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Optimizing Electrodialytic Recovery of Mineral Ions from Bittern Wastewater Using D-Optimality Design

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Journal of Ecological Engineering 2023, 24(10), 198–204 https://doi.org/10.12911/22998993/170291 ISSN 2299–8993, License CC-BY 4.0

## Accumulation of Lead and Cadmium by Vegetables at Different Levels of Gray Forest Soil Moistening in the Conditions of the Right Bank Forest Steppe of Ukraine

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#### **ABSTRACT**

Providing a sufficient level of moisture while growing vegetables is the key to a high yield, its excessive or insufficient amount can lead to negative phenomena - disrupt the normal functioning of plants, deteriorate their chemical composition, etc. Every year, in certain areas of Ukraine, in particular, the Right Bank Forest Steppe, one can observe unevenness of the amount in precipitation (from a very low level to an abnormally high level in a short period of time). During heavy rainfall, the plant nutrition system is disrupted due to the movement of chemicals into deeper layers of the soil, which may become inaccessible to the root system of plants, thereby changing the quantitative and qualitative indicators of their production. The purpose and main direction of the research was aimed at studying the influence of different levels of gray forest soil moisture in the conditions of the Right Bank Forest Steppe of Ukraine on the content, accumulation coefficients and danger of lead (Pb) and cadmium (Cd) in the leaf mass of parsley, dill and spinach grown in the zone of man-made influence (from mobile sources of pollution). According to research results, it was established that vegetable plants (parsley, dill, spinach) can accumulate several times more Pb and Cd per unit mass compared to the content of these toxicants in the same mass of soil. At a high level of soil moisture (98-134 mm) during the formation of the leaf mass of vegetables, a lower content and coefficient of accumulation of Pb and Cd in the leaf mass of parsley, dill, and spinach was observed, compared to moderate soil moisture (30-37 mm). The results of the research indicate that when growing parsley, dill, and spinach on gray forest soils under man-made conditions with a high (98–134 mm) level of moisture during the formation of their leaf mass, a decrease in the content of Pb and Cd in the leaf mass of these plants is observed.

Keywords: parsley, dill, spinach, heavy metals, moisture, precipitation, soil, accumulation coefficient.

### **INTRODUCTION**

Vegetable growing is an important and, at the same time, complex plant-growing branch of Ukraine. Vegetable products are valuable and irreplaceable in the diet of the population, which is the reason for the introduction of their production all over the world. The industry includes a large number of vegetable crops, for which different growing technologies are defined, being diverse in terms of ripening, harvesting, storage and cost (Salo, 2021).

In human nutrition, green vegetables have always been and remain a popular component. Galat (2019) stated that the wide range of these products, as well as favorable natural and climatic conditions for their cultivation in Ukraine can provide for the needs of consumers almost in full at the expense of their own resources. In recent years, there has been a tendency to increase the area under green vegetables.

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Sarkar et al. (2022) reported that green leafy vegetables have extraordinary nutritional value

and can even be used for medicinal purposes. They are rich in minerals (iron, calcium, zinc) and vitamins (beta-carotene, vitamin E, K, B, C, etc.). Vidrih et al. (2009) believe that from the nutritional point of view, the most important components in vegetables are antioxidants and dietary fiber; the green vegetables appear to be a good source of  $\alpha$ -linolenic acid. Parsley, spinach and dill are well-known among the vegetables that are grown for obtaining green leafy mass with a short growing season. Their inherent precociousness makes it possible to sow green plants multiple times both in open and closed soil and to create a constant conveyor of fresh useful products.

Garden parsley is a popular vegetable crop. It has unique taste, nutritional, dietary and medicinal properties. It is characterized by a high content of minerals, vitamin C (ascorbic acid) and provitamin A (carotene) in the leaves. Essential oils give it a pleasant smell and taste, which also promote digestion (Poznyak, 2015). Punoševac et al. (2021) noted that the predominant compounds in parsley leaves are flavonoids, which are carriers of the plant's antioxidant and anti-inflammatory activity and which are 3 times more abundant compared to fruits and roots. Parsley is used in cooking, canning, pharmaceutical and perfume industries (Poznyak, 2015). As of March 2023, there are 30 varieties of garden parsley in Ukraine (Karakutsia, 2023).

Spinach is an early and easy to grow vegetable plant. It is included by specialists of many countries in the top ten most useful plants for humans. Juicy spinach leaves are rich in vitamins (A, B, C, E), minerals (Mg, K, Zn, Mg), as well as digestible Ca and Fe salts. Roberts and Moreaua (2016) investigated that spinachderived phytochemicals and biologically active substances are capable of scavenging reactive oxygen species and preventing macromolecular oxidative damage, modulating gene expression and activity, and restraining food intake by inducing the secretion of satiety hormones. Such biological actions, scientists believe, will contribute to the anti-cancer, anti-obesity, hypoglycemic and hypolipidemic properties of spinach (Roberts and Moreaua, 2016).

Vdovenko (2018) notes that the benefit of spinach is due to the approximation of its chlorophyll structure to the hemoglobin of human blood, so it should be used for blood diseases and people with low hemoglobin levels. Spinach leaves also contain a lot of coarse dietary fiber

and vegetable protein (more of it only in green peas and beans) (Melnyk et al., 2019). Such a rich composition makes it a valuable product of healthy nutrition, dietary and medicinal product. Also, spinach has a neutral taste, so it can be combined with various food products and widely used in cooking.

Dill is a plant that is resistant to cold (seedlings withstand frost) and sunstroke, precocious and generally undemanding. It is suitable for growing both in open and closed soil, with the possibility of repeated sowing. Dill is grown as a medicinal and spicy-tasty plant. Dill seeds and leaves contain up to 4-6% essential oil; vitamins; pectin substances; coumarins; flavonoids: rutin, quercetin; mineral substances (Lisiewska et al., 2006; Gupta et al., 2012; Singh et al., 2016).

Dill plants need fertile soil, the application of mineral and organic fertilizers has a positive effect on the productivity of dill, in particular, the vegetative weight, percentage of chlorophyll, percentage of dry matter, yield, etc. increases (Rostaei et al., 2018; Elsayed et al., 2020; Al-Dulaimy et al., 2022). Also, the plant needs moderate moistening of the soil (with a lack of moisture, dill begins to bloom, which leads to a decrease in the marketability of products). Setayesh-Mehr and Ganjeali (2013), when studying the effect of drought stress on the growth and physiological characteristics of dill, found that with increasing drought stress, the amount of chlorophyll, carotenoid, soluble proteins, vitamins K, P, and Ca decreases, and the amount of phenolic compounds in the shoot and roots, on the contrary, increases, which must be taken into account when growing dill.

The use of green parts of dill and seeds in food, as well as preparations made on its basis, strengthen the separation of secretions by digestive glands, the motility of the digestive tract, improve appetite, contribute to the normalization of metabolism in the body and in obesity, diseases of the liver, gall bladder, kidneys, antacid gastritis, flatulence, etc. (Duke, 2002; Masoody et al., 2023).

Considering the fact that green leafy vegetables are widely used in human nutrition and treatment, it is important that their products are of high quality and do not contain toxicants, in particular, heavy metals, the content of which in the environment is constantly increasing due to man-made activities of the population. Mining, chemical, metallurgical, agro-industrial,

transport, residential and communal and other complexes can be singled out among the most well-known sources of environmental pollution with heavy metals (Mir et al., 2021).

Agricultural activity, especially plant growing, creates a high burden on the environment. Use of mineral and organic fertilizers, polluted irrigation water, etc. is a source of entry of heavy metals into the soil, the ecological danger of plant products depends on the content of excess concentrations (Jalali et al., 2020; Razanov et al., 2020; Razanov et al., 2022a). Contamination of agricultural soils with heavy metals is one of the urgent environmental problems: soils lose their ability to self-clean, which leads to a significant accumulation of mobile forms of heavy metals, their accumulation by plants and migration through trophic food chains to the human body, creating a health hazard (Zaakour et al., 2022; Razanov et al., 2022b).

The accumulation of heavy metals by plants, in particular, vegetables, depends on a number of factors, one of which is the level of soil moisture (Razanov et al., 2023). It is known that efficient use of water is an important component of sustainable vegetable production. Applying the right amount of water helps to maximize yield, improve product quality, and reduce the risk of nutrient leaching from the root zone (Schattman et al., 2023).

Recently, various adverse anomalous weather phenomena have been observed in Ukraine, in particular, changes in the precipitation regime, which in certain periods can be abnormally high (exceed the norm by several times), which can negatively affect the condition of the soil and the quality of crop production (Zubov, 2020). Under such conditions, there is a need to study the impact of precipitation on the translocation of heavy metals in vegetables, especially under the conditions of man-made load.

Thus, the goal of the conducted research was to study the concentration and coefficients of accumulation and danger of Pb and Cd in the leaf mass of parsley, dill, and spinach under moderately and abnormally high soil moisture rates under the conditions of constant exposure to mobile sources of pollution.

MATERIALS AND METHODS

Research on the intensity of accumulation of Pb and Cd by vegetable plants was carried out under the conditions of the Forest Steppe of the Right Bank of Ukraine on gray forest soils in the zone of man-made influence of motor vehicles. Leaf mass of green leafy vegetables was used in the research: parsley – variety Naida, dill – variety Atlant, spinach – variety Peremozhets (varieties of Ukrainian selection, recommended for use in the conditions of the Forest Steppe of Ukraine). The study of the accumulation of Pb and Cd by vegetables at different levels of soil moisture was carried out according to the research scheme (Table 1).

Each crop was sown in four replicates in both the experimental and control variants for two years. To moisten the soil, artificial irrigation (sprinkling) was used during the formation of the leafy mass of vegetables. The amount of water that entered the soil during artificial moistening (raining) was monitored using a rain gauge.

The coefficient of accumulation of Pb and Cd in the leaf mass was determined by the ratio of the content of the toxicant in vegetables to its content in the soil. The hazard ratio of Pb and Cd in the leaf mass was determined by the ratio of the content of the toxicant in vegetables to the maximum permissible concentration (MPC). The concentration of Pb and Cd in the leaf mass was determined by using the atomic absorption method.

The research was conducted under the conditions of man-made influence of mobile sources of environmental pollution within a 300-meter zone from the highway. The content of Pb in the soils of the 300-meter zone was 1.72-1.84 mg/kg, Cd -0.08-0.12 mg/kg.

#### RESULTS AND DISCUSSION

The use of agricultural soils in the zone of man-made load can cause a decrease in the quality and safety of plant raw materials. The research

Table 1. Scheme of research

Product	Research period	Soil moisture level, mm	Research indicators	
Leaf mass of parsley Leaf mass of dill Leaf mass of spinach	2021	108-134	Content.	
	2021	30-37	accumulation factor, danger	
	2022	98-118	factor of Pb and Cd in leaf	
		30-31	mass	

Product	Research period	Soil moisture level, mm	Pb	MPC	Cd	MPC
Leaf mass of parsley	2021	134	0.62 ± 0.042	0.5	0.053 ± 0.002	0.03
	2021	37	0.77 ± 0.037	0.5	0.071 ± 0.003	0.03
	2022	112	0.57 ± 0.041	0.5	0.051 ± 0.004	0.03
	2022	31	0.58 ± 0.027	0.5	0.067 ± 0.004	0.03
Leaf mass of dill	2021	108	0.71 ± 0.012	0.5	0.058 ± 0.001	0.03
	2021	30	0.84 ± 0.030	0.5	0.082 ± 0.002	0.03
	2022	118	0.68 ± 0.040	0.5	0.057 ± 0.004	0.03
	2022.	34	0.86 ± 0.034	0.5	0.084 ± 0.001	0.03
Leaf mass of spinach	2021	122	0.64 ± 0.052	0.5	0.054 ± 0.001	0.03
	2021	37	0.78 ± 0.047	0.5	0.077 ± 0.002	0.03
	2022	98	0.67 ± 0.031	0.5	0.066 ± 0.003	0.03
	2022	30	0.81 ± 0.030	0.5	0.080 ± 0.001	0.03

Table 2. Concentration of heavy metals in vegetable products, mg/kg

results (Table 2) showed that during the cultivation of vegetable crops (parsley, dill, spinach) under the influence of mobile sources on polluted soils, an excess of the maximum permissible concentrations was observed: Pb (MPC = 0.5 mg/kg), Cd (MPC = 0.03 mg/kg).

The research results showed that the concentration of Pb was higher than the maximum permissible levels (on average over two years of research at high and moderate levels of soil moisture) in the leaf mass of parsley by 19.0% and 35.0%, dill by 39.0% and 70.0% and spinach – by 31.0% and 59.0%, respectively. The concentration of Cd at a high and moderate level of soil moisture with the content of this toxicant in them from 0.08 mg/kg to 0.12 mg/kg was higher on average for two years of research than the maximum permissible levels by 73.3% and 2, respectively. 3

times in the leaf mass of parsley, by 91.6% and 2.7 times in the leaf mass of dill as well as 2.0 times and 2.6 times in the leaf mass of spinach.

It is known that the level of soil moisture to one degree or another affects the nutrition of plants and the accumulation of chemicals in them. According to the results of the conducted research, it was established that at an extremely high level of soil moisture (created artificially as a result of irrigation), a decrease in Pb and Cd was observed in the leaf mass of the studied vegetable plants.

Thus, at a high level of soil moisture (98-134 mm) during the period of vegetative mass formation, a decrease in the concentration of Pb and Cd in parsley was found – by 11.8% and 24.6%, dill – by 18.2% and 29.7% and spinach – by 17.6% and 23.5%, respectively, compared to moderate moisture (30–37 mm).

Product perio	Research	Pb			Cd		
	period, year	Content in soil, mg/kg	Content in leaf mass, mg/kg	Coefficient of accumulation	Content in soil, mg/kg	Content in leaf mass, mg/kg	Coefficient of accumulation
Leaf mass of parsley 2022	2021	1.77 ± 0.2	0.62 ± 0.042	0.35 ± 0.034	0.09 ±0.004	0.053 ± 0.002	0.58 ± 0.047
	2021	1.79 ±0.31	0.77 ± 0.037	0.43 ± 0.021	0.08 ±0.003	0.071 ±0.003	0.88 ± 0.053
	2022	1.76 ±0.3	0.57 ± 0.041	0.32 ± 0.011	0.09 ±0.001	0.051 ±0.004	0.56 ± 0.07
	2022	1.78 ±0.17	0.68 ± 0.027	0.38 ± 0.041	0.11 ±0.004	0.067 ±0.004	0.61 ± 0.037
Leaf mass 20 of dill 20	2021	1.74 ±0.14	0.71 ± 0.012	$0.40 \pm 0.032$	0.011 ± 0.001	0.058 ±0.001	0.52 ± 0,07
	2021	1.73 ±0.20	0.84 ± 0.03	$0.48 \pm 0.031$	0.10 ±0.002	0.082 ±0.002	0.82 ± 0.08
	2022	1.79 ±0.31	0.68 ± 0.04	0.40 ± 0.022	0.09 ±0.004	0.057±0.004	0.63 ± 0.07
	2022	1.81 ±0.41	0.86 ± 0.034	0.47 ± 0.031	0.09 ±0.004	0.084 ±0.001	0.93 ± 0.005
Leaf mass of spinach	2021	1.72 ±0.31	0.64±0.052	0.37 ± 0.027	0.11 ±0.003	0.054 ±0.001	0.49 ± 0.04
	2021	1.74 ±0.20	0.78±0.047	0.45 ± 0.028	0.12 ±0.003	0.077 ±0.002	0.64 ± 0.03
	2022	1.82 ±0.14	0.67±0.031	0.37 ± 0.027	0.10 ±0.004	0.066 ±0.003	0.6 6± 0.06
	2022	1.84 ±0.14	0.81±0.03	0.44±0.017	0.11 ±0.002	0.080 ±0.001	0.61 ± 0.037

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Product	Research period, year	PI			Cd		
		Actual concentration	MPC	Hazard ratio	Actual concentration	MPC	Hazard ratio
Leaf mass of parsley	2021	0.62 ± 0.042	0.5	1.24 ± 0.43	0.053 ± 0.02	0.03	1.76 ± 0.09
	2022	0.077 ± 0.037	0.5	1.54 ± 0.11	0.071 ± 0.003	0.03	2.36 ± 0.82
	2021	0.57 ± 0.041	0.5	1.14 ± 0.49	0.051 ± 0.004	0.03	1.70 ± 0.31
	2022	0.68 ± 0.027	0.5	1.36 ± 0.73	0.067 ± 0.001	0.03	2.23 ± 0.49
Leaf mass of dill	2021	0.71 ± 0.012	0.5	1.42 ± 0.67	0.058 ± 0.001	0.03	1.93 ± 0.68
	2022	0.84 ± 0.03	0.5	1.68 ± 0.54	0.082 ± 0.002	0.03	2.73 ± 0.87
	2021	0.68 ± 0.04	0.5	1.36 ± 0.42	0.057 ± 0.004	0.03	1.90 ± 0.49
	2022	0.86 ± 0.034	0.5	1.72 ± 0.44	0.084 ± 0.001	0.03	2.80 ± 0.76
Leaf mass of spinach	2021	0.64 ± 0.052	0.5	1.28 ± 0.65	0.054 ± 0.001	0.03	2.80 ± 0.09
	2022	0.78 ± 0.047	0.5	1.56 ± 0.81	0.077 ± 0.002	0.03	2.56 ± 0.42
	2021	0.67 ± 0.031	0.5	1.34 ± 0.47	0.066 ± 0.003	0.03	2.20 ± 0.74
	2022	0.81 ± 0.030	0.5	1.62 ± 0.47	0.080 ± 0.001	0.03	2.60 ± 0.52

**Table 4.** The hazard ratio of heavy metals in vegetable products

While analyzing the coefficient of accumulation of heavy metals in the leaf mass (Table 3), it should be noted that at a high level of soil moisture, a lower level of heavy metal accumulation was observed, compared to moderate moisture. Thus, at a high level of soil moisture, the coefficient of accumulation of Pb and Cd, obtained in the second year of research, was lower in the leaf mass of parsley by 17.5% and 22.9%; in the leaf mass of dill – by 14.9% and 34.4% and in the leaf mass of spinach – by 15.9% and 16.1%, compared to the low level of moisture.

According to the results of the research (table 4), it was established that when growing parsley, dill and spinach on soils with a content of Pb (1.72–1.8 mg/kg) and Cd (0.053–0.084 mg/kg), the threshold level exceeded hazard ratio (1.0) in the leaf mass of these plants. Thus, the Pb hazard ratio at a high level of soil moisture in the leaf mass of parsley was 1.19 and 1.45 times higher than the threshold level; in the leaf mass of dill – by 1.39 and 1.7 times, in the leaf mass of spinach – by 1.3 and 1.59 times. A similar trend of exceeding the threshold level of the hazard ratio was also observed for Cd.

While analyzing the data in Table 4, changes in the hazard ratio of Pb and Cd in the leaf mass of parsley, dill, and spinach were also found, depending on the high and moderate level of soil moisture. Thus, at a high level of soil moisture, the hazard ratio of Pb and Cd was lower, respectively, by 17.9% and 24.4% in parsley, by 18.2% and 30% in dill, and by 17.6% and 3.1% in in spinach, compared to low soil moisture.

#### **CONCLUSIONS**

It was established that the cultivation of parsley of the Naida variety, dill of the Atlant variety and spinach of the Peremozhets variety in the 300-meter zone of influence of road transport on gray forest soils with the content of Pb (1.72– 1.84 mg/kg), Cd (0.08–0.012 mg/kg) an excess of the maximum permissible concentrations of these toxicants was observed, which are 0.5 mg/ kg for Pb and 0.03 mg/kg for Cd in the leaf mass of these vegetables, both at moderate and high levels of moisture soils. Lower level of Pb and Cd concentrations in the leaf mass of parsley by 11.8% and 24.6%, dill – by 18.2% and 29.7%, spinach - by 17.6% and 23.5% was revealed at the ultra-high level soil moisture (98–134 mm), compared to moderate (30–37 mm).

For the cultivation of parsley, dill, and spinach under the conditions of man-made stress, it is necessary to take into account the high ability of these vegetables to accumulate Pb and Cd and the influence of the level of soil moisture to predict the entry of these toxicants into their leaf mass.

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