^{210}Po characteristic in selected thermal water sources in Northern Vietnam

Van-Hao Duong[1] · Trinh Trong Phan[2,3,4] · Bach Thao Nguyen[1] · Duc Bang Dao[1] · Miklós Hegedűs[5] · Tibor Kovacs[5]

Abstract

There are eight famous thermal water sources, with medium temperature, neutral pH, high ranges of TDS values located in different carbonate formations in Northern Vietnam. The chemical composition results showed the major elements present were Na, K, Mg, Ca, Sr, while trace amounts of rare earth elements (REE), Ag, As, Pb, Th, U were observed. The ^{210}Po activity concentration and the annual committed effective doses for adults, children, and infants in all study areas were far less than 100 mBq L^{-1} and 0.1 mSv y^{-1}, respectively. Some significant correlations between ^{210}Po and other chemical components have been observed.

Keywords ^{210}Po · Thermal water · Northern Vietnam · Effective dose · Chemical concentrations

Introduction

Thermal water sources have well-known uses, such as medical treatment, balneotherapy, spas and thermal-mineral water due to their health-improving effects on the human organism, the development of tourism, and fulfilling the mineral water demand in Northern Vietnam. Previous studies reported that thermal waters contain metal ions and radionuclides with varying concentration [1]. Thermal waters are found at a greater depth, and on its way up they are heated by the warm rocks and the minerals from the rock dissolve in the water. Natural radionuclides in thermal and underground waters have been investigated by many authors [2–8]. As special type of underground water (high temperature), the thermal water sources during their travel to the surface come into contact with a large surface area of rock formations that have potentially high natural radioactivity such as granite, porphyry or basalt [9]. Therefore, the natural radionuclides can enter from the surrounding geological formations to the thermal water during interactions between the liquid and solid phases [10, 11].

Due to of its potential for significant negative health effects and just long enough half-life to play an important role in environmental processes [12], ^{210}Po (138 day of half-life) is one of the most toxic radionuclides [1, 13]. The ^{210}Po activity concentration depends on the geological structure of the aquifer and distribution of the parent element in the rock matrix and the thermal water [14–16]. In addition, the solubility and mobility of ^{210}Po are also affected by the chemical and physical composition characteristics of the aquifer [16].

The geochemical properties of ^{210}Po are quite complex in behavior, the transport process and the eventual fate of ^{210}Po in groundwater or thermal water is a challenging re-search question, and is expected to differ significantly based on the local properties. The ^{210}Po generally can be readily removed from groundwater by co-precipitation with Fe-hydroxides, Mn-oxides, colloids and sulfides and be adsorbed onto solid surfaces in the system of aquifers [6, 11, 12]. Therefore, the presence of ^{210}Po in groundwater is mostly detected in low concentrations [10], rarely exceeding 37 mBq L^{-1} in the aquifer [2, 17]. However, some previous studies reported the ^{210}Po levels exceeding 5000 mBq L^{-1} (up to 16,600 mBq L^{-1}) in the US and Finland [6, 18–21]. High activity of ^{210}Po

✉ Tibor Kovacs
   kt@almos.uni-pannon.hu

1   Hanoi University of Mining and Geology, No 18, Vien street, Bac Tu Liem district, Hanoi, Vietnam

2   Institute of Geological Sciences, Vietnam Academy of Science and Technology, Hanoi, Vietnam

3   Graduate University of Science and Technology, Vietnam Academy of Science and Technology, Hanoi, Vietnam

4   Royal Academy for Overseas Sciences, Brussels, Belgium

5   Institute of Radiochemistry and Radioecology, University of Pannonia, Veszprem, Hungary

is observed in regions with waters that tend to be fairly acidic and have a high content of parent radioisotopes such as ^{222}Rn [2, 10, 22]. A previous study reported that in un-buffered distilled water at a pH of < 2 or > 10 nearly 100% passed through 0.45 μm filters but at pH of 6–7 only about 20% of the polonium passed through the filters [23]. The pH could be a parameter influencing the ^{210}Po concentration in groundwater.

The close binding of ^{210}Po to aquifer surfaces and mineral grains with its relatively short half-life often reflects on local supply rates and bulk adsorption coefficients [24, 25], in addition to the relationship between ^{210}Po and physico-chemical parameters of water as a means of studying geochemical processes. This indicates that the determination of the natural ^{210}Po and the chemical properties in thermal water are necessary for the determination of the geochemical behavior of ^{210}Po with respect to the formation and interaction in the aquifer.

In this study, the ^{210}Po activity concentration and the chemical composition of eight thermal water sources located in Northern Vietnam were investigated. The selected infiltration type sources are located in limestone on both sides of the Red River fault system, are expected to be representative only of their near vicinity. The selected water sources also have local economic significance both as a popular tourism destination and as a water resource. The main objective of this paper is to identify some of geochemical factors responsible for the mobilization of ^{210}Po in thermal water at the study areas. In addition, the results of the study will provide a typical case study on low level of ^{210}Po activity in thermal water sources for identifying the geochemical and radiological processes occurring. Furthermore, the baseline data of effective annual dose was calculated as the information for the assessment of water quality and radiological safety.

Materials and methods

The water samples were collected in My Lam—Tuyen Quang (ML), Thanh Thuy—Phu Tho (TT), Kim Boi—Hoa Binh (KB), Quang Hanh—Quang Ninh (QH), Tien Lang—Hai Phong (TL), Kenh Ga—Ninh Binh (KG), Ban Moong (BM), and It Ong—Son La (IO). The studied sampling locations are shown in Fig. 1. During sampling, the pH, TDS, and temperature values were measured in situ by Hanna instruments model HI8314 and HI2003-02 devices. All the collected water samples are from aquifers hosted in various limestone formations [26]. Therein, the mineral water in My Lam aquifer is formed and stored in crystalline limestone, marble, and sericite slate [27]. For other locations, the mineral water is formed and stored within fault systems and in a carboniferous limestone formation at different depths. Each water sample was taken with a 5-L

plastic can and acidified to pH 2 to prevent polonium from being hydrolyzed and absorbed to the surface of the plastic can wall [12]. The followed water sampling procedure is described in [26].

A radiological method was employed to determine ^{210}Po activity concentration in the water samples. In the laboratory, from each of the studied samples 2 L subsamples were taken, then weighted. The chemical separation procedure can be briefly described as: A well-known amount of ^{209}Po tracer was added to the water sample at the beginning of the chemical procedure. The polonium isotopes were precipitated in $(NH_4)_2U_2O_7$ together with MnO_2 through first adding ammonia into the water sample, then adding $KMnO_4$, and $MnCl_2$ to form the precipitate at pH > 9 [28]. The precipitate was washed with distilled water. Subsequently, the obtained precipitate was dissolved in HCl acid. A chromatographic column with Dowex 1 × 8, 100–200 mesh anion resin has been used to separate Po, U, Pb, and Bi in the solution [29]. The obtained solution was evaporated to dryness, then it was dissolved in 0.5 M HCl acid and ~ 0.5 g of ascorbic acid was added. Polonium isotopes were spontaneously deposited on a silver disk from the solution for ~ 4 h at temperature of about 80 °C. The obtained silver disk source was left to dry at room temperature and was measured using an ORTEC Alpha-Ensemble-4 spectrometer with Alpha-vision software and ALPHA-DUO-M1 − 450 mm^2 area detectors. The detection limit of the equipment was 0.5 mBq. A background sample from distilled water was also prepared and measured to account for the background derived from the chemical reagents, electronic noise or alpha particles emitted from the chamber. The calculated recovery rate of the ^{209}Po tracer and the test samples is approximately 90%. The measurement time of each sample is chosen in a way to account for the count rate uncertainty at the ^{210}Po and ^{209}Po peaks to be below 5%, respectively.

The activity concentration of ^{210}Po isotope in the water samples was calculated using Eq. 1:

$$C_{210} = \left(A_{209} \cdot \frac{I_{210}^{sp} - I_{210}^{bg}}{I_{209}^{st} - I_{209}^{bg}} \right) / V \qquad (1)$$

C_{210}—the concentration of ^{210}Po isotope in thermal water sample [mBq L^{-1}]; A_{209}—activity tracer ^{209}Po isotope added to the thermal water sample [mBq]; $I_{210}^{sp}, I_{210}^{bg}$, and $I_{209}^{sp}, I_{209}^{bg}$ are the count rates (counts/min) in the peak of ^{210}Po and ^{209}Po for the studied and background samples respectively; V—Volume of the water samples used for the measurement [L].

The chemical analysis was performed at the Radioactive & Rare Minerals Division. From each of the thermal water samples 50 mL subsamples were pre-concentrated
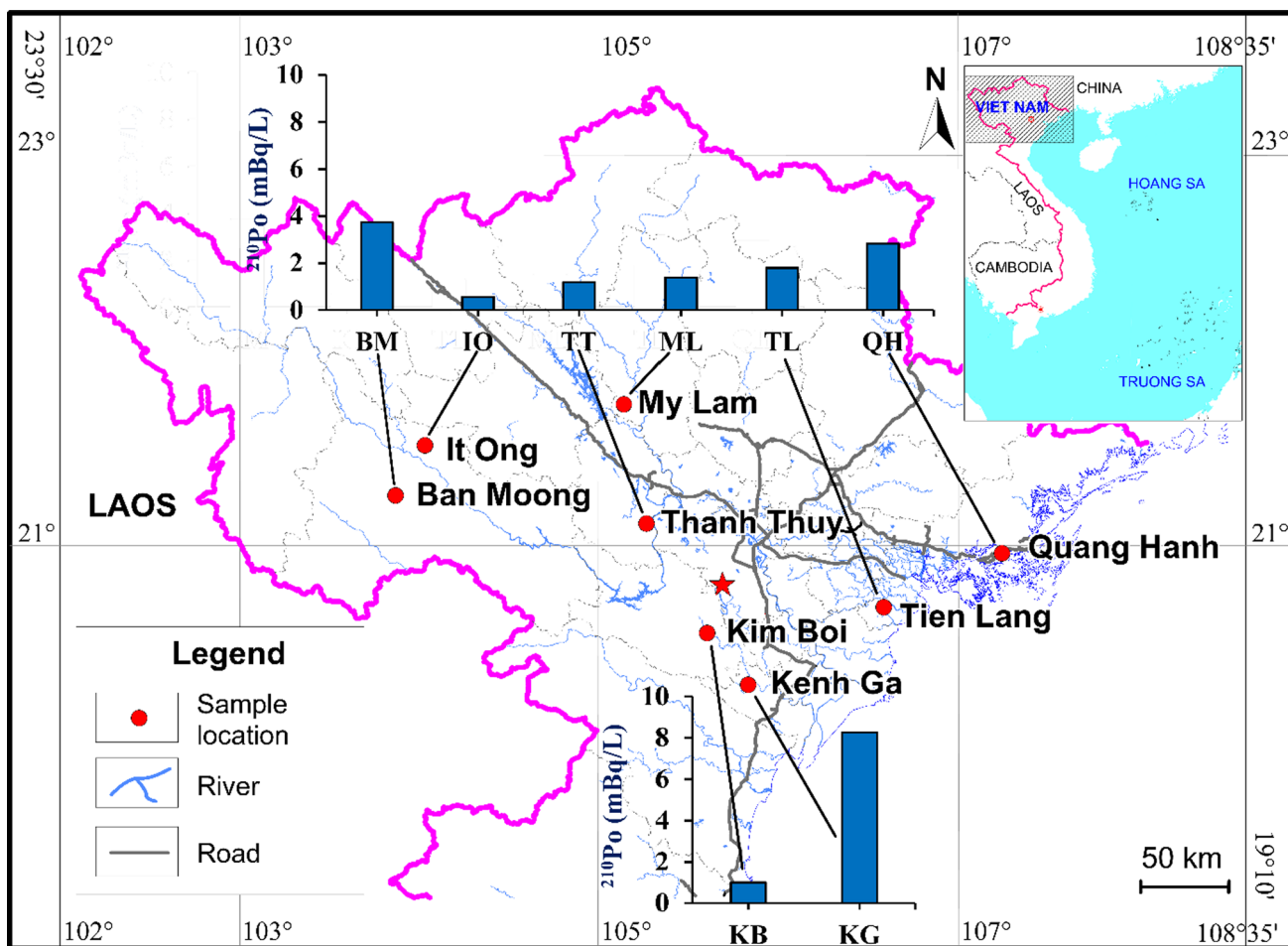
Fig. 1 The sampling locations and the measured ^{210}Po activity concentrations

in Teflon cups at 120 °C and the residual liquid was mixed with a HNO$_3$ (2%) solution to reach a final weight of 10 g. The samples were measured using an Agilent − 7700 × type ICP-MS. The concentration of chemical elements in the analytical samples were determined by comparing them to the calibration series performed with multi-element standard solutions (ICP multi-element standard solutions— MerckTM). The detection limits of the analysis were at the 0.1 ng L^{-1} level.

Annual effective dose calculation

The annual dose contributed from ^{210}Po due to drinking water was calculated using Eq. (2) [30].

$$AED = A \times C \times D \qquad (2)$$

AED: is the annual effective dose (μSv y^{-1}), A is the activity concentration of isotopes (mBq L^{-1}) in water, C is the consumption of drinking water for one year (L y^{-1}), and D is the dose conversion coefficient (Sv Bq^{-1}). The

annual drinking water intake for adults, children and infants is 730, 350, and 250 L, respectively. The dose conversion factor for adults, children and infants to calculate the annual effective dose used for ^{210}Po was 1.2×10^{-6}, 2.6×10^{-6} and 8.8×10^{-6} Sv Bq^{-1} [31, 32].

Results and discussion

The coordinates, the pH value, temperature, TDS, the ^{210}Po activity concentration, and the observed chemical components in the investigated thermal water samples are presented in Table 1. Therein the pH, temperature and TDS were previously reported by Van-Hao [26]. The pH value for all investigated water samples is neutral, except for water samples from KB and IO, which are slightly alkaline. The ICP-MS measurements showed that the major elements present are Na, K, Mg, Ca, Sr with concentrations ranging from a few mg L^{-1} up to 1000 mg L^{-1}, while trace amounts of rare earth elements (REE), as well as Ag, As, Pb, Th, and U were identified. The Fe level of all investigated water sources were

Table 1 ^{210}Po activity and chemicals concentration of studied areas

	TL	QH	TT	ML	KG	KB	BM	IO
X	20°43′00″	20°59′10″	21°09′10″	21°46′10″	20°19′30″	20°35′30″	21°17′40″	21°33′25″
Y	106°33′00″	107°11′50″	105°15′40″	105°08′20″	105°48′30″	105°35′10″	103°53′20″	104°02′50″
^{210}Po (mBq L^{-1})	1.79±0.18	2.83±0.26	1.19±0.09	1.39±0.12	8.26±0.66	1.01±0.05	3.73±0.22	0.56±0.02
pH	6.9±0.6	7.4±0.7	7.2±0.5	7.3±0.7	7.1±0.7	7.9±0.5	7.1±0.7	7.6±0.8
Depth (m)	400	210	55	90	Spring	125	10	47
TDS (mg L^{-1})	326±33	735±96	3153±236	4064±272	9270±927	354±46	319±38	3009±241
T (C^0)	55±2	43±1	41±1	61±1	53±1	44±1	39±1	41±1
Li (µg L^{-1})	7.8±0.9	65.8±5.9	54.6±4.1	49.2±3.4	101±8.0	6.0±0.7	2.3±0.2	71.1±4.3
Be (ng L^{-1})	4.5±0.4	22.7±1.5	6.1±0.7	1.5±0.2	LLD	LLD	LLD	43.9±3.1
Na (mg L^{-1})	78±6	190±11	120±5	111±4	0.12±0.01	3.4±0.1	3.7±0.2	31±2
Mg (mg L^{-1})	2.5±0.1	173±7	651±39	607±30	924±37	9.4±0.3	6.5±0.3	112±1
P (µg L^{-1})	173±10	14.6±2	LLD	LLD	2.6±0.3	28±2	52.7±4.5	15.6±1.2
K (mg L^{-1})	4.6±0.2	106±3.2	6.1±0.3	5.6±0.2	30±1	1.2±0.1	0.50±0.05	8.4±0.1
Ca (mg L^{-1})	3.2±0.2	147±3	185±2	172±3	155±5	200±4	176±7	140±4
Sc (µg L^{-1})	3.2±0.3	0.93±0.08	3.8±0.3	3.1±0.3	1.6±0.2	1.0±0.1	1.8±0.17	3.2±0.1
Ti (µg L^{-1})	2.9±0.3	1.4±0.1	2.3±0.3	1.9±0.2	1.2±0.1	1.2±0.1	1.4±0.1	2.3±0.2
V (µg L^{-1})	0.34±0.03	1.2±0.1	1.2±0.1	1.3±0.1	1.0±0.1	0.11±0.01	0.22±0.02	0.41±0.04
Cr (µg L^{-1})	0.62±0.06	4.1±0.4	1.0±0.1	1.2±0.1	2.6±0.3	1.1±0.1	2.2±0.2	1.1±0.1
Mn (µg L^{-1})	0.16±0.02	LLD	LLD	LLD	41.8±3.1	LLD	LLD	LLD
Co (µg L^{-1})	LLD	2.7±0.2	3.4±0.3	2.8±0.2	2.5±0.2	0.20±0.02	0.17±0.02	1.9±0.2
Fe (µg L^{-1})	LLD	LLD	LLD	LLD	LLD	LLD	LLD	LLD
Ni (µg L^{-1})	LLD	LLD	LLD	LLD	LLD	LLD	LLD	LLD
Cu (µg L^{-1})	LLD	LLD	LLD	LLD	LLD	LLD	LLD	LLD
Zn (µg L^{-1})	LLD	LLD	LLD	LLD	LLD	LLD	LLD	LLD
As (µg L^{-1})	2.3±0.2	21.8±2.0	1.8±0.1	1.7±0.2	20.9±2	1.3±0.1	5.8±0.3	3.4±0.2
Se (µg L^{-1})	6.1±0.6	14.5±1.6	2.0±0.2	1.4±0.2	8.6±1.7	0.21±0.20	0.36±0.48	0.77±0.31
Rb (µg L^{-1})	43±4	196±16	168±13	156±11	234±14	20±1	8±1	232±9
Sr (mg L^{-1})	0.10±0.01	2.4±0.2	8.3±0.6	7.6±0.9	26.2±2.1	1.00±0.01	0.010±0.001	8.5±0.6
Y (ng L^{-1})	62±9	143±29	251±40	161±35	472±80	9.9±1.5	1.5±0.2	119±19
Zr (µg L^{-1})	0.11±0.01	82.9±7.5	55.0±4.1	36.2±2.5	90.7±7.3	17.7±0.9	47.2±2.8	153.7±10.8
Nb (µg L^{-1})	1294±129	425±38	450±34	277±24	328±26	251±13	413±25	522±26
Mo (µg L^{-1})	15.7±1.6	6.4±0.6	2.99±0.21	2.06±0.18	1.55±0.11	1.83±0.09	1.64±0.10	4.18±0.17
Ag (ng L^{-1})	6.0±0.7	184±17	89±7	66±6	255±20	56±6	37±2	51±6
Cd (µg L^{-1})	1.3±0.1	5.2±0.5	9.5±0.7	4.9±0.4	5.3±0.4	6.6±0.5	6.8±0.4	7.1±0.6
Sb (µg L^{-1})	0.53±0.05	LLD	LLD	LLD	2.1±0.1	LLD	LLD	LLD
Cs (µg L^{-1})	0.19±0.02	0.63±0.08	0.45±0.04	0.42±0.04	8.03±0.04	0.31±0.03	0.54±0.04	2.61±0.13
Ba (µg L^{-1})	8.8±0.9	14.4±1.2	5.6±0.6	4.7±0.5	110±1	1.4±0.2	LLD	LLD
La (ng L^{-1})	383±25	333±20	160±14	85.4±6.2	41.0±3.5	LLD	LLD	LLD
Ce (ng L^{-1})	LLD	45.4±7	126±11	LLD	LLD	LLD	LLD	LLD
Pr (ng L^{-1})	87.4±5.6	51.7±4.5	37.0±3.2	9.4±0.8	4.8±0.5	LLD	LLD	LLD
Nd (ng L^{-1})	232±15	190±16	117±10	17.7±1.3	2.7±0.3	LLD	LLD	LLD
Sm (ng L^{-1})	62.1±5.8	46.1±4.5	54.1±4.6	LLD	3.3±0.3	LLD	LLD	LLD
Eu (ng L^{-1})	10.6±1.1	14.3±0.1	LLD	LLD	97.2±8.1	LLD	LLD	LLD
Gd (ng L^{-1})	47.4±4.5	38.1±3.2	19.9±1.2	0.59±0.02	LLD	LLD	LLD	LLD
Tb (ng L^{-1})	0.75±0.08	LLD	LLD	LLD	LLD	LLD	LLD	LLD
Dy (ng L^{-1})	18.3±1.8	15.4±1.5	17.9±1.5	LLD	LLD	LLD	LLD	LLD
Ho (ng L^{-1})	LLD	LLD	LLD	LLD	LLD	LLD	LLD	LLD
Er (ng L^{-1})	3.1±0.3	9.0±0.8	4.0±0.8	0.6±0.01	LLD	LLD	LLD	LLD
Tm (ng L^{-1})	LLD	LLD	LLD	LLD	LLD	LLD	LLD	LLD
Yb (ng L^{-1})	LLD	LLD	LLD	LLD	LLD	LLD	LLD	LLD

Table 1 (continued)

	TL	QH	TT	ML	KG	KB	BM	IO
Lu (ng L^{-1})	LLD	LLD	LLD	LLD	LLD	LLD	LLD	LLD
Hf (µg L^{-1})	0.49 ± 0.04	3.7 ± 0.4	1.9 ± 0.2	1.8 ± 0.2	2.3 ± 0.2	0.66 ± 0.06	1.5 ± 0.1	5.6 ± 0.6
Ta (µg L^{-1})	1438 ± 144	298 ± 27	219 ± 16	146 ± 13	155 ± 12	116 ± 6	195 ± 12	230 ± 7
W (µg L^{-1})	1719 ± 69	854 ± 43	484 ± 29	298 ± 21	244 ± 15	217 ± 9	602 ± 18	224 ± 7
Pb (ng L^{-1})	11 ± 2	482 ± 58	491 ± 69	406 ± 49	490 ± 74	699 ± 77	504 ± 55	594 ± 59
Th (ng L^{-1})	LLD	LLD	LLD	LLD	LLD	LLD	LLD	LLD
U (ng L^{-1})	9 ± 2	3595 ± 324	292 ± 32	253 ± 22	440 ± 35	241 ± 27	229 ± 28	2877 ± 288

LLD lower limit of detection

lower than the limit of detection and a high concentration was observed for both Mn and ^{210}Po for the KG NB water source.

In this study, the ^{210}Po activity concentration ranged from 0.56 to 8.26 mBq L^{-1} and had a mean value of 2.6 mBq L^{-1}. The mean activity was observed to be significantly lower than the 100 mBq L^{-1} limit activity according to the WHO drinking water guidelines [33]. The mean value of the investigated water samples is also generally much lower than some previous studies on the activity of ^{210}Po in groundwater or thermal water. Specifically, according to the results of the investigation of ^{210}Po content in some areas in the US, the activity of ^{210}Po can be up to 6590 mBq L^{-1} for some basalt aquifers in the Lahontan Valley [7], 1700 mBq L^{-1} was recorded in the metropolitan area Charles County, Maryland [34] or in Madera and San Bernadino counties, California, which had a ^{210}Po activity concentration of 555 and 444 mBq L^{-1} respectively [35]. Contamination levels of ^{210}Po were detected with activity values > 1000 mBq L^{-1} in the town of Fallon in Northern Nevada [7]. Meanwhile, the North and West-Central Florida regions recorded ^{210}Po activity concentrations possibly up to 14,400 mBq L^{-1}, which is related to phosphate deposits and mining activity occurring in the area [19]. In some other parts of the world the reported activity concentration of ^{210}Po up to 19,000 mBq L^{-1} in saline aquifers around Lake Tyrrell in the Australian state of Victoria [22], wells in granite formation in Finland has been reported to have contamination levels of up to 16,000 mBq L^{-1} [21, 36–39]. Meanwhile, in Sweden, the highest recorded level was 947 mBq L^{-1} [40].

Previous studies have shown that ^{210}Po strongly binds to sediment particles [2, 24], so its activity in groundwater is often recorded with values below 40 mBq L^{-1} [2, 24, 41]. Reports of ^{210}Po activity below the limit include a study in southern China's Guangxi Province with ^{210}Po activity of 0.24 to 6.96 mBq L^{-1} [11], Guarani aquifer, Brazil with the largest activity of ^{210}Po recorded at 3.7 mB.L^{-1} [10]. Waters originating from different geological regions of Croatia are recorded at ^{210}Po levels of 0.25–5.20 mBq L^{-1} [42]. Tap water from private wells in the area around the Žirovski

Vrh uranium mine, Croatia had a ^{210}Po activity concentration of 0.28–8.0 mB.L^{-1} [43]. The first deep geothermal doublet in found Flanders, Belgium had a very low content of ^{210}Po, 36 mBq L^{-1} [1]. The differences in the distribution and content of ^{210}Po in these areas are attributed to the complex geochemical behavior of ^{210}Po. Besides, there are major differences under different environmental conditions related to the mobilization and collection of ^{210}Po in groundwater as well as thermal water.

Radioisotopes occurring in groundwater are primarily due to the solubility of minerals in aquifer rocks and leaching [44]. Groundwater is in contact with aquifer rock, so the activity concentration of natural radionuclides is closely related to the geological and environmental features of the aquifer [9, 44–46]. Areas with high background radiation concentrations such as granite, phosphate, shale formations can have elevated levels of radioactivity in ground or thermal waters [47–50]. On the other hand, areas with low natural radioactivity are often found in carbonate or limestone formations, which often correspond to lower levels of natural radioactivity in the water resources in those areas [44, 51–56]. In this study, the ^{210}Po characteristics in the thermal water at these eight sites is a case study for an area believed to have a low radioactive background with a carbonate host formation. Specifically, these are cracked carbonate formations containing hot mineral water. The low radioactive background feature of host formation may also be the primary cause of the low concentrations of U and Th in the measured samples, specifically U in the range from 9 to 3595 and a mean value of of 992 ng L^{-1} while Th is lower than detection limit. The results show that the average concentration of U is about 300,000 times lower than the allowable limit in drinking water of 30,000 µg L^{-1} (370 Bq L^{-1}) [57, 58]. For comparison, the potable groundwater in Uttarakhand state of India has uranium concentrations between 0.02 ± 0 µg L^{-1} 63.7 ± 4.3 µg L^{-1} [58]. The low concentration of U in the water samples in this study was not closely correlated to the low activity of ^{210}Po. Seiler [7] suggested that the U content often has no close relationship with ^{210}Po in groundwater because the half-life of ^{238}U is

very large [6]. However, the presence of ^{238}U or other parent isotopes in the decay series is a fundamental condition for the occurrence of ^{210}Po in groundwater or thermal water [2, 24, 41]. Increased ^{210}Po occurrence in groundwater could be due to the recoil following the alpha decay of precursor atoms in the uranium decay chain [25].

The low ^{210}Po activity in hot mineral water sources in the study area may be also related to the physicochemical properties of the water sources. The hot water storage area is in fractured carbonate strata, which has been clarified in the study of Van Duong [26], allowing for the possibility of radon gas escape for aquifers, which directly supply ^{210}Po. Research by Harada [2] and Seiler [7] suggested that ^{210}Po in groundwater is often not supported by ^{210}Pb because in this environment there is no radioactive equilibrium between ^{210}Po and ^{210}Pb, so ^{210}Po is mobilized from aquifer sediments [2, 6]. The relationship of ^{210}Po to parent radioisotopes and geological formations in the study area still needs further study. Due to the limitation of the scope of the study project, the authors were limited to determine the concentration of ^{210}Po in the eight mine areas and to the interpretation of the relationship of ^{210}Po with the measured physical and chemical parameters of the thermal waters in question.

The oxidation–reduction processes of Fe hydroxide and Mn oxide may be involved in the mobilization of ^{210}Po in groundwater. The study by Seiler et al. [6] showed that the level of ^{210}Po is positively correlated with the level of Mn and Fe. This is supported by the fact that under strongly reducing conditions, the solubility of Fe and Mn-oxyhydroxide/hydroxide increases leading to an increase in the adsorption capacity of the aquifer for ^{210}Po, hence the ^{210}Po content in water tends to decrease [11]. In this study, the ^{210}Po content was found to be relatively low. In our case, in the study area, the Fe content was below the detection level, while for Mn, the highest concentration was recorded in the KG area where the ^{210}Po activity was highest. Research by Balistrieri [24] and Benoit and Hemond [59] showed a strong positive relationship between ^{210}Po and Mn in water, the authors suggested that redox dissolution of Mn oxides contributes to ^{210}Po release and increases ^{210}Po content in groundwater [24, 59]. This result is consistent with the study of Persson [60] and could be a major factor explaining highest ^{210}Po concentration in the study aquifers.

The presence of Arsenic (As) is one of the factors controlling redox potential and pH, thereby affecting the presence of ^{210}Po in groundwater [13, 61]. Arsenic content in groundwater was determined to depend on the ability to co-precipitate with iron sulfide [62], pH [63–66] and the binding properties of redox components [64, 67]. Research by Seiler et al., [6] showed that wells with high ^{210}Po activity tend to have high As concentrations. The redox process of Fe and Mn oxides (oxyhydroxides) releasing trace elements may be responsible for the increased As concentration in water.

As content was found to be strongly correlated according to the Pearson correlation coefficient with ^{210}Po activity in the study areas in Vietnam as well (R ~ 0.75). The concentrations pass the Kolmogorov–Smirnov Test of Normality. It has to be admitted that this is based on 8 data points, and one location, QH is an outlier, showing the highest As concentration, but only a moderate ^{210}Po activity concentration, without it the correlation is even stronger (R ~ 0.97).

Water evolution processes (cation exchange, salinization) also contribute to the change ^{210}Po concentration in groundwater. For this process, the exchange of soluble cations of Na while removing Ca and Mg from groundwater results in Na-dominant water [68–70], this event causes the water to be less saturated with carbonate minerals (CO_3^{2-}) (calcium and dolomite). This process leads to additional dissolution of carbonate minerals accompanied by an increase in pH and alkalinity that reduces the absorption of As for iron oxy-hydroxide (FeO(OH)) thereby enhancing solubility of As. Surveys on groundwater potential in the Northern provinces of Vietnam show that two types exist simultaneously, freshwater and saltwater. Fresh water usually has a chemical form of Sodium Bicarbonate Chloride, Sodium Calcium or Sodium Bicarbonate Chloride, which indicates that there is salinization of groundwater in freshwater bodies but they are frequently supplied from rain and surface water, even is irrigation water. Salt water usually has the form of Sodium Chloride. The chemical type of water also changes from Calcium Bicarbonate to Sodium Bicarbonate Chloride. In this study, the concentration of ^{210}Po seems to decrease with increasing sodium, however the correlation is not statistically significant. A negative correlation between ^{210}Po activity and Na content was also shown in the study of [11, 71].

The variation in the content of ^{210}Po is associated with Ca, most likely due to calcite precipitation and ion exchange [1, 6] It is expected that in wells with high ^{210}Po activity the Ca content is low and the pH is usually more than 9 [7]. However, in our study, there was no significant correlation between ^{210}Po and Ca. The only thing in common is that they all have relatively low concentration. In addition, in the study area the neutral pH condition is also different from previous studies reporting on high ^{210}Po activity concentrations. The pH is one of the factors potentially affecting the ^{210}Po activity concentration significantly [6, 10, 11, 13, 71]. The pH value is often strongly connected to the oxidizing nature of water. In our samples pH was not strongly associated with ^{210}Po concentration, but our samples cover a relatively narrow pH range. According to Seiler [7], ^{210}Po can be present over a wide range of pH from more than 5 to less than 9, however it is often suggested that at neutral or high pH, information of colloidal Po(OH)$_4$ and precipitation with Fe oxyhydroxide could result in the polonium getting fixed [6]. ^{210}Po is highly reactive under most conditions associated with groundwater. Therefore, the distribution of ^{210}Po in

Table 2 Annual effective dose contribution from ^{210}Po in thermal water for adults, children, and infants

^{210}Po (μSv y^{-1})	TL	QH	TT	ML	KG	KB	BM	IO
Adults	1.61	2.55	1.07	1.25	7.43	0.91	3.36	0.50
Children	1.63	2.58	1.08	1.27	7.52	0.92	3.40	0.51
Infants	3.94	6.23	2.61	3.06	18.2	2.21	8.21	1.22

groundwater is tightly controlled by the adsorption properties of surrounding minerals under different conditions [25]. The oxidation state Po^{4+} is believed to be the most stable in aqueous solutions, Po has a high surface reactivity and is readily hydrolyzed and adsorbed onto mineral surfaces, particles and colloids [3, 12, 71]. In highly acidic environments, Po^{4+} can form complexes with acids and anions. However, in neutral and mildly acidic environments, ^{210}Po absorbs into inorganic and organic colloids of different sizes, but because it is usually present in very low concentrations in groundwater, the possibility of colloid formation is very low [12, 72].

Temperature is also one of the factors affecting the concentration of ^{210}Po in the aquatic environment, both by changing solubility and by potentially causing losses by evaporation. It has been shown that ^{210}Po at high temperatures is volatile in separation procedures and laboratory measurements [12, 73–76]). In these studies, the loss of ^{210}Po is thought to be from 50 °C in Heyraud [72] study or about 100 °C in Martin [71] study with 90% loss at about 300 °C. The evaporation of ^{210}Po has been shown to depend on the oxidation state [12, 77]. However, it remains unclear which oxidation state of polonium is most volatile. In this study, the temperature of the thermal waters was defined as warm and slightly hot water with an average temperature of about 47 °C and the highest recorded at 61 °C, which is thought to initiate the evaporation of polonium, but at low concentration. As for the Po^{4+} oxidation state, due to its low concentrations and low colloidal ability, ^{210}Po remains in the dissolved state and can be evaporated due to increased temperature.

Significant coefficients values were observed for ^{210}Po with TDS, Ag, Sr, Y, and Cs, 0.68, 0.77, 0.72, 0.69, and 0.83 respectively. ^{210}Po is one of the natural isotopes, which emits alpha particles and contributes the gross alpha dose in the water samples. A high correlation between gross alpha and TDS was reported previously by Van Duong [26] for the water sources in the current study (R = 0.94 and correlation is significant at the 0.01 level (2-tailed).

In the observed area TDS has high correlation coefficient values with Li, Ca, Rb, Sr, Y, Ag, and Cs with R = 0.81, 0.62, 0.69, 0.99, 0.93, 0.7, and 0.89 respectively, therein Ca and Sr are the two major components.

U, Th, and Pb are present only in trace amounts in the samples. The Th concentration is under the detection limit of the equipment. The ^{210}Po and U, Pb concentrations were not correlated in the samples. This can happen due to the complex geochemical behavior of ^{210}Po, the concentration could be reduced by precipitation or absorption as mentioned above, or there can be excess ^{210}Po in the water originating from the host formation or the sediment of the aquifer [6].

On the other hand, besides the influence of the physico-chemical parameters of water listed above, the appearance and content of ^{210}Po can be affected by additional factors mentioned by the previous authors including the dissolved oxygen (DO) [6, 13, 78], microbial activity [2, 3, 10] or sulfide [2, 3, 6, 12, 19]. However, because the scope of the topic was limited, investigation of these factors needs further study in the area.

The annual effective dose contribution of ^{210}Po was calculated and is presented in Table 2. The calculations were made using the annual drinking water intake for adults, children and infants 730, 350, and 250 L, respectively, which will be an overestimation for people consuming such water occasionally or for medical purposes, who would receive proportionally less according to their consumption, and would represent people relying on these hot water springs as their main source of drinking water.

The ^{210}Po in all studied thermal water sources was far below the guidance level of ^{210}Po concentration for drinking water suggested by the WHO (Table 1) [79]. Consequently, it is clear that the calculated annual committed effective doses from the ingestion of ^{210}Po for adults, children, and infants were also far less than the guidance level of WHO, 0.1 mSv y^{-1} [79].

Conclusions

The ^{210}Po concentration and chemical composition were determined in eight famous thermal water sources in Northern Vietnam. Based on the research results, the following conclusions were drawn:

All of the characteristics studied thermal water sources have similar geologic origin, they all originate from a limestone aquifer, the temperature ranges from 39 to 60 °C, the pH value from 6.9 to 7.9, but the TDS had a higher range, from 326 to 9270 mg L^{-1} and was 2650 mg L^{-1} on average. The chemical analysis showed that the major elements present were Na, K, Mg, Ca, and Sr while trace amounts of rare earth elements (REE), Ag, As, Pb, Th, U were also found.

The active concentrations of ^{210}Po were found to range from 0.56 to 8.26 mBq L^{-1} and have an average of 2.6 mBq L^{-1}. Physical and chemical factors possibly influencing the presence of low ^{210}Po concentration in the thermal water have been discussed. Some, such as red-ox processes through Fe or Mn oxides and oxi-hydroxides, cation exchange or salinization can be observed in the study area, while the effects of pH and temperature described in the literature seem to be less pronounced.

The ^{210}Po activity and other observed radioactive elements concentration in all of the studied thermal water sources were far under the guidance level, as suggested in WHO [79]. Consequently, the annual committed effective doses calculated for adults, children, and infants were also far less than the recommended limit of 0.1 mSv y^{-1} [79].

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