UDC 631.4:504.5:628.4.041]::550.4

RESTORATION OF SOILS CONTAMINATED WITH RADIONUCLIDES BY PHYTOREDOMEDIATION METHOD

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The possibility of soil restoration by means of phytotechnology and artificial geochemical barriers (GB) from contamination by radionuclides (RN) and toxic elements (TE) is methodologically substantiated. For this purpose, a number of artificial GBs were created at a special landfill within the framework of a model experiment. The process of formation and development of barriers, their parameters are investigated. Agrophytocenosis cultures were selected for optimal phytostabilization of soil conditions. The study of phytoextraction of TE and RN by agrophytocenosis cultures during one complete vegetation period was performed. Some selectivity of the investigated plants for extraction of different TEs and RNs from soils and material of barriers was revealed.

INTRODUCTION

Soil protection and their rational use are one of the most important priorities for the sustainable economic and social development of our country. The ecological status of domestic soils is no longer an agrarian issue, but an overriding problem of our country's environmental security. Particularly dangerous are the contamination of soil by TEs and RNs.

After the Chernobyl accident in Ukraine there was a danger of contamination of soil with radiation materials. And today this issue remains relevant not only for the Exclusion Zone, but also for some other territories of Ukraine. This article is an attempt to methodologically justify the possibility of using the phytoremediation method for the environmentally safe restoration of soil from contamination of RNs and TEs.

Intense and various forms of negative technogenic impact on natural landscapes lead to the formation of different in origin structural and functional features of the development of ecological systems, which are complicated by the difference of their transformation under the influence of natural factors and lead to many, including specific forms of technogenic fashion biocenological methods of soil contamination restoration.

An important factor in the technogenic contamination of soils is the increase in the soil content of TE – such as Pb, Cd, Cr, Fe, Cu, Zn, radioactive isotopes and other RN.

Because contamination disrupts the natural biochemical cycles of chemical elements, the natural diversity of the plant's properties in terms of selective absorption from the soil of these elements has been successfully applied to clean the environment from TEs and RNs. This principle is based on methods of soil restoration with the use of phytotechnology or the use of vegetation to remove, transfer, stabilize, and eliminate soil pollutants [1–3].

The main idea of the work is to intensify the processes of phytoremediation by creating conditions on the routes of man-made migration conditions for the concentration of chemical elements, or the purposeful formation of artificial (engineering) GB. Special agrophytocenoses are created at the locations of these GBs and at a certain stage of vegetation a vegetation cover with high content of TE absorbed from the soil is eliminated. In several cycles of elimination, the content of soil contaminants is practically reached the acceptable level.

It is established that different types of plants have the ability to remove different chemical elements with different intensities. Also, different types of artificial GBs that concentrate TE and RN have certain physicochemical features [4–7]. This requires a detailed study of the kinetics and mechanisms of TE and RN migration processes in the soil-plant system. Adequate understanding of the dynamics of migration of chemical elements in such systems allows to develop a set of measures for the implementation of natural soil restoration by forming appropriate agrophytocenoses on special artificial GBs. To implement such measures, it is necessary to develop specific methodological and technical means of obtaining prompt information on the processes of accumulation of TE and RN in artificially created GBs and in vegetation on these barriers.

ANALYSIS OF PREVIOUS RESEARCH

The development of phytotechnology makes it beneficial for their practical application, in connection with which the US Environmental Protection Agency has since 2000 approved a program for the use of plants for the purification of the environment from TE [8]. In China, there are studies of phytorecovery of contaminated TE soil by means of plants-hyperaccumulators, as well as studies on phytoextraction, which is one of the main approaches to the problems of phytoextraction and phytopurification of soils, with subsequent identification of TE-storage plants [4]. In Russia, work is underway to use as phytomeliorants for the biological purification of buckwheat soils and fodder beans [9].

In Ukraine the prospects of phytopurification of soil from RN and TE have been investigated [10]. Also in

Ukraine, the phytoremediation processes and the development of environmentally safe technologies, in particular phytostabilization, are being studied at the Institute of Agroecology of the UAAS and the National University of Bioresources and Environmental Management of Ukraine.

The results of previous research and development of the authors, which are the basis of the work:

– development of methods for collecting and processing environmental information and methods for analyzing the quantitative composition of a substance and developing recommendations for the use of information on contamination of TE and RN for the prompt implementation of measures for the natural restoration of soil of agricultural sites (lands);

– development of state-of-the-art environment monitoring methods and methods that allow maintaining the ecological balance of both individual territories and significant regions;

– methodological recommendations for the operational control of the environmental status of environment contaminated with TE and RN, and recommendations for the optimal natural recovery of these objects through the formation of appropriate biogeocenoses;

– identification of agrocenoses cultures characterized by high productivity and content of TE within the maximum permissible concentration as an optimal variant of phytostabilization of soils contaminated with TE.

Purpose and tasks of research. The purpose of the work is to develop the concept and develop the principles, methodological and technical means of restoring the condition and structure of contaminated TE soils, man-made and existing natural GB.

Achieving the goal of work involves the following practical tasks:

– comprehensive assessment of the soil status of territories and agricultural lands in potentially technogenic-dangerous regions, depending on landscape conditions;

– development of methods of measurement of elemental composition and activity of PH and identification of quantitative characteristics of natural man-made GB;

– development of methods of creation of artificial (engineering) GB on the way of distribution of polluting components (TE and RN);

– determination of agrocenoses cultures for the optimal variants of soil phytostabilization for specific components of contamination;

– development and improvement of existing phytotechnologies of soil purification due to the use of GB, based on specific landscape conditions and needs of rational nature management.

MATERIALS AND METHODS

To achieve the main result of the research – creation of an effective method of restoration of technogenically contaminated TE and RN soil of the territories and, in particular, agricultural land – as the main working tool is envisaged the use of phytotechnology or the use of plants for removal, transfer, stabilization and elimination (destruction) of soil pollutants. The main types of phytotechnology for the purification of soil contaminated with TE, their radioactive isotopes and other RN are considered phytoextraction or phytoaccumulation (removal of soil contamination by the root system, transfer and accumulation in the stems and leaves of plants) and phytostabilizations layers between root surface and soil [11].

The intensification of the processes of phytochemical extraction from TE and RN soil is achieved by creating areas with high levels of contamination in the contaminated territories. The formation of such sites is carried out by the method of creation on the way of distribution of contaminants of artificial (engineering) GB, on which these contaminants are concentrated, or the use of existing natural man-made barriers for the same purpose.

The effectiveness of such measures is directly dependent on the efficiency of the system of control of the content of TE and RN in soils, which can be realized only with the use of modern high-speed nuclear-physical methods and methods of analysis of the quantitative elemental composition of the substance and the activity of radioactive isotopes [7, 12].

At present, the use of various carbonate GBs is considered to be the most promising and expedient for the removal of TEs from wastewater and groundwater or for linking moving metal forms. Complex sludge-carbonate and sludge-sulfate-carbonate GBs, in which the latter component must efficiently immobilize pollutants from concentrated solutions, should be even more effective [7].

When selecting material to create barriers, you must follow the following basic criteria:

– the barrier must effectively intercept the pollutants and retain them during the estimated lifetime;

– the material chosen should have relatively little value;

– the material should not be an additional source of contamination.

Technology of phytoextraction of TE from contaminated soil includes two stages: preparatory and phytoextraction. In the first stage, the contaminated site is identified by sampling soil samples for analysis on the TE content and comparing the analysis results with the maximum permissible concentration. Special attention should be paid to the analysis of the content of the mobile form TE, that is accessible to plants, which is solved by obtaining from the soil samples various extracts [13].

In geochemical investigations of the pH of sputtered fuel (Chernobyl) in soils and sediments, a time-varying ratio of the forms of anthropogenic RN has been established and a combined change in their migration ability. This allowed us to formulate new provisions of the concept of formation of man-made RN [14]:

1. The technogenic form of radioactive fallout is usually thermodynamically nonequilibrium in soils and sediments and is prone to transformation with the formation of mobile and fixed forms of RN.

2. Intensity of biogenic and abiogenic.

3. The combination of migration and transformation processes allows us to use the kinetic model of

transformation of ^{90}Sr and ^{137}Cs to predict the dynamics of self-purification of trophic chains and natural waters.

The physicochemical processes occurring in the soil cover and other objects of the environment and which determine the dynamics of chemical element migration do not depend on the isotopic state of these elements. That is, the rate and direction of migration are the same for all isotopes of a given chemical element. Therefore, green plants are removed from the environment and concentrate in their tissues not only TE, such as As, Cd, Cu, Hg, Se, Pb, but also the radioactive isotopes of Sr, Cs, U and other RN [5].

Model experiment. A model experiment was planned and performed to determine the effectiveness of conservation measures using artificial GBs and phytoremediation of soils. A land plot was rented in the Borovsky forestry of Kharkiv region (landfill) for a model experiment. Landscape features of the landfill minimize the possibility of flushing rain and storm flows of artificially contaminated soil and the risk of their spread in the environment located outside the landfill. The proximity of the landfill to the large potential pollutants, which are the enterprises of Kharkiv and Donetsk region, creates conditions for an objective assessment of the migration processes under study, which are characteristic of the residential areas.

For creation of artificial GB, materials of Chemical Industry dump (Sumy city) were used, which are iron domes of $FeSO_4 \cdot nH_2O$, where n is the degree of hydration ($n \leq 7$).

The polygon for conducting a model experiment to investigate the functioning of artificial GB consisted of three control test sections (Fig. 1).

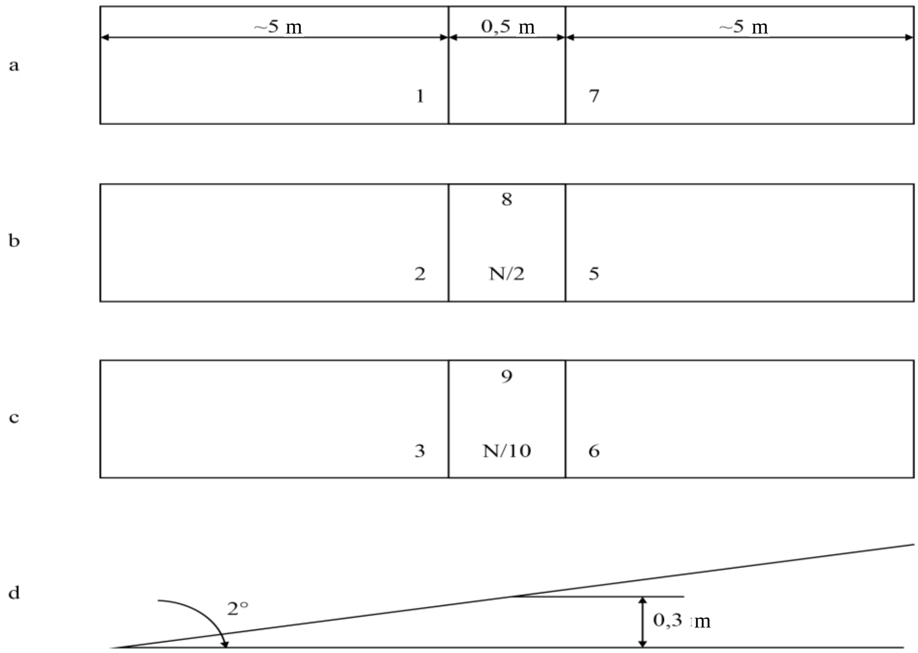

Fig. 1. The scheme of the polygon for conducting a model experiment

The model range was broken down into test sections as follows. Only three test sections measuring 3×10 m each.

Trench 0.5 m wide and 0.3 m deep were dug in the middle of each section.

The trench in section a) (see Fig. 1) was filled completely with the material of the dumps (iron sulfate).

The trench in section (b) was filled with a mixture of heaps of material with soil removed from the trenches in a ratio of 1:1.

The trench in section (c) was filled with a mixture of dumps with soil removed from the trenches in a ratio of 1:10.

The average slope of the site is $\sim 2^{o}$.

Phytoextraction of RN on artificial GB. To determine the activity of RN at the sites of the model polygon samples were used to analyze the content in the soil layer and vegetation cover TE. Express methods of determination of RN activity in environment objects were applied, which in any objects allow to measure specific activity of the sample or surface radioactive contamination directly (express) without enrichment of the samples, i.e. without the use of concentration of radioactive substances in the sample materials (evaporation, ashing, pressing, chemical enrichment, etc.). This method is the so-called “Method for express determination of the bulk and specific activity” of beta-emitting nuclides by the method of “direct” measurement of “thick samples”, which is widely used in the laboratories of SES, the State Agricultural Industry and other ministries and departments [15].

There are five basic operations in this method:

– sampling and preparation of samples of the test material for measurements;

– preparation of the radiometer for work;

– background measurement;

– measurement of samples of the investigated material of environment objects;

– calculation of radioactivity (specific mass or volume activity) of samples and their comparison with the acceptable norm.

This work used radiometers SRP-68-01, “Beta” and “Search”. This choice of measuring equipment is due both to the simplicity and reliability of the equipment, and to the fact that in previous studies the authors found that the main radioactive soil pollutants in the Kharkiv region are ^{90}Sr and ^{137}Cs, which are β-emitters [16].

The results of measuring the activity of RN in soil samples of the tested components of the landfill are given in Table 1. From the Table 1 shows that the migration of RN ^{90}Sr and ^{137}Cs occurs relative to the created artificial GB in both directions, but at the GB itself (sections N 7, 8, 9) the activity is significantly increased, ie the pH at GB is concentrated.

Table 1

RN activity in soil samples of landfill components, Bq/kg

RN	Area numbers								
	1	2	3	4	5	6	7	8	9
Analysis Completion Date – August, 2017									
^{90}Sr	10	12	11	12	14	12	6	8	8
^{137}Cs	38	41	40	42	44	40	12	14	14
Analysis Completion Date – October, 2017									
^{90}Sr	12	11	12	14	14	16	16	18	16
^{137}Cs	44	46	49	44	44	46	54	56	62
Analysis Completion Date – May, 2018									
^{90}Sr	15	17	22	15	16	14	26	28	29
^{137}Cs	46	46	52	48	50	54	64	73	79

In the second stage of the work, the activity of the investigated RN was determined in the plants of phyto-extractors: Calendula officinalis (Calendula officinalis), annual lupine (Lupinus angustifolius) and dwarf sunflower (Helianthus sp.). Sampling of plant material was carried out on the same sites as samples of the soil layer, in sites N 1, 2, 3, 7, 8, 9.

The results of measuring the activity of RN in plant samples obtained from sown areas of the landfill are shown in Table 2. From the Table 2 shows that the best phytoextractor of both RNs studied is dwarf sunflower (Helianthus sp.), but it produces slightly less biomass per unit time. Therefore, it is not possible to unequivocally recommend it as the most effective phytoremediator on GB of this type.

Obtaining more representative results in order to provide more detailed recommendations requires additional research, both in terms of observation and in the use of more plants under study.

Table 2

RN activity in plant samples on sown areas of landfill, Bq/kg

Date (month)	Plant	RN	Area numbers					
			1	2	3	7	8	9
August, 2018	Calendula	^{90}Sr	14	16	20	18	18	22
		^{137}Cs	32	34	50	36	38	52
	Lupine	^{90}Sr	22	28	30	24	32	32
		^{137}Cs	26	29	44	30	31	48
	Sunflower	^{90}Sr	28	34	34	32	38	42
		^{137}Cs	42	40	44	52	54	60
September, 2018	Calendula	^{90}Sr	18	20	22	24	24	26
		^{137}Cs	36	36	42	44	52	54
	Lupine	^{90}Sr	26	32	34	28	38	38
		^{137}Cs	34	37	48	36	42	52
	Sunflower	^{90}Sr	36	40	42	42	48	50
		^{137}Cs	48	52	54	60	60	66
October, 2018	Calendula	^{90}Sr	22	26	30	30	30	32
		^{137}Cs	44	48	49	48	56	58
	Lupine	^{90}Sr	30	36	38	34	42	46
		^{137}Cs	42	45	52	42	44	56
	Sunflower	^{90}Sr	40	45	48	50	54	60
		^{137}Cs	54	56	56	76	78	84

CONCLUSIONS

1. The methodology of creation of artificial (engineering) GB on the way of distribution of TE and RN has been developed.
2. Developed, improved and modified methods for measuring the content of TE and RN in the soil layer and vegetation.
3. A model experiment was performed to create an artificial GB at the experimental site, which resulted in quantitative barrier values.
4. Cultures of agrophytocenoses for optimal phytostabilization of soil conditions for specific components of contamination have been determined.

5. Existing phytotechnology of soil purification due to the use of GB, based on specific landscape conditions and needs of rational use of nature, has been developed and improved.

6. Cultures of agrophytocenoses for optimal variants of soil phytorestoration for different components of contamination (TE and RN) were determined.

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Article received 04.03.2020

ВОССТАНОВЛЕНИЕ ПОЧВ ЗАГРЯЗНЕННЫХ РАДИОНУКЛИДАМИ МЕТОДОМ ФИТОРЕМЕДИАЦИИ

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Методологически обоснована возможность восстановления состояния почв с помощью фитотехнологий и искусственных геохимических барьеров (ГБ) от загрязнения радионуклидами (РН) и токсичными элементами (ТЭ). Для этого создан ряд искусственных ГБ на специальном полигоне в рамках модельного эксперимента. Исследован процесс формирования и развития барьеров, определены их параметры. Выбраны культуры агрофитоценозов для оптимальных вариантов фитостабилизации состояния почв. Выполнены исследования фитоизвлечения ТЭ и РН культурами агрофитоценозов в течение одного полного вегетационного периода. Выявлена определенная селективность исследуемых растений по изъятию различных ТЭ и РН из почвы и материала барьеров.

ВІДНОВЛЕННЯ ҐРУНТІВ ЗАБРУДНЕНИХ РАДІОНУКЛІДАМИ МЕТОДОМ ФІТОРЕМЕДІАЦІЇ

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Методологічно обґрунтована можливість відновлення стану ґрунтів за допомогою фітотехнологій та штучних геохімічних бар’єрів (ГБ) від забруднення радіонуклідами (РН) і токсичними елементами (ТЕ). Для цього створено ряд штучних ГБ на спеціальному полігоні в рамках модельного експерименту. Досліджено процес формування та розвитку бар'єрів, визначені їх параметри. Вибрано культури агрофітоценозів для оптимальних варіантів фітостабілізації стану ґрунтів. Виконано дослідження фітовилучення токсичих елементів (ТЕ) і РН культурами агрофітоценозів протягом одного повного вегетаційного періоду. Виявлена певна селективність досліджуваних рослин щодо вилучення різних ТЕ і РН з ґрунтів і матеріалу бар'єрів.