

CONSEQUENCES OF THE CADMIUM CONTAMINATION FOR THE PHYSICAL AND CHEMICAL STATUS OF THE DARK GRAY PODZOLIC SOIL IN THE WESTERN FOREST-STEPPE OF UKRAINE

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Kachmar N., Datsko T., Ivankiv M., Dydiv A., Panasiuk R. Consequences of the cadmium contamination for the physical and chemical status of the dark gray podzolic soil in the Western Forest-Steppe of Ukraine

Contamination with heavy metals is a major concern because of their toxicity and threat to human life and environment. The object of the study was dark gray podzolic soil polluted with cadmium. The samples were taken from the research field of Lviv National Environmental University, from the layer of 0–60 cm deep. Cadmium ($\text{CdCl}_2 \cdot 2.5 \text{H}_2\text{O}$) was applied to the top layer of soil as water-salt solutions in different doses, namely 0; 3; 15; 30 mg kg^{-1} . The basic chemical and physical properties, such as soil reaction, organic carbon content, grain size composition, total surface area, porosity, and hydrolytic acidity of the samples were analyzed using routine laboratory procedures. The soluble forms of Cd were also investigated. The soil reaction ranged between 6.9 and 7.6 in 1M KCl and 7.4–8.1 in H_2O , whereas the content of organic C ranged between 0.62 and 1.59 %. For Cd-treated samples, the content of sand fraction changed from 7 to 25 %, silt fraction – from 47 to 63 %, and clay – from 18 to 43 %. The pore volume of polluted soil ranged from 411 to 515 $\text{mm}^3 \text{g}^{-1}$. The total surface area of the soils varied from 26.8 $\text{m}^2 \text{g}^{-1}$ to 40.0 $\text{m}^2 \text{g}^{-1}$. The content of available forms of cadmium was the highest in the top layers of soils. The presence of this element was similar to that in the control sample at the depth of 30 cm only for small initial doses of Cd. The content of Cd for the highest dose and at the deepest soil level was higher than for the control sample. The behaviour of cadmium in soil and the influence of cadmium on the basic characteristics of dark gray podzolic soil can be caused by the chemical properties of this metal and the properties of the soil. The rate of migration of mobile forms of cadmium in the soil may be an indication of its self-purification.

Keywords: soil pollution, heavy metals, cadmium, dark gray podzolic soil, physical and chemical properties, soluble forms of heavy metals.

Качмар Н., Дацко Т., Іванків М., Дидів А., Панасюк Р. Наслідки кадмієвого забруднення темно-сірого опідзоленого ґрунту для його фізико-хімічного стану в умовах Західного Лісостепу України

Забруднення важкими металами зумовлює серйозне занепокоєння через їхню токсичність і загрозу життю людини та навколишньому середовищу. Досліджено забруднений кадмієм темно-сірий опідзолений ґрунт. Зразки ґрунту відбирали із глибини 0–60 см на дослідному полі Львівського національного університету природокористування. Кадмій ($\text{CdCl}_2 \cdot 2.5 \text{H}_2\text{O}$) вносили у верхній шар ґрунту у вигляді водно-сольових розчинів у різних дозах: 0; 3; 15; 30 mg/kg ґрунту. Основні хімічні та фізичні властивості, як-от реакція ґрунту, вміст органічного вуглецю, гранулометричний склад, загальна площа поверхні, пористість, гідролітична кислотність зразків, проаналізовано за допомогою стандартних лабораторних методів. Досліджено також уміст розчинних форм кадмію. Зауважено, що реакція ґрунту коливалася від 6,9 до 7,6 в 1М KCl і 7,4–8,1 в H_2O , тоді як уміст органічного вуглецю був у межах 0,62–1,59 %. Для досліджуваних зразків уміст фракції піску змінювався від 7 до 25 %; фракції мулу – від 47 до 63 %, і фракції колоїдної глини – від 18 до 43 %. Об'єм пор забруднених зразків ґрунту становив від 411 $\text{mm}^3 \text{g}^{-1}$ до 515 $\text{mm}^3 \text{g}^{-1}$. Загальна площа поверхні ґрунтових зразків змінювалася в межах від 26,8 $\text{m}^2 \text{g}^{-1}$ до 40,0 $\text{m}^2 \text{g}^{-1}$. Найвищий вміст рухомих форм кадмію виявився у верхніх шарах ґрунту. Вміст забруднювача був на одному рівні з контрольними зраз-

ками на глибині 30 см за умови низького рівня забруднення. Вміст кадмію за високого рівня забруднення на найбільшій глибині ґрунту був значно вищим, ніж у контрольному варіанті. Особливості поведінки кадмію в ґрунті та вплив досліджуваного полютанта на основні характеристики темно-сірого опідзоленого ґрунту можна пов'язати з хімічними властивостями цього металу та властивостями, притаманними досліджуваному ґрунту. Швидкість міграції рухомих форм кадмію у ґрунті може бути свідченням і показником його самоочищення.

Ключові слова: забруднення ґрунту, важкі метали, кадмій, темно-сірий опідзолений ґрунт, фізико-хімічні властивості, розчинні форми важких металів.

Formulation of the problem. One of the factors contributing to the chemical degradation of soils is the presence of heavy metals, which are among the primary pollutants in the environment. More than 85% of the total heavy metal content in soils comes from human activities. Contamination with heavy metals is a major concern due to their toxicity and the threat they pose to human life and the environment. Soils accumulate large amounts of heavy metals and their distribution and movement within the soil depend largely on their adsorption by soil particles. Specifically, soil organic and mineral particles can bind toxic elements by forming complexes.

Analysis of recent research and publications. Three principal stages of technogenic heavy metals transformation in soil are 1) the formation of complexes; 2) heavy metals' highly intensive migration; 3) high humus horizon intrusion [2; 3]. Some agricultural soils are contaminated with cadmium (Cd). Cadmium belongs to 10 chemical elements that are the basic contaminants of the environment and they can be found in solid as well as in liquid phase. The parent rock of which the soils are developed is the natural source of heavy metals in those soils. Soils exhibit high absorbing capacity to cadmium. Several soil properties, such as the pH value, organic carbon content, grain size composition, specific surface area, porosity, and hydrolytic acidity, can influence the availability of exchangeable and water-soluble Cd determined as available for plants [5; 12]. On the other hand, several physicochemical processes occurring in soils, such as water and ions adsorption, acid-base equilibrium, and transport phenomena, are related to or governed by the surface properties of the soil solid phase. The main factor influencing the mobility of heavy metals in the soil environment is its reaction (pH) which affects the stability of humus complexes with metals. In alkaline and high-sorption capacity carbonate soils with pH above 7, heavy metals are naturally transformed into non-soluble forms without any additional agricultural treatments [12]. The relationship between the amount of metal adsorbed and composition of the soil is quite complex, due to solid phase heterogeneity and influence of soil solution chemistry [2; 7]. The solution activity of Cd is consistently higher than other heavy metals, indicating that Cd is more mobile in the environment [8]. In soils dominated by permanent charge surface, heavy metals are not mobile, but in variable charge soils, the low surface charge density creates

conditions conducive to increased mobility. Consequently, the adsorption of heavy metals, in particular cadmium, by soils in relation to the effects of inorganic and organic ligands and the implications for metal transport were reviewed by researchers [1; 11].

Setting objectives. The aim of this study was to investigate the basic properties of the dark gray podzolic soil polluted with cadmium. Basic chemical and physical properties, such as soil reaction, hydrolytic acidity, organic carbon, grain size composition, total surface area, soil porosity and content of water-soluble forms of Cd were measured.

Presenting main material. The soil samples were taken from the research field of Lviv National Environmental University. The experimental area of 100 m² was divided into 20 plots of 2 m² each. The effect of cadmium on physical and chemical properties of the dark gray podzolic soil was investigated at the contamination levels of 1, 5 and 10 of the Threshold Limit Value. Heavy metals were applied onto the top layer of soil as water-salt solutions of CdCl₂ at different doses, namely 0; 3; 15 and 30 mg kg⁻¹ of soil. The soil samples were taken from every next 10 cm layer of the soil profile (0–60 cm depth). Soil reaction, organic carbon, grain size composition, specific surface area, porosity, hydrolytic acidity of the studied soil were measured using routine laboratory analyses on the basis of Institute of Agrophysics, Polish Academy of Sciences in Lublin. Soil reaction was measured by a potentiometer with a combined glass/calomel electrode in 1M KCl and in H₂O at 1:2.5 soil-to-solution ratio. Organic carbon was determined oxidometrically with potassium dichromate in hot sulphuric acid, according to the modified Tiurin method. The grain size composition was evaluated by the areometric Cassagrande method modified by Prószyński. The specific surface area of investigated soil samples was obtained according to the Polish Standard PN-Z-19010-1. Before adsorption measurements, the soil samples were dried at 105 °C in a vacuum chamber with concentrated sulphuric acid until the weight of the samples reached constant values. The amount of adsorbed water vapour at T = 20 °C was computed as the difference between the weight of the sample with water and the dry sample. The relative water pressures were obtained

from the density of sulphuric acid solutions. The adsorption measurements were replicated three times. Soil porosity was measured using a Micrometrics Mercury Porosimeter Autopore IV 9510 Model and applying the pressures from the range from 0.0036 to 413 MPa. This range allowed for the determination of pores with equivalent radii ranging from 0.003 μm to 360 μm . Before porosity measurements, the samples were oven-dried at 105 °C and then degassed up 10^{-3} Pa to remove physically adsorbed water from their surface. The pore radii were calculated from the Washburn equation [6]. The surface tension and the contact angle of mercury were assumed to be 480 dynes cm^{-2} and 141.3 °C, respectively. All calculations from obtained porosimetric data, i.e. the bulk density, pore surface area, average pore radius, and total porosity, were carried out using the cylindrical pore model by computer program Autopore IV Version 1.06. The content of available forms of cadmium in soils was investigated by atomic absorption spectrometry (AAS) using

a Perkin Elmer 3300 apparatus. The soil was stressed with cadmium (CdCl_2) with concentrations of 0; 3; 15 and 30 mg Cd per kg of soil. Soil samples for those studies were collected in the second year of the experiment from three depths – 10, 20, and 30 cm. Afterwards, equal-weight amounts of dried soils were extracted for 24 hours by the mixture of 1 M hydrochloric (HCl) and 1 M nitric acid (HNO_3) at the ratio of 1:1. Received extracts of available Cd forms were filtrated. The content of cadmium was analyzed in clear solutions [4]. Received data were statistically calculated using a t-student test for equal expectation value.

From the results obtained in this study, it follows that the reaction of polluted soil samples was 6.9–7.6 in 1M KCl and 7.4–8.1 in H_2O , while the pH of the control soil sample was 6.9–7.4 in 1M KCl and 7.5–7.9 in H_2O (see Table 1). The reaction of the soil was neutral.

Table 1

Basic properties of samples contaminated with cadmium

No	Depth (cm)	Grain size composition (%)			C _{orgs} (%)	pH		(TSA m^2g^{-1})
		Sand	Silt	Clay		H ₂ O	1M KCl	
Soil + Cd 3 (mg kg^{-1})								
1	0–10	20	62	18	1.58	7.8	7.3	36.3
2	10–20	19	57	24	1.52	7.9	7.4	29.8
3	20–30	15	55	30	1.44	8.0	7.5	28.8
4	30–40	19	51	30	1.28	7.7	7.1	35.5
5	40–50	21	47	32	0.92	7.8	7.3	33.9
6	50–60	11	50	39	0.62	7.4	7.0	40.0
Soil + Cd 15 (mg kg^{-1})								
1	0–10	25	50	25	1.55	7.9	7.4	30.2
2	10–20	19	58	23	1.49	8.1	7.6	30.8
3	20–30	13	60	27	1.39	7.8	7.4	29.3
4	30–40	14	53	33	1.30	7.9	7.3	33.9
5	40–50	7	50	43	0.85	7.7	7.2	39.2
6	50–60	9	63	28	0.72	7.5	6.9	36.7
Soil + Cd 30 (mg kg^{-1})								
1	0–10	20	60	20	1.57	7.9	7.4	30.5
2	10–20	20	47	33	1.47	8.1	7.5	30.7
3	20–30	12	58	30	1.42	7.8	7.3	30.2
4	30–40	10	60	30	1.24	7.7	7.1	37.6
5	40–50	13	55	32	0.89	7.5	7.0	37.8
6	50–60	11	49	40	0.66	7.6	7.0	36.5
Control								
1	0–10	20	54	26	1.59	7.7	7.2	30.1
2	10–20	18	59	23	1.50	7.9	7.4	30.4
3	20–30	13	57	30	1.46	7.9	7.3	26.8
4	30–40	9	56	35	1.23	7.6	7.2	30.4
5	40–50	15	55	30	0.94	7.7	7.1	33.9
6	50–60	13	54	33	0.71	7.5	6.9	38.7

Abbreviation: sand fraction: 1–0.1 mm, silt: 0.1–0.02 mm, clay: < 0.02 mm, C_{orgs} – Organic carbon, TSA – Total surface area

The fraction of organic carbon in all investigated samples was rather low. Indeed, the organic carbon content in the samples polluted with Cd ranged from 0.62 % to 1.58 %, whereas in the control soil, it changed from 0.71 % to 1.59 %. Within the layers of 0–20 cm (they exhibited the highest organic carbon content), significant differences in organic carbon content between contaminated and control samples were observed for all soils treated with Cd.

The transport and deposition of pollutants in soil profiles strongly depend on pH and the amount of organic matter. Several researchers have shown that heavy metals get bound to dissolved humic substances and this phenomenon significantly decreases the negative impact of heavy metals on plants and soil organisms [9; 10].

For Cd polluted soils the content of sand fraction was from 7 to 25 %, silt fraction – from 47 to 63 %, and clay – from 18 to 43 %. The grain size composition of the control soil was as follows: sand – 9–20 %, silt – 54–59 %, and clay – 23–35 %. The grain size composition depends on the soil horizon (Table 1). However, one can state that the grain size compositions of the polluted soil samples were not significantly different from the composition of the control soil. For all studied samples the TSA evaluated from the adsorption isotherms ranged from 28.8 to 40.0 m²g⁻¹ for Cd-polluted soils.

The BET specific surface area for control soil ranged from 26.8 to 38.7 m²g⁻¹ (Table 1) and there were no essential differences between the polluted soil samples and the control soil. The average values of specific surface area were 33.8 m²g⁻¹ and 31.7 m²g⁻¹ for soil-Cd and control soil, respectively. The highest values of specific surface area were observed for samples taken from layers 40–60 deep and contaminated with cadmium. The differences between the surface area of the control sample and soil polluted by heavy metals were rather low. That may be connected with a different factor, such as low concentration of metals in soil and heterogeneity of samples which were taken from the experimental plots.

The results of the mercury porosimetry measurements are given in Table 2. The samples were taken from the layers of 0–10 cm and 10–20 cm deep. The total intrusion volume (TV) was directly measured in a quantitative way, whereas the total pore area (TPA), average pore diameter (PD_{av}), and bulk density were calculated using the cylindrical pore model. The pore volume (TV) of investigated soil samples ranged from 411 mm³g⁻¹ to 515 mm³g⁻¹. Polluted soils exhibited also different values of TV for the upper and lower horizons. TV increased for the soil containing Cd. The changes in TP (total porosity) with depth were similar to those already observed for TV.

Table 2

Parameters of pore structure of the dark gray podzolic soil degraded by cadmium

No	Depth (cm)	TV (mm ³ g ⁻¹)	TPA (m ² g ⁻¹)	PD _{av} (nm)	D (g mL)	TP (%)
Soil + Cd 30 (mg kg ⁻¹)						
1	0–10	0.426	3.44	495.3	1.211	51.63
2	10–20	0.515	3.73	552.2	1.100	56.61
Control						
3	0–10	0.420	3.50	481.1	1.223	51.42
4	10–20	0.411	3.74	438.8	1.244	51.09

Abbreviations: TV – total intrusion volume, TPA – total pore area, PD_{av} – average pore diameter, D – bulk density, TP – total porosity

Generally, the samples of Cd-soil were characterized by high values of all investigated parameters, i.e. total volume of intruded mercury, pore volume, total porosity, average pore radius, and the amounts of storage and residual pores. It can be connected with the behavior of Cd in the environment. The influence of cadmium on the porosity of the dark gray podzolic soil

can be related to both the chemical nature of the metal and the properties of the soil. The results of mercury porosimetry from samples taken from the experimental plot were compared with those from samples prepared in the laboratory. The cumulative curves for the laboratory and plot samples are shown in the Figure.

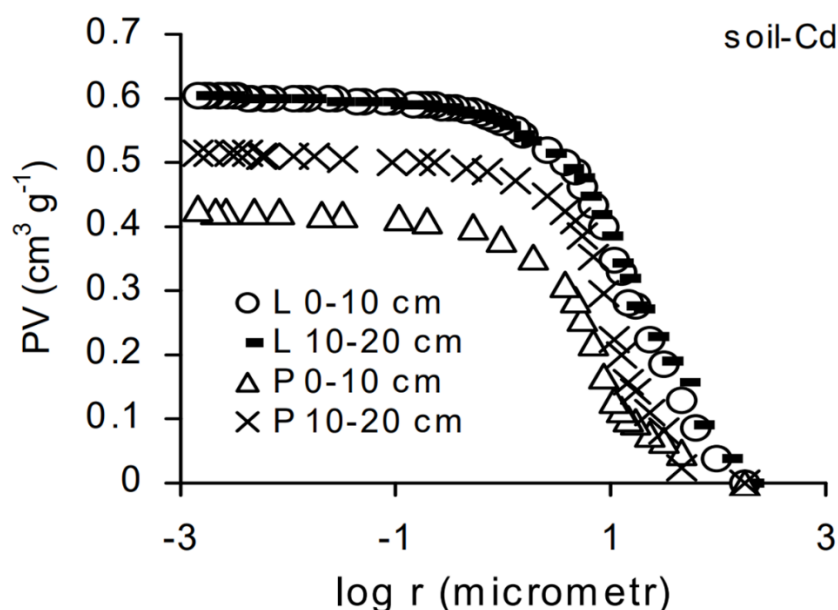


Fig. Cumulative curves for the dark gray podzolic soil polluted by cadmium (30 mg kg^{-1})
 Abbreviations: r – pore radius, PV – pore volume, L – samples prepared in the laboratory,
 P – samples taken from the experimental plot, 0–10 cm and 10–20 cm – depth

The difference between the PV of polluted soil samples prepared in the laboratory and those from the experimental plot is rather connected with the hetero-

geneity of the samples. The results of studies of cadmium content in selected levels of investigated soil are presented in Table 3.

Table 3

Cadmium content at selected depths of soil and for different initial doses of metal

Depth (cm)	Metal content (mg dm^{-3})			
	Control soil	Soil+dose of Cd (mg kg^{-1})		
		3	15	30
10	0.101	0.182	0.224	0.535
20	0.077	0.122	0.195	0.166
30	0.099	0.114	0.112	0.209

The results show that after two years of the experiment, the highest concentration of cadmium remained constantly in the shallowest soil layer, irrespective of the initial dose of cation. The highest dose ($30 \text{ mg Cd per kg of soil}$) was illuviated faster than smaller doses of cadmium (3 and $15 \text{ mg Cd per kg of soil}$). The control sample contained also a small amount of cadmium, but it was smaller in all layer levels than for the soils with metal. After two years of the experiment, the content of Cd at the depth of 30 cm and for initial doses of 3 and $15 \text{ mg Cd per kg of soil}$ was still similar to the control sample. Only soil samples with the highest concentration of Cd showed a higher content of Cd at the depth of 30 cm than the control sample at the same level.

The decrease of heavy metal content with depth is connected with the process of gradual migration and

illuviation to the soil profile. Similar contents of cadmium as for the control samples can be evidence of a weak rate of migration of small amounts of Cd (3 and 15 mg kg^{-1}). The highest doses of heavy metals migrate to the soil faster, and after the second year, a slightly higher content of cadmium can be observed at a depth of 30 cm . The presence of cadmium in soil can be influenced by the creation of less mobile and sparingly soluble organomineral forms of cadmium in the upper soil layers. This can result in small doses of cadmium remaining in the $0\text{--}20 \text{ cm}$ layer for longer periods of time. When large doses of metals are applied, a portion of them can become chemically bound, while the rest may move deeper into the soil. Consequently, higher levels of cadmium can be found at a depth of 30 cm .

Conclusions. The behavior of cadmium in soil and the different influences of cadmium on the basic characteristics of the dark gray podzolic soil can be connected with the chemical properties of this metal and the properties of the soil. The pore volume of investigated polluted soil ranged from 411 to 515 mm³ g⁻¹. The reaction of the soil samples was neutral. Within 0–20 cm layers significant differences between average values of pH (in H₂O) for polluted and control soils were detected only in the case of samples contaminated with 15 mg and 30 mg doses Cd (per 1 kg of soil). The soil samples were characterized by a low content of organic carbon fraction. Statistically significant differences ($P > 0.05$) between the average fraction of organic carbon in the whole soil profile (0–60 cm) occurred only for samples contaminated with 15 and 30 mg of Cd per 1 kg of soil. In the case of results obtained from mercury intrusion experiments, the Cd-polluted samples possessed higher values of all investigated parameters, i.e. the total intrusion volume of mercury, pore volume, total porosity, average pore radii, and amounts of storage and residual pores. The above-listed parameters varied with the soil horizon, but they did not essentially change with the dose of the applied pollutant. The highest level of cadmium was found at a depth of 0–20 cm regardless of the amount of cadmium applied. At a depth of 30 cm, the presence of cadmium was significantly lower for smaller doses, likely due to the formation of less mobile and sparingly soluble organomineral forms of cadmium in the upper layers of soil. The movement of cadmium forms in the soil can be an indication of the soil's ability to purify itself.

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