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The assessment of natural and artificial radionuclides in river sediments in the Czech Republic

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Abstract The concentrations of natural radionuclides, radium-226, radium-228, and potassium-40, and the artificial radionuclide caesium-137, in river sediments were monitored in the Czech Republic by the Czech Hydrometeorological Institute during the period 2000–2008. The data were used to evaluate the natural background levels of these radionuclides and the impact of human activities on the water environment. 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.

Key words river sediments; surface water; uranium industry; radioactive contamination; radium-226; radium-228; potassium-40; caesium-137

INTRODUCTION

Monitoring of radioactive substances in river sediments in the Czech Republic has a long history (Mansfeld & Hanslík, 1983; Beneš & Nondek, 1993; Hanslík, 1996; Hanslík *et al*., 2002). The permanent monitoring of river 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 solids. The results of the monitoring for the period 2000–2008 are evaluated in the paper.

METHODS

The monitoring network covered the Czech Republic and included 22 river sites in the first year (1999), 44 sites in 2000, and 45 sites in 2003 (hereinafter referred to as basic sites). Based on the evaluation of the results in 2004 (Hanslík *et al*., 2005a), the monitoring was extended by an additional 33 sites in 2006, which cover the areas of former uranium 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. Grain size of the sediment samples was generally less than 2 mm. Samples were analysed 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) (CNS, 1999). The results were expressed in Bq kg^{-1} dry sample. The minimum detectable activities in the sediments at the 95% level of significance were approx. 0.5 Bq kg^{-1} for ^{137}Cs, 10 Bq kg^{-1} for ^{40}K, and 2 Bq kg^{-1} for the radium radioisotopes. Values below the detection limit were included in the assessment as they were assumed to equal the minimum detectable activity. The measured values were used for calculation of annual average activities (excluding data from 1999).

RESULTS AND THEIR EVALUATION

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 year (Lederer & Shirley, 1978). Annual average, minimum and maximum activities at the monitored sites are summarized in Table 1. Values ranged from 0.5 to 124 Bq kg^{-1}, with an average of 13.4 Bq kg^{-1}.

Table 1 Annual average, minimum and maximum ^{137}Cs activities in river sediments during 2000–2008.

		^{137}Cs (Bq kg^{-1})		
Year	Number of sites	Mean	Minimum	Maximum
2000	44	15.8	1.61	120
2001	44	17.5	1.55	99.4
2002	44	16.4	1.79	113
2003	45	13.7	1.05	49.6
2004	45	13.3	1.63	55.3
2005	45	13.8	0.83	64.3
2006	77	9.9	0.51	83.2
2007	76	11.7	0.53	124
2008	76	13.1	1.14	92.6
2000–2008		13.4	0.51	124

Differences in the ^{137}Cs concentrations of sediment between the monitored sites correspond to the available information on the distribution of ^{137}Cs in the Czech Republic after the accident at the Chernobyl nuclear reactor (Hanslík *et al*., 2005b). The highest activities of ^{137}Cs, with an average of 88 Bq kg^{-1} and range from 38.9 to 124 Bq kg^{-1}, were detected at the Topělec site on the Otava River.

The data from the basic sites were analysed for possible time trends in the ^{137}Cs values (equation (1)). The trend was considered to be significant for values of R^2 greater than 0.2. Effective half-life was calculated according to equations (2) and (3) (Hanslík *et al*., 2000; Smith & Beresford, 2005):

$$\ln a = -\lambda_{eff}.t + q \tag{1}$$

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

$$T_{eff} = \frac{\ln 2}{\lambda_{eff}} \tag{2}$$

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

$$\frac{1}{T_{eco}} = \frac{1}{T_{eff}} - \frac{1}{T_P} \tag{3}$$

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

The annual average values were used for determining the effective half-life of ^{137}Cs (14 years) and ecological half-life (26.1 years) (see Fig. 1). The average decrease in the ^{137}Cs exceeds that of the physical half-life (30.2 years). 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.

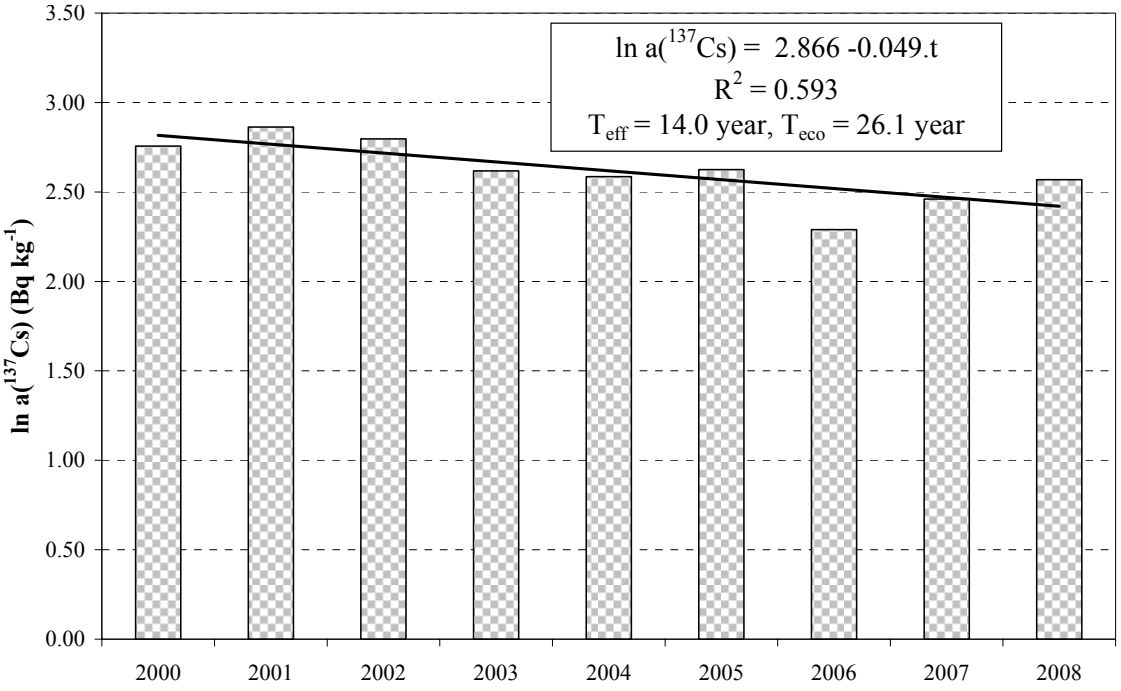

Fig. 1 The decrease in annual average ^{137}Cs activities in sediments for the period 2000–2008.

Table 2 Annual average, minimum and maximum ^{40}K activities in river sediments during 2000–2008.

Year	Number of sites	^{40}K (Bq kg^{-1}): Mean	Minimum	Maximum
2000	44	605	299	932
2001	44	529	188	976
2002	44	513	233	1021
2003	45	575	355	936
2004	45	552	239	941
2005	45	576	169	1031
2006	77	597	108	1152
2007	76	573	95	1054
2008	76	589	176	1051
2000–2008		570	95	1152

A more detailed assessment was carried out for the individual basic sites. A decreasing trend was observed at 19 sites, an increasing trend was observed at four sites, while 22 sites exhibited no trend ($R^2 < 0.2$). Reasons for the variation in the temporal trends in the ^{137}Cs activity could include spatial variations in sediment transport and removal from the channel during high water flows, uncertainty associated with sampling, and different physicochemical properties of sediments in different years.

Potassium-40

Potassium-40 is a natural isotope with very long half-life (1.28×10^9 year) (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 (Švec *et al.*, 2003). Annual average, minimum and maximum ^{40}K activities in the sediments for the monitoring sites in the Czech Republic are listed in Table 2. Observed annual average values range from 513 to 605 Bq kg^{-1}. In the monitoring period, the observed values did not exhibit any significant trend

(i.e. $R^2 < 0.2$), using equation (1) (Fig. 2). A more detailed assessment of the basic sites showed no trend at 37 sites, a decreasing trend at two sites, and an increasing trend at six sites. 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 solids, which is 500–700 Bq kg^{-1} (Mundschenk, 1996).

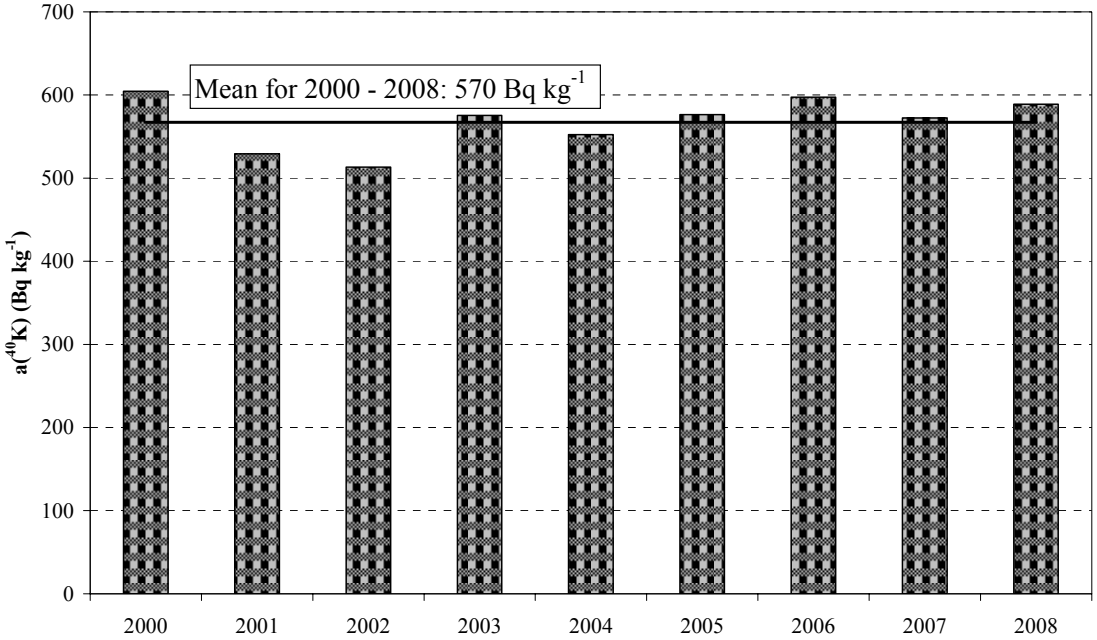

Fig. 2 Annual average ^{40}K activities in sediments for the period 2000–2008.

Table 3 Annual average, minimum and maximum ^{226}Ra and ^{228}Ra activities in river sediments during 2000 to 2008.

		^{226}Ra (Bq kg^{-1})			^{228}Ra (Bq kg^{-1})		
Year	Number of sites	Mean	Minimum	Maximum	Mean	Minimum	Maximum
2000	44	50.8	20.4	182	43.9	20.1	115
2001	44	61.6	16.3	182	49.7	15.5	127
2002	44	60.4	20.9	182	52.6	20.1	133
2003	45	64.1	17.9	186	53.9	17.6	127
2004	45	65.3	11.6	371	52.6	13.4	146
2005	45	59.1	13.0	283	45.0	11.9	112
2006	77	76.1	14.3	315	41.9	13.4	122
2007	76	86.4	12.3	393	44.9	12.0	122
2008	76	90.4	11.8	396	48.6	10.5	129
2000–2008		71.3	11.6	396	48.2	10.5	146

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 years and 5.7 years, respectively (Lederer & Shirley, 1978). Annual average, minimum and maximum ^{226}Ra and ^{228}Ra activities for the river sediments for the period 2000–2008 are shown in Table 3. The average activity of ^{226}Ra in river sediments (calculated for all sites in the observation period) was 71.3 Bq kg^{-1}. The average value for the period 2000–2005 was 60.2 Bq kg^{-1}, with a range from 11.6 to 371 Bq kg^{-1}, while the average

value for the period 2005–2008 is 84.3 Bq kg^{-1}, with a range from 11.8 to 396 Bq kg^{-1}. These results illustrate that the new sites (included in 2006 for monitoring of the impacts of uranium ore mining and processing) affect the mean value calculated from all of the observation sites.

Measured values of ^{228}Ra activities of sediments are summarized in Table 3. Anthropogenic pollution of the aquatic environment by ^{228}Ra is unlikely, because thorium ores are not mined in the Czech Republic. The average value for the period 2000–2008 is 48.2 Bq kg^{-1}. The range of annual minimum and maximum activities is 10.5–146 Bq kg^{-1}. Observed values correspond to the natural occurrence of ^{228}Ra in watercourses (Lederer & Shirley, 1978).

Hanslík (1997) 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 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 (1997) proposed five classes of river sediment contamination by ^{226}Ra according to the ^{226}Ra:^{228}Ra ratio (see Table 4).

These classes were used for classification of sediments collected in the individual sites in the years 2000–2008. The numbers of the sites in the individual classes are shown in Fig. 3. In the period 2000–2005, most of the sites were classified as class I (84–91%), i.e. as uncontaminated. Class II had 2–9% of the sites, class III had 5–9%, class IV had 0–2%, and class V (extremely high contamination) had 0% of the sites. Since 2006, the inclusion of the sites affected by former mining and processing of uranium ore has been reflected by an increase in the representation of contaminated classes. In the period 2006–2008, 62–70% of the sites were classified as class I, while class II had 8–18%, class III had 16%, class IV had 1–5%, and class V had 0–3% of the river sites.

Table 4 Classification of river sediments contaminated by ^{226}Ra into classes I–V according to the ratio of the activities of ^{226}Ra and ^{228}Ra (Hanslík, 1997).

^{226}R ^{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

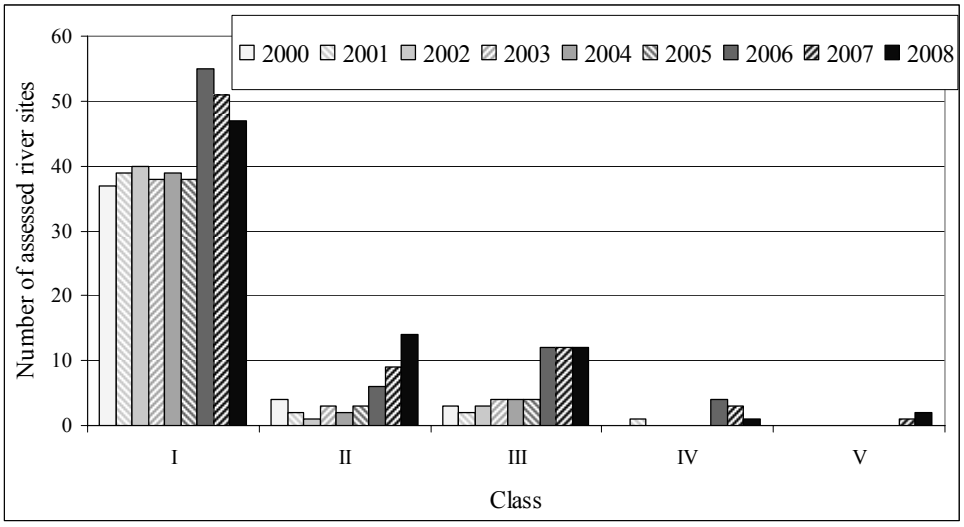

Fig. 3 Classification of river sediments into classes I–V according to the ^{226}Ra:^{228}Ra ratio for annual average activities (see Table 4 for class description).

The activities of radium isotopes were also evaluated for the basic sites. Trends were derived both for the individual sites and for the annual averages. The results of the analysis did not show any trends in the time series ($R^2 < 0.2$).

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 ± 157 Bq kg^{-1}. 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 into class I were used for the analysis. The average natural background values for ^{226}Ra and ^{228}Ra were essentially identical at 48.2 ± 23.5 Bq kg^{-1} for ^{226}Ra and 48.2 ± 25.4 for ^{228}Ra. The uncertainty of the background values was expressed as the standard deviation.

CONCLUSIONS

Activities of ^{137}Cs, ^{40}K, ^{226}Ra and ^{228}Ra in river sediments were monitored during the period 2000–2008. The mean concentration of ^{137}Cs in the sediments was 13.6 Bq kg^{-1} and this reflects the residual contamination after nuclear weapons tests and the Chernobyl accident. Natural background levels were 570 ± 157 Bq kg^{-1} for ^{40}K, 48.2 ± 23.5 Bq kg^{-1} for ^{226}Ra and 48.2 ± 25.4 Bq kg^{-1} for ^{228}Ra. The river 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.

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