Radionuclides' Activity Analysis in the Environmental Samples

Eva Singovszka, Adriana Estokova and Magdalena Balintova

Abstract Sediment quality monitoring are amongst the highest priorities of environmental protection policy. Their main objective is to control and minimise the incidence of pollutant—oriented problems, and to provide for water of appropriate quality to serve various purposes such as drinking water supply, irrigation water etc. The present work aimed to investigate the pollutants levels of some heavy metals (Fe, Mn, Al, Cu, Zn, As, Cd, Pb) in the sediments relate to acid mine drainage (AMD) producing from abandoned sulphide mine in Smolnik in eastern of Slovakia. Studies on environmental radioactivity in this area is scarce. Therefore, a baseline study of natural (238U, 226Ra, 40K) radionuclides was carried out on Smolnik Creek surface sediments and on their radiological significance. Grab surface sediment samples were collected from 5 stations and their radioactivity concentrations measured by gamma spectrometry. The estimated radionuclide activity index, total absorbed dose rate in air (D), radium equivalent activity (Raeq), external hazard index (Hex), annual effective dose equivalent (AEDE) and indicated no significant radiological risks from the sediment radioactivity concentrations.

Keywords Acid mine drainage · Heavy metals · Natural radioactivity · Radiological parameters

1 Introduction

Radionuclides such as ^{226}Ra, ^{228}Th and ^{40}K are widely distributed in the environment as a result of their natural occurrence in the Earth's crust or the atmosphere. The human population worldwide receives an average annual radiation dose of 2.4 mSv/y, about 80% of which comes from naturally-occurring radionuclides, the remaining part is largely due to artificial sources of which fallout radionuclides account for only

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0.4% (UNSCEAR 2000). Sediment contamination by radionuclides of the ^{238}U and ^{232}Th decay-series and ^{40}K is of particular interest from radiological point of view, as they can form the basis of radiological assessments for the human population. The Environmental Risk from Ionising Contaminants Assessment and Management tool (ERICA) developed by the European Commission provides an integrated approach to the assessment and management of environmental risks from ionising radiation (Beresford et al. 2007) and can be applied to assess the potential ecological impact of radionuclide-contaminated environments.

The activity concentrations of various radionuclides in natural resources play an essential role as regards the public and environmental health. The naturally occurring radioisotopes ^{40}K-as well as ^{238}U-series and ^{232}Th-series are the main sources of gamma radiation in rocks, soils and water. Human body could be subjected to such radiation sources, either externally or internally (through inhalation and/or ingestion ways). During the last decades, there has been an increasing interest in the study of radioactivity in environmental samples such as bottom sediment (Ahmed et al. 2006; Harb et al. 2008; El Mamoney and Khater 2004; Abdel-Razek et al. 2008; EL Saharty and Dar 2008; El-Taher and Madkour 2011; Orgun et al. 2007). In the Slovak Republic, overflowed mine Smolnik produces acid mine drainage with high metal concentrations and low value of the pH (about 3–4) as a result of chemical oxidation of sulphides and other chemical processes. This was the reason for starting a systematic monitoring of geochemical development (Singovszka et al. 2016). The most critical values of heavy metals were observed also in the abandoned deposit Smolnik (Balintova and Petrilakova 2011; Singovszka et al. 2017). Another significant issue could be connected with the possible radiological risk of sediment. The aim of this study was to assess the mass activities of natural radionuclides in bottom sediments from Smolnik creek in the East of Slovakia and their radiological significance to provide a prognosis in terms of environmental risk.

2 Materials and Methods

The samples of the sediment were collected from the Smolnik creek from five sampling stations (S1–S5) creek in November 2018. The sampling sites were located at 48° south latitude and 20° east longitude (Fig. 1). The two sampling sites were situated in the upper part of the Smolnik creek not contaminated by acid mine water from the Pech shaft and another two sampling localities were located under the shaft. The outflow of AMD from Pech shaft (Smolnik mine) is numbered as Site 3 (Balintova and Petrilakova 2011). The sediment samples are marked as S1, S2, S3, S4 and S5 according to the location of sampling.

The samples of sediment were air-dried and ground by using a planetary mill to a fraction of 0.063 mm. TFirst af all the samples were characterized by its chemical composition using of X-ray fluorescence (XRF) method (SPECTRO iQ II, Ametek, Germany). The measured concentration of heavy metals in sediment were compared

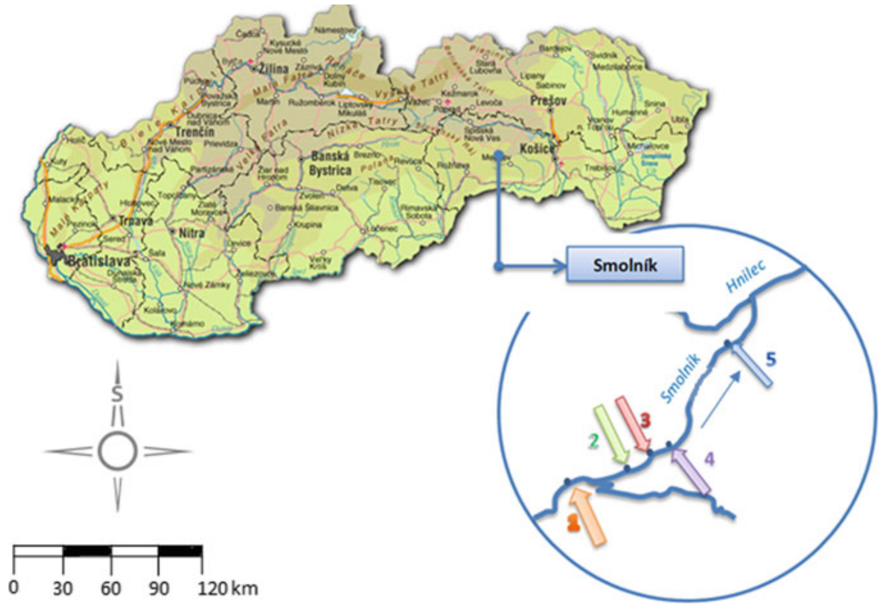

Fig. 1 Location of five sediment samples from Smolnik Creek

with limit value by Slovak legislation (Act. No. 188/2003 Coll of Laws on the application of treated sludge and bottom sediments to fields) (188/2003).

Afterwards, the powdered samples were under radiological investigation. The samples were weighted and stored in the Marinelli containers until radioactive equilibrium was stated.

The mass activities of radionuclides (^{226}Ra, ^{232}Th and ^{40}K) in sediment were measured by gamma ray spectrometry. Measurements were carried out using an EMS-1A SH (Empos, Prague, Czech Republic) detection system equipped with a NaI/Tl scintillation detection probe and a MC4K multichannel analyzer with optimized resolution of 818 V, 4.096 channel and with 9 cm of lead shielding and internal lining of 2 mm tinned copper.

The specific activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K were determined in Bq.kg^{-1} using the count spectra. The ^{40}K radionuclide was measured directly through its gamma ray energy peak at 1461 keV, while activities of ^{226}Ra and ^{232}Th were calculated based on the mean value of their respective decay products. Activity of ^{226}Ra was measured using the 351.9 keV gamma rays from ^{214}Pb and the activity of ^{232}Th was measured using the 238.6 keV gamma rays of ^{212}Pb. The same counting time of 86,400 s (24 h) was used for all measured samples.

2.1 Radiological Risk Assessment

Characterisation of associated potential radiological risk is essential to protection for human and appropriate handling of radioactive—contaminated sediments, Radionuclide activity index, radium equivalent activity (Raeq), total absorbed dose rate in air (D), external hazard index (Hex), annual effective dose rate (AEDR) and gamma radiation representative level index (RLI) are six most often used radiological hazard indices for radiological assessment.

UNSCEAR 2000 defined index of radionuclide activity. The gamma index of materials recommend limit values depending on the dose criterion ($I\gamma \leq 1$) (UNSCEAR 2000). Radionuclides' activity index, Iγ is exúressed according to the following Eq. (1):

$$I\gamma = (A_{Ra}/300) + (A_{Th}/200) + (A_{K}/3000) \quad (1)$$

According to Sugandhi et al. (2014), Botwe et al. (2017) the Ra_{eq} is weight sum of activity concentration of measured radionuclides in a study sediment, which allows comparison with their individual ^{226}Ra, ^{232}Th and ^{40}K activity concentration. Radium equivalent activity is expressed by the following Eq. (2).

$$Ra_{eq} = A_{Ra} + 1.43A_{Th} + 0.077A_{K}\ (Bq/kg) \quad (2)$$

The total absorbed dose rate in air (D) expresses the rate of exposure to gamma radiation in air at 1 m above the ground due to measured activities in sediment samples (Sugandhi et al. 2014). The D rates were calculated using the Eq. (3).

$$D = 0.462A_{Ra} + 0.604A_{Th} + 0.0417A_{K}\ (nGy/h) \quad (3)$$

Beretka and Mathew (1995) defined index that represent External hazard index, which is obtained from Rae_q expression, that its allowed maximum value corresponds to the upper limit of Ra_{eq} (370 Bq/kg). The limit value for H_{ex} must not exceed 1.0 for human health (UNSCEAR 2000; Beretka and Mathew 1995). The H_{ex} can be defined as:

$$H_{ex} = (A_{Ra}/370) + (A_{Th}/259) + (A_{K}/4810) \quad (4)$$

Annual effective dose rate as a result from total absorbed dose values was calculated using the next equal (4) (Ravisankar et al. 2012; Kurnaz et al. 2007):

$$AEDR = D \times 1.23 \times 10^{-3}\ (mSv/y) \quad (5)$$

Association with different concentration of some specific radionuclide can be estimated by level of gamma radioactivity known as the representative level index (RLI)

Gamma radiation representative level index is given as:

$$RLI = (A_{Ra}/150) + (A_{Th}/100) + (A_K/1500) \quad (6)$$

where A_{Ra} is average activity concentration of ^{236}Ra in Bq/kg, A_{Th} is average activity concentration of ^{232}Th in Bq/kg and A_K is average activity concentration of ^{40}K in Bq/kg.

3 Result and Discussion

3.1 Chemical Analysis

The results of the chemical analysis of sediment samples, originated from the Smolnik creek are presented in Table 1.

Based on the analyses of sediments quality in the Smolnik creek oriented towards the influence of heavy metals concentration; and on the comparison of limit values, it can be stated that the sediment does not show a significant risk with respect to the heavy metal content except copper and arsenic. The concentration of popper was higher than the limit value in all sediment samples while arsenic in one sample (S3) of the Site 3 (1406 mg/kg). This points to the extra high content of arsenic in AMD since Site S3 was located at the outflow of the contaminated water from the mine.

Table 1 Chemical analysis of sediments regarding the metals content from the Smolnik creek

Metals	Sediment samples					Limits
(mg/kg)	S1	S2	S3	S4	S5	(mg/kg)
Fe	29510	27910	302100	85540	64840	–
Mn	568.5	426.4	383	558	755	–
Al	62,450	54,520	8267	5,7460	7,4320	–
Cu	**113.0**	**147.4**	**360**	**249.5**	**338.1**	100
Zn	121.0	135.2	1.0	94.6	215.8	2500
As	2.1	6.1	**1406**	18.7	39.2	20
Cd	5.1	3.2	5.1	5.1	1.7	10
Pb	5.9	22.8	222	4.5	20.3	750

Table 2 Natural activity of radionuclides and gamma indexes of the samples $I\gamma$

	Sample	^{226}Ra	^{232}Th	^{40}K	$I\gamma$
		Bq/kg			
Sediment sample sites	S1	11.11	76.96	1148.75	0.80
	S2	9.18	81.84	1082.38	0.79
	S3	4.30	53.97	350.39	0.40
	S4	10.01	64.16	846.57	0.66
	S5	7.52	69.29	946.77	0.68

Table 3 Radiological parameters in bottom sediment samples from Smolnik creek

	Ra_{eq}	D	H_{ex}	AEDR	RLI
	Bq/kg	nGy/h	–	mSv/y	–
S1	201.58	99.86	0.57	0.12	1.61
S2	201.98	99.13	0.57	0.12	1.60
S3	106.02	49.31	0.29	0.06	0.80
S4	168.17	81.95	0.47	0.10	1.32
S5	172.88	85.09	0.48	0.10	1.37

3.2 Radiological Risk Assessment

3.2.1 Concentrations of Radionuclides

The activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in the bottom sediment are shown in Table 2.

The natural activity concentration of radionuclide ^{40}K is relatively higher than of radionuclides ^{226}Ra and ^{232}Th, ranging from 350.39 to 1148.75 Bq/kg. The activities range for ^{226}Ra and ^{232}Th are 4.30–11.11 and 53.96–81.84 Bq/kg, respectively. The comparison of the measured radionuclides in our study with the worldwide average values (35 Bq/kg for ^{226}Ra, 30 Bq/kg for ^{232}Th and 400 Bq/kg for ^{40}K) show that radionuclides ^{232}Th and ^{40}K exceed multiply worldwide average values (UNSCEAR 2000) measured in sediments.

3.2.2 Assessment of the Radiological Hazard

The results of six radiological hazard indexes are given in Table 3. The radium equivalent activity Ra_{eq} was calculating according Eq (2). The maximum admissible value of Ra_{eq} is 370 Bq/kg (Beretka and Mathew 1995). As it can be seen in Table 3, the Ra_{eq} values for the bottom sediments rangeg from 106.02 to 201.98 Bq/kg. Any values of Ra_{eq} did not exceed the allowed value.

The absorbed gamma dose rates D ranged from 49,31 to 99,86 nGy/h. In this study, estimated mean value of absorbed gamma dose rate.

The range of annual effective dose rate AEDR is between 0.06 and 0.12 mSv/y and mean value is 0.1 mSv/y. According (UNSCEAR 1993) the average annual indoor effective dose from natural radionuclides in normal background areas is 0.46 mSv/y. The calculated mean value (0.1 mSv/y) from five evaluated sediment samples is lower than average value. The values for external hazard index are between 0.29 and 0.57 (Table 3). The recommended values of the Hex should be <1. It is observed in Table 3 that the values of H_{ex} is below the criterion value (<1). The RLI values for the evaluated sediment samples varies from 0.80 to 1.61. The limit values of RLI is $\leq$1 (Mahur et al. 2008). Except one location (S3) all sediment sample exceed recommend value.

4 Conclusion

The radioactivity levels of ^{226}Ra, ^{232}Th and ^{40}K in bottom sediment from Smolnik creek in Slovakia have not been studied before. The measured activity concentrations of the radionuclides were the basis for the calculation of the main radiological hazard indicators to determine a possible risk effect from natural radionuclides in sediments. The result indicated that values of all radiological hazard parameters were under the world average value reported in (UNSCEAR 2000), expect for RLI for sediment sample site S1, S2, S4, S5.

Assessment of radioactivity in the environment is useful for the protection of human health and environment from dangerous ionizing radiation. Consequently the assessed radiological parameter in this study can be used as a basis for next research.

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