RADIONUCLIDE BIOSORPTION BY THE AQUATIC PLANTS OF *PISTIA STRATIOTES*

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The activity of leaves and roots of *Pistia stratiotes* from the Seversky Donets river has been measured. The visible activity of ^{131}I in roots of plant is found. The content estimate of ^{131}I in water of Seversky Donets river before extraction of samples of a hydrophyte gives value exceeding 1 Bk/l. The detection of activity of ^{131}I in roots of *Pistia stratiotes* can be used for its monitoring in the biosphere. The photoactivation analysis has been used for measuring of element content in leaves and roots of *Pistia stratiotes*. Accumulation in roots versus leaves of *Pistia stratiotes* Mn, Co, Ni, Mo, I, Pb and also isotopes ^{228}Ac, ^{214}Pb and ^{214}Bi was detected.

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1. INTRODUCTION

Water contamination by radio nuclides, heavy metals and industrial pollutants is a very important problem in the world. Last years the phytotechnologies are used for contamination removal by plants. The principal mechanism for contamination uptake is sorption by roots [1]. The main mechanism involved in biosorption is ion exchange between monovalent metals as counter ions present in macrophytes biomass and heavy metal ion and protons taken up from water [2]. A review of literature shows that metals can be removed by inexpensive biological materials as algae, fungi and bacteria [3, 4].

In 2011 *Pistia stratiotes* has appeared in the waste canal of thermal power station-2 which takes places on the Seversky Donets river near the settlement Eshar of the Kharkov region. The significant amounts of *Pistia stratiotes* have been discovered in the Seversky Donets river in 2013 year (Fig.1). The water temperature in Seversky Donets river was 25.1°C in July 2013. The temperature in the waste canal of thermal power station-2 (0.5 km below the water discharge) was 30.2°C. Water plant of *Pistia stratiotes* is a plant of warm water aquariums and botanic gardens from tropical fields from Africa. The facts of the occurrence of this water plant in Europe are registered [5]. Most likely, this plant is brought in reservoirs from decorative ponds and aquariums. The tropical water plant has appeared in natural reservoirs of medial latitudes for refining of city sewage, waste of factories, enterprises of the textile industry. This water plant is used also in a combination to other water plants for sewage treatment of pig-breeding complexes.

The given water plant is a plant-introdutsent (immigrant). This plant grows and multiplies rapidly and also intensively absorbs almost all biogenic elements and their compounds from water. Efficacy of compound cleaning is ∼95%. The cleared water is used for watering of agricultural crops.

Fig.1. *Surface of the Seversky Dontets covered by Pistia stratiotes*

Last years it is observed dilating of a geographic range of diffusion and acceleration invasion processes of *Pistia stratiotes*. It is promoted processes of warming of a climate observed in last year's, and also the thermal contamination of water objects. The *Pistia stratiotes* can hibernate if water does not freeze [6] in the winter.

Strong development of *Pistia stratiotes* can cause of shadowing of the water areas of the river. In such conditions the vegetation in the water will die off and the hydrochemical state of the river, first of all an

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oxygen regimen to worsen. It can cause local (or mass) destruction of fish and other hydrobionts that will lead to the further deterioration of river water.

The *Pistia stratiotes* is object of intensive study because of a series of unique its properties. The *Pistia stratiotes* produce a big amounts of Ca oxalate crystals in specialized cells called crystal idioblasts [7]. It has been determined that Ca^{2+} channels play a key role in Ca oxalate crystal formation in this plants.

Table 1. *Concentration of radioactive isotopes in the coals of Donetsk basin used on the Zmievsky state district power station, Bq/kg [8, 9]*

Coal type	^{226}Ra	^{232}Th	^{40}K
Anthracite culm	17	≤5	226
sludge	30.3	17.3	305
Ordinary coal	39.2	52.6	684
Donetsk coal [8]	18.5...107		
Donetsk coal [9]	22.2...51.8		

By thermal power station operation the greatest contribution to environmental contamination bring such radio nuclides, as ^{210}Pb (∼25%), ^{232}Th (∼30%), ^{228}Th (∼20%), ^{238}U (∼10%), ^{40}K (∼2%), ^{226}Ra (∼2%), ^{228}Ra (∼1.0%). Concentration of natural radio nuclides in the coals used on the Zmievsky state district power station is presented in Table 1.

Table 2. *Atmospheric isotopes release from NPP in Ukraine (the data of project INPRO ENV), Bq/y*

isotope	Bq/year	isotope	Bq/year
^{1}H	$1.50\cdot10^{11}$	^{89}Sr	$1.10\cdot10^{6}$
^{47}Ar	$1.70\cdot10^{10}$	^{90}Sr	$1.50\cdot10^{5}$
^{51}Cr	$2.60\cdot10^{6}$	^{95}Zr	$5.30\cdot10^{5}$
^{54}Mn	$1.30\cdot10^{6}$	^{95}Nb	$4.60\cdot10^{5}$
^{59}Fe	$5.50\cdot10^{5}$	^{110m}Ag	$4.50\cdot10^{5}$
^{58}Co	$8.50\cdot10^{5}$	^{133}Xe	$6.10\cdot10^{12}$
^{60}Co	$2.30\cdot10^{6}$	^{135}Xe	$1.10\cdot10^{12}$
^{85}Kr	$5.10\cdot10^{11}$	^{131}I	$4.80\cdot10^{7}$
^{85m}Kr	$4.60\cdot10^{11}$	^{134}Cs	$7.10\cdot10^{5}$
^{87}Kr	$8.40\cdot10^{10}$	^{137}Cs	$1.50\cdot10^{6}$
^{88}Kr	$1.90\cdot10^{11}$		

Nuclear power plants (NPP) also cause releasing of radioactive isotopes into the atmosphere (Table 2). Thereupon some isotopes represent danger at incorporation into a human body. Owing to the high rate of metabolic processes in children the ^{131}I is especially dangerous. The transport of ^{131}I through the grass → cow → milk → man food chain is caused primarily by the interception efficiency of typical pasture vegetation for the radionuclide, the unique secretion of iodine into milk by the cow, and the rapidity with which milk is processed and reaches the consumer.

The aim of the present study is to investigate the mechanism of the simultaneous removal of metals derived from industrial activities from dead freshwater macrophytes and the creation of a method of monitoring of ^{131}I in biosphere by means of detection of its activity in roots of *Pistia stratiotes.*

2. MATERIALS AND METHODS

Samples of *Pistia stratiotes* from the Seversky Donets river were investigated. Samples *Pistia stratiotes* were taken in October, 2013. Investigation of radionuclide activity in dry native samples (roots, leaf) of *Pistia stratiotes* was conducted using Ge(Li)-detector with energy resolution of 3.2 keV at the energy of 1333 keV. Time of activity measurements of samples weighing up to 0.5 kg was 6...12 hours. Natural isotopes – ^{40}K, ^{235,238}U, ^{232}Th families, cosmic – ^{7}Be, and anthropogenesis - ^{137}Cs and ^{131}I were detected in native samples. The errors of measurements were from 3 to 25%. Activation of samples has been conducted with use brake radiation of the linear accelerator electrons NSC KIPT with electron energy 23 MeV and a current 500 μA. Activation of samples was carried out on air, the temperature of samples in the course of activation did not exceed 40°C. Trace elements Zn, Ni, Ca, I, Mn, Rb, Zr, Na and others were determined. The limit of detection elements for photoactivation analysis was $10^{-4}...10^{-7}$wt. The ashing of samples was spent at temperature 700°C.

3. RESULTS AND DISCUSSION

In Fig.2 the γ-spectrum of the initial sample of the leaf of *Pistia stratiotes* is presented. In γ-spectrum of investigating sample the various elements are observed (^{226}Ra, ^{7}Be, ^{214}Pb, ^{208}Tl, ^{137}Cs, ^{40}K and others) (Table 3). Special interest causes ^{7}Be ($T_{1/2}$=53 days). ^{7}Be is generated by cosmic rays in the upper troposphere and stratosphere, and is a tracer of downward aerosol transport.

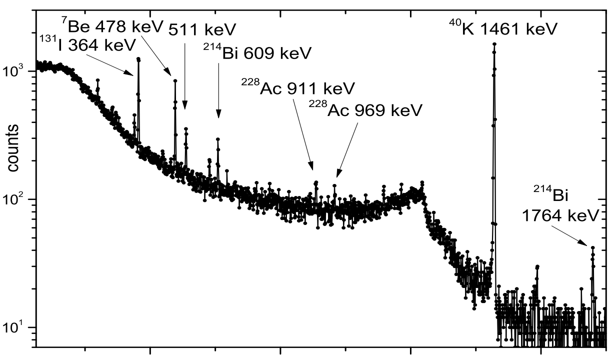

Fig.2. *Energy spectrum of own radioactivity of leaf of Pistia stratiotes*

It is especially necessary to note detection ^{131}I. It arrives into the water of the river in the course of deposition of aerosols of the working NPP. The high coefficient of accumulation *Pistia stratiotes* iodine allows to register isotope ^{131}I (see Table 3). Considerable quantity of iodine collects by roots of *Pistia stratiotes.* Therefore the possibility of determination of ^{131}I by means of activity of *Pistia stratiotes* allows to carry out radioiodine monitoring in an environment.

In Fig.3 the gamma spectrum of the irradiated sample of root of *Pistia stratiotes* is given. A considerable quantity of elements (Table 4) were registered.

Table 3. The activity of root and leaf of Pistia stratiotes and activity ratio of root vs leaf (dry wt.)

	root, Bq/kg	leaf, Bq/kg	root vs leaf
^{40}K	604	2573	0.23
^{131}I	2032	153	13.3
^{7}Be	138	287	0.48
^{226}Ra	119	23.9	4.98
^{228}Ac	81.3	7.65	10.62
^{214}Pb	41.8	2.7	15.50
^{214}Bi	38.1	3.61	10.55
^{208}Tl	10.6	4.41	2.41
^{212}Pb	9.56	2.15	4.45
^{137}Cs	1.3	0.90	1.14

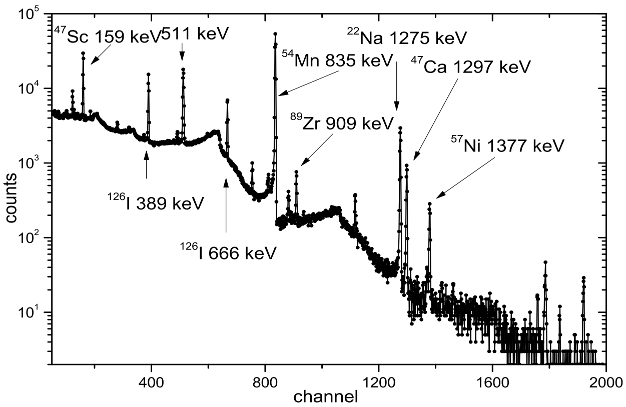

Fig.3. Energy spectrum of root of Pistia stratiotes after an irradiation on the electronic accelerator

The content of elements in the leaves and roots of *Pistia stratiotes* from Seversky Donets has the singularities. The Seversky Donets river is not pure. We will note in *Pistia stratiotes* high enough concentrations of essential elements of Ca and K. The content of elements in roots of *Pistia stratiotes* is big due to accumulation of conventionally essential elements of Mn, Co, Ni, Mo and I. Also high value of accumulation by roots of *Pistia stratiotes* toxic elements of Pb, U and As.

The iodine content in roots of *Pistia stratiotes* from the Seversky Doners river is $\sim 10^{-4}$ g/g. Assuming that the coefficient of accumulation of iodine by roots of *Pistia stratiotes* is ~1000 it is possible to estimate the iodine content in the water: $\sim 10^{-7}$ g/g [10]. In turn, it is possible to estimate the content of ^{129}I and ^{131}I. For Europe the attitude ^{129}I/I is $\sim 10^{-6}$ [11]. Hence, the ^{129}I and ^{131}I contents in water the Seversky Doners river were $\sim 10^{-13}$ g/g and ~2 Bk/l, accordingly. The estimate of the content of ^{137}Cs in water is $\sim 10^{-3}$ Bq/l that coincides with mean values in Ukraine [12]. The estimate of value of the ratio of ^{137}Cs/Cs is $\sim 10^{-8}$. The ratio ^{137}Cs/Cs for leaves of *Pistia stratiotes* is 27.8 Bq/mg. For example, of the most polluted wood in Finland (Kullaa, 18.2 kBq/m^2) the ratio ^{137}Cs/Cs is 5100 Bq/mg [13]. The difference between the ratios of ^{137}Cs/Cs is partly attributable to the different deposition levels of ^{137}Cs. A positive correlation between the total deposition of ^{137}Cs and the ^{137}Cs/Cs ratio was observed for the different sites. However, different concentrations of stable Cs in soil and rivers (e.g. vegetation, geology, soil type) also affect the ^{137}Cs/Cs ratio.

Table 4. The elements content in root and leaf of Pistia stratiotes and ratio of elements content in root versus leaf (dry weight)

	root, g/g	leaf, g/g	ratio root/leaf
Na	$1.78 \cdot 10^{-2}$	$5.38 \cdot 10^{-3}$	3.32
K	$1.99 \cdot 10^{-2}$	$8.49 \cdot 10^{-2}$	0.23
Ca	$1.75 \cdot 10^{-2}$	$2.0 \cdot 10^{-2}$	0.87
Ti	$6.01 \cdot 10^{-4}$	$1.62 \cdot 10^{-4}$	3.71
Cr	$4.32 \cdot 10^{-6}$	$5.65 \cdot 10^{-5}$	7.65
Mn	$2.03 \cdot 10^{-2}$	$7.26 \cdot 10^{-4}$	27.90
Co	$2.62 \cdot 10^{-5}$	$1.03 \cdot 10^{-6}$	25.44
Ni	$9.79 \cdot 10^{-5}$	$5.65 \cdot 10^{-6}$	17.32
Zn	$7.46 \cdot 10^{-4}$	$1.19 \cdot 10^{-4}$	6.27
As	$4.95 \cdot 10^{-6}$	$7.2 \cdot 10^{-7}$	7.05
Br		$6.33 \cdot 10^{-6}$	
Rb	$1.63 \cdot 10^{-5}$	$1.77 \cdot 10^{-5}$	0.92
Sr	$4.25 \cdot 10^{-4}$	$5.87 \cdot 10^{-4}$	0.72
Y	$3.38 \cdot 10^{-6}$	$4.96 \cdot 10^{-6}$	6.81
Zr	$1.19 \cdot 10^{-5}$	$4.79 \cdot 10^{-6}$	2.48
Nb	$2.2 \cdot 10^{-6}$	$1.37 \cdot 10^{-6}$	1.60
Mo	$9.93 \cdot 10^{-6}$	$6.26 \cdot 10^{-7}$	15.86
I	$1.55 \cdot 10^{-4}$	$1.11 \cdot 10^{-5}$	14.02
Cs		$3.25 \cdot 10^{-8}$	
Ce	$3.94 \cdot 10^{-6}$	$1.67 \cdot 10^{-6}$	2.37
Pb	$1.28 \cdot 10^{-4}$	$5.13 \cdot 10^{-6}$	24.96
U	$3.74 \cdot 10^{-6}$	$5.27 \cdot 10^{-7}$	7.10

Table 5. The ratio of elements content of ash vs leaf and root (dry weight) of Pistia stratiotes

elem.	ash vs leaf	ash vs root	elem.	ash vs leaf	ash vs root
Na	4.2	3.02	Br	3.4	nd
Ca	4.06	3.39	Rb	4.19	2.68
Ti	4.48	2.87	Sr	4.11	2.68
Cr	4.0	3.08	Zr	3.73	3.78
Mn	4.15	3.08	Nb	2.21	2.24
Ni	3.75	3.16	Mo	4.26	2.48
Zn	4.51	3.31	I	3.87	1.73
As	4.6	2.69	Ce	3.05	3.03
Pb	3.10	2.61	U	4.05	3.65

In Table 5 the ratio of element content in ashes versus initial *Pistia stratiotes* (dry weight) are given. These ratios for leaves were ~4 and ~3 for roots. Considerable calcium quantity is caused the formation of compounds of type of $KAlSi_3O_8$, SiO_2, Fe_2O_3 and others which cause the formation of small amounts of flying compounds [14]. That in turn is the positive factor at use of *Pistia stratiotes* as an absorption material for heavy metals, Sr, As and I.

4. CONCLUSIONS

1. The ^{131}I activity of one of dangerous radioisotopes from NPP has been registered in roots of *Pistia stratiotes* by γ-spectrometry.

2. Accumulation of Mn, Co, Ni, Mo, I, Pb and isotopes ^{228}Ac, ^{214}Pb and ^{214}Bi has been detected in

roots and leaves of *Pistia stratiotes* (their ratios were counted).

3. Photoactivation analysis possesses advantages at the determination of sorption of radioisotopes by plants.

4. The developed methods allow carrying out radioisotopes monitoring in the biosphere.

References

1. H. Denny, D. Wilkins. Zinc tolerance in Betula spp.II. Microanalyticalstudies of zinc uptake into root tissues // *New Phyt.* 1987, v. 106, p. 525-534.
2. P. Miretzky, A. Saralegui, A.F. Cirelli. Simultaneous heavy metal removal mechanism by dead macrophytes // *Chemosphere* 2006, v. 62 p. 247-254.
3. Y. Ho, J. Porter, G. McKay. Equilibrium isotherm studies for sorption of divalent metal ions onto peat: Cu, Ni and Pb single component systems // *Water Air Soil Pollut.* 2002, v. 141, p. 1-33.
4. P. Kaewarn. Biosorption Cu (II) form aqueous solution by pre-treatrd biomass of marine algae // *Chemosphere* 2002, v. 47, p. 1081-1085.
5. V.V. Soloveva. Floristic finds and unusual occurrences bioecologists of hydrophytes in ponds of Samara // *Phytodiversity of the Eastern Europe* 2006, N.2, p. 174-180 (in Russian).
6. A.V. Shcherbakov, S.P. Mayorov. Water adventive plants of the Moscow region // *Bull. Udmurt univ., Biol. Sci. Earth.* 2013, iss. 2, p. 57-61.
7. G.M. Volk, L.J. Goss, V.R. Franceschi. Calcium Channels are Involved in Calcium Oxalate Crystal Formation in Specialized Cells of Pistia stratiotes // *Annals Botany.* 2004, v. 93, p. 741-753.
8. V.A. Knizhnikov, R.M. Barhudarov. Relative estimate of radiative danger to the population from outliers in atmosphere of thermal and atomic stations // *AE* 1977, v. 43, p. 191-196 (in Russian).
9. L.A. Ilin, V.A. Knizhnikov, N.K. Shandala, et al. *Oncologic "price" of thermal and atomic energy*, Moscow: "Medicine", 2001, 240 p. (in Russian).
10. Q. Lu, Z.L. He, D.A. Graetz et al. Uptake and distribution of metals by water lettuce (P. stratiotes) // *Environ. Sci. Pollut. Res.* 2011, v.18, p.978-986.
11. J.E. Moran. Sources of I and ^{129}I in rivers // *Water Resources Research.* 2002, v. 38, N.8, p. 1149.
12. G.D. Kovalenko. *Radioecology Ukraine*, Kharkov: "PH INGEK", 2008, 264 p. (in Russian).
13. S. Yoshida, Y. Muramatsu, M. Steiner, et al. Relationship between radiocesium and stable cesium in plants and mushrooms collected from forest ecosystems with different contamination levels // *IRPA-10*, 2000, p. 11-244.
14. M.K. Misra, K.W. Ragland, A.J. Baker. Wood ash composion as a function of furnace temperature // *Biomass Bioenergy*, 1993, v. 4, N.2, p. 103-116.

БИОСОРБЦИЯ РАДИОНУКЛИДОВ ВОДНЫМИ РАСТЕНИЯМИ *PISTIA STRATIOTES*

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Была измерена активность листьев и корней *Pistia stratiotes* из Северского Донца. Зарегистрирована заметная активность ^{131}I в корнях растения. Оценка содержания ^{131}I в воде Северского Донца перед извлечением образцов гидрофита дает значение, превышающее 1 Бк/л. Метод детектирования активности ^{131}I в корнях *Pistia stratiotes* может быть использован для мониторинга его в биосфере. Фотоактивационный анализ был использован для измерения содержания элементов в листьях и корнях *Pistia stratiotes* из Северского Донца. Обнаружено накопление в корнях относительно накопления в листьях *Pistia stratiotes* Mn, Co, Ni, Mo, I, Pb, а также изотопов ^{228}Ac, ^{214}Bi и ^{214}Pb.

БІОСОРБЦІЯ РАДІОНУКЛІДІВ ВОДНИМИ РОСЛИНАМИ *PISTIA STRATIOTES*

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Була виміряна активність листя і корення *Pistia stratiotes* із Сіверського Донця. Зареєстрована помітна активність ^{131}I у коренях рослини. Оцінка вмісту ^{131}I у воді Сіверського Донця перед витяганням зразків гідрофіта дає значення, яке перевищує 1 Бк/л. Метод детектування активності ^{131}I у коренях *Pistia stratiotes* може бути використаний для моніторінгу його в біосфері. Фотоактиваційний аналіз був використаний для вимірювання вмісту елементів у листках і кореннях *Pistia stratiotes* із Сіверського Донця. Виявлено накопичення в коренях відносно накопичення в листях *Pistia stratiotes* Mn, Co, Ni, Mo, I, Pb, а також ізотопів ^{228}Ac, ^{214}Bi і ^{214}Pb.