ANTHROPOGENIC RADIONUCLIDE AND TRACE ELEMENTS OF SOIL AND CELANDINE IN KHARKIV CITY

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Samples of celandine and soil from Kharkiv city territory were researched. Gamma spectrometric measurements have shown that the samples contain natural radionuclides of families of ^{238}U, ^{235}U, ^{232}Th, and also ^{40}K and anthropogenic radionuclide ^{137}Cs. The average values of specific activities (Bq/kg) of radionuclides in the soil are 625.2, 38.4, 25.7, 21.5 for ^{40}K, ^{228}Ac, ^{226}Ra, ^{137}Cs, respectively.There is a strong fixation of ^{137}Cs in studied soil. The accumulation factors for natural Sr and ^{40}K in the celandine are significant in contrast to other radionuclides and elements.

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1. INTRODUCTION

Artificial radionuclides mainly introduced into the environment following nuclear power plant accidents or nuclear weapons tests, by careless use in engineering, medicine etc. In addition, soil may interact with radioactive waste materials that have been buried for disposal. Radionuclide can travel around the world on air streams. Their own weight, and also the weather determine their deposition to the ground. Also, the heavy rains can bring the radioactive particles to the ground. Soils possess sorbent and complexing capacities which contribute to the immobilization of radionuclide from water in the underlying layers, after they were displaced from complexes or adsorption sites. Radionuclide existing in soil can be dissolved in solution, or ion exchanged in reaction, complexed with soil organics or precipitate as pure or mixed solids. They can move into the water, air and the food supply. The immobility of these radioactive elements in uppermost soil layers represents a problem for environment and human health, since they can be easily integrated in the food chain. A scheme for radionuclide movement in soil was proposed by Igwe et al. [1] Consequently, the major part of radionuclide released into the environment will finally accumulate in either the upper layer of soils or interstitial system of sediments in aquatic systems. As a consequence, a risk for ecosystems, agro-systems and health could be induced [2].

Content of radionuclide in plants depends on their individual ability to selectively accumulate certain chemical elements and on soil properties. In particular, some members of the plant communities concentrate radioactive substances. First of all these plants are mosses and lichens. Artificial radionuclides enter the lichens and mosses in the main by aerial way. Other plants accumulate some radionuclide mainly from the soil. Some kinds of medicinal plants accumulate significant quantities of radionuclide, while the neighbor herbs do not have this ability.

It is interesting to investigate accumulation ability of radionuclides of such medicinal plant as celandine. The greater celandine (Chelidonium majus L.) belongs to the Papeveraceae family. As a specific feature of the family is the orange coloured latex. The Papaveraceae family is rich in specific alkaloids. Some of them are important in medicine and some others can be considered as promising in this regard. Chelidonium majus exhibits multiple biological actions such as antiviral, antitumour, antibacterial/antifungal and anti-inflammatory effects.

This work contains information about content of anthropogenic ^{137}Cs and other radionuclides in the soil of Kharkiv city territory. And also about abilities of celandine to accumulate trace elements, natural and anthropogenic radionuclides from the soil.

2. MATERIALS AND METHODS

Samples of soil were collected by an envelope method in five places of Kharkiv city. Depth of soil samples selection was up to 12 sm. Then the extraneous inclusions (stones, roots of plants, etc.) were removed from the samples. Soil samples were dried up to an air-dry condition, and then the average sample was selected.

Determination of the radionuclides in soil samples was performed by gamma spectrometer method on Ge(Li) detector with volume of 50 cm^3 and resolution of 3.2 keV at 1332 keV line. To reduce the influence

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of background, the detector is equipped with a three-layer Pb-Cu-Al protection. During the measurement of radionuclides samples were placed in thin-walled plastic container with volume of 1 liter. Measurements of background conditions (Table 1) which were considered further were carried out previously.

Table 1. *Background conditions during measurements*

Eγ (keV)	Radio-nucl.	Counts per 1 h
511	$^{-}e+^{+}e$	26
1461	^{40}K	24
239	^{212}Pb	15
609	^{214}Pb	14
352	^{214}Pb	13
186	$^{226}Ra+^{235}U$	8
583	^{208}Tl	7
911	^{228}Ac	6
1120	^{214}Bi	5
1764	^{214}Bi	5
295	^{214}Pb	5
662	^{137}Cs	4
338	^{228}Ac	3

The weights of the soil and celandine samples were 1100 g and 300 g, respectively. The exposure time was about 24 hours. Despite these conditions, the errors of determination of radionuclides activities reached up to an order 10^{-2} Bq/g.

Determination of various forms of radionuclides by mechanisms of connections in the soil was performed by sequential extraction using different leaching solutions. To do this, one of the five soil samples was selected. This sample was collected on the territory of an old oak forest. Water soluble forms of the radionuclides were isolated by distilled water H_2O (in a ratio of soil and leach solution 1:3). Exchange forms were isolated using 1M solution CH_3COONH_4. Nonexchange (acid soluble) forms were isolated by 6N solution of HCl. Strongly bound forms which are not supplanted by the above reagents, was determined directly in the soil residues after extraction.

The time of contact of the soil with a leach solution was not less than 24 hours at all stages of the experiment (Fig 1). It is known that cations of radionuclide which are desorbed by ion-exchange mechanism, and soluble complex compounds of radionuclides with soil components, proceed to water extract. Radionuclides in exchange condition proceed to ammonium acetate extract [3-5]. Acid soluble compounds include nonexchange forms of radionuclides. These forms of radionuclides do not proceed into soil solution in the environment under usual conditions, but they can be absorbed by plants at a root pathway of receipt [3, 6]. Strongly bound forms contain radionuclides that are not dissolved by any above mentioned reagents and are unavailable for plants.

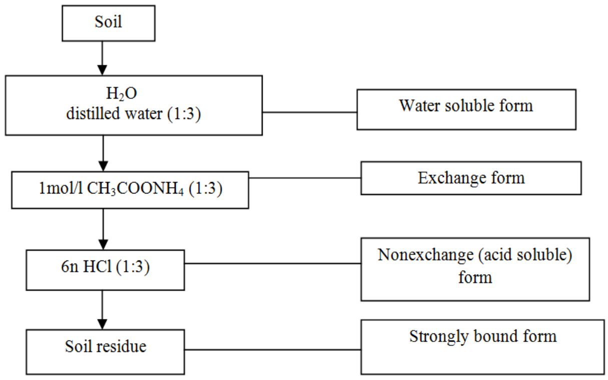

Fig.1. *General plan of sequential extraction*

Celandine samples were collected in the center part of the city at the same site with the soil sample. Plant samples were collected together with roots, thoroughly laundered by water. And then celandine samples were thoroughly dried up.

Composition of elements of the samples was investigated by photoactivation analysis. Samples with masses up to 2 g. have been activated on the accelerator "EPOS" NSC KIPT with energy of 23 MeV and a current of 700 mA. And then the gamma-spectrometric analysis was performed.

3. RESULTS AND DISCUSSION

There are registered $\gamma - lines$ from natural radionuclide of families of ^{238}U, ^{235}U,^{232}Th, and also ^{40}K and anthropogenic radionuclide ^{137}Cs on the spectrum of samples (Fig.2).

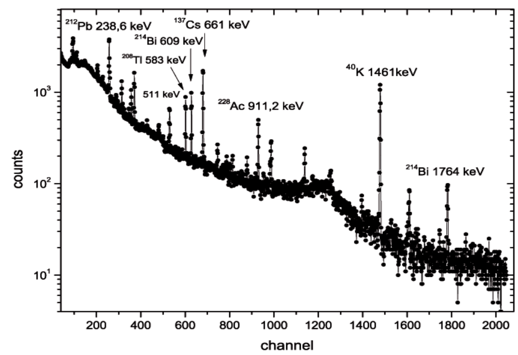

Fig.2. *Typical gamma-spectrum of the soil sample*

The average values of specific activities of radionuclides in the soil for the study area are presented in the Table 2. At a general level samples from the central and north-western part of the city stand out. In first sample the content of ^{40}K (363.9 Bq/kg) and other radionuclides are lower. This is probably connected with observed extensive celandine bushes here. The second sample is the richest in content of ^{137}Cs (37.6 Bq/kg). This is apparently connected with fact that soil from old oak forest significantly fixed radionuclide Cs, which has been located in it for a long time.

Table 2. *The average value of specific activities of radionuclides in the soil for the study area*

element	activities (Bq/kg)
^{40}K	625.2
^{228}Ac	38.4
^{212}Pb and ^{208}Tl	36
^{226}Ra	25.7
^{214}Pb and ^{214}Bi	24
^{137}Cs	21.5

The results of the extraction of different (by connection mechanisms in soil) forms of radionuclides from the soil are presented in the Table 3.

Physicochemical state of radionuclide, entering to the land cover, changes with time. Such changes depend on own chemical properties of elements, duration of stay in the soil, features of absorbing complex, features of genetic structure of the soil profile, as well as a number of environmental factors. As a result, the migratory ability of radionuclides and their availability to plants is changing. It is known that the radionuclide ^{137}Cs is more connected with the mineral part of the soil-absorbing complex, which plays a very important role in its mobility in the soil and in transition to plants [11].

Table 3. *The content of different (by connection mechanisms in soil) forms of radionuclides* ^{137}*Cs and* ^{40}*K in the soil*

Forms of radionuclide	^{137}Cs(%)	^{40}K(%)
water-soluble	2,5	5,1
exchange	0,5	2,8
nonexchange (acid soluble)	2,0	7,5
strongly bound	95	84,6

The content of radionuclide ^{137}Cs in exchange and nonexchange forms is 0.5 and 2.0 %, respectively, that is insignificant. Apparently, it is related to the presence in the forest soils of clay minerals group of illite. It is known that illite has high selectivity in relation to the trace amount of Cs ions. This is caused by presence of selective adsorption places on the weathered side surfaces of illite. Such adsorption places are localized in the region of wedge extensions of three-layer packages. [8, 10]

The main content of ^{137}Cs and ^{40}K radionuclides about 95 and 84.6 % respectively is presented in the strongly bound form. All three mobile forms ^{40}K in average are 3.5 times more than that of ^{137}Cs. For other radionuclides (e.g. ^{228}Ac and ^{214}Pb) the values are close to values for ^{40}K. Finnaly, all radionuclides are more mobile in the soil, than ^{137}Cs. It can be connected with features of behavior of these elements in the soil. And also it testifies to long-term stay of ^{137}Cs in the soil.

There are also natural radionuclides of families of ^{238}U, ^{235}U, ^{232}Th, radionuclides ^{40}K and ^{137}Cs, and additionally cosmogenic ^{7}Be in the celandine sample. However, intensity of the corresponding peaks on a spectrum is lower, than ones in soil samples. Only ^{40}K stands out.This is connected with the fact that potassium is one of the most necessary elements of mineral nutrition of plants. It is found in structure of minerals, in particles of colloids, in organic residues and in the form of mineral salts in the soil (KCl, $KHCO_3$, K_2HPO_4 - in plants). Potassium is an essential element of plant nutrition, besides it, as a competitor, reduces the accumulation of ^{137}Cs in plants. Consequently, the higher content of potassium is in the soil relative to ^{137}Cs, the smaller amount of the radionuclide will be absorbed by the plant roots [7].

The intensity of the transfer of radionuclides or elements from soil into plants is being measured by the accumulation factor (K_{af}). Last equals the ratio of the specific activities of radionuclide or a content of element in the plant to the soil. Accumulation factor in dry matter of celandine equals for ^{137}Cs - 0.01, ^{40}K - 5.53, ^{228}Ac -0.23, ^{226}Ra - 0.21, respectively.

As can be seen K_{af} for ^{40}K reaches a significant value in contrast to radionuclide Cs, which has a low value of K_{af}. Also there are observed relatively high values of accumulation factors of actinium and radium (thorium and uranium groups) in celandine.

Composition of trace elements of the samples was investigated by photoactivation analysis (Fig.3). Celandine sample includes such elements as calcium, sodium, zirconium, chrome, titanium, strontium, cesium, rubidium, yttrium, iodine, etc. Most of these elements are essential for normal growth and development of plants. However some of them are toxic at the high concentrations. Accumulation of certain elements greatly varies depending on the type of plant, and also on content them in the soil.

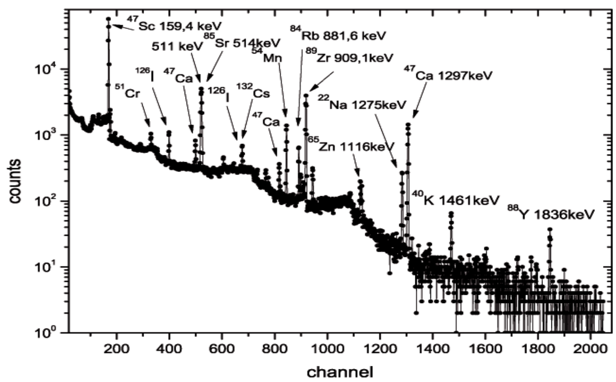

Fig.3. *Typical gamma spectrum of celandine sample after* γ*-activation*

A similar set of elements (Table 4) are observed in the soil sample from under the plants. The elemental composition of the soil sample depends on the type of soil, its mineralogical composition, acidity, etc.

Table 4. *The content of some trace elements in the leaves, roots of celandine and soil sample from under the plant*

element	leaves	roots	soil
Na	$3.79 \cdot 10^{-5}$	$2.71 \cdot 10^{-4}$	$1.04 \cdot 10^{-3}$
Ca	$8.52 \cdot 10^{-3}$	$9.69 \cdot 10^{-3}$	$5.70 \cdot 10^{-3}$
K*	$6.87 \cdot 10^{-2}$	$4.33 \cdot 10^{-2}$	$1.20 \cdot 10^{-2}$
Ti	$4.97 \cdot 10^{-5}$	$3.77 \cdot 10^{-4}$	$2.79 \cdot 10^{-3}$
Cr	$1.82 \cdot 10^{-7}$	$1.03 \cdot 10^{-6}$	$6.08 \cdot 10^{-6}$
Mn	$1.55 \cdot 10^{-5}$	$9.27 \cdot 10^{-5}$	$2.62 \cdot 10^{-4}$
Ni	$6.16 \cdot 10^{-7}$	$3.48 \cdot 10^{-6}$	$5.73 \cdot 10^{-6}$
Zn	$2.34 \cdot 10^{-5}$	$8.73 \cdot 10^{-5}$	$1.69 \cdot 10^{-4}$
As	$2.43 \cdot 10^{-7}$	$7.64 \cdot 10^{-7}$	$6.19 \cdot 10^{-6}$
Rb	$4.64 \cdot 10^{-6}$	$6.12 \cdot 10^{-6}$	$2.84 \cdot 10^{-5}$
Sr	$8.21 \cdot 10^{-5}$	$1.76 \cdot 10^{-4}$	$4.39 \cdot 10^{-5}$
Y	$2.27 \cdot 10^{-7}$	$1.46 \cdot 10^{-6}$	$1.13 \cdot 10^{-5}$
Zr	$2.40 \cdot 10^{-6}$	$3.27 \cdot 10^{-5}$	$2.56 \cdot 10^{-4}$
I	$1.63 \cdot 10^{-6}$	$1.99 \cdot 10^{-6}$	$3.40 \cdot 10^{-6}$
Cs	$6.28 \cdot 10^{-8}$	$2.16 \cdot 10^{-7}$	$1.48 \cdot 10^{-6}$
Ce	$2.88 \cdot 10^{-7}$	$2.93 \cdot 10^{-6}$	$2.85 \cdot 10^{-5}$
Pb	$9.57 \cdot 10^{-6}$	$9.12 \cdot 10^{-6}$	$2.88 \cdot 10^{-5}$
U	$2.73 \cdot 10^{-7}$	$1.93 \cdot 10^{-7}$	$1.93 \cdot 10^{-6}$

* - by results for radionuclide ^{40}K

Such elements as Na, Ti, Cr, Mn, Ni, Y, Zr, Nb, Ce is being accumulated in the roots of celandine (Table 5)

Table 5. *The content of elements in ratio: roots/leaves, leaves/soil, roots/soil*

element	roots/leaves	leaves/soil	roots/soil
Na	7.15	0.04	0.26
Ca	1.20	1.57	1.89
K*	0.63	5.72	3.60
Ti	7.60	0.02	0.14
Cr	5.67	0.03	0.17
Mn	5.97	0.06	0.35
Ni	5.65	0.11	0.61
Zn	3.74	0.14	0.52
As	3.14	0.04	0.12
Rb	1.32	0.16	0.22
Sr	2.14	1.87	4.00
Y	6.46	0.02	0.13
Zr	13.66	0.01	0.13
Nb	6.50	0.05	0.35
I	1.22	0.48	0.58
Cs	3.44	0.04	0.15
Ce	10.19	0.01	0.10
Pb	0.95	0.33	0.32
U	0.71	0.14	0.10

As shown the accumulation factor of K for celandine leaves is significant. It is connected with fact that K is one of the most important elements for plants.

Plants absorb Cs less efficiently than its nutrient analogue, potassium. The mechanisms by which Cs is taken up by plant roots are not completely understood. At least at low K concentrations there is evidence that Cs^+ is absorbed by the K^+ uptake system of the root. This evidence is derived from the observations that K^+ strongly suppresses Cs^+ uptake and that Cs^+ is efficiently transported by an isolated high affinity K^+ uptake transporter of root cells [9].

The accumulation factor of Ca is also great. A chemical analogue of calcium is strontium. Accumulation factor of Sr in celandine roots is equal 4. This is a very high rate of accumulation factor. Therefore, strontium (including radionuclide ^{90}Sr) also easily comes into celandine and accumulates more considerably in the root system.

Obtained large value of K_{af} for natural cesium compared with the radionuclide ^{137}Cs indicates on significant fixing in the soil of this radionuclide. This suggests that ^{137}Cs has been in the soil for a long time.

4. CONCLUSIONS

1. Results are obtained about: almost all content of the radionuclide ^{137}Cs in soil is presented in the strongly bound form; all other radio nuclides, that were registered in the soil, are more mobile, than ^{137}Cs; radionuclide ^{137}Cs is bound in the soil more than natural cesium. All these indicate that ^{137}Cs has being in the soil for a long time. Therefore pollution in the city of Kharkiv is mainly a consequence of nuclear weapons tests in the 1960s, and not by Chernobyl accident.
2. Strontium is being absorbed and accumulated by celandine from the soil more than other elements and radionuclides. This indicates about selectivity of celandine to strontium. And it also suggests that this plant can be used for remediation soil from radionuclides, primarily from ^{90}Sr. However, in this case, it is required to find the optimal method of celandine utilization without intake of radionuclides to the environment.
3. Obtained results about good accumulation of ^{40}K as against of ^{137}Cs by celandine, confirmed literature data that potassium is a chemical competitor of cesium, and it is reducing Cs accumulation by plants.
4. Microelements that were received by plant from the soil are distributed unevenly. Such elements as Na, Ti, Cr, Mn, Ni, Y, Zr, Nb, Ce are contained in the roots of celandine greater than in leaves.

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АНТРОПОГЕННЫЕ РАДИОНУКЛИДЫ И МИКРОЭЛЕМЕНТЫ В ПОЧВЕ И ЧИСТОТЕЛЕ ГОРОДА ХАРЬКОВА

Н. П. Дикий, Ю. В. Ляшко, Д. С. Каталевская, Ю. Г. Пархоменко, М. А. Ботова

Исследовались образцы чистотела и почвы города Харькова. Гамма-спектрометрические измерения показали, что образцы содержат естественные радионуклиды семейств ^{238}U, ^{235}U, ^{232}Th, а также ^{40}K и техногенный радионуклид ^{137}Cs. Среднее значение удельной активности (Бк/кг) радионуклидов в почве составляет: 625.2, 38.4, 25.7, 21.5 для ^{40}K, ^{228}Ac, ^{226}Ra, ^{137}Cs, соответственно. В исследованной почве обнаружена сильная фиксация ^{137}Cs. Коэффициенты накопления естественного Sr и ^{40}K в чистотеле являются значительными, в отличие от остальных элементов и радионуклидов.

АНТРОПОГЕННІ РАДІОНУКЛІДИ ТА МІКРОЕЛЕМЕНТИ У ГРУНТІ ТА ЧИСТОТІЛІ МІСТА ХАРКОВА

Н. П. Дикий, Ю. В. Ляшко, Д. С. Каталевська, Ю. Г. Пархоменко, М. О. Ботова

Досліджувалися зразки чистотілу і ґрунту міста Харкова. Гамма-спектрометричні виміри показали, що зразки містять природні радіонукліди сімейств ^{238}U, ^{235}U, ^{232}Th, а також ^{40}K і техногенний радіонуклід ^{137}Cs. Середнє значення питомої активності (Бк/кг) радіонуклідів у ґрунті становить: 625.2, 38.4, 25.7, 21.5 для ^{40}K, ^{228}Ac, ^{226}Ra, ^{137}Cs, відповідно. У дослідженому ґрунті виявлена сильна фіксація ^{137}Cs. Коефіцієнти накопичення природного Sr і ^{40}K в чистотілі є значними, на відміну від інших елементів і радіонуклідів.