**Introduction**

Substances containing radioactive elements belong to dangerous and persistent contaminants in the environment. The elements can be divided into two classes: natural and artificial (anthropogenic).

Mean content of natural radioactive isotopes in the lithosphere is around 0.1%, among which the most important ones are uranium, thorium, and potassium (238U, 232Th, 40K). These elements are widely distributed in rocks, soil, and surface waters.

Among the natural radionuclides some can be characterized by a long time of half-decay, comparable to the age of the Earth. One such isotope is 40K isotope, which consti-
tutes 0.0117% of natural potassium concentration. Its half-decay time $T_{1/2}$ is $1.28 \cdot 10^9$ years. When it decays, 89% of events lead to the emission of beta radiation with a maximum energy of 1.33 MeV. The remaining 11% of the decays produce gamma radiation with the energy of 1.46 MeV [1].

The main sources of artificial radioactive elements in the environment are:
- nuclear weapon testings carried out in the atmosphere during the 1950s
- nuclear reactor catastrophes (the biggest one, in Chernobyl in 1986, released to the atmosphere substantial amounts of $\alpha$, $\beta$, and $\gamma$-radionuclides)
- nuclear power plants

The elements, among them $^{137}$Cs, were introduced to the stratosphere, distributed globally, moved back to the troposphere and precipitated on the earth surface [1, 2].

The radioactive isotope levels in the environment of Poland was widely studied. Particular attention was paid to the $^{137}$Cs presence in soil, water, and sediments. The radioactivity measurements of this radionuclide have been carried out in the threshold region of the Carpathian Foothills. As a result, substantial variations of $^{137}$Cs concentrations in soil were found. This fact was a direct consequence of the amount of atmospheric fallout in days following the Chernobyl disaster and the movement of the radioactive cloud in the area [3, 4]. The fate (including transport and distribution) of the cesium isotope delivered into the earth surface, strongly depends on the elements’ chemical features and soil and sediment sorptive properties (considering water environment).

A similar problem refers to the accumulation of other elements (heavy metals) in soil and sediments. Lead is such an element. Although its concentration in the surface waters might be low, sorption on mineral particles and organic compounds can result in substantial accumulation of the element in sediments (which in turn might be a threat for living organisms). On the other hand, lead is a contaminant that is delivered to the environment constantly, both from natural and anthropogenic sources.

Sediments play a fundamental role in the distribution of toxic compounds in aquatic systems. On the one hand they interact with water and, in consequence, they influence water quality. But on the other hand, sediments can be treated as a buffer that can reduce unfavourable changes and stabilize the system. Sediments consist of minerals and organic compounds and usually they have good sorptive properties. Thanks to these properties, sediments can accumulate large quantities of toxic substances but, in certain conditions, contaminants can be released into water in an unpredictable way [5-8].

The authors decided to study sediments’ sorptive properties in relevance to the three analytes: two radionuclides, $^{137}$Cs, $^{40}$K, and Pb. The sediment samples were collected from the Dobczyce Reservoir located on the Raba River, in southern Poland. The reservoir supplies 60% of drinking water for the Kraków agglomeration (over 1 million inhabitants). The composition and the properties of sediments substantially influence reservoir water quality.

Considering remarks mentioned above, the following goals of the study were defined:

a) Determination of the radioactivity and spatial distribution of two radionuclides – anthropogenic $^{137}$Cs and natural $^{40}$K and concentration of Pb – in the sediments of the Dobczyce Reservoir

b) Analysis of the radionuclides and lead distribution in the sediment core samples

c) Determination of the $^{137}$Cs and Pb distribution coefficients in the presence of K and Ca ions relative to the sorptive properties of the sediments

d) Estimation the levels of K and Ca concentrations which may cause $^{137}$Cs and Pb desorption from the sediments

Fig. 1. The Dobczyce Reservoir on the Raba River in southern Poland. Sampling points for spatial element distribution (black dots), sampling points for core samples collection P1-P6 (white dots).
Study Area

The reservoir was built in 1986 on the Raba River, the right-hand Carpathian tributary to the Vistula river. The catchment area of the reservoir is about 768 km². Due to hydrology, Dobczyce Lake can be divided into three parts: Myslenice Basin, Dobczyce Basin, and Wolnica Gulf. Average depth of Dobczyce Lake is 12.3 m; the bottom is aslant in the dam direction and the maximum depth is around 24 m.

The reservoir is an open ecosystem consisting of water, sediments and living organisms. Water quality is influenced by numerous factors like amount of atmospheric fallout, soil erosion in the catchment area, variations of weather conditions (e.g. temperature), and water physical and chemical properties (pH, content of oxygen, chemical composition).

Dobczyce Reservoir is the main drinking water reservoir for the city of Kraków. Secondly, it supplies technological water to the hydroelectric power station (plant) in Dobczyce. Thirdly, it protects the land below the dam from flooding.

The topography of the reservoir controls sedimentary regimes, coarse material is deposited in the Myslenice Basin, fine material is transported further and sedimented in the Dobczyce Basin (Fig. 1). Due to the mountainous character of the river, a substantial amount of drained material is deposited as sediment every year at the lake bottom [5].

Methods

Spatial distribution of cesium and potassium isotopes, and lead in the sediment layer in contact with water (upper 10-15 cm) was analyzed based on measurements at 17 points (marked 1-17) in the reservoir (Fig. 1). The samples were collected using Eckman’s device. After drying and homogenizing the sediment samples, the radioactivities of $^{137}$Cs and $^{40}$K were measured. Similarly, after sediment samples wet digestion, concentration of Pb was measured using AAS.

Based on the data obtained and taking into account geomorphology of the reservoir, at 6 points (marked as P1-P6) the sediment core samples were collected (Fig. 1). The core samples were collected using a custom designed sediment sampling device (LIMNOS, Poland). Each profile was divided into three layers (layer A, 0 to 6 cm, layer B, 6 to 12 cm, and layer C, 12 to 18 cm). Samples were air-dried, homogenized and passed through a 0.4 mm screen using a vibrating shaker.

Gamma Spectrometry Measurements

The sediment samples were analyzed using a low background gamma spectrometer equipped with an HPGe detector (21% efficiency, FWHM=1.9 keV at 662 keV ($^{137}$Cs) and 1,463 keV ($^{40}$K). The gamma ray spectra processing were performed with a Canberra and Ortec electronic system together with the Maestro program. The spectrometer was calibrated using the standard IAEA –154 from IAEA of Vienna. All radioactivities refer to dry mass of the samples and the results are calculated for the day of 01. 09. 2000.

Atomic Absorption Spectrometry Measurements

Quantitative analysis of Pb was performed with atomic absorption spectrometry, electrothermal technique (ET AAS) using Perkin Elmer Model 3110 spectrometer with an HGA 600 graphite furnace. The measuring conditions were optimized by the method development program.

Prior to analysis, the sediment samples were wet digested (with the use of conc. HNO$_3$ and perhydrol, both suprapure, Merck, Germany) in a Plazmatronica UniClever (Poland) microwave digestion system.

X-ray Diffraction Measurements (XRD)

Before XRD analysis the samples were split using a riffle splitter and a portion of 2.7 g from each sample was mixed with 0.3 g of Fisher Scientific ZnO. The mixtures were loaded to McCrone micronizing mill and ground for 5 minutes in ethanol. The ground samples were air-dried, carefully mixed, passed through a 0.4 mm sieve and side loaded (using a custom designed side loading holder) to obtain random powder mounts. X-ray diffraction analyses were performed using a Bruker D8 advance diffractometer with variable divergence and an anticatter slit system, incident beam soler slit and the sol-x solid state detector. CuKα radiation was used with an applied voltage of 40 kV and 30 mA current. The mounts were scanned in the range of 2º to 65º ($\Theta$) at a counting time of 4 s per 0.02º step. The obtained XRD patterns were analyzed quantitatively using Rietveld Autoquan/BGMN software [9].

Determination of the Distribution Coefficient

Sediments are composed of layered silicates and amorphous substances characterized by specific sorption and ion exchange properties. These properties play an important role in water purifying processes by retention of many harmful substances in the sediments. In our experiments the sediment samples were treated as a material characterized not only by its ability to ion exchange, but also having certain sorptive properties. The sorption of cesium from aqueous solution was investigated using a radiometric determination of the distribution coefficient $K_{D}$.

The static ion-exchange chromatography was utilized in the performed analysis. The influence of other ions (K and Ca) in the solution on Cs sorption was determined. The research was carried out in different concentrations of potassium and calcium ions from 5·10$^{-5}$ to 10$^{-4}$ mol·dm$^{-3}$ (added as KNO$_3$ and Ca(NO$_3$)$_2$, respectively) [10]. The distribution coefficient was calculated according to the following formula (1):

$$K_{D} = \frac{(A_{p} - T) - (A_{i} - T)}{(A_{i} - T)} \times \frac{V}{m}$$  \hspace{1cm} (1)

...where $K_{D}$ – distribution coefficient  
$A_{p}$ – initial number of counts  
$A_{i}$ – final number of counts, after reaching an equilibrium-state
Similarly, the process of lead sorption on the sediments was tested based on the measurements of Pb concentrations in the solution being in contact with solid sediments (suspension) at the beginning of the experiment and after two hours of continued stirring. The distribution coefficient was calculated taking into account the initial lead concentration and its concentration after sorption in the presence of calcium or potassium ions. All Pb concentration measurements were made with ET AAS [11].

Results and Discussion

The radioactivities of anthropogenic $^{137}$Cs and, in comparison, natural $^{40}$K isotopes in the surface layer of sediments were measured at 17 points distributed in the whole lake area and at 6 points in core samples (P1-P6) (Fig. 1). The relationship between radioactivity of $^{137}$Cs and $^{40}$K and the sampling point location is shown in Fig. 2 (a and b).

The radioactivity of $^{137}$Cs varies from 6.1 to 86.2 [Bq·kg$^{-1}$]. $^{137}$Cs radioactivity values are twice as high as the radioactivity indicated in the sediments of rivers in France [12] or Tyrrhenian Sea sediments [13], but are almost the same as in lake sediments of northern Patagonia and Zigetang Lake [14, 15].

According to Chełmicki [3], $^{137}$Cs concentration in the soils surrounding the Dobczyce Reservoir is within the range of 11 to 160 [Bq·kg$^{-1}$]. Variations of $^{137}$Cs radioactivity in the upper layer of the sediments result mainly from hydrological and geochemical factors. The radioactivity of $^{137}$Cs is lower in the Myślenice Basin (points 1-9), where mainly coarse materials, silica, and carbonates with low sorption properties are deposited. The basin is also characterized by low content of organic matter (from 1 to 7% wt.) in the sediments, which also influences sorptive properties of the sediments. Points from 10 to 15 are located in Dobczyce Basin, which is characterized by higher $^{137}$Cs radioactivity. This, in turn, is connected with the higher content in the sediments of materials, exhibiting good sorption capacity in relation to that radionuclide – fine grained minerals (i.e. layered silicates), amorphous substances, and organic matter (up to 10% of dry weight). The highest cesium radioactivity was found in the sediments of points 16 and 17 located in Wolnica Gulf. The Gulf characteristics are hydrologically completely different compared to the rest of the Reservoir. The relatively polluted Wolnica stream flows into the gulf. Wolnica Gulf is surrounded by cultivated fields that favor soil erosion processes. Also, the exchange of water between the gulf and the main part of the Dobczyce Reservoir is relatively small. Probably, similar to the Dobczyce Basin, the high concentration of $^{137}$Cs is influenced by good sorptive properties of fine grained mineral compounds and high content of organic matter in the gulf sediments (up to 12%) [6, 16, 17].

It was found that the concentration of potassium varies from 499.6 to 947.9 [Bq·kg$^{-1}$]. These values are almost two
times higher than the radionuclide radioactivity in soils of the lake catchment. It is most likely caused by a relatively high concentration of K-bearing minerals (micas mainly) in the sediments. Distribution of \(^{40}\)K content in fine-grained sediments corresponds to the sedimentation of fine-grained silicates in the reservoir – the lowest levels were recorded near the estuary of the Raba to the reservoir, the highest in the sampling points near the dam (points 13, 15) [18].

Similar distribution pattern in the sediments of Dobczyce Reservoir was found for Pb (Fig. 2 c, d). The lowest concentrations were found in the sampling points located in the shallow part of the Lake (points 1-5, Myslenice Basin) and in points located close to the Lake’s banks (points 6 and 10). Wolnica Gulf is also characterized by a relatively low Pb concentration (32-36 mg·kg\(^{-1}\)). On the other hand, high values of Pb concentration were noted in the deeper part of the lake (the Dobczyce Basin) (49-47 mg·kg\(^{-1}\)). All these suggest that the element is accumulated in the lake regions in which sediments are rich in fine-grained minerals and organic matter. This is in agreement with the literature data [19-21]. Lead is readily sorbed on layered silicates – illite and montmorillonite (sorptive capacity of Pb ions on this compound is in the range 20 – 110 c mol·kg\(^{-1}\)). Also, amorphous iron and manganese compounds (oxides and hydroxides) reveal high sorptive properties in reference to Pb [19-21].

The radioactivities of \(^{40}\)K and \(^{137}\)Cs were also measured in the sediment core samples (Fig. 3 a, b). The tendency of increasing \(^{137}\)Cs radioactivity with the depth of the sediments was observed. The highest radioactivity is in the deepest layer (sampling points P2 – 17.4, P3 – 136.3, P4 – 48.6, P5 – 141.5, P6 – 43.2 [Bq·kg\(^{-1}\)]). This is consistent with expectations, because the largest \(^{137}\)Cs deposition has taken place in the years following the Chernobyl accident. Leaching of this isotope from the catchment soils decreases with time, since there are no factors providing new amounts of \(^{137}\)Cs into the environment. Thus its accumulation in the sediments of the reservoir is decreasing. The dependence does not refer to P1 point. The layer of 18 cm (the thickness of the entire collected profile) was deposited during only a few months, and therefore we can not observe any differences in cesium concentration (the total thickness of the sediments which have been deposited at this sampling point since the reservoir was filled with water, is near 3 m). Sediments collected at this point are characterized by low organic matter content and the presence of coarse material that creates unfavorable conditions for sorption of cations, including cesium.

Table 1 shows the mean concentrations of Pb in selected core samples.

Table 1. The mean concentrations of Pb in core samples P2, P3, and P6.

<table>
<thead>
<tr>
<th>Pb in core samples</th>
<th>Mean of Pb[ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2A</td>
<td>17.84</td>
</tr>
<tr>
<td>P2B</td>
<td>18.69</td>
</tr>
<tr>
<td>P2C</td>
<td>20.03</td>
</tr>
<tr>
<td>P5A</td>
<td>25.64</td>
</tr>
<tr>
<td>P5B</td>
<td>28.07</td>
</tr>
<tr>
<td>P5C</td>
<td>28.07</td>
</tr>
<tr>
<td>P6A</td>
<td>24.27</td>
</tr>
<tr>
<td>P6B</td>
<td>24.73</td>
</tr>
<tr>
<td>P6C</td>
<td>25.57</td>
</tr>
</tbody>
</table>

Fig. 3. Changes of gamma radionuclide activities a) \(^{137}\)Cs and b) \(^{40}\)K in the core sediment samples.
influence of K and Ca ions on Cs and Pb sorption in the sediments were performed. The experimental material was constituted by the core sediments from sampling point P3. For this sampling point (P3) the mineral composition was also examined (Table 2). As one may see, the mineral composition of core samples remains practically homogeneous, although their time of sedimentation covers more than 10 years. Thus, the observed variations in activities or concentrations of the examined analytes in the sediments result most likely from the amount of the element supplied to the reservoir with water, and physical and chemical conditions of sorption in a given period of time.

<table>
<thead>
<tr>
<th>Sediments’ layer in point P3</th>
<th>Amorphous substances [%]</th>
<th>Layered silicates [%]</th>
<th>Feldspar K</th>
<th>Feldspar Na-Ca</th>
<th>Quartz</th>
<th>$^{137}$Cs [Bq·kg$^{-1}$]</th>
<th>Pb [µg/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3a (0-6 cm)</td>
<td>18.9</td>
<td>47.4</td>
<td>2.4</td>
<td>6.3</td>
<td>24.0</td>
<td>18.9</td>
<td>52.7</td>
</tr>
<tr>
<td>P3b (6-12 cm)</td>
<td>19.9</td>
<td>46.8</td>
<td>4.5</td>
<td>5.3</td>
<td>21.6</td>
<td>20.1</td>
<td>50.5</td>
</tr>
<tr>
<td>P3c (12-20 cm)</td>
<td>21.7</td>
<td>43.0</td>
<td>4.8</td>
<td>5.9</td>
<td>22.9</td>
<td>151.7</td>
<td>48.8</td>
</tr>
</tbody>
</table>

Fig. 4. Dependence of $^{137}$Cs distribution coefficients on potassium ion concentrations in core sediment samples.

Fig. 5. Changes of $^{137}$Cs distribution coefficients as a function of potassium and calcium ion concentrations in P3 core sediment samples.
As quartz in general exhibits low sorption of metals, most important in this respect is the sorption of Cs on amorphous substances (organic matter, iron, and manganese oxides and hydroxides) and layered silicates, while in the case of Pb most important are layered silicates.

As was noticed earlier, it is important to determine the conditions under which accumulated, potentially harmful cesium or lead may be released from the sediments to the water body. In all presented graphs (Fig. 5a), one may observe that while the concentration of potassium ion increases, the value of Cs distribution coefficient decreases. On the basis of the performed measurements it was found that the limiting concentration of potassium ions in water at which desorption of cesium from the sediment to water might be possible was 10^-1 mol·dm^-3. Such a situation may occur when a sudden supply of compounds containing potassium ions into the water of the reservoir would happen. Potassium is therefore a competitive element in relation to 137Cs ions. A similar effect was observed in the case of cesium sorption on insoluble hexacyanoferrates of transition metals in the presence of potassium [22].

The influence of calcium ions on the desorption of cesium from the sediments was also studied, since there is a relatively high concentration of this element in the aquatic environment. Similar relations were studied for the influence of potassium and calcium ions on the desorption of lead from sediments [23-25].

The sorption of cesium in the presence of calcium ions was investigated (Fig. 5b). Calcium ions weakly influence the value of the distribution coefficient for cesium.

In the presence of potassium ions the value of distribution coefficient decreased 13 times, and that change for calcium ions was only 2.5 times.

Desorption of Pb (Fig. 6) from the sediments to water might be possible if the concentration of Ca ions approaches 10^-3 mol·dm^-3. This is undoubtedly related to the mechanism of sorption of these ions. Sediments mainly consist of layered silicates that have good sorptive and ion exchange properties. Therefore, they are considered ionite-sorbents or sorbent-ionites. The influence of potassium and calcium ions on lead sorption has been analyzed and the results are shown in Fig. 6. Lead belongs to a group of cations that are well sorbed by its sediments, but its concentration in water and sediments in relation to concentrations of calcium or potassium is much lower. Potassium ions have no significant influence on lead sorption in the sediments of core sample P3A shown in Fig. 6. By contrast, the value of Pb distribution coefficients b in the presence of calcium are 3 times higher relative to the value for potassium. It means that calcium ions have a higher impact on lead sorption than potassium.

Conclusions

1. Spatial distribution of anthropogenic 137Cs in the sediments of the Dobczyce Reservoir results from hydrological conditions of sedimentation process and from the sorptive properties of the deposited material. The lowest radionuclide radioactivity was found in Myślenice Basin (the most shallow), the highest in Wolnica Gulf (the deepest).

2. Distribution of natural 40K isotope is connected mainly with sedimentation of fine-grained minerals – thus its highest radioactivity was observed in the samples of sediments taken from the deepest part of the reservoir close to the dam. In contrast, the lowest activities were measured in Myślenice Basin, where the river stream is strong and only coarse material is deposited.

3. Spatial distribution of lead in sediments reflects the sedimentation processes and is directly connected with the element delivery to the Lake with the Raba River waters and its sorption on deposited material. Thus, higher Pb concentrations were found in the Dobczyce Basin, where fine material containing layered silicates, organic compounds, iron and manganese oxides, and hydroxides is deposited.

4. The measurements of 137Cs radionuclide radioactivities in the core samples proved that the element presence in the sediments is a direct result of washing it out from the soil in the reservoir catchment. So the highest radioactivities of 137Cs were found in the deepest samples of the cores – the sediments deposited closer to date of the Chernobyl disaster (when the high amount of the isotope contaminated soils in Poland).

5. Accumulation of 137Cs isotope in sediments depends on numerous physical and chemical factors, including the sorptive properties of mineral and organic compounds constituting the sediments. On the other hand, competitive effects of other ions may be expected. It was shown that in case of 137Cs sorption, pronounced competitive effect was observed for K ions, much less effect was
found for Ca. On contrary, in case of Pb such competitive effect was seen for Ca, much less for K. The conditions of Cs desorption from the sediments due to the K and Ca ions present in water were estimated. Some of the results presented in this publication will be used in the forthcoming dissertation of Katarzyna Szarłowicz.

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References

1. HRYNKIEWICZ A. Z. Human and ionizing radiation, Warszawa, PWN, 2001 [In Polish].
5. STARMACH J., MAZURKIEWICZ-BORON G. Dobczyce Reservoir, ecology- eutrofisation- protection, Karol Starmach Department of Water Biology PAN, Kraków, 2000 [In Polish].
12. KUBICA B. Application the insoluble hexacyanoferrates of transition metals as sorbents, Akapit, Kraków, 2008 [In Polish].