

# Studies on concentration of some heavy metals and strontium $^{90}\text{Sr}$ and cesium $^{137}\text{Cs}$ isotopes in bottom sediments of selected lakes of Łęczyńsko-Włodawskie Pojezierze

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**Abstract** Research on concentration of radionuclides and heavy metals in bottom sediments of three different lakes is presented. The lakes were located in the vicinity of the National Park in the Lublin (Poland) region. Bottom sediments were collected from various depths. In all studied sediment, sample concentration of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  isotopes ranged from 2.07–11.76 to 5.67–67.7 Bq/kg, respectively. The amount of radioactive  $^{137}\text{Cs}$  increased with depth of the lake. The same dependence for  $^{90}\text{Sr}$  was not observed. The level of radioactivity originated from natural isotopes was much lower in bottom sediments than that measured in related soils. Most of radioactivity in bottom sediments comes from anthropogenic isotopes.

**Key words** strontium • cesium • lakes • sediments • heavy metals

## Introduction

Along with industrial development of the world a water reservoirs, such as soil become, although in considerably smaller degree, the place of accumulation of different kind of contaminations. Introduction of organic, inorganic, and radioactive substances produces dramatic, often irreversible changes of physicochemical and biological properties of these reservoirs. The geochemical composition of sediments, gathering on the bottom of rivers and water reservoirs it is a very good indicator of quality of surface waters and the presence of contaminants. Usually, such sediments are a mixture of natural (autochthonous) matter and anthropogenic (allochthonous) one transported often from distant places. Generally, one may distinguish three kinds of water sediments differing in a way of formation and properties, i.e. river, marine and lake sediments. Because concentration of these substances is several times higher in sediments than in water, the former enable their detection and observation of changes in their content even at small concentrations.

In the literature, much attention has been paid to studies on anthropogenic isotopes [3–5, 7–12, 14], and heavy metals contents [11, 15] in bottom sediments. Authors focus on transportation of these isotopes along the rivers and their deposition in river sediments or inlet reservoirs (lake, sea) [4, 8, 9, 14]. Some papers deal with studies on influence of the depth of the reservoir on the concentration of isotopes in the sediment layers [3, 7, 12].

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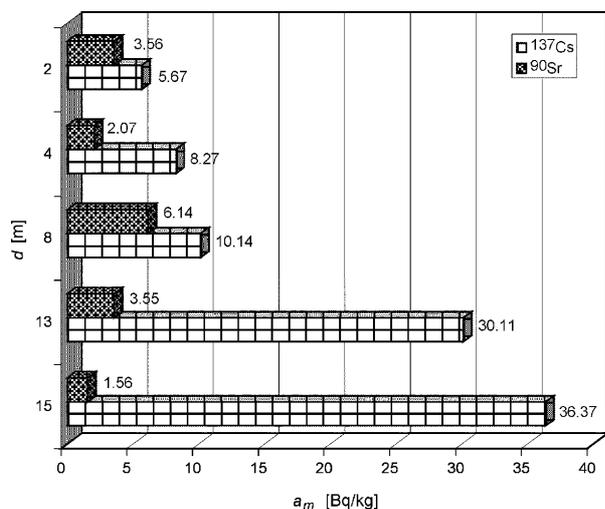
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It the present paper, studies on chosen natural isotopes, anthropogenic ( $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ) as well as on heavy metals in bottom sediments from the three lakes of Pojezierze Łęczyńsko-Włodawskie – the Lublin Region are presented. The area is free of heavy industry and is part of Poleski National Park. The selected lakes are the reservoirs of closed character without a tributary of rivers and streams. The investigations of sediments coming from these reservoirs may give information concerning radioactive fallout on this territory and some data concerning transportation of contaminations from surrounding fields and meadows.

## Experimental

The samples of bottom sediments were collected from the three lakes: Krasne, Uścimowskie, Zagłębozce located on the area of Pojezierze Łęczyńsko-Włodawskie, Lublin Region, in September 2004. From each lake, five points of different depth was set using a bathygraphic map (Fig. 1). In each point, the bottom sediment was taken from the boat using a Kajak sampler [17] many times to ensure satisfying mass of the sample. The sampler allows to collect the upper layer of the sediment, down to the compact layer, i.e. several cm. Drained of water, the samples were transported to laboratory where they were air dried and then, after grinding in a porcelain mortar, dried at  $80^\circ\text{C}$  to constant mass. In lakes, at the distance no longer than 5 m from bank and places of undisturbed structure, several superficial (5 cm) soil samples were taken. All samples were coded according to first letters of the lake with a depth index (in m) as follows: Krasne K-; Uścimowskie U-; Zagłębozce Z-. In such prepared samples the presence of gamma emitters was analyzed using a gamma spectrometer by Silena with a germanium detector IGC-13 (Princeton Gamma-Tech) cooled with liquid nitrogen and set with a 4096 channel analyzer.

The relative efficiency of the detector, measured at the  $^{60}\text{Co}$  peak (1.75 and 1.33 MeV) was 15%. The qualitative and quantitative analysis was realized using



**Fig. 1.** Concentration of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  [Bq/kg] in samples of the bottom sediments taken from the Krasne lake vs. depth of the lake [m].

computer program GENIE 2000. All samples were measured in standard Marinelli vessels of volume  $0.5\text{ dm}^3$  during 10 h.

Next, the sediment samples were prepared to  $^{90}\text{Sr}$  determine in the following way: about 200 g of the sediment was subjected to the thermal mineralization to remove organic parts. The combustion was led in a muffle stove at a temperature of  $550\text{--}600^\circ\text{C}$  during 8 h. After incineration, the ash sample was weighed to calculate the organic carbon contents.

Determination of  $^{90}\text{Sr}$  content in the samples of bottom sediments was done according to an earlier worked out, here modified, analytic procedure [6, 16], i.e. the yttrium path. Basing on the conducted earlier measurements of the gamma emitters contained in yttrium oxalate sediment, two cleaning stages were introduced which considerably improved the accuracy and credibility of the obtained results. As was learned from the earlier experiences [16], this method permits also on the control of degree of removal of natural isotopes by observing  $^{90}\text{Y}$  decay curve.

The first of the added stages (well-known already from earlier experiments) comprise the use of Dowex  $1\times 8$  100–200 mesh ionite to dispose of thorium and actinium isotopes. The second stage removes  $^{210}\text{Pb}$  as  $\text{PbI}_2$  sediment. The chemical yield of the process was controlled by the yttrium oxalate ( $\text{Y}_2(\text{C}_2\text{H}_4)_3\cdot 9\text{H}_2\text{O}$ ) reaction. An efficiency of strontium extraction with concentrated  $\text{HNO}_3$  was checked by the XRF method [13, 16] that also permitted the determination of the heavy metals in studied sediments. Determination of the XRF sensitivity is made from a calibration curve, obtained from several spectra of matrix made of metal oxides and silica with bromine as standardization element. Bromine is added to each measured sample.

The beta radioactivity measurements were made with use of a liquid scintillation counter QUANTULUS from Wallac. The sample was in the form of a gel suspension prepared as follows: the sample of yttrium oxalate was transferred to a measurement vessel,  $2\text{ cm}^3$  of distilled  $\text{H}_2\text{O}$ , was added and after shaking  $6\text{ cm}^3$  of Insta-Gel Plus scintillator was added. Each sample was measured during 5 h. After 21 days, the sample was measured again and the result was accepted as a background. The counting efficiency, established by measurement of the standard  $^{90}\text{Sr}\text{--}^{90}\text{Y}$  source performed in the identical way as the samples is equal to 97% in channels 150 to 900. The accuracy of the obtained results was 3% and was controlled with an IAEA Soil 6 sample. The average error of the sediment samples was 4.5%. The error of radioactivity measurement ranged from 0.11 to 0.84 Bq/kg (d.w.), and the MDA value ranged from 0.16 to 0.40 Bq/kg (ash).

## Results and discussion

The obtained results are presented in figures and in tables. The data listed in Table 1, concerning to the presence of heavy metals in the studied sediments are in a good correlation with those published in Geologiczny Atlas Polski [11] and obtained earlier for the Piaseczno and Maśluchowskie lakes located in the same terrain [15].

**Table 1.** Concentration of selected metals in soils and bottom sediments of studied lakes

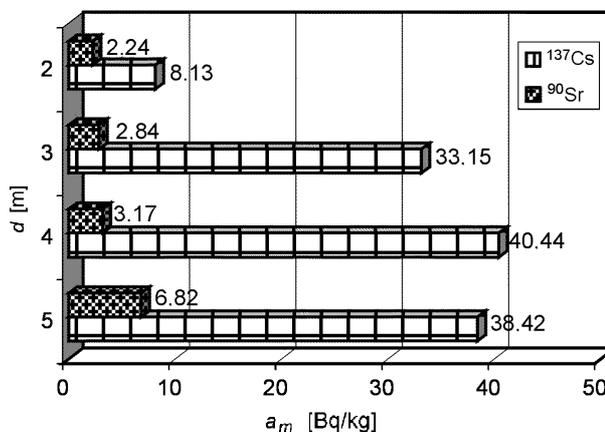
Sample	Metal concentration [mg/g]									
	K	Ca	Cr	Mn	Fe	Cu	Zn	Sr	Y	Pb
K-2	14.7	60.8		0.2	4.2	0.04	0.05	0.22	0.006	0.03
K-4	6.9	26.3		<0.1	2.8	0.03	0.03	0.09	0.007	0.04
K-8	9.3	16.0		0.1	2.7	0.03	0.02	0.06	0.005	0.03
K-13	11.9	68.6	0.16	0.3	9.3	0.03	0.13	0.30	0.012	0.10
K-15	10.3	79.7		0.4	12.7	0.04	0.15	0.37	0.014	0.12
K-G	9.8	3.4		0.1	2.1	0.04	0.02	0.03	0.004	0.03
U-2	8.3	27.1		0.9	38.1	0.04	0.08	0.06	0.006	0.06
U-3	10.4	<2.9		0.2	2.2	0.03	0.03	0.03	0.006	0.04
U-4	13.1	8.7	0.14	0.3	11.5	0.03	0.13	0.07	0.010	0.10
U-5	12.2	7.7		0.3	10.7	0.03	0.12	0.07	0.014	0.10
U-G	15.0	6.6		0.2	4.1	0.04	0.04	0.04	0.008	0.04
Z-2.5	5.2	225.3		0.6	14.6	0.03	0.05	0.30	0.004	0.05
Z-6	10.5	9.0		0.5	14.1	0.02	0.07	0.07	0.009	0.09
Z-13	7.2	8.5		0.7	19.6	0.03	0.14	0.06	0.009	0.12
Z-15	6.6	9.6	0.09	0.4	13.9	0.02	0.11	0.07	0.011	0.12
Z-20	7.0	6.9		1.1	26.7	0.03	0.18	0.06	0.008	0.17
Z-G	<5.3	<2.7	0.18	<0.1	1.6	0.03	0.03	0.02	0.003	0.03
Average*	9.5	25.3		0.42	13.1	0.03	0.09	0.13	0.009	0.08

\* Arithmetic average does not include metals in soil.

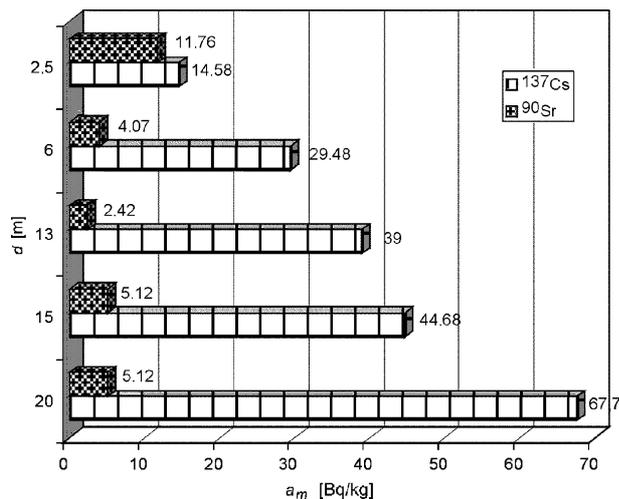
Appearance of chrome in a few samples drew our attention (K-13, U-4, Z-15, Z-G). Because this contamination was not detected in other samples, one should rather consider it as accidental. XRF measurements give standard deviation (s.d.) of the measured concentration within ± 4–25%. For example, at a concentration of 0.09 mg/kg s.d. is equal to 0.025 and for 0.18 mg/kg – 0.05.

The <sup>90</sup>Sr and <sup>137</sup>Cs isotopes were present in all studied samples of sediments and soils. Their concentration is shown in Figs. 1 to 4. The data on drawings 1–3 show, that the concentration of radioactive <sup>137</sup>Cs is considerably higher than that of <sup>90</sup>Sr and rises along with depth of lakes. Similar measurements made in 1995 for sediments from the Piaseczno and Maśluchowskie lakes [3] did not show so clear relation between the radioactivity and the depth of the lake. The average concentration of radioactive <sup>137</sup>Cs in the sediments from these two lakes, calculated for the year 2004 was considerably higher (70.5 Bq/kg) [3] than that in the three now studied lakes (29 Bq/kg). In experiments on lake sediments, Ioannides *et al.* [7] stated that radiocesium is immobilized at a distance no greater than a few cm from the water sediment interface. A comparison of the above radioactivities may prove the higher solubility of cesium or its migration downwards. The adopted method of bottom sediment collection did not allow to verify this. As was mentioned previously, all these lakes lie in the relatively close neighborhood and the size of radioactive fallout was of similar intensity.

For <sup>90</sup>Sr isotope the above-mentioned dependence was not observed. Contamination of the lake environment by this radionuclide is unequal and does not show systematic dependence on the depth of the lakes. A similar phenomenon was observed for the bottom sediments from lakes of Greece and Sweden [7, 12]. The reason of such behavior one may assume in the different affinity of cesium and strontium cations to the sediments and their migration velocity. The quicker migration of strontium may result from the various amounts of organic substances, pH and type of the sediment.



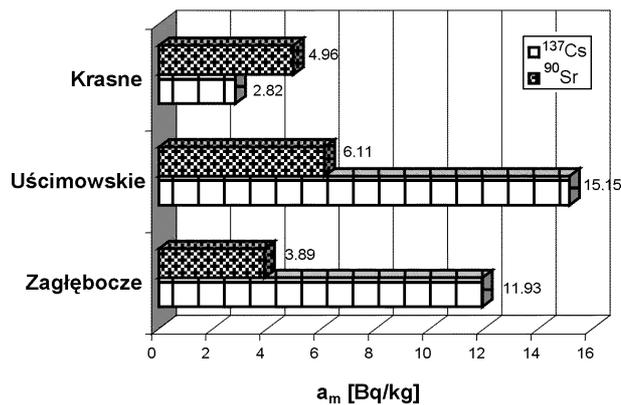
**Fig. 2.** Concentration of <sup>90</sup>Sr and <sup>137</sup>Cs [Bq/kg] in samples of the bottom sediments taken from the Uścimowskie lake vs. depth of the lake [m].



**Fig. 3.** Concentration of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  [Bq/kg] in samples of the bottom sediments taken from the Zagłębcze lake vs. depth of the lake [m].

Studies by Manjona *et al.* [12] on the presence of both isotopes in successive layers of the bottom sediments show that the largest concentration of  $^{137}\text{Cs}$  was at a 15 cm layer to 15 cm whereas  $^{90}\text{Sr}$  at about 40 cm. In studies of Ioannides *et al.* [7],  $^{137}\text{Cs}$  was immobilized in the upper 6 cm of the sediment layer. This phenomenon proves the larger speed of downwards migration of  $^{90}\text{Sr}$ . Because the bottom sediments in our studies were taken from the layers of several centimeters, the obtained concentrations of both isotopes may be different.

A comparison of the  $^{90}\text{Sr}$  to  $^{137}\text{Cs}$  concentration ratio listed in Table 3 proves much lower deposition of  $^{90}\text{Sr}$  than of  $^{137}\text{Cs}$  on the Pojezierze territory.



**Fig. 4.** Concentration of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  [Bq/kg] isotopes in of soils taken in the vicinity of the studied lakes.

A comparison of the concentrations of studied isotopes in soil presented in Fig. 4 and the bottom sediments of the respective lakes in Figs. 1–3 reveals lack of univocal dependency. It shows that the content of isotopes in the superficial layers of soil in the vicinity of the lakes has no direct connection with their concentration in the bottom sediments. Generally, the concentration of both the isotopes is lower in the soils than in the sediments.

Amounts of the selected natural isotopes measured in the bottom sediments of the lakes and the neighboring soils are listed in Table 2. Radioactive concentration of these isotopes in the bottom sediments is much lower than those published in [1, 2].

As was shown in Table 3, the share of anthropogenic isotopes in the total radioactivity of the bottom sediments is higher than in the soils and reaches 30.1%

**Table 2.** Radioactivity ( $a_m$ ) in Bq/kg of main natural isotopes in studied samples of soils and bottom sediments

Sample	$^{40}\text{K}$	$^{212}\text{Bi}$	$^{212}\text{Pb}$	$^{214}\text{Bi}$	$^{214}\text{Pb}$	$^{224}\text{Ra}$	$^{226}\text{Ra}$	$^{228}\text{Ac}$
K-2	55.9	0.94	1.21	1.38	1.13	1.11	0.51	1.65
K-4	53.1	0.86	1.18	1.29	1.14	1.38	1.38	<0.24
K-8	91.9	1.65	2.32	2.22	2.08	2.09	0.57	2.93
K-13	112.3	4.08	4.87	4.47	3.80	6.22	1.60	5.48
K-15	93.6	3.81	4.61	3.06	3.48	3.00	1.82	5.62
K-G	164.4	4.71	6.66	4.97	4.96	6.04	10.48	5.91
U-2	66.0	1.16	1.14	1.51	1.32	1.85	0.51	1.59
U-3	79.4	2.65	2.82	2.53	2.20	7.38	2.59	5.74
U-4	110.3	4.37	3.67	3.67	3.33	6.14	1.49	5.39
U-5	96.6	2.13	3.45	2.13	1.49	6.76	2.54	5.56
U-G	247.0	6.31	<0.19	9.19	9.79	6.06	21.42	9.72
Z-2	81.9	2.65	2.96	2.28	2.04	5.91	1.38	3.84
Z-6	72.7	2.42	3.23	1.63	1.83	6.39	2.12	5.04
Z-13	54.1	3.59	2.81	1.93	1.29	5.11	2.26	3.83
Z-15	197.8	8.16	15.21	7.49	7.98	12.04	4.97	11.42
Z-20	67.5	3.28	3.65	3.17	2.68	6.00	1.74	5.12
Z-G	134.8	3.06	3.42	4.54	4.28	4.74	9.96	4.88

**Table 3.** Percent of the anthropogenic isotopes in total radioactivity and <sup>90</sup>Sr to <sup>137</sup>Cs ratio for studied samples of soils and bottom sediments

Sample	$a_m^{90}\text{Sr} + a_m^{137}\text{Cs}$	Total radioactivity	% of anthropogenic isotopes	<sup>90</sup> Sr/ <sup>137</sup> Cs
K-2	9.2	84.1	11.0	0.63
K-4	10.3	82.8	12.5	0.25
K-8	16.3	140.6	11.6	0.61
K-13	33.7	214.7	15.7	0.12
K-15	37.9	199.4	19.0	0.04
K-G	7.8	226.7	3.4	1.76
U-2	10.4	97.6	10.6	0.28
U-3	36.0	182.0	19.8	0.09
U-4	43.6	229.3	19.0	0.08
U-5	45.2	216.0	20.9	0.18
U-G	21.3	355.8	6.0	0.40
Z-2.5	26.3	158.8	16.6	0.81
Z-6	33.5	166.3	20.2	0.14
Z-13	41.4	161.6	25.6	0.06
Z-15	49.8	372.1	13.4	0.11
Z-20	72.8	242.0	30.1	0.08
Z-G	15.8	203.8	7.8	0.33

(Z-20) while in the soils only 7.8% (Z-G). This fact results from both: the lower radioactivity of natural isotopes and the higher of the anthropogenic ones in the bottom sediments. We can generally state that the bottom sediments of the studied lakes reveals a larger contamination by the studied isotopes than the neighboring soil.

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