.8	7.8	8.5	16.6	1.0
Sokobanja 4	34.8	31.2	24.6	9.4	7.2	7.7	17.1	5.8

Table 3. Radioactivity of soil, ADER in air, and radon concentration in water

	Radioactivity in soil						**ADER in air [nSv h^{-1}]**		**Rn in water**	
	^{40}K [Bq kg^{-1}]	**^{226}Ra [Bq kg^{-1}]**	**^{232}Th [Bq kg^{-1}]**	**^{137}Cs [Bq kg^{-1}]**	**D_E [μSv y^{-1}]**	**$ELCR$ 10^{-4}**	**0 m**	**1 m**	**C_{Rn} [Bq L^{-1}]**	**E_{wing} [μSv y^{-1}]**
Mataruška 1	305	17.2	25.1	70.8	54.7	2.11	138	145	<LLD*	-
Mataruška 2	378	24.3	39.4	78.5	74.3	2.86	148	150	-	-
Ovčar1	413	24.4	36.6	12.1	63.9	2.46	143	115	-	-
Ovčar2	553	23.3	35.3	95.8	82.2	3.17	178	120	4.9	2.9
Ovčar3	381	24.5	33.2	35.9	63.4	2.44	110	113	-	-
Vrnjačka1	364	23.4	31.8	4.1	56.1	2.16	118	108	4.2	2.5
Vrnjačka 2	398	20.1	35.3	111.9	75.0	2.89	158	63	5.5	3.3
Vrnjačka 3	405	30.9	43.3	40.7	76.5	2.95	108	120	1.5	0.9
Bogutovačka1	410	30.4	31.2	12.1	63.1	2.43	123	120	6.1	3.7
Bogutovačka2	322	34.9	28.8	16.3	60.0	2.31	105	95	-	-
Gornja Trepča1	399	22.6	18.9	21.1	50.4	1.94	170	115	-	-
Gornja Trepča2	394	23.9	34.4	42.0	65.6	2.52	120	160	6.4	3.8
Gornja Trepča3	342	21.5	31.3	95.2	67.4	2.59	123	98	8.9	5.3
Sokobanja 1	381	46.2	27.9	16.4	68.8	2.65	103	133	-	-
Sokobanja 2	407	26.7	24.6	0.8	54.3	2.09	140	105	9.9	5.9
Sokobanja 3	381	26.4	33.1	3.3	59.5	2.29	110	93	60.7	36.4
Sokobanja 4	463	32.3	30.6	16.4	67.1	2.59	155	103	59.4	35.6

*LLD – Lower Limit of Detection

Table 4. Heavy metal concentrations (in mg kg^{-1}), total hazard index (THI) and total carcinogenic risk (TCR) from heavy metals in soils.

	As	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Hg	Children		Adults	
										THI	**TCR**	**THI**	**TCR**
Mataruška 1	35.4*	446**	86.8*	13150	642	401**	64.9	193*	0.693*	7.65	1.14E-02	0.92	1.66E-04
Mataruška 2	31.8*	308*	37.1*	12920	648	452**	85.7*	209*	0.727*	6.02	8.10E-03	0.72	1.22E-04
Ovčar1	14.6	52.6	38.8*	9215	305	72.7*	16.9	86.7	0.146	1.46	1.63E-03	0.17	2.96E-05
Ovčar2	50.8*	46.0	57.9*	11840	725	56.3*	35.4	114	0.329*	3.10	2.43E-03	0.35	6.22E-05
Ovčar3	13.5	50.8	51.7*	10000	327	64*	368.6*	175*	0.137	2.72	1.56E-03	0.30	2.98E-05
Vrnjačka 1	32.6*	292*	28.2	10710	534	275**	64.5	185*	0.160	5.51	7.76E-03	0.65	1.18E-04
Vrnjačka 2	21.1	485**	31.9	11300	669	299**	39.8	130	0.148	7.16	1.20E-02	0.87	1.64E-04
Vrnjačka 3	24.2	131*	31.6	9604	791	143*	40.8	119	0.132	2.99	3.73E-03	0.35	6.22E-05
Bogutovačka1	19.2	315*	27.8	12820	642	368**	26.3	111	0.124	5.14	7.93E-03	0.62	1.12E-04
Bogutovačka2	75.1**	495**	38.7*	13500	707	455**	42.3	484*	4.557*	10.27	1.37E-02	1.21	2.19E-04
Gornja Trepča1	55.7**	135*	22.5	8109	350	106*	16.6	60.8	4.304*	4.60	4.65E-03	0.53	9.31E-05
Gornja Trepča2	26.4	126*	41.5*	10480	585	166*	35.4	110	0.278	3.06	3.68E-03	0.36	6.28E-05
Gornja Trepča3	4.7	20.4	15.2	9977	1056	22	24.4	141*	0.136	0.59	6.05E-04	0.07	1.06E-05
Sokobanja 1	29.5*	30.4	25.1	10370	1222	26.4	19.1	84.6	0.100	1.82	1.50E-03	0.20	3.72E-05
Sokobanja 2	7.4	21.5	17.5	8469	425	15.5	10.6	44.7	0.071	0.66	7.02E-04	0.08	1.35E-05
Sokobanja 3	5.7	17.9	15.9	7642	330	11.5	9.5	40.6	0.041	0.53	5.75E-04	0.06	1.08E-05
Sokobanja 4	9.3	22.3	31.1	8414	408	14.6	25.4	82.8	0.306*	0.83	7.73E-04	0.09	1.56E-05

*Exceeded the regulatory limit

**Exceeded the remediation value