Journal of Environmental Protection, **2014, 5, 114-119**
Published Online February 2014 (http://www.scirp.org/journal/jep)
http://dx.doi.org/10.4236/jep.2014.52015

Natural and Artificial Radionuclides in River Bottom Sediments and Suspended Matter in the Czech Republic in the Period 2000-2010

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Received November 29th, 2013; revised December 28th, 2013; accepted January 27th, 2014

ABSTRACT

The concentrations of natural radionuclides, radium-226, radium-228, and potassium-40, and the artificial radionuclide caesium-137, in river bottom sediments and suspended matter were monitored in the Czech Republic by the Czech Hydrometeorological Institute during the period 2000-2010 and 2001-2010 respectively. The data were used to evaluate the natural background levels of these radionuclides and the impact of human activities on the water environment. For potassium-40 in sediments, the natural background level was estimated to be 570 Bq/kg. To evaluate the background level for radium-226, the river sites affected by human activities (mining and processing uranium ore, coal) were eliminated from the assessment. The average natural background values were 47.8 Bq/kg for radium-226 and 47.2 Bq/kg for radium-228 in sediments and 86.5 Bq/kg for radium-226 and 87.9 Bq/kg for radium-228 in suspended matter. The river sediments were identified as good indicators of radioactive contamination, especially radium-226, which recorded historic contamination due to former uranium mining and milling. The radium-226 contamination rate was assessed using the ratio of radium-226 to radium-228. This ratio was used to classify sediment according to the relative contamination from the uranium industry. The residual contamination of caesium-137 due to the Chernobyl accident in 1986 was also assessed. Average values of caesium-137 were 14.0 Bq/kg in sediments and 25.0 Bq/kg in suspended matter.

KEYWORDS

River Bottom Sediments; Suspended Matter; Surface Water; Uranium Industry; Radioactive Contamination; Radium-226; Radium-228; Potassium-40; Caesium-137

1. Introduction

Monitoring of radioactive substances in river bottom sediments in the Czech Republic has a long history [1-4]. The permanent monitoring of river bottom sediments and suspended matter, which includes gamma-spectrometric analysis, was initiated in 1999 under a programme carried out by the Czech Hydrometeorological Institute (CHMI). The aim was to improve the knowledge of natural background levels and anthropogenic influences on the content of radionuclides in sediments and suspended matter. The results of the monitoring for the period 2000-2010 and 2001-2010, respectively, are evaluated in the paper.

2. Methods

The monitoring network of river bottom sediments covered the Czech Republic and included 44 river sites (hereinafter referred to as "basic network"). Based on the evaluation of the results in 2004 [5], the monitoring was extended by an additional 33 sites in 2006-2008 (hereinafter referred to as "extended network"), which cover the areas of former uranium and coal mining and processing. The sampling was carried out mainly by staff of CHMI and since 2006 the new sites were also sampled

by staff of river basin companies and the T. G. Masaryk Water Research Institute (TGM WRI). The frequency of the sampling was twice per year.

Suspended matter were sampled by using a mobile centrifuge ALFA LAVAL WSB 203B-34 with a pump ALFA LAVAL IP 200 and maximal power 1 800 l/s since the year 2001 [6]. In the period 2001-2005, the sampling was carried out in the same monitoring network as of river bottom sediments (basic network). The monitoring was narrowed to ten selected sites in 2006.

Grain size of the sediment samples was generally less than 2 mm. Samples were analyzed at the Radiological Laboratory of the TGM WRI. Sediment samples were dried at 105˚C, hermetically sealed in containers and measured for the activities of caesium-137 (^{137}Cs), potassium-40 (^{40}K), radium-226 (^{226}Ra) and radium-228 (^{228}Ra) by using gamma-spectrometric methods in accordance with Czech National Standard ISO 10703 (75 7630) [7]. Samples of suspended matter were measured for the activities of ^{137}Cs, ^{226}Ra and ^{228}Ra. The amount of dry sample was about 0.5 kg (sediments) and 1 - 25 g (suspended matter) respectively. The results were expressed in Bq/kg dry sample. The minimum detectable activities (MDA) in the sediments at the 95% level of significance were approx. 0.5 Bq/kg for ^{137}Cs, 10 Bq/kg for ^{40}K, and 2 Bq/kg for the radium radioisotopes. The MDA in the suspended matter at the 95% level of significance was approx. 5 Bq/kg for ^{137}Cs, 20 Bq/kg for the ^{226}Ra and 30 Bq/kg for ^{228}Ra.

Values below the MDA were included in the assessment as they were assumed to equal the MDA. The measured values were used for calculation of annual average activities. Comprehensive assessment of radionuclides in river sediments was done for basic network for the period 2000-2010. The extended network was included only for assessment of impacts of former uranium mining and processing. Assessment of radionuclides in the suspended matter was done only for ten sites where the monitoring was carried out for the whole period 2001-2010.

The monitoring network of river bottom sediments and suspended matter is shown in **Figure 1**.

3. Results and Their Evaluation

3.1. Caesium-137

The concentrations of artificial radionuclides were assessed by using ^{137}Cs, which represents the residual contamination in the environment after nuclear weapons tests in the atmosphere, mainly in the 1950s and 1960s, and also the nuclear reactor accident at Chernobyl in 1986. The half-life of ^{137}Cs is 30.2 y [8]. Annual average activities in river sediments at the monitored sites ranged from 11.4 to 17.5 Bq/kg, with an average of 14.0 Bq/kg.

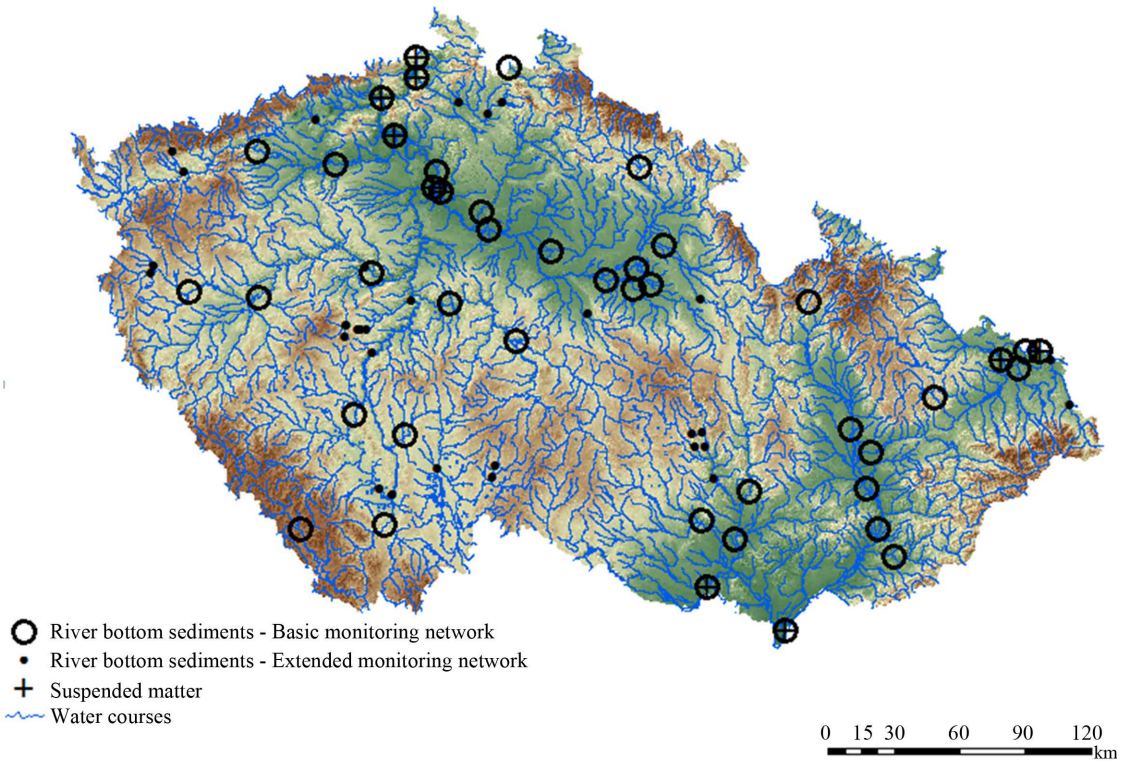

Figure 1. Map of sampling sites.

Differences in the ^{137}Cs concentrations of sediment between the monitored sites correspond to the available information on the distribution in the Czech Republic after the accident at the Chernobyl nuclear reactor [9]. The highest activities of ^{137}Cs, with an average of 87.6 Bq/kg and range from 38.9 to 124 Bq/kg, were detected at the Topělec site on the Otava River.

Annual average activities in suspended matter ranged from 16.8 to 31.4 Bq/kg, with an average of 25.0 Bq/kg. The average activity of ^{137}Cs in the suspended matter was nearly two times higher than that in river sediments.

Further, the assessment of ratio of ^{137}Cs activities in suspended matter and sediments at individual sites was performed. The ratio ranged from 1 to 36.8, with an average 6.2. The activity of ^{137}Cs was higher in suspended matter than in river sediments at all sites.

The data from the basic network were analysed for possible time trends in the ^{137}Cs values (Equation (1)). Statistical significance of regression curve was tested by using F-test. Effective half-life was calculated according to Equations (2) and (3) [10,11]:

$$\ln a = -\lambda_{eff} \cdot t + q \quad (1)$$

where a is radionuclide activity in sediments (Bq/kg); λ_{eff}, effective decay constant of ^{137}Cs (1/y); t, time (y); and q, natural logarithm of radionuclide activity in sediments (suspended matter) at the beginning of observation (Bq/kg).

$$T_{eff} = \ln 2 / \lambda_{eff} \quad (2)$$

where T_{eff} is effective half-life of ^{137}Cs (y).

$$1/T_{eco} = 1/T_{eff} - 1/T_P \quad (3)$$

where T_{eco} is ecological half-life of ^{137}Cs (y) and T_P is physical half-life of ^{137}Cs (y).

The annual average values were used for determining the effective half-life of ^{137}Cs in sediments 23.8 y and ecological half-life 112 y (see **Figure 2**).

The average decrease in the ^{137}Cs in sediments exceeds that of the physical half-life (30.2 y). We assume that the quicker reduction of ^{137}Cs is caused by natural fluvial and biological processes, and thus that the effective and ecological half-lives are less than the radioactivity decay.

The annual average values of ^{137}Cs in suspended matter were used for determining the effective half-life of ^{137}Cs in suspended matter 11.4 y and ecological half-life 18.4 y (**Figure 2**). Observed decrease of ^{137}Cs in suspended matter was faster than in sediments.

3.2. Potassium-40

^{40}K is a natural isotope with very long half-life (1.28×10^9 y) (with an abundance of 0.0118%) and classified among the so-called primordial radionuclides (radionuclides which arose with the emergence of the Earth). In the Earth's crust, it is dispersed homogeneously [8,12]. Observed annual average values ranged from 513 to 605 Bq/kg, with an average of 570 Bq/kg. In the monitoring period, the observed values did not exhibit any significant trend, using Equation (1) (**Figure 3**).

The results of the monitoring programme in the Czech Republic are in good agreement with the range of ^{40}K activities reported in the literature for sediments and suspended matter, which is 500 - 700 Bq/kg [13].

The assessment of ^{40}K in suspended matter was not performed.

3.3. Radium-226 and 228

The isotopes ^{226}Ra and ^{228}Ra are among the most representative of the natural decay series of uranium and thorium, with half-lives of 1600 y and 5.7 y, respectively [8].

Development of annual average ^{226}Ra activities in river sediments and suspended matter for the period 2000-2010 and 2001-2010 respectively is showed in the **Figure 4**.

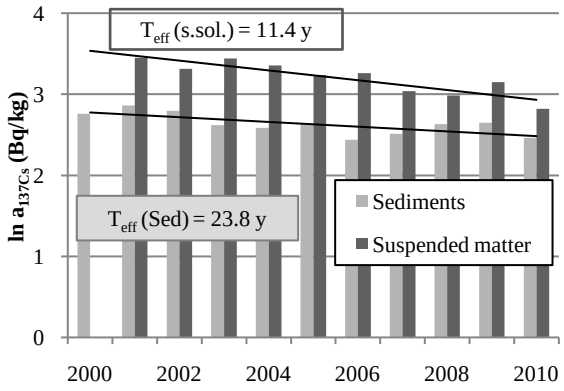

Figure 2. The decrease in annual average ^{137}Cs activities in river sediments and suspended matter for the period 2000-2010 and 2001–2010 respectively.

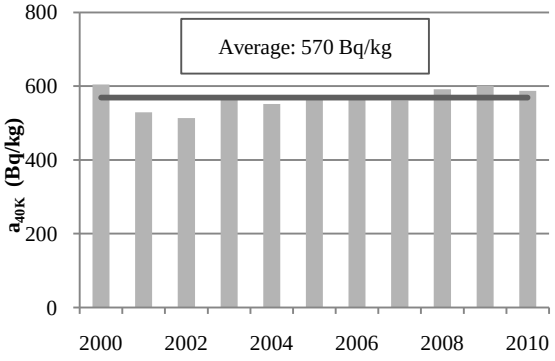

Figure 3. Annual average ^{40}K activities in river sediments for the period 2000-2010.

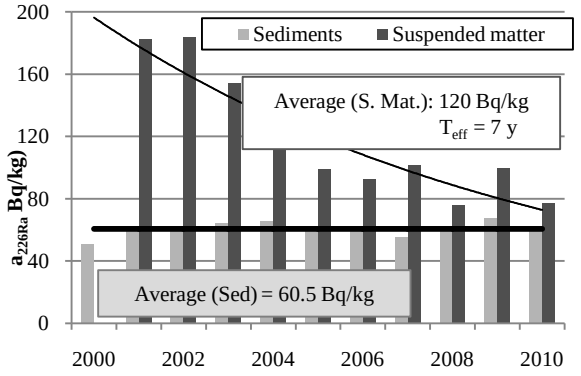

Figure 4. Development of annual average ^{226}Ra activities in river sediments and suspended matter for the period 2000-2010 and 2001-2010 respectively.

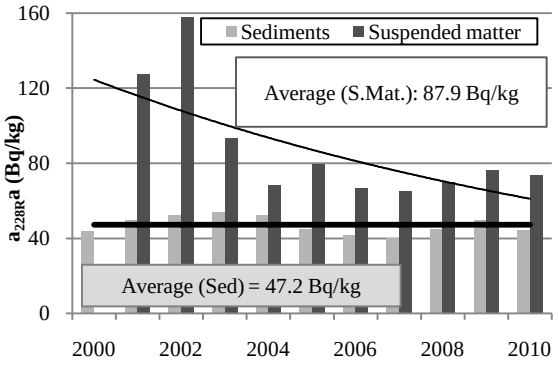

Figure 5. Development of annual average ^{228}Ra activities in river sediments and suspended matter for the period 2000-2010 and 2001-2010 respectively.

Annual average values of ^{226}Ra in river sediments for the whole territory of Czech Republic ranged from 50.8 to 67.9 Bq/kg, with an average of 60.5 Bq/kg. In the monitoring period 2000-2010, the observed annual average values for basic network did not exhibit any significant trend, using Equation (1).

Annual average values of ^{226}Ra in suspended matter ranged from 75.5 to 184 Bq/kg, with an average of 120 Bq/kg. In the monitoring period 2001-2010, the observed annual average values were used for determining the effective half-life of ^{226}Ra in suspended matter 7 y, using Equation (1).

Development of annual average ^{228}Ra activities in river sediments and suspended matter for the period 2000-2010 and 2001-2010 respectively is showed in the **Figure 5**.

Anthropogenic pollution of the aquatic environment by ^{228}Ra is unlikely, because thorium ores are not mined in the Czech Republic.

Annual average values of ^{228}Ra in river sediments ranged from 40.2 to 53.9 Bq/kg, with an average of 47.2 Bq/kg. In the monitoring period 2000-2010, the observed annual average values of ^{228}Ra for basic network did not exhibit any significant trend, using Equation (1).

Annual average values of ^{228}Ra in suspended matter ranged from 65 to 158 Bq/kg, with an average of 87.9 Bq/kg. In the monitoring period 2001-2010, the observed annual average values were used for determining the effective half-life of ^{228}Ra in suspended matter 9.7 y, using Equation (1).

Observed values correspond to the natural occurrence of ^{228}Ra in watercourses.

Activities of ^{228}Ra in suspended matter are in greater range than activities in sediments. Also decrease of activity of ^{228}Ra in suspended matter exceeded that of the physical half-life at most sites. This we attribute to presence of parent radionuclide ^{232}Th with physical half-life of 1.4×10^{10} y [8]. However decrease of activity ^{228}Ra should be studied in more details.

Additionally was carried out monitoring activity of ^{226}Ra and ^{228}Ra in sediments at sites of former uranium (and coal) mining and processing in the period 2006-2008 (extended network). Observed annual average values ^{226}Ra ranged at these sites from 102 to 133 Bq/kg, with an average of 123 Bq/kg. Observed annual average values of ^{228}Ra ranged from 42.5 to 54.4 Bq/kg, with an average of 49.8 Bq/kg. While average activity of ^{228}Ra for extended network was same as that in other (basic network), average activity of ^{226}Ra was two times greater.

The ratio of ^{226}Ra and ^{228}Ra activities in suspended matter and in sediments was assessed. The ratio of ^{226}Ra activities ranged from 0.3 to 4.6 with an average 1.9. The ratio of ^{228}Ra activities ranged from 0.7 to 6.9 with an average 2.3. Activity of ^{226}Ra and ^{228}Ra was higher in suspended matter in 82 % and 94 % respectively.

Hanslík [14] proposed that it is possible to use the ^{226}Ra:^{228}Ra ratio to identify the degree of radionuclide contamination in the environment from uranium ore (and coal) mining activities. The ratio is around 1.0 in natural samples, while in areas affected by uranium ore mining, it is significantly higher. The activity of ^{226}Ra is increased as a result of contamination, while the activity of ^{228}Ra corresponds to the natural radium levels. On this basis, Hanslík [14] proposed five classes of river sediment contamination by ^{226}Ra according to the ^{226}Ra:^{228}Ra ratio (see **Table 1**).

These classes were used for classification of river sediments collected in the individual sites in the period 2000-2010. Results from extended network were included to the assessment too. The numbers of the sites in the individual classes are shown in **Figure 6**.

In the period 2000-2005 and 2009-2010, most of the sites were classified as class I (84% - 91%), *i.e.* as uncontaminated. In the period 2006-2008, the inclusion of the sites affected by former mining and processing of

Table 1. Classification of river sediments (and suspended matter) contaminated by ^{226}Ra into classes I–V according to the ratio of the activities of ^{226}Ra and ^{228}Ra [14].

$\frac{^{226}Ra}{^{228}Ra}$	*Class*	*Description*
≤1.5	I	Natural occurrence of natural radionuclides
>1.5 - 2.0	II	Moderate contamination by wastes from uranium industry, coal mining, industrial wastes
>2.0 - 5.0	III	Contamination by wastes from uranium industry
>5.0 - 10.0	IV	High contamination by wastes from uranium industry
>10	V	Extremely high contamination by wastes from uranium industry

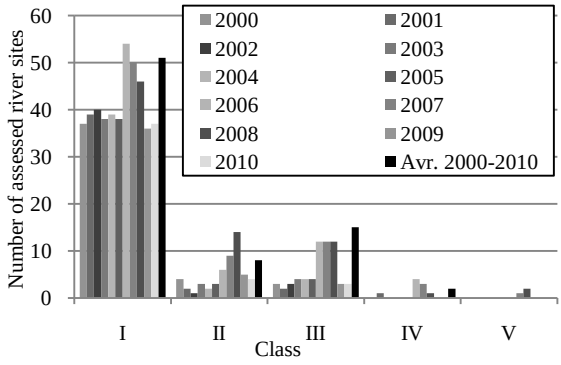

Figure 6. Classification of river sediments into Classes I–V according to the ^{226}Ra:^{228}Ra ratio for annual average activities (see Table 1 for class description).

uranium ore has been reflected by an increase in the representation of contaminated classes.

These classes were used also for classification of suspended matter. The numbers of the sites in the individual classes are shown in **Figure 7**. Most of the sites were classified as class I (from 50% to 100%) too.

The ratio of ^{226}Ra and ^{228}Ra activities from 5 selected sites with former uranium mining and processing was in average higher in sediments than in suspended matter. Only at one site was evaluated ratio higher in suspended matter. We think it is because of better conditions of water and stopping of mining and on-going mining water treatment respectively.

3.4. Natural Background Levels

The average values were used further to determine natural background levels of radionuclides in the Czech Republic. For ^{40}K, the natural background level was estimated to be 570 Bq/kg. To evaluate the background level for ^{226}Ra, the river sites affected by human activities (mining and processing uranium ore, coal) were eliminated from the assessment, and only river sites falling

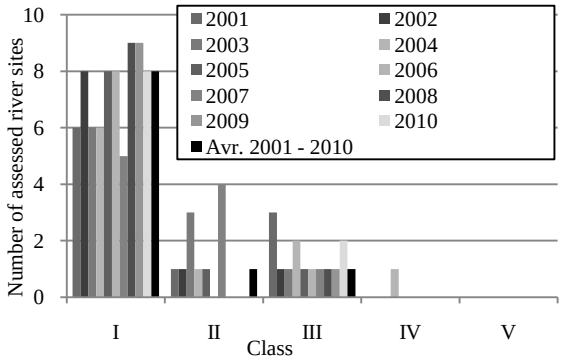

Figure 7. Classification of suspended matter into Classes I-V according to the ^{226}Ra:^{228}Ra ratio for annual average activities.

into class I were used for the analysis. The average natural background values for ^{226}Ra and ^{228}Ra in sediments were essentially identical at 47.8 Bq/kg for ^{226}Ra and 47.2 for ^{228}Ra. In suspended matter it was 86.5 Bq/kg for ^{226}Ra and 87.9 Bq/kg for ^{228}Ra.The uncertainty of the background values was expressed as the standard deviation.

4. Conclusions

Activities of ^{137}Cs, ^{40}K, ^{226}Ra and ^{228}Ra in river bottom sediments and suspended matter were monitored during the period 2000-2010 and 2001-2010 respectively. The mean concentrations of ^{137}Cs in the sediments were 14.0 Bq/kg and 25.0 Bq/kg in the suspended matter. This reflects the residual contamination after nuclear weapons tests and the Chernobyl accident. Annual average values were analyzed for possible time trends in the monitored period. Evaluated effective half-lives of ^{137}Cs in the river sediments were 23.8 y and 11.4 y in the suspended matter respectively. The assessment of ratio of ^{137}Cs activities in suspended matter and sediments at individual sites was performed. The ratio ranged from 1 to 36.8, with an average 6.2. The activity of ^{137}Cs was higher in suspended matter than in river sediments at all assessed sites.

Natural background levels in river sediments were 570 Bq/kg for ^{40}K, 47.8 Bq/kg for ^{226}Ra and 47.2 Bq/kg for ^{228}Ra. In suspended matter it was 86.5 Bq/kg for ^{226}Ra and 87.9 Bq/kg for ^{228}Ra.

In the monitoring period, the observed annual average values of ^{40}K, ^{226}Ra and ^{228}Ra in river sediments from the whole territory of Czech Republic did not exhibit any significant trend. The decrease of annual average values of ^{226}Ra and ^{228}Ra in suspended matter was observed. Evaluated effective half-lives of ^{226}Ra and ^{228}Ra in suspended matter were 7 y and 9.7 y.

The ratio of ^{226}Ra and ^{228}Ra activities in suspended

matter and in sediments was assessed. The ratio of ^{226}Ra activities ranged from 0.3 to 4.6 with an average 1.9. The ratio of ^{228}Ra activities ranged from 0.7 to 6.9 with an average 2.3. Activity of ^{226}Ra and ^{228}Ra was higher in suspended matter in 82% and 94% respectively.

The river bottom sediments are still contaminated by ^{226}Ra which stems from mining and processing of uranium ore. Contamination by ^{226}Ra can be assessed by using the ^{226}Ra:^{228}Ra ratio, which is up to 1.5 for unaffected river sites, and exceeds this value for the affected sites. This approach can be used as a complementary assessment to that based solely on the activity of ^{226}Ra to identify sites contaminated by uranium mining and processing.

Acknowledgements

This paper was prepared with the support of the project MŽP CR 0002071101.

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