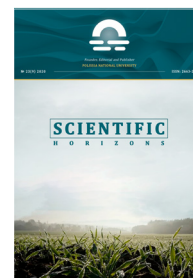


# SCIENTIFIC HORIZONS

Journal homepage: <https://sciencehorizon.com.ua>

*Scientific Horizons*, 24(3), 52-57



UDC 631.453/631.459.21

DOI: 10.48077/scihor.24(3).2021.52-57

## Intensity of Soil Pollution by Toxic Substances Depending on the Degree of Its Washout

Oleksandr Tkachuk\*, Victoria Verhelis

Vinnytsia National Agrarian University  
21008, 3 Soniachna Str., Vinnytsia, Ukraine

### Article's History:

Received: 12.06.2021

Revised: 15.07.2021

Accepted: 22.08.2021

### Suggested Citation:

Tkachuk, O., & Verhelis, V. (2021). Intensity of soil pollution by toxic substances depending on the degree of its washout. *Scientific Horizons*, 24(3), 52-57.

**Abstract.** A significant degree of ploughness of agricultural lands of Ukraine has led to increased erosion and the creation of soils of varying degrees of washout, which leads to dehumification and contamination of soils with toxic substances. Therefore, the purpose of the study was to establish the features of horizontal migration and accumulation of heavy metals of lead, cadmium, copper, and zinc, trace elements of boron and manganese, radionuclides of caesium and strontium on podzolic heavy loamy chernozems with varying degrees of washout: non-eroded, weak and medium washout, conditioned by the development of erosion processes. During the study, spectrophotometric, colorimetric, gamma-spectrometric, and radiochemical methods were used to determine the content of toxic substances in the soil. The study results showed that on slightly washed soils, the content of humus is 12.9% less, easily hydrolysed nitrogen – 13.3%, mobile forms of phosphorus – 51.1%, mobile potassium – 34.9% less than on slightly washed soils. The humus content on medium-washed soil was 8.8% less than on lightly washed soil, easily hydrolysed nitrogen – 14.3% less, mobile phosphorus – 15.3% more, mobile potassium – 42.9% more. A strong horizontal migration of mobile lead forms in washed podzolic heavy loamy chernozem was established, which increases with increasing degree of soil washout with the content of mobile lead forms on medium-washed soil by 24% more than on non-eroded soil. The same dependence was established on the content of mobile forms of zinc in the soil, with their predominance on medium-washed soil by 17 %, compared to non-washed. The content of mobile forms of copper is lower on slightly washed soil, compared to non – washed soil by 5%, boron – 18.8% less on non-washed soil, compared to medium-washed, and the content of mobile forms of manganese increases by 3.3% from slightly to medium-washed soil. It was also found that the concentration of caesium decreased by 25.6% on medium-washed soils, compared to non-washed ones

**Keywords:** heavy metals, trace elements, radionuclides, horizontal migration, soil erosion



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\*Corresponding author

## INTRODUCTION

The modern use of land resources in Ukraine is characterised by intensity and does not meet the requirements of rational use of natural resources. Land resources lose their fertility and degrade due to crop rotation irregularity, ploughing soils on slopes, applying high rates of mineral fertilisers and pesticides, and over-compaction with machinery [1]. One of the defining agroecological problems of agriculture in Ukraine is the high degree of ploughness of agricultural soils. The ploughness of soils in Ukraine is one of the largest in the world and accounts for 57% of the country's territory, and the ploughness of agricultural land reaches 80%. Intensive ploughing of lands, including inclined ones, leads to a decrease in soil fertility due to their over-compaction, deterioration of the structural condition, reduction of water permeability, aeration, and contamination with toxic substances [2].

In Ukraine, the following degradation processes in soils are most widespread: dehumidification and reduction of the content of nutrients, physical degradation (over-compaction), erosion, pollution, etc. [2]. Especially dangerous for soils is erosion, which has significantly accelerated with the introduction of intensive farming technologies and significant ploughing of protected land on the slopes. Due to the development of erosion processes caused by anthropogenic activity, the soil is washed away, which leads to a decrease in its fertility and contamination with toxic substances [2].

Accelerated erosion is estimated by the volume of soil washout per year: weakly washed soils – 0.5-1.0 t/ha; medium-washed soils – 1.0-5.0 t/ha; heavily washed soils – 5-10 t/ha; very strongly washed soils – more than 10 t/ha [3]. In Ukraine, the area of eroded and erosive soils is approximately 17 million hectares. Most of the washed-off soils were found in Luhanska, Vinnytska, Dnipropetrovska, and Odeska oblasts, where the share of washed-off soils reaches 53-66% of the total arable land area [4]. The number of polluted and unproductive soils on the territory of Ukraine reaches 15 million hectares, while over the past 130 years their number has increased significantly, which is also affected by a decrease in the humus content in the soil. On such soils, along with the problem of acidification, pollution with heavy metals, radionuclides, pesticide residues, and salts is growing. Data from the Institute of Soil Science and Agrochemistry show that 20% of the soil area in Ukraine is contaminated with heavy metals [4], which requires their constant agroecological monitoring.

Studies by E.Ya. Zhovinsky, A.I. Samchuk [5], and A.I. Fateev [6] are devoted to the issues of heavy metal contamination of the soil cover. Considerable attention of researchers is focused on the study of issues of landscape ecogeochemistry in agrogenesis zones: T.M. Myslyva [7], O.I. Trunova [8]. Part of the research concerns the features of migration and accumulation of certain chemicals in the soil. Study by Yu.M. Dmytruk [9] is aimed at

investigating the features of the movement of copper and zinc in the soil thickness of the Carpathian region, A.I. Melnyk [10] – migration and accumulation of heavy metals in the soils of the Chernihivska Oblast, S.S. Rudenko and S.S. Kostyshin – in the soils of agricultural land of the Chernivetska Oblast [11; 12]. Features of distribution of Zn in agricultural soils of the Kharkivska Oblast are considered by M.M. Miroshnichenko and A.I. Fateev [13], the nature of migration and accumulation of heavy metals in the soils of protected areas – by A.I. Samchuk and E.Ya. Zhovinsky [5], agro-cultural landscapes – T.M. Myslyva [7]. A small amount of research papers concerns the study of the horizontal movement of toxic substances and their accumulation in the soil. There are almost no data on the horizontal redistribution of toxicants in soils undergoing erosion.

Considering the above, *the purpose of the study* is to establish the features of horizontal migration and accumulation of heavy metals, some trace elements and radionuclides under conditions of varying degrees of washout of soils due to the development of erosion processes.

## THEORETICAL OVERVIEW

According to the degree of mobility, all heavy metal compounds in the soil are divided into stationary, potentially mobile, and mobile components. Among them, heavy metals in mobile form have the most negative effect on living organisms, including humans. Agrochemical properties of soils significantly affect the mobility of heavy metals: in soils with low buffering, the number of mobile forms of heavy metals will be significantly higher than in soils with high buffering with the same other characteristics: the background content of heavy metals, the level of anthropogenic pollution, and others. Based on this, "the buffer capacity directly determines the protective properties of soils, so to determine the actual danger of heavy metals, it is necessary to monitor the content of their mobile forms. The value of the gross content of heavy metals should be used only to establish the general characteristics of soil contamination and identify their potential danger" [14].

It was found that the transfer of heavy metals from landscapes located above the landform leads to an increase in the content of Pb in the lowlands by 4.5 times, Sr – by 1.7, Ag – by 2.2, Cu – by 1.7, Zn – by 2.5, Ga – by 1.5, Sn – by 1.6 and Yb – by 1.5 times [15]. Admittedly, the reaction of the soil environment also directly affects the mobility of chemical elements. In an acidic environment, most cationic elements (Cd, Hg, Pb, Ni, Co, Mn, Zn, Cu, etc.) easily migrate, and an increase in PH leads to a sharp decrease in the intensity of migration processes due to the generation of poorly soluble compounds of these substances.

An important factor in the intensity of movement of heavy metals in the soil is its redox properties. Heavy

metals are the least mobile in the soil under highly reducing conditions (50-150 mV), and Co, Cd, Mn, Fe, Ni, and Zn are the most mobile at the reducing properties of soils of 400 mV, and Cu – at 700-800 mV [16]. However, since the redox potential of soils is a very dynamic value, its study is rarely conducted.

A significant part of heavy metals is bound in the soil by the organic matter of humus – humic and fulvic acids. Fertile soils with a high humus content are able to retain high concentrations of heavy metals compared to sandy or humus-poor soils [17]. At the same time, the long-term supply of heavy metals to the soil, even in low concentrations, causes their significant accumulation in the soil [18]. The toxic effect of heavy metals in heavy soils with a high humus content is less than in light and humus-poor soils. This can be explained by the property of clay particles and organic matter of humus to transfer heavy metals to a bound and sedentary state.

When pollutants enter the soil, its structure is destroyed, which leads to preconsolidation of the soil. The consequences of this are a decrease in water permeability, the generation of a soil crust, and the deterioration of the water-air regime. When heavy metals accumulate in the soil, its physical and chemical properties deteriorate: the mobility of the clay fraction increases, the acid reaction of the soil environment changes, the concentration of calcium and magnesium exchange compounds decreases, compounds of carbonates and iron hydroxides are destroyed, the quantitative composition of humus decreases, and the mobility of humic acids of humus increases [19].

## MATERIALS AND METHODS

The study was conducted during 2017-2020 based on processing materials for monitoring and ecological and agrochemical certification of agricultural land of the farm "Avgust VA" in the village of Markovka, Tomashpol district, Vinnytska Oblast, which were developed by the Vinnytsia branch of the state institution "Institute of soil protection of Ukraine" [20]. The soil of the experimental site is podzolic heavy loamy chernozem with varying degrees of washout: non-eroded, slightly washed, medium washed. The following ecological and agrochemical parameters of the soil were analyzed: the content of mobile forms of heavy metals: lead (Pb), cadmium (Cd), copper (Cu) and zinc (Zn) – by spectrophotometric method; the content of trace elements: boron (B) – by colorimetric method, manganese (Mn) – by spectrophotometric method; the density of radioactive contamination: Caesium – 137 (Cs) – by gamma spectrometer, strontium-90 (Sr) – by radiochemical method [20].

Agrochemical survey of the soils was carried out on a total area of 740.5 hectares. Sampling was carried out in accordance with the guidelines for large-scale agrochemical survey of soils in the agrochemical service of Ukraine. The study was conducted on two adjacent soil areas with different degrees of washout: non-eroded and slightly washed soil and slightly washed and medium-washed soil. On the experimental non-eroded

podzolic heavy loamy chernozems by mechanical composition, the humus content was 2.94%. On slightly washed soils, the humus content was 12.9% lower. The content of easily hydrolysed nitrogen on non-eroded soils was 113 mg/kg, and on slightly washed soils – 13.3% less. The content of mobile forms of phosphorus on non-eroded soils was 137 mg/kg, and on slightly washed soils – decreased by 51.1%. The content of mobile potassium on non-eroded podzolic heavy loamy chernozems was 152 mg/kg. This was 34.9% more than on lightly washed soil.

Observation of a section of podzolic heavy loamy chernozem with a weak and medium-washed degree showed that the humus content on slightly washed soil was 2.94%, and on medium-washed soil it decreased by 8.8%. The content of lightly hydrolysed nitrogen on lightly washed podzolic heavy loamy chernozem was 112 mg/kg, and on medium-washed – decreased by 14.3%. The content of mobile forms of phosphorus on lightly washed soil was 50 mg/kg, and on medium-washed soil – increased by 15.3%. The content of mobile forms of potassium on lightly washed podzolic heavy loamy chernozems was 89 mg/kg, and on heavily washed – increased by 42.9%.

The hydrolytic acidity of non-eroded soil was 2.34 mg-eq/100 g, and slightly washed – increased by 4.9%. The reaction of the soil solution on unwashed soil was 5.5 pH, and on slightly washed soil – increased by 1.8%. The sum of the absorbed bases of non-eroded podzolic heavy loamy chernozem was 25.6 mg-eq/100 g, and slightly washed – increased by 11.4%.

Observations of the acidity indicators of another soil area, where the degree of washout was higher, revealed the hydrolytic acidity of slightly washed soil of 1.72 mg-eq/100 g. Medium-washed podzolic heavy loamy chernozem had a hydrolytic acidity of 11.3% higher. The reaction of the soil solution of slightly washed soil was 5.8 pH, and the reaction of medium-washed soil was 1.7% less. The sum of the absorbed bases of weakly and medium-washed soils was the same and amounted to 29.2 mg – eq/100 g.

## RESULTS AND DISCUSSION

The main toxic substances in soils that can negatively affect plant growth and development are heavy metals, radionuclides, pesticide residues, salts and acids. At high concentrations in soils, trace elements can also be toxic to plants.

Among the group of heavy metals, lead and cadmium are the most dangerous. At the same time, copper and zinc can act in soils, depending on their concentration, as heavy metals, and microelements useful for plants. In this study, the influence of the degree of washout of podzolic heavy loamy chernozem on the concentration of mobile forms of heavy metals in it was revealed. In particular, on non-eroded soil, the content of mobile forms of lead was 1.13 mg/kg, and on lightly washed soil, it increased by 6.6% and amounted to 1.21 mg/kg (Table 1).

**Table 1.** Intensity of soil contamination with heavy metals depending on the degree of its washout, mg/kg

Soil type	Mechanical composition	Degree of washout	Heavy metals							
			Pb		Cd		Cu		Zn	
			Content	MPC	Content	MPC	Content	MPC	Content	MPC
Podzolic chernozem	Heavy loam	Non-eroded	1.13	6.00	0.07	0.70	0.20	3.00	0.47	23.0
		Slightly washed	1.21	6.00	0.07	0.70	0.19	3.00	0.49	23.0
Podzolic chernozem	Heavy loam	Slightly washed	0.85	6.00	0.06	0.70	0.24	3.00	0.41	23.0
		Medium washed	1.03	6.00	0.06	0.70	0.24	3.00	0.47	23.0

**Notes:** MPC – maximum permissible concentrations

**Source:** compiled based on [20]

The content of mobile forms of cadmium in the soil did not depend on the degree of its washout and amounted to 0.07 mg/kg on unwashed and slightly washed soil. The concentration of mobile forms of copper on unleaded podzolic chernozem was 0.20 mg/kg, and on slightly washed chernozem it was 5% less and amounted to 0.19 mg/kg. The content of mobile forms of zinc on unwashed soil was 0.47 mg/kg, and on lightly washed soil – increased by 4.1% and amounted to 0.49 mg/kg.

Comparison of indicators of the content of mobile forms of heavy metals between lightly and medium-washed podzolic heavy loamy chernozem revealed an increase in lead concentration by 17.5% on medium-washed soil: from 0.85 mg/kg on slightly washed – to 1.03 mg/kg on medium washed. The concentration of mobile cadmium forms did not depend on the degree of soil washout and was 0.06 mg/kg. In addition, there was no effect of the degree of soil washout on the content of mobile forms of copper in it – 0.24 mg/kg. At the same time, the content of mobile forms of zinc on slightly washed soil was 0.41 mg/kg, and on medium-washed soil it increased by 12.8% and amounted to 0.47 mg/kg.

Analysis of indicators of the content of heavy metals in soils of various degrees of washout showed that the concentration of mobile forms of lead and zinc increases from unwashed to medium-washed soil, and the concentration of mobile forms of cadmium and copper

does not depend on the degree of its washout. At the same time, the concentration of mobile forms of lead and zinc in the soil increases three times more intensively during the transition from slightly washed to medium-washed than from unwashed to slightly washed. This indicates a horizontal migration of lead and zinc along the slope. Lead has a greater horizontal migration in the soil compared to zinc. At the same time, cadmium and copper migrate in a horizontal plane along soil slopes less intensively. In particular, only copper migration was detected in slightly washed soil compared to non-eroded soil, while such migration between slightly and medium-washed soil was not detected.

Assessment of the content of heavy metals in experimental soils in comparison with maximum permissible concentrations (MPC) did not detect that the permissible limits were exceeded. In particular, the content of mobile forms of lead was 0.14-0.20 MPC, cadmium – 0.09-0.10 MPC, copper – 0.06-0.08 MPC, zinc – 0.02 MPC. The study analysed changes in the concentration of trace elements in the soil depending on the degree of its washout. In particular, the content of mobile forms of boron on unwashed soil was 0.84 mg/kg, and on lightly washed soil – decreased by 9.5% and amounted to 0.76 mg/kg. The manganese content on non-eroded soil was 35.80 mg/kg, and on lightly washed soil it decreased by 0.2% and amounted to 35.74 mg/kg (Table 2).

**Table 2.** Content of trace elements boron and manganese in the soil depending on the degree of its washout, mg/kg

Soil type	Mechanical composition	Degree of washout	Trace elements			
			B		Mn	
			Content	Background	Content	MPC
Podzolic chernozem	Heavy loam	Non-eroded	0.84	6.0	35.80	700
		Slightly washed	0.76	6.0	35.74	700
Podzolic chernozem	Heavy loam	Slightly washed	0.86	6.0	35.64	700
		Medium-washed	0.78	6.0	36.84	700

**Source:** compiled based on [20]

During the transition of soil from slightly to medium washed, the content of mobile forms of boron decreased by 9.3% (from 0.86 to 0.78 mg/kg), and manganese – increased by 3.3% (from 35.64 to 36.84 mg/kg). The results of the conducted studies indicate that with an increase in the degree of soil washout, the boron content in it decreases – evenly between weakly and medium-washed soil, but the manganese content increases, especially in medium-washed soils. The background content of boron in the soils of the forest-steppe of Right-Bank Ukraine is 6.0 mg/kg, which is significantly higher than the actual content of boron in the soil of experimental sites. The maximum permissible concentration

of mobile forms of manganese in the soil is 700 mg/kg, and the actual content is 0.05 maximum permissible concentration.

The influence of varying degrees of soil washout on the content of radionuclides in it is revealed. In particular, the caesium content in the undisturbed soil was 0.37 Ki/km<sup>2</sup>. On slightly washed soil, the caesium content decreased by 18.9% and amounted to 0.30 Ki/km<sup>2</sup>. On medium-washed podzolic chernozem, the caesium content also decreased by 16.7% (0.25 Ki/km<sup>2</sup> against 0.30 Ki/km<sup>2</sup>). The content of strontium in the studied soils did not depend on the degree of its washout (Table 3).

**Table 3.** Intensity of changes in soil contamination with radionuclides depending on the degree of its washout, Ki/km<sup>2</sup>

Soil type	Mechanical com-position	Degree of washout	Trace elements			
			Cs		Sr	
			content	MPC	content	MPC
Podzolic chernozem	Heavy loam	Non-eroded	0.37	1.0	0.02	0.15
		Slightly washed	0.30	1.0	0.02	0.15
Podzolic chernozem	Heavy loam	Slightly washed	0.30	1.0	–	0.15
		Medium-washed	0.25	1.0	–	0.15

**Source:** compiled based on [20]

At the maximum permissible concentration of caesium in the soil of 1.0 Ki/km<sup>2</sup>, its actual content at the experimental sites was 0.3-0.4 MPC, and strontium – 0.1 MPC.

## CONCLUSIONS

According to the study results, the migration ability of toxic substances in the soil was revealed, depending on the degree of its washout. A strong horizontal migration of mobile forms of lead in the soil was established, which grows from non-eroded to medium-washed soil with the highest lead content on medium-washed podzolic heavy loamy chernozems, which is 24% more than on non-eroded soil. A similar relationship was found in the content of mobile forms of zinc in the soil, where its

concentration on medium-washed soil was 17% higher than on non-eroded soil. The content of mobile forms of copper decreases on slightly washed soils by 5% compared to non-eroded ones, boron – by 18.8% from non-eroded to medium-washed soils, and the content of manganese increases from slightly to medium-washed soil by 3.3%. A decrease in the concentration of caesium was revealed on medium-washed soils compared to non-eroded soils by 25.6%.

Prospects for further research are to investigate the features of accumulation of toxic substances: heavy metals, radionuclides, salts and acids in crop products grown on soils with varying degrees of washout and develop measures to reduce the horizontal migration of such toxicants along soil slopes.

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## **Інтенсивність забруднення ґрунту токсичними речовинами залежно від ступеня його змитості**

**Олександр Петрович Ткачук, Вікторія Ігорівна Вергеліс**

Вінницький національний аграрний університет  
21008, вул. Сонячна, 3, м. Вінниця, Україна

**Анотація.** Значний ступінь розораності сільськогосподарських ґрунтів України призвів до посилення ерозійних процесів та утворення ґрунтів різного ступеня змитості, що призводить не тільки до дегуміфікації, але й до забруднення ґрунтів токсичними речовинами. Тому метою дослідження було встановити особливості горизонтальної міграції та накопичення важких металів свинцю, кадмію, міді та цинку, мікроелементів бору та марганцю, радіонуклідів цезію і стронцію на чорноземах опідзолених важкосуглинкових із різним ступенем змитості: незмиті, слабо- та середньозмиті, зумовленої розвитком ерозійних процесів. Під час дослідження було використано спектрофотометричні, колориметричні, гамма-спектрометричні та радіохімічні методи визначення вмісту токсичних речовин у ґрунті. Результатами досліджень виявлено, що на слабозмитих ґрунтах вміст гумусу на 12,9 % менший, азоту легкогідролізованого – на 13,3 %, рухомих форм фосфору – на 51,1 %, рухомого калію – на 34,9 % менший, ніж на слабозмитих ґрунтах. Вміст гумусу на середньозмитому ґрунті був на 8,8 % меншим, ніж на слабозмитому, азоту легкогідролізованого – на 14,3 % меншим, рухомого фосфору – на 15,3 % більшим, рухомого калію – на 42,9 % більшим. Встановлено сильну горизонтальну міграцію рухомих форм свинцю у чорноземі опідзоленому важкосуглинковому змитому, що зростає із збільшенням ступеня змитості ґрунту із вмістом рухомих форм свинцю на середньозмитому ґрунті на 24 % більшому, ніж на незмитому ґрунті. Така ж залежність встановлена за вмістом у ґрунті рухомих форм цинку, з їх переважанням на середньозмитому ґрунті на 17 %, порівняно із незмитим. Вміст рухомих форм міді менший на слабозмитому ґрунті, порівняно із незмитим на 5 %, бору – на 18,8 % менший на незмитому ґрунті, порівняно із середньозмитим, а вміст рухомих форм марганцю збільшується на 3,3 % від слабо- до середньозмитого ґрунту. Також встановлено зниження концентрації цезію на 25,6 % на середньозмитих ґрунтах, порівняно із незмитими

**Ключові слова:** важкі метали, мікроелементи, радіонукліди, горизонтальна міграція, ерозія ґрунту