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PRELIMINARY STUDY OF ELEMENTAL AND RADIONUCLIDES COMPOSITION IN SEDIMENT SAMPLES FROM DOBCZYCE WATER RESERVOIR

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Abstract

Sediments play fundamental role in toxic compounds distribution in aquatic systems and in the evaluation of current state and course of changes taking place in environment. On the other hand physical, chemical, biochemical and geochemical processes that influence toxic compounds and elements fate in sediments are numerous and complex (for example: adsorption – desorption, oxidation – reduction, ion-exchange, biological activity). River and lake sediments constitute also very difficult analytical samples. Due to the above mentioned general statements only long term and as complex as possible research can lead to satisfactory answers to the question about drinking water quality for the city of Cracow. Therefore in this paper, introductory results concerning determination of concentration of chosen elements such as Al, P, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, NI, Cu, Zn and radionuclids natural (^{40}K) and artificial (^{137}Cs) in the depth profile of sediment samples from the Dobczyce Reservoir are presented. For the best quality of experimental work several analytical techniques, were applied namely: Proton Induced X-ray Emission (PIXE), Rutherford Back-Scattering (RBS), Atomic Absorption Spectroscopy (AAS), gamma spectrometry, and x-ray diffraction.

Introduction

Among components of aquatic environment, sediments can be recognized as a factor playing fundamental role in a circulation of toxic compounds. Potentially harmful elements and compounds are effectively accumulated in the sediments and, in certain conditions, can be readily released into water in an unpredictable way. On the other hand, concentration of elements in sediments can serve as an indicator of water quality. If one can analyze chemical composition of separate layers in depth profile of sediments, the "history" of water contamination in the area might be distinguished. Numerous factors, physical and chemical, influence process of toxic compounds accumulation in sediments. These are: sediments mineral composition, organic matter content, concentration of elements such as Al, Ca, Mn, Fe, Co red-ox potential, pH, temperature ect. Very complex nature of the sedimentation processes requires interdisciplinary studies with application of numerous analytical methods and techniques.

Experimental

Site description

The Dobczyce Reservoir construction was completed in 1985 and filled with water in 1987. It is situated in the South of the city of Cracow on Raba river at 60 km of its course, 270 m above sea level with an area of 970 ha. The Raba river basin consists mainly of suburban areas with small cities like Myślenice and Dobczyce. Thus, main contaminants that can be expected come from agriculture and municipal activity, less from industry.

Due to the very dry weather in 2003 in Poland, the water level of the Dobczyce Reservoir dropped markedly (about 6 m below typical water level). It happened for the first time since the reservoir was filled with water. Vast areas of sediments emerged then. It enabled a sampling of sediments from the reservoir banks.

The sampling site is marked in the Reservoir map (Fig. 1). At the place marked as "A" sediments were taken up in a depth profile, up to 90 cm below the ground level. Due to morphological reasons 7 sediments layers were distinguished and subsequently seven samples of the sediments were taken up (Fig. 2).

The samples were taken and transported to the laboratory in polyethylene containers and air-dried. The samples were thoroughly mixed and prepared for further analysis according to a given analytical method requirements.
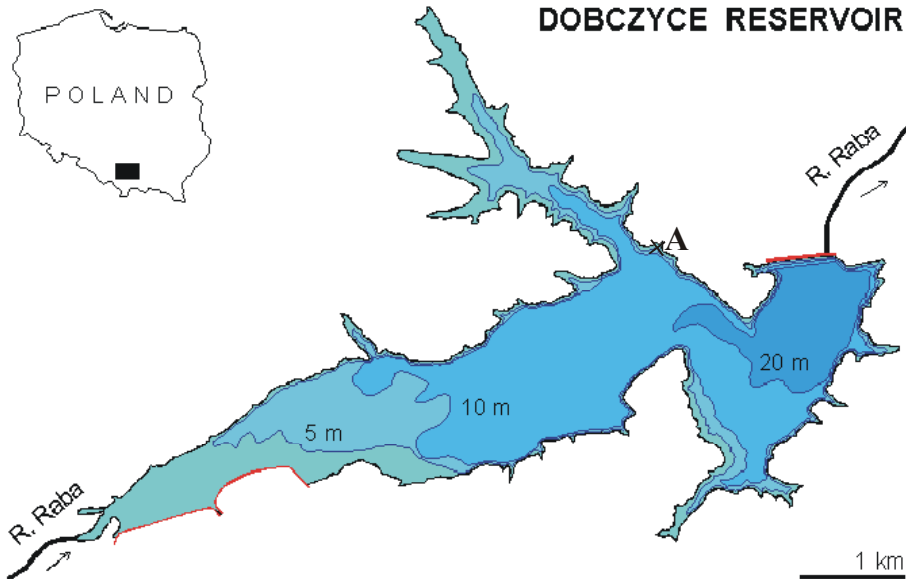

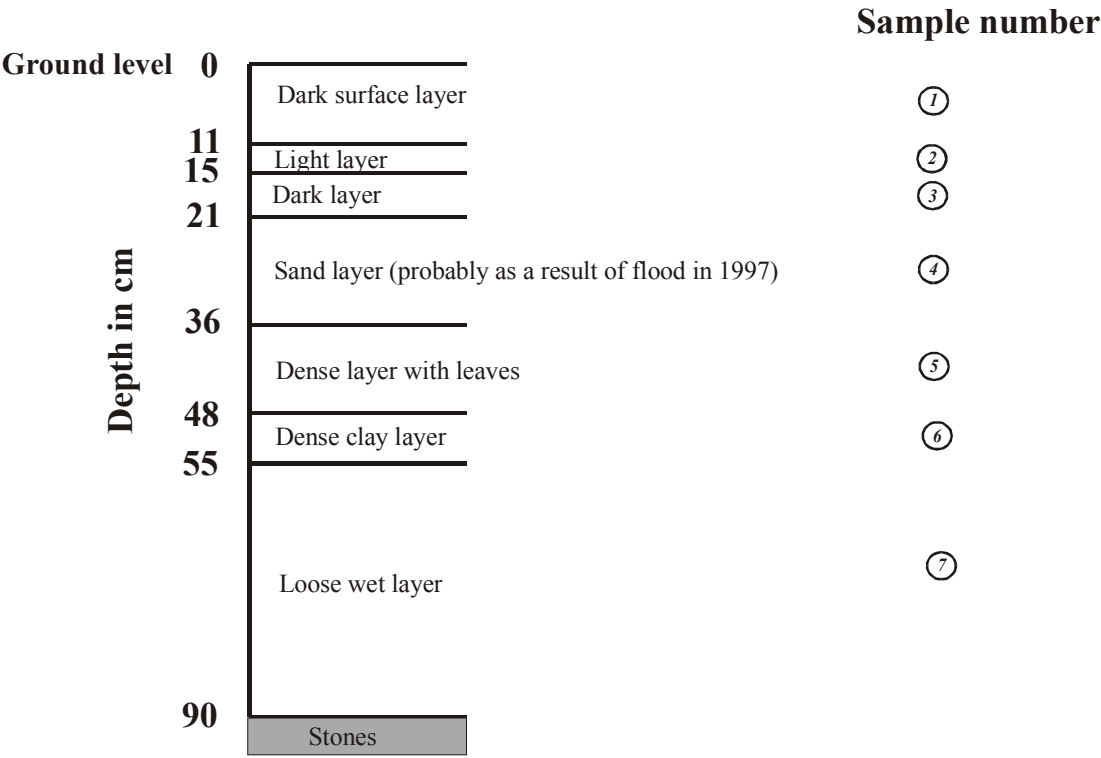Fig. 1. Sampling site at the Dobczyce Reservoir.

Fig. 2. Diagram of depth profile.

Mineral composition of the sediment samples.

The sediments samples consist mainly of quartz and feldspars (K-feldspars as well as Na-plagioclase). Small amount of layered silicates (mainly mica, chlorite and/or vermiculite) can also be detected. The composition of sediment was presented in diffractogram of samples number 2 in Fig 3.
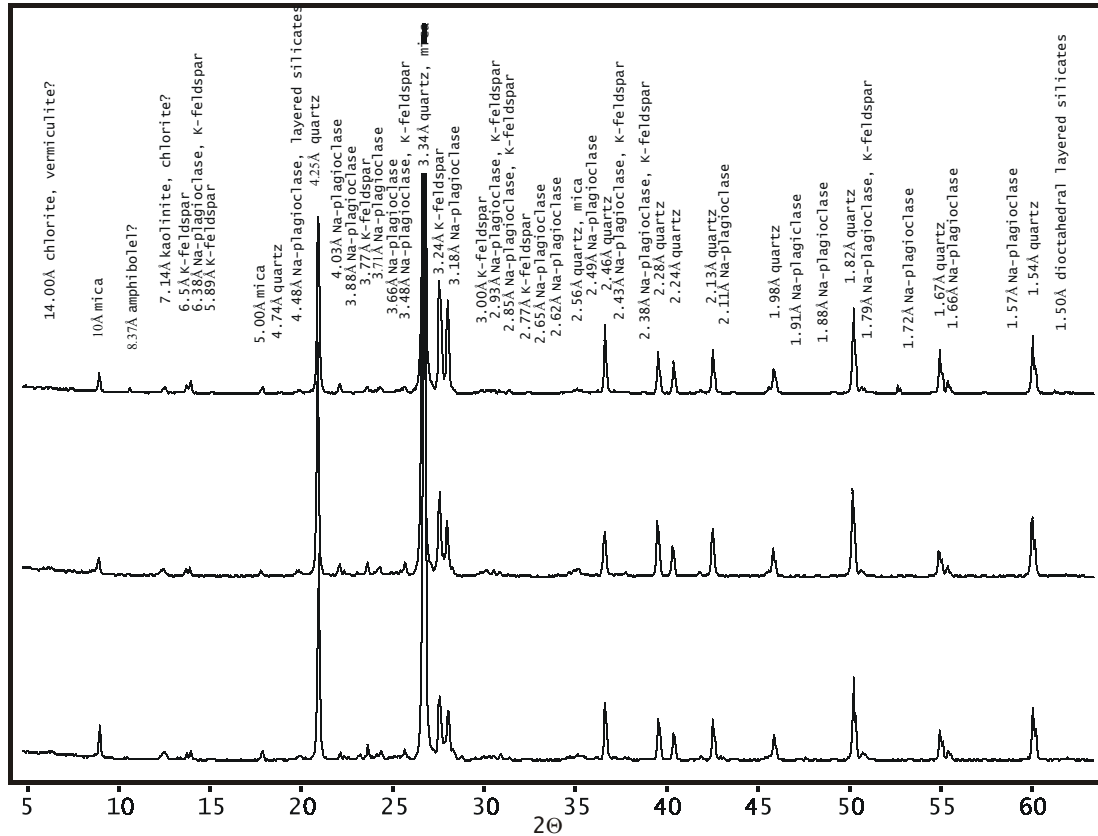

Fig. 3. Random powder diffraction patterns of the selected fractions.

Organic matter content in the sediment samples

Organic matter content in the samples was determined by means of samples roasting in an oven at 600°C for 6 hours. The results are presented in Fig. 4.

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 adsorption of heavy metals in sediments. Organic matter is an important scavenger for metals in lake and river sediments.
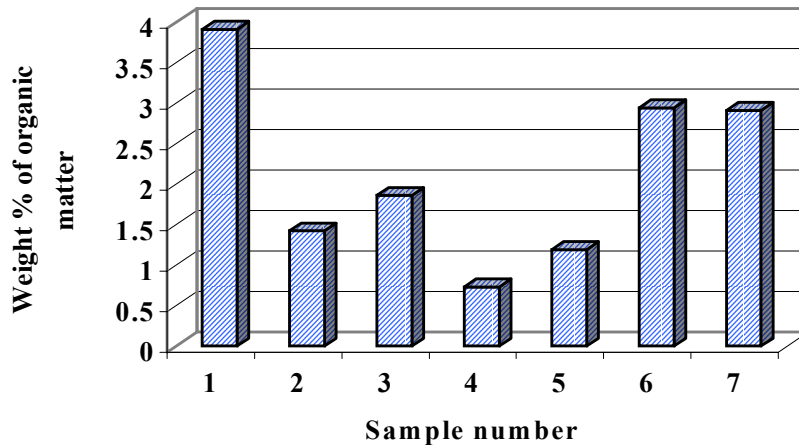
Fig. 4. Organic matter content in sediment samples.

Particle size distribution in the sediment samples

The sediment samples were analysed for a grain size with the use of a set of sieves. The collected samples were sieved on vibrating screen (diameter circular – hole screen were in range between 2,5 mm to 0,04 mm).
Seven fractions of grains were collected and weighted. In the Fig. 5 certain fractions are identified by the sieve mesh diameter in mm.
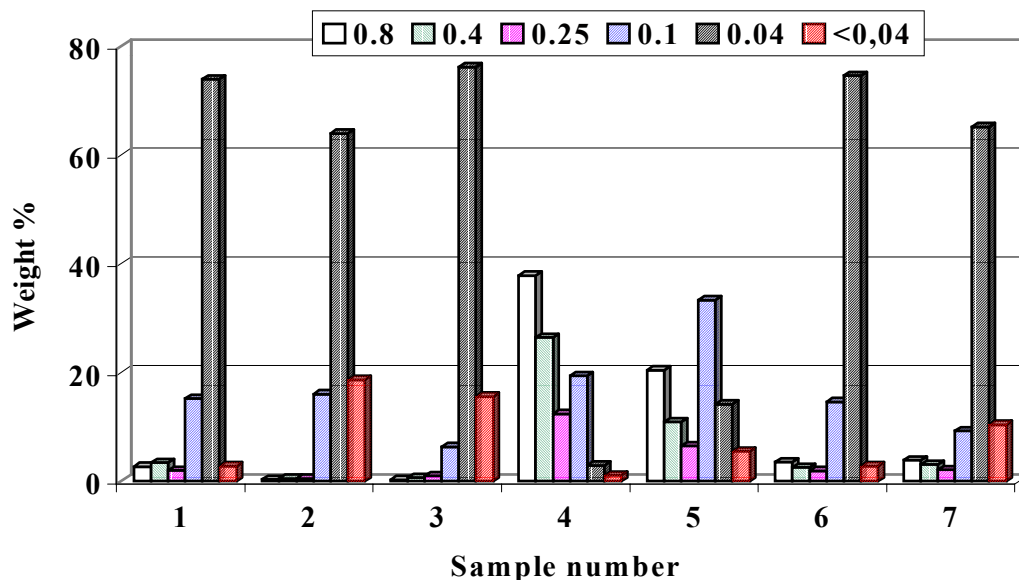
Fig. 5. Particle size distribution in the sediment samples

Determination of elemental concentration by means of PIXE method

Since the trace element distribution in a sample may give a lot of information about trace elements their self, their functionin living organisms and indicate pollution of environmentthe PIXE technique, as a very sensitive and powerful, have been applied in this study. 2.4 MeV proton beam at the Institute of Nuclear Physics in Cracow has been applied to the

trace element analysis using PIXE, and RBS techniques. Those two techniques were simultaneously applied. Proton beam was collimated down to 1 mm^2.

The experimental set-up for PIXE experiments allows to collect 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 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 on an aluminum thin foil. The foil separates the high vacuum volume of target chamber from low vacuum region, where the investigated sample is placed. This arrangement, known as an external beam technique allows to avoid target charge deposition. Such normalization 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.

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. The Table 1 presents results taken on samples prepared in the form of pellet of 12 mm in diameter and 0,5 mm thick. The samples were mounted on Scotch tape attached to the aluminum frames. Each pellet was irradiated for 900 s live time. Elemental concentrations were normalized to the element concentration in the first sample. Such data presentation enables comparison of elemental composition changes of the sediments in time.

Tab. 1. Elemental concentration normalized to the concentration determined in sample No. 1.

Sample No	P	K	Sc	Ti	V	Cr	Co	Cu	Zn
1	1	1	1	1	1	1	1	1	1
2	0.75	1.28	0.91	1.27	0.11	1.87	1.53	2.36	1.05
3	0.16	0.91	0.01	0.82	0.06	0.51	1.23	4.33	1.77
4	0.01	1.17	1.66	0.47	0.07	0.35	0.77	2.11	0.45
5	0.01	0.85	0.43	0.53	0.05	0.40	0.68	0.79	0.00
6	0.66	0.96	0.56	0.97	0.08	0.55	1.18	0.95	0.90
7	0.17	0.95	0.51	0.97	0.10	0.48	1.34	0.77	1.53

Determination of elemental concentration by means of Atomic Absorption Spectrometry

In addition to PIXE analysis the 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 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_2O – acetylene flame.

Each determination was performed three times. Concentrations of Fe, Mn, Ca and Al are presented in table 2.

Tab. 2. Concentrations of elements in sediment samples [ppm ±SD] determined by means of F AAS method.

Sample No	Al	Ca	Mn	Fe
1	6171±200	196±16	145±4	8268±200
2	5212±170	97±8	120±4	6768±160
3	6069±200	187±15	150±4	7340±180
4	2352±75	30±3	128±4	3792±90
5	3214±100	50±4	154±4	5810±140
6	6112±200	444±40	139±4	8442 ±80
7	7378±240	438±40	153±4	8528±200

Also, arsenic concentration was determined. In that case Electrothermal Technique (ET) was applied. 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. An accuracy of the analytical procedure for arsenic analysis was tested with the use of the certified reference material BCR No 320 River Sediment. Satisfactory results were obtained and presented in Fig 6.
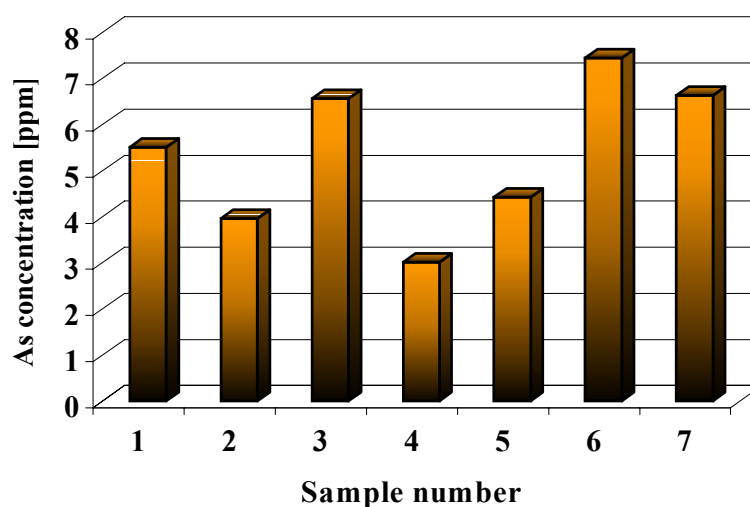

Fig. 6. Concentration of As in the sediment samples determined by means of ET AAS (relative standard deviation of As determination was 2%).

Determination of mercury in the sediment samples by means of spectrophotometric method.

Determination of Hg in the sediment samples was performed by means of the automatic mercury analyzer AMA-254. Results are presented in Table 3.

Table 3. Concentrations of Hg in sediment samples [ppb ±SD].

Sample No	Hg
1	11.4 ± 1.4
2	8.7 ± 1.2
3	13.6 ± 9.2
4	5.5 ± 1.0
5	10.8 ± 0.4
6	14.4 ± 2.0
7	24.5 ± 1.9

Same as in the case of the results of element concentrations in the sediments samples obtained by means of PIXE method, the concentrations of Al, Ca, Mn, Fe, As and Hg were normalized (table 4).

Tab. 4. Elemental concentration normalized to the concentration determined in sample No. 1.

Próbka	Fe	Mn	Ca	Al	As	Hg
1	1	1	1	1	1	1
2	0,82	0,83	0,49	0,84	0,72	0,76
3	0,89	1,04	0,96	0,98	1,19	1,19
4	0,46	0,89	0,15	0,38	0,55	0,63
5	0,70	1,06	0,25	0,52	0,80	0,79
6	1,02	0,95	2,27	0,99	1,35	2,62
7	1,03	1,06	2,24	1,20	1,20	2,27

The determination of natural and artificial radionuclides concentration

In the 20th century the natural environment has been contaminated with artificial radioactivity. In the northern hemisphere the atom bomb explosions increased the radioactivity, most significantly in the first half of the 1960. In 1986 after the Chernobyl accident, the deposition of radioactive cesium increased considerably in large areas of Europe.

The concentration of artificial ^{137}Cs and natural ^{40}K isotopes in the sediment profiles were investigated. The radionuclide concentration in the sediment samples were measured using the gamma spectrometry technique. The gamma spectrometer with HPGe detector (10% efficiency) was calibrated by the standard IAFA-154 from IAEA. All activities refer to dry mass of samples and the results are calculated for the day of 01.09.2000 for each of the samples. Artificial ^{137}Cs and natural ^{40}K radionuclides activity in sediment samples collected from region Dobczyce Lake were presented in Table 5 and in Fig .7 and Fig.8.

Table 5. The contents of the level activity of cesium and potassium in sediment samples [Bq/kg±SD].

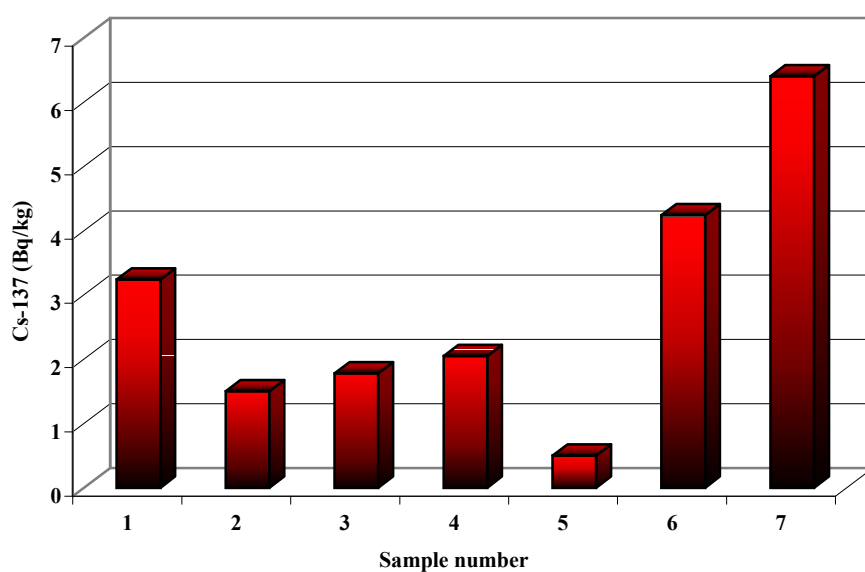| Sample No	^{137}Cs	^{40}K
1	3.2 ± 0.5	520 ± 22
2	1.5 ± 0.4	428 ± 18
3	1.8 ± 0.5	432 ± 18
4	2.1 ± 0.5	675 ± 28
5	1.5 ± 0.4	396 ± 16
6	4.2 ± 0.5	515 ± 22
7	6.4 ± 0.6	478 ± 20

Fig.7. Dependence of ^{137}Cs activity on depth of sediment layer from the Dobczyce Reservoir.
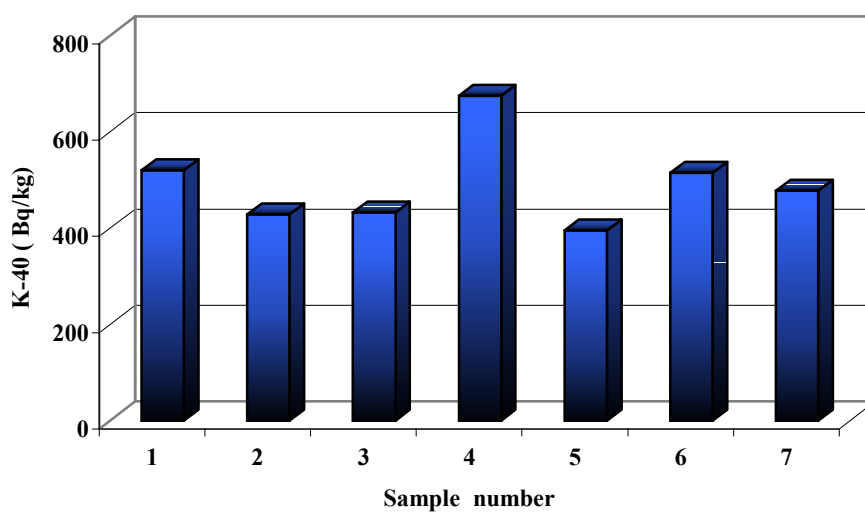

Fig.8. Dependence of ^{40}K activity on depth of sediment layer from the Dobczyce Reservoir.

As it is seen on the presented graphs, the level of natural ^{40}K isotope is not correlated with the depth of the sediment but depends mainly on the geological structure. Insouluble K is probably associated with the clay mineral illite,which is present in this sediment. Contrary, changes of ^{137}Cs concentration in the sediments are more visible.

Discussion

At the sampling site, seven layers of the sediments were distinguished in the depth profile, basing on their morphological features – colour, water saturation, and density. Of all distinguished layers, one differed significantly (sample no 4, depth from 21 to 36 cm below the surface). It was characterised by much lower content of the clay material, light colour, and abundance of the coarse-grained sand. The deepest layer (below 55 cm) was saturated with water (sample 7) and deposited on a layer of stones placed there during the reservoir construction. Thus, by analysing sediments in the depth profile, some conclusions concerning a "history" of the water contamination in the reservoir might be drown out.

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, a part of organic matter originated from dead leaves (they were found during sampling) as well as from a biological life in water. The lowest content of the organic matter was found in the samples 4 and 5. Determined values were much lower than the organic matter content in the Dobczyce Reservoir sediment samples taken from the central part of the reservoir – being in the range 5 – 9,4 % [WIOŚ report 2001].

The distribution of grain size in the sediment samples reveals certain stability. In the samples No 1-3 and 6 and 7, 64 up to 76 weight % constitute particles of size between 0,04 mm and 0,1 mm. It results form hydrological and mineralogical characterisation of reservoir itself and its basin. The part of the Reservoir close to 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 4 and 5. It will be discussed later.

As shown in Table 1 the depth profile of elemental concentrations normalized to the concentration determined in sample no. 1 depends on the element. Mostly, one can observe an characteristic behaviour of the each profile. Some of them are very well correlated while the others are not. The first layer mostly accumulates P and V, second layer K, Ti, Cr, and Co, third layer Cu and Zn, whereas the fourth one does not accumulate Al, Ca, Mn, and Fe.

Concentrations of metals presented in sediments at high concentration levels (Fe, Mn, Ca, Al) varied in the examined samples in broad ranges. The most significant were for Ca (from about 30 ppm in the sample 4 to 444 ppm in the sample 6). Generally the highest concentrations of metals were found in the samples taken from the deepest level. The elements correlate with mineral composition of sediments [Helios-Rybicka and Kyziol, 1991; Manning and Goldberg, 1996] as well as with organic matter content [Lin and Chen, 1998].

It is worth to stress that determined values were (as far as Fe and Mn are concerned, but there is no data for Ca and Al concentrations) lower than published by Starmach and Mazurkiewicz-Boron (Mn concentration was in the range 0,3 – 3,3 mg/g; Fe – 0,9 – 35,9 mg/g) [2000].

Of potentially toxic elements, concentration of As was determined in sediment samples. As for the other metals, the highest concentrations were found in the samples 6 and 7. It may result from two reasons: a) higher inflow of arsenic containing compounds with water (for example: in the 80-s As containing pesticides were still used in Poland) and b) higher concentration of elements that influence process of immobilisation of trace elements in sediments (Fe, Mn, Al and Ca) in those samples [Belizile and Tessier, 1990]. Similar trend was observed for Hg concentration changes in the sediments.

The sediment layer, marked as 4 was deposited during the severe flood in Poland in 1997. Coming water firstly washed out clay material as well as organic matter and metals from the sediments (thus low concentrations of them in the sample 5). Later there was deposited coarse-grained material consisting mainly of sand with much lower concentrations of all examined components.

The Dobczyce Reservoir was built when the effects of the Chernobyl accident were visible. It could be the cause of the ^{137}Cs activity is the highest in the deepest layers. In the more shallow layers, the ceasium concentration is lower resulting probably from the intensive rinsing of this element from sediments during the flood in 1997.

From the potential health risk point of view, the level of cesium is low. The concentration level 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 [Vray and Debayle, 2003] or Tyrrhenian Sea [Desideri and Meli,2002]. According to the W.Chełmicki, the level of cesium ascertained in soil samples from The Wielickie Pogórze [Chełmicki and Klimek, 1996-1997]. In comparison to these data, the average ceasium content in soil originated from Carpathian Foothills is about 3,67 Bq/m^2 [Strzelecki and Wołkowicz, 1993].

According to the results of our preliminary studies, since the concentrations of elements and radionuclides in sediment layers significantly vary the more detailed and systematic research program is being elaborated and it will be implemented in the nearest future.

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