Preliminary Studies of Sediments from the Dobczyce Drinking Water Reservoir

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Abstract

The analysis of river and lake sediments indicates that the physical, chemical, biochemical and geochemical processes that influence the fate of toxic compounds and elements in sediments are numerous and complex (for example: sorption – desorption, oxidation – reduction, ion-exchange, biological activity). Due to the above-mentioned general statement, only a long term and complex research programme can lead to satisfactory answers to the questions relating to possible changes of water and environmental quality in the future.

The aim of our study consisted in physical and chemical characterisation of sediments in in-depth profiles taken from the Dobczyce reservoir in southern Poland that is a main source of drinking water for the city of Kraków. Due to morphological reasons, 7 layers of sediment samples were distinguished from the ground level to about 90 cm below (total thickness of the sediments in the sampling site). Analysis of grain size distribution and application of x-ray diffraction method, enabled mineralogical description of sediments.

The use of proton-induced x-ray emission (PIXE) and atomic absorption spectrometry (AAS) revealed elemental composition of the samples (Al, P, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn). Concentrations of natural ^{40}K and artificial ^{137}Cs radionuclides were determined by the use of gamma spectrometry.

The following facts were established: 1) the oldest (deepest) and newest, recently deposited layers of sediments are similar in their physical and chemical properties. It means that the inflow of contaminants and biogenic compounds to the reservoir has changed little since it was constructed and filled with water; 2) the severe flood in 1997 changed significantly sediment composition and, in fact, led to purification of sediments in the Dobczyce reservoir.

Keywords: sediments, Dobczyce reservoir, trace elements, natural and artificial radionuclides

Introduction

Among the components of the aquatic environment, sediments can be recognized as a factor playing a fundamental role in circulation of toxic compounds. Potentially harmful elements and compounds are effectively accumulated in the sediments and, in certain conditions, can be rapidly released into the water column in an unpredictable way [1-3]. On the other hand, concentration of elements in sediments can serve as an indicator of water quality. If one can analyze

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chemical composition of separate layers in in-depth profiles of sediments, the "history" of water contamination in the area might be established. Numerous physical and chemical factors influence the accumulation of toxic compounds in sediments. These include: sediment mineral composition, organic matter content, concentration of elements (such as Al, Ca, Mn, Fe, Co), red-ox potential, pH, temperature, etc. The very complex nature of the sedimentation processes requires interdisciplinary studies and the application of different analytical methods and techniques.

During the 20th century the natural environment has been contaminated with artificial radioactivity. The atomic bomb explosions in the northern hemisphere increased radioactivity, most significantly in the first half of the 1960s. In 1986, after the Chernobyl accident, the deposition of radioactive cesium increased considerably in large areas of Europe [4-7].

The Dobczyce Reservoir construction was completed in 1985 and filled with water in 1987. It is situated to the south of the city of Kraków on the Raba River at 60 km from the source, 270 m above sea level and with an area covering 970 ha. The Raba basin consists mainly of suburban areas with little towns like Myślenice and Dobczyce. Thus, the main contaminants originate from agriculture and municipal activities with smaller industrial contributions.

Materials and Methods

Site Description

Due to very dry weather conditions in 2003 in Poland, the water level of the Dobczyce Reservoir dropped markedly (about 6 m below its typical level), the first time since the reservoir was filled. Vast areas of sediments emerged and facilitated sampling of sediments from the reservoir banks.

The sampling site is marked on the reservoir map (point "A") (Fig. 1).

Sediments were taken up as a core that extended 90 cm below the sediment surface. Due to morphological reasons seven layers were distinguished and the samples of sediments were prepared from them (Table 1).

The samples of sediments were air-dried and homogenized by means of grinding. Then they were sieved on vibrating screens with circular holes ranging from 0.04 to 2.5 mm in size. The samples were prepared for further analysis according to requirements of each analytical method.

Mineral Characterization of the Sediment Samples

For mineral analysis, 3 grams of each sediment sample were ground in an agate mortar to a size of less than 20μm. The ground samples were analyzed according to the technique described by Moore and Reynolds [8]. X-ray diffraction analyses were performed with the use of Philips X'Pert diffractometer with a vertical goniometer PW3020 equipped with a 1° divergence slit, 0.2 mm receiving slit, incident and diffracted beam Soller slits as well as graphite-diffracted beam monochromator. Cu-K_α radiation was used. A voltage of 40 kV and current of 30 mA were used for the analyses. The random powder
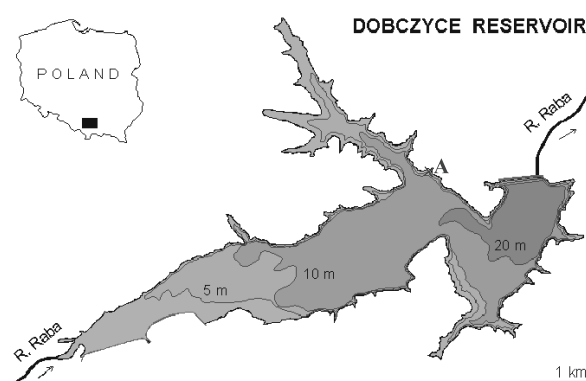

Fig. 1. Sampling site at the Dobczyce Reservoir

Table 1. Organic matter content vs. particle size distribution in sediment samples [wt.%].

Sediment layer	Depth [cm] (0 - ground level)	Weight of organic matter [%]	Particle size [mm]					
			2.5 - 0.8	0.8 - 0.4	0.4 - 0.25	0.25 - 0.1	0.1 - 0.04	<0.04
1	0 – 11	3.91	2.70	3.38	1.99	15.18	73.94	2.82
2	11 – 15	1.42	0.30	0.47	0.51	16.05	63.99	18.68
3	15 – 21	1.86	0.25	0.66	0.99	6.31	76.19	15.61
4	21 – 36	0.73	37.86	26.43	12.37	19.38	2.89	1.08
5	36 – 48	1.19	20.46	10.88	10.15	33.32	19.71	5.48
6	48 – 55	2.94	3.53	2.54	1.91	14.59	74.64	2.79
7	55 – 90	2.91	3.85	3.09	2.07	9.27	71.32	10.40

mounts were scanned from 2° to 64° 2θ with the counting time of 2s per 0.02° step.

Determination of Elemental Concentration by Means of PIXE Method

The PIXE technique has been applied in this study. 2.4 MeV proton beam at the Institute of Nuclear Physics, Polish Academy of Sciences in Kraków has been applied to the trace element analysis. Proton beam was collimated down to 1 mm^2 on the sample.

The experimental set-up for the PIXE experiments allows collecting two independent spectra at the same time. The PIXE spectrum was detected by a Si (Li) detector with an energy resolution of 180 eV for Mn-K$_\alpha$ line. The spectrum of back-scattered protons used for normalization of all registered PIXE spectra are provided by the surface-barrier detector with an energy resolution of 18 keV for an Am^{241} source. The surface-barrier detector detects particles back-scattered from a thin aluminum foil. The foil separates the high vacuum volume of the target chamber from the low vacuum region where the investigated sample is placed. This arrangement, known as an external beam technique, avoids target charging effects. Such normalization also provides independence on target types and is directly proportional to the number of incident particles. The two input data acquisition system is built around the ORTEC 919 Multichannel Buffer controlled by a PC computer.

Determination of Elemental Concentration by Means of Atomic Absorption Spectrometry

Additionally, determination of elemental concentration of Al, Ca, Mn and Fe was made by means of the Atomic Absorption Spectrometry method (at the Department of Analytical Chemistry, AGH – University of Science and Technology). Samples were wet digested with the use of microwave system (Plazmatronica, Poland). Concentrations of iron, manganese and calcium were determined in the air-acetylene flame, aluminum in the N$_2$O – acetylene flame (Perkin-Elmer AAS spectrometer, Model 3110, USA). Each determination was performed three times.

Arsenic concentrations were determined with the electrothermal technique (ET) of AAS. The analysis was made with HGA-600, AAS spectrometer Model 3110, Perkin-Elmer, USA. Working conditions for ET AAS were established using the method development program [9]. The accuracy of the analytical procedure for arsenic analysis was tested with the use of the certified reference material BCR No 320 River Sediment. Satisfactory accuracy was achieved. Determination of Hg in the sediment samples was performed by means of the automatic mercury analyzer AMA-254.

The Determination of Natural and Artificial Radionuclide Concentrations

The concentration of artificial ^{137}Cs and natural ^{40}K isotopes in the sediment profiles were investigated. The radionuclide concentrations in the sediment samples were measured using the gamma spectrometry technique. The gamma spectrometer with well-type, high-purity germanium (HPGe) detector (10% efficiency was calibrated by the IAEA standard IAFA-154). The spectra were taken with standard electronics (EG&G) and evaluated with commercial software (MAESTRO FOR WINDOWS 95). The sediment samples were analyzed in three-day mode of measurements. Spectrometer was calibrated according to the method described previously [10]. Half-lives and gamma energies were taken from Schotzing and Schrader (1998) [11].

Results

Each sediment sample was characterized by a certain distribution of particle sizes and organic matter content (expressed in weight percent) (Table 1).

Mineral Composition of the Sediment Samples

X-ray diffraction patterns of the studied samples are presented in Fig. 2. The main mineral present in the sediment samples is quartz. The samples also contain different amounts of feldspars (K-feldspars as well as Na-plagioclase). A small amount of layered silicates (probably of dioctahedral type – mica, chlorite and/or vermiculite and/or kaolinite) was also identified in all the samples by the presence of their basal (near 14 Å, 10 Å, 7 Å) and hkl reflections (near 4.4 Å, 2.56 Å, 1.50 Å). The samples taken from layers 1 and 6 seem to be slightly richer in layered silicates than the other samples studied. The samples taken from layers 4 and 5 were relatively poor in the layered silicates.

Proton-Induced X-ray Emission (PIXE)

The concentration of several elements such as: P, K, Sc, Ti, V, Cr, Co, Cu, Zn were calculated according to the external standard procedure. The International Atomic Energy Agency (IAEA) standards such as IMEP-14, IAEA-433, Soil-5, Soil-7 were used for this purpose. Table 2 presents results taken on samples prepared in the form of pellets, 12 mm in diameter and 0.5 mm thick. The samples were mounted on scotch tape attached to aluminum frames. Each pellet was irradiated for 900 s live time using a proton beam current of 10 µA. Elemental concentrations were normalized to the element concentration in the sample taken from the first layer (surface). Such data presentation enables comparison of elemental composition changes of the sediments in time.
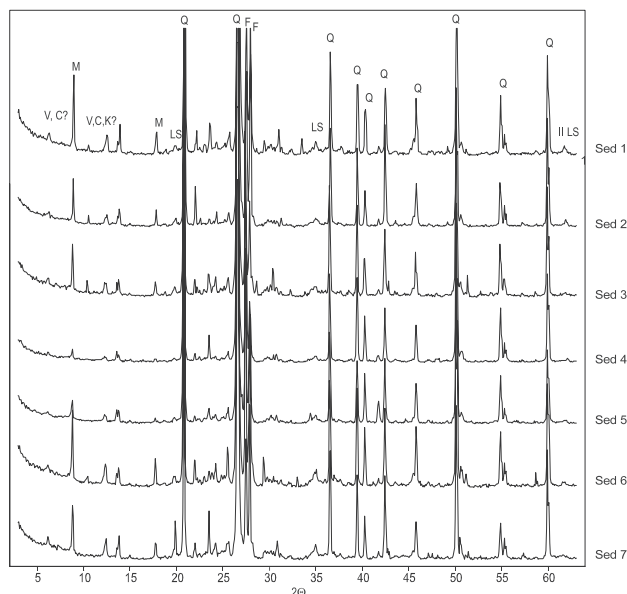
Fig. 2. X-ray diffraction patterns of the studied sediment samples. Q quartz, F – feldspars, LS – layered aluminosilicates, II LS – dioctahedral layered aluminosilicates, V – vermiculite, C – chlorite, M – mica, K – kaolinite.

Atomic Absorption Spectrometry (AAS)

Concentrations of Fe, Mn, Ca and Al in the sediment samples are presented in Table 3. Concentrations of Al and Fe are of the same magnitude, with the highest values in sediment sample no. 7 and lowest in sample no. 4.

Determination of Mercury Concentrations in Sediment Samples

Determination of Hg in sediment samples presented in table 4 were performed by means of automatic mercury analyzer AMA-254, or Advanced Mercury Analyzer AMA 254 (Altec). AMA 254 is a direct mercury analyzer which was conceived for determination of mercury

traces in liquid and solid samples. Total mercury determination involves the evaporation of Hg compounds by progressive heating of the sample (pyrolysis), until 800 ^{0}C is reached. The heating is performed in the oxygen stream for 3 min. During the sample heating the Hg vapors are collected by means of amalgamation on the Au net. After the amalgamation step the gold net is heated to liberate the collected mercury which is subsequently measured by UV atomic absorption spectrometry.

The concentrations (C_i) of Al, Ca, Mn, Fe and As obtained by AAS and Hg were normalized in the same way as in the case of the PIXE (Fig. 3).

The activity of artificial radionuclide ^{137}Cs, natural radionuclide ^{40}K and organic matter content in sediment samples are presented in Fig. 4.

Discussion

It is well known that environmental data are usually characterized by high variability, because of a variety of natural (geogenic, hydrological, meteorological), artificial and anthropogenic influences. Uncertainties from sample preparation and analytical signal measurement are also included in the data and affect their quality. The best approach to avoid incorrect interpretation of environmental data is the application of chemometric methods for data processing. Several useful literature surveys on the topic are available [12-15].

In this paper the squared Euclidian distance and the agglomerative hierarchical cluster analysis according to Ward [16] was applied to detect multivariate similarities between the river sediments in different annual layers. This method is distinct from all other methods because it uses an analysis of variance approach to evaluate the distances between clusters. Ward's method yields clearly structured and relatively stable clusters in which homogeneity is satisfied in environmental data sets applications.

Final results of the cluster analysis are presented graphically in the form of a dendrogram. On dendogram x-axis the indices of clusters objects (or variables) are displayed whereas the y-axis represents the correspond-

Table 2. Element concentrations (C_i) normalized to the concentration (C_1) determined in sample taken from the first layer.

Sediment layer	Depth [cm] (0 - ground level)	Ratio C_i/C_1							
		P	K	Ti	V	Cr	Co	Cu	Zn
1	0 – 11	1	1	1	1	1	1	1	1
2	11 – 15	0.75	1.28	1.27	0.11	1.87	1.53	2.36	1.05
3	15 – 21	0.16	0.91	0.82	0.06	0.51	1.23	4.33	1.77
4	21 – 36	0.01	1.17	0.47	0.07	0.35	0.77	2.11	0.45
5	36 – 48	0.01	0.85	0.53	0.05	0.40	0.68	0.79	0.00
6	48 – 55	0.66	0.96	0.97	0.08	0.55	1.18	0.95	0.90
7	55 – 90	0.17	0.95	0.97	0.10	0.48	1.34	0.77	1.53

Table 3. Concentrations of elements in sediment samples [ppm ± SD] determined by means of the F-AAS method.

Sediment layer	Depth [cm] (0 - ground level)	Al	Ca	Mn	Fe	As
1	0 – 11	6171±200	196±16	145±4	8268±200	5.5±0.3
2	11 – 15	5212±170	97±8	120±4	6768±160	3.9±0.2
3	15 – 21	6069±200	187±15	150±4	7340±180	6.6±0.4
4	21 – 36	2352±75	30±3	128±4	3792±90	3.0±0.2
5	36 – 48	3214±100	50±4	154±4	5810±140	4.4±0.3
6	48 – 55	6112±200	444±40	139±4	8442 ±80	7.4±0.5
7	55 – 90	7378±240	438±40	153±4	8528±200	6.6±0.4

Table 4. Concentrations of Hg [ppm ±SD] in sediment samples.

layer No	Hg concentration [ppb]
1	11.4 ± 0.05
2	8.7 ± 0.05
3	13.6 ± 2.7
4	5.5 ± 7.0
5	10.8 ± 0.1
6	14.4 ± 0.6
7	24.5 ± 0.3

Fig. 3. Elemental concentration normalized to the concentration determined for samples from layer 1, where C_i – element concentration and C_1- element concentration determined for layer 1.

Fig. 4. Dependence of ^{137}Cs, ^{40}K activity and organic matter content on depth of sediment layer.

ing linkage distance (or an adequate measure of similarity) between the two objects or clusters which are merged.

The aim to apply intelligent data analysis methods is to obtain specific information about the hidden structure of the environmental data sets from the Dobczyce water reservoir. In this study cluster analysis was applied to multidimensional data sets, in order to study similarities (or dissimilarities) of objects in the variable space or similarities of variables in the object's space. In our work the annual layers of sediments are the objects and concentration of some elements in the individual layers are the variables. Chemometric data interpretation has the advantage of confirmation of the typical parameter changes and notices the features, which are specific for sediments from the mentioned region.

If one considers the dendrogram characterizing the sediment samples (Fig. 5), three groups could be distinguished: first – consisting of the samples 1. 6 and 7; second to which samples 2 and 3 belong; and third containing samples 4 and 5. The first group represents layers 6 and 7 and layer 1. As their chemical composition is similar it can be assumed that the inflow of the examined elements in time at typical weather conditions is almost invariable. The third group consisting of layer 4 (most probably deposited during the severe flood in 1997) is characterized by the lowest concentrations of all analyzed elements and completely different grain size profile compared with the other samples (with the exception of layer 5). The flooding water washed out layer 5, 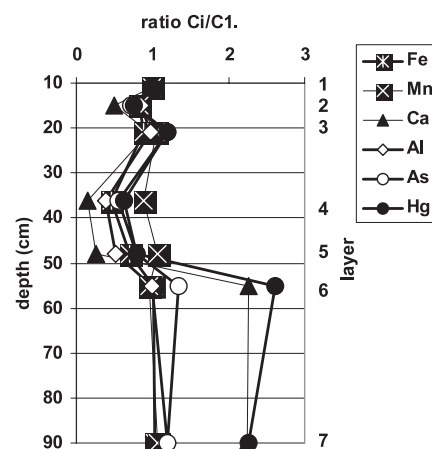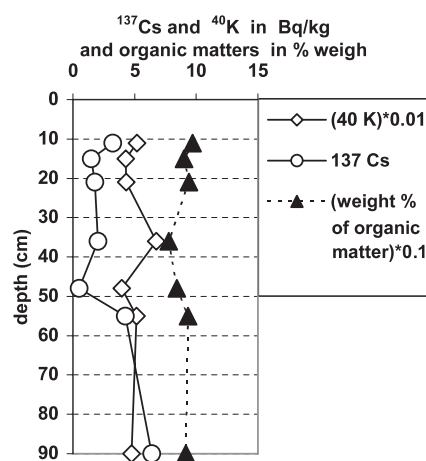which results in low concentrations of the elements and different grain size distribution close to what was found in layer 4). The second group seems to represent layers of "post flood" sediments. The lower level of element concentrations in those layers may result from weaker erosion of the Raba river basin (the river banks were washed out by heavy rainfall during the flood).
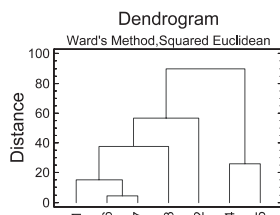
Dendrogram
Ward's Method,Squared Euclidean

Fig. 5. Hierarchical dendrogram for the clustering of sediment layers (1-7).

Dendrogram
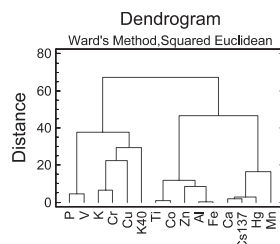Ward's Method,Squared Euclidean

Fig. 6. Hierarchical dendrogram for the clustering of concentration of elements

There is not enough data referring to similarities of variables to make possible more than a limited discussion of the presented dendrogram for the elemental clustering (Fig. 6). The first group consisting of P, V, Cr and Cu can be considered as "anthropogenic" elements. K and ^{40}K were observed in this group. K P and Cu originate from fertilizers used in the area whereas Cr appears in the sediments most probably from tanneries located along the upper Raba River. K and ^{40}K are also incorporated into the structure of sediments' mineral compounds. The activity of ^{40}K is directly proportional to the total activity of potassium in the soil or sediment; 1 g of potassium always contains 31.7 Bq kg^{-1} of ^{40}K [4]. The second group (Ti, Co, Zn, Al and Fe) can be recognized as elements either naturally constituting soil particles (Ti, Al, Fe) or having strong affinity to sediment particles (Co and Zn). Very similar characteristics of Ca and Cs^{137} (the latter being totally artificial) suggests that the elements originate predominantly from soil erosion.

At the sampling site seven layers of sediments were distinguished in the in-depth profile based on their morphological features. The fourth one (depth from 21 to 36 cm below the surface) differed significantly from the others. That layer was characterized by light colour, much lower content of clay material and an abundance of coarse-grained sand. The deepest layer (below 55 cm) was saturated with water (layer 7). That layer was deposited on a layer of stones placed there during reservoir construction.

The content of organic matter changes significantly in sediments (from less than 1% up to about 4%). As the sampling site was located near the reservoir shore part of the organic matter originated from dead leaves (they were found during sampling) as well as from biological life in water (Tabl. 1). The lowest content of organic matter was found in layers 4 and 5. Those values were

much lower than the organic matter content found in the Dobczyce Reservoir sediment samples taken from the central part of the reservoir – being in the range of 5 – 9.4% [17].

The grain size distribution in the sediment samples reveals certain similarities. Samples from layers 1, 2, 3, 6 and 7 consist mainly (64 up to 76 weight%) of particles of size between 0.04 mm and 0.1 mm. This can be understood from the hydrological and mineralogical characterization of the reservoir itself and its basin. The part of the reservoir close to the Raba river estuary (named Myślenice Basin) works as a settler for coarse grains while the other part (Dobczyce Basin) is reached only by smaller particles of suspended particles. However, it was not true for samples from layers 4 and 5. Such phenomena will be discussed later.

As shown in Table 2, the depth profile of elemental concentrations normalized to the concentration determined in the sample taken from layer 1 is characteristic. The first layer reveals high accumulation of P and V, second layer of K, Ti, Cr and Co, third layer of Cu and Zn, whereas the fourth one accumulates only small amounts of Al, Ca, Mn and Fe. Metal concentrations in the sediments are positively correlated with the organic matter content. It is connected with cation exchange capacity (CEC). Organic matter and clay colloid increase the CEC and adsorbability of heavy metals in sediments. Organic matter is an important scavenger for metals in lake and river sediments.

Concentrations of metals found in sediments at high concentration levels (Fe, Mn, Ca, Al) varied in the examined samples over a broad range. The most significant differences were determined for Ca (from about 30 ppm in the layer 4 to 444 ppm in the layer 6). Generally the highest concentrations of metals were found in the samples taken from the deepest layer. The element concentration correlate with mineral composition of sediments [1-2] as well as with organic matter content [3]. It is worthwhile to mention that concentrations of Fe and Mn are lower than those reported by Starmach [18].

The concentration of arsenic a potentially toxic element was determined in the analyzed samples. As for the other metals, highest concentrations were found in the samples taken from layers 6 and 7 (Fig. 3). This may result from two reasons: a) higher inflow of compounds containing arsenic (for example: in the 80's pesticides containing As were still used in Poland) and b) higher concentration of elements that influence the process of immobilization of trace elements in sediments (Fe, Mn, Al and Ca) in those samples [19]. A similar trend was observed for the Hg concentration changes in the sediments.

It seems to be justified that the sediment layer 4 was deposited during the severe flood in Poland in 1997. The incoming water first washed out clay material as well as organic matter and metals from the sediments (thus low concentrations of them in the samples taken from layer 5). Later there was a deposition of coarse-grained mater-

ial consisting mainly of sand with much lower concentrations of all examined components.

The Dobczyce Reservoir was built when the results of the Chernobyl accident were visible. Thus it could be the reason for the highest ^{137}Cs activity in the deepest layers. In the more shallow layers the active cesium concentration is lower, resulting probably from the intensive rinsing of this element from sediments during the flood in 1997.

From the point of view of potential health risk, the level of cesium is low. The concentration level of the activity is in range between 6.4 Bq/kg to 1.1 Bq/kg. These values are comparable with the data collected from the river sediments in France [20] or the Tyrrhenian Sea [6]. The level of potassium was compared with the values of the concentration for Carpathian Foothills [21,22]. In comparison with these data the average caesium content in soil originating from the Carpathian Foothills is about 3.67 Bq/m^2 [23]. The sorption mechanism of caesium and potassium is dependent either on the amount of organic components or on the quantity of mineral components found in tested sediment samples (Fig. 4) [7].

As seen in the presented graphs the level of the natural ^{40}K isotope activity is correlated with the depth of the sediment and depends mainly on the mineralogical structure (Fig. 1). However, changes of ^{137}Cs concentration in the sediments are connected with the concentration of organic matter in investigated sediment samples (Fig 4).

Acknowledgements

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