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RESULTS FROM RADIONUCLIDE INTERLABORATORY COMPARISON IN SEDIMENT AND FISH

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Abstract. *The results of an intercomparison exercise, designed for the determination of anthropogenic and natural radionuclides in sediment and fish samples from the Danube River, are reported. The methods of gross beta and gamma spectrometry measurements were compared. Considering the uncertainties of measurements, a good agreement between the results obtained by two laboratories has been ascertained.*

Key words: *radionuclides, intercomparison, sediment, fish, Danube River*

1. INTRODUCTION

The Paks Nuclear Power Plant, located 5 kilometres from Paks, is the first and only operating nuclear power station in Hungary. Its four reactors produce more than 40 percent of the electrical power generated in the country. The water of river Danube cools the reactors and and receives authorized radioactive liquid releases during normal operating conditions.

The radioactivity control of the Danube River was performed by water quality experts of Serbian-Hungarian Subcommittee from Serbian-Hungarian Commission for management of water resources. The radionuclide content and gross beta activity were measured in the samples of filtrated water, suspended material, sediment, algae and fish, but ^{90}Sr activity was determined in all samples except algae due to small quantity of the sample [1]. From 1997 to 2012 samples were collected 2 times per year at Bezdan in Serbia and 2 times per year at Mohács in Hungary. In 2013 and 2014 sampling was performed only in Mohács. ^{137}Cs activity in sediments ranged from 20 Bq/kg to 30 Bq/kg in 2000 [1].

Regarding the external quality control of the measurements, during 2014 the Vinča Institute for Nuclear Sciences from Belgrade in Serbia and South Transdanubian Inspectorate for Environmental Protection, Nature Conservation and Water Management from Pécs in Hungary, have participated in intercomparison exercise, which has been organized and developed in the framework of Serbian-Hungarian Subcommittee for water quality. The subcommittee experts have coordinated an intercomparison exercise on gross beta activity and gamma spectrometry measurement in the sediment and fish samples with natural and artificial radionuclides. The scope of the intercomparison was to obtain information on the degree of agreement between the two laboratories. Authors expected that radioactivity control of the Danube River will continue on regular basis in the next year and it is very important to have very reliable measurement in both laboratories.

2. MATERIAL AND METHODS

2.1. Sampling technique and sample preparation

The samples were collected in October 2013 from Danube River near Mohács. The samples were taken downstream from the nuclear power plant. Surface sediments were collected at four locations close to riverbank, 2 on the left and 2 on the right coast. Sediment samples were collected from the top 5 cm layer of the material, taken by a grab sampler, in polyethylene bottles.

The samples were prepared in laboratory in Pécs. The sediment samples were packed in a container made from nonradioactive material, sealed and labelled to avoid mix up and contaminations. Each sediment is dried at 105°C to constant weight, sieved and the fraction of the particles with diameter smaller than 250 μm is taken.

Two species of fish were collected: Crucian Carp (*Carassius carassius*) and Zander (*Stizostedion lucioperca*). Each fish was cooked

at 100°C and after that dried at 105°C to constant weight, fragmented and homogenized.
The samples were homogenized in Hungary and we only transferred them to cylindrical containers or Marinelli beaker and sealed. The samples were kept hermetically closed 6 weeks in order to reach the equilibrium due to radon emanation. Since all the samples contained natural radionuclides, the emanation and consequently the loss of radon, as a decay product of some of these radionuclides, changes the activity concentration of said radionuclides. When the samples are sealed and stored for a certain amount of time, the radon does not escape but instead reaches the equilibrium with its decay products. Rn decays to ^{218}Po which in turn decays to ^{214}Pb, which is used for measurement of ^{226}Ra.

2.2. Experimental technique and method of measurements

Participating laboratories had to measure the activity of the radionuclides detected in each sample, with particular attention to natural radionuclides (from the uranium and thorium series and ^{40}K) and ^{137}Cs. Each laboratory was requested to apply its own routine procedure for such measurements using its most recent efficiency calibration and its usual source of nuclear data.

The measurement of gross beta activity is carried out by α-β-proportional gas counter "Thermo Eberline FHT770T" in both laboratories. The counting gas is a mixture of 90 % argon and 10 % methane. The level of background radiation is from 0.005 - 0.01 imp/s. The size of planchet is 6 cm in diameter. In Serbia calibration was performed by using standard source of ^{90}Sr (EM 145, Czech Metrological Institute, Inspectorate for Ionizing Radiation, Prague) with an activity of 189.4 Bq on the 1st August 2011, while in Hungary calibration was done with KCl. The counting efficiencies for beta counting is 35 % in Serbia and 25 % (for fish) and 35 % (for sediment) in Hungary. The efficency for fish is lower because the fish sample amount is higher than sediment sample amount in the planchete and atenation occurs. The background of each detector was determined by counting an empty planchet for 3600 s.

A high-purity germanium detector system was used for gamma spectrometry. Each sample was mesured using standard method [2]. In Serbia two HP Ge p-type detectors Canberra with relative efficiencies of 20 % and 50 % were used for gamma spectrometry measurement. Duration of each measurement was 60000 s. Calibration of detectors for sediment measurements was performed using silicone resin matrix spiked with a series of radionuclides (^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{203}Hg, ^{88}Y, ^{113}Sn, ^{85}Sr and ^{137}Cs) with total activity of 41.48 kBq on the day 31st August 2012 (Czech Metrological Institute, Inspectorate for Ionizing Radiation, Prague, 9031–OL– 420/12, type ERX). Efficiency calibration for fish samples (the cylindrical geometry 120 cm^3) is performed with secondary reference materials which was produced using certified radioactive mixture solution ER X 9031-OL-427/12, issued by Czech Metrological Institute, Inspectorate for Ionizing Radiation, Prague. The radioactive solution contained following radionuclides: ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{203}Hg, ^{113}Sn, ^{85}Sr , ^{88}Y and ^{210}Pb, with the energies that span from 59 keV to 1898 keV with total activity of 72.4 kBq at reference date 31.08.2012. In Hungary one HP Ge p-type detector Canberra and one HP Ge n-type detector ORTEC both with relative efficiencies of 30% were used. Calibration of detectors was performed using calibrating source in cylindrical geometry, 220 cm^3. Duration of measurement was 60000 s for the sediment and 250000 s for the fish samples.

Gamma lines used for determining the activity concentrations of the different natural radionuclides studied in the intercomparison were 295.22, 351.92, 609.32 and 1120.28 keV for ^{226}Ra, 338.3 and 911.07 keV for ^{232}Th and 1460.7keV for ^{40}K. The activities of ^{137}Cs was determined from its 661 keV γ–energy. For spectra processing the program Genie 2000 was used.

The accuracy and reproducibility of gamma spectrometry systems are verified on a weekly basis. The detector-shield background, detector efficiency, peak shape and peak drift are measured and verified to be within the acceptance limits [3].

Beside that both laboratories used a Certified Reference Material for radionuclides in sediment IAEA-385 for quality assurance/quality control of the analysis of radionuclides in sediment samples.

3. RESULTS AND DISCUSSION

Results obtained by the two laboratories participating in the intercomparison exercise, along with their respective combined standard uncertainties, are summarized in the Tables 1-4. We used the detector efficiency and counting uncertainty as the main contributor to the total uncertainty in the gross beta and gamma spectrometriy measurement. The measurement uncertainties are presented at the 95 % confidence level. In the figures and tables we used acronym SRB for the laboratory from Serbia and HU for the laboratory from Hungary.

The results of gross beta measurement for the sediments and fish are presented in Tables 1 and 2. There is good agreement between SRB and HU

results for gross beta activity in all sediment and fish samples. The results differ less than 15 % and all are within the limits of measurement uncertainty.

Table 1 Gross beta activity in the sediments

Sample	SRB Activity (Bq/kg dry weight)	HU Activity (Bq/kg dry weight)
Sediment 1	880 ± 140	850 ± 100
Sediment 2	900 ± 140	930 ± 110
Sediment 3	940 ± 140	820 ± 100
Sediment 4	970 ± 140	830 ± 100

Table 2 Gross beta activity in the fish

Sample	SRB Activity (Bq/kg)	HU Activity (Bq/kg)
Crucian Carp	95 ± 12	83 ± 10
Zander	89 ± 7	90 ± 10

The results of gamma spectrometry measurements for the sediments are presented in Table 3. The spectra for all sediments are similar. If we observe only Serbian or Hungarian results of measurement we notice that the natural radionuclide levels did not change statistically significantly between the samples because all sediments were collected from the same river basin not far from each other. The results for ^{137}Cs activity also showed that there is no large difference between the samples (17 Bq/kg to 28 Bq/kg). Because of the long half life of ^{137}Cs the obtained results were similar as the previous measurements in 2000 [1].

Comparing the results between the two laboratories for each radionuclide for sediment 1-4 we noticed that the results for ^{232}Th, ^{40}K and ^{137}Cs activity are the same within the measurement uncertainty. The results for ^{226}Ra activity differ 20% between the two laboratories, which corresponds to the tolerances for this radionuclide in intercomparison organized by IAEA [4].

The results of gamma spectrometry measurements for the fish are presented in Table 4. The spectrum of Zander showed that natural radionuclides could be also measured in fish, but because of the small amount of catched fish their values are very low and cannot be easily determined, except for ^{40}K. The spectrum for Crucian Carp is similar.

Table 3 Radionuclide activity in the sediments

Sample		SRB Activity (Bq/kg dry weight)	HU Activity (Bq/kg dry weight)
Sediment 1	^{226}Ra	43 ± 3	33 ± 4
	^{232}Th	40 ± 3	39 ± 3
	^{40}K	530 ± 34	555 ± 61
	^{137}Cs	17 ± 2	18 ± 2
Sediment 2	^{226}Ra	46 ± 4	39 ± 5
	^{232}Th	39 ± 3	42 ± 3
	^{40}K	585 ± 37	609 ± 60
	^{137}Cs	22 ± 2	25 ± 2
Sediment 3	^{226}Ra	48 ± 4	37 ± 4
	^{232}Th	43 ± 3	44 ± 4
	^{40}K	622 ± 40	633 ± 63
	^{137}Cs	28 ± 2	28 ± 2
Sediment 4	^{226}Ra	44 ± 3	37 ± 4
	^{232}Th	42 ± 3	42 ± 3
	^{40}K	608 ± 40	631 ± 63
	^{137}Cs	27 ± 2	28 ± 2

Table 4 ^{40}K and ^{137}Cs activity in the fish

Sample		SRB Activity (Bq/kg)	HU Activity (Bq/kg)
Crucian Carp	^{40}K	108 ± 9	98 ± 10
	^{137}Cs	< 0.4	< 0.05
Zander	^{40}K	105 ± 9	120 ± 10
	^{137}Cs	0.5 ± 0.3	0.30 ± 0.01

Comparing the results between the two laboratories we noticed that the results are the same within the measurement uncertainty for ^{40}K activity in both fish and for ^{137}Cs activity in Zander. ^{137}Cs activity in Crucian Carp is lower than MDA. In Hungary duration of measurement was 250000 s for the fish samples and because of that their values for MDA were much lower.

4. Conclusion

This intercomparison exercise was organised with the aim of providing the participating laboratories with the possibility of testing the performance of their analytical methods on a fish and sediment samples with elevated radionuclide levels due to the contamination of samples by the reprocessing nuclear plant.

Considering the uncertainties of measurements, a good agreement between the results obtained by two laboratories has been ascertained. Such a comparison gave laboratories an opportunity to compare their work and results and help in evaluation of their analytical performance.

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