ЕКОЛОГІЯ

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MIGRATION OF TOXIC METALS FROM VEGETABLE WASTE IN COMPOST

The article presents the results of studies of the heavy metals transformation from the raw plant materials (dry leaf, lawn grass, vegetable wastes) in the process of composting using the Californian worm. It is known that in cities during the growing season, a large number of fallen leaves is accumulated. It is a valuable raw material for fuel production; it is an excellent thermal insulator, it is considered to be a good mulch and can be recycled. We have developed a humus technology based on vegetable waste (fallen leaves) with the help of a Californian worm. Before composting, the concentration of heavy metals (lead, cadmium, copper and zinc) was determined in foliage collected from the streets of Vinnitsa. Analyzes showed that the background of these metals in plant waste did not exceed the maximum permissible norms. It has been experimentally proved that composting involves the conversion of heavy metals from fallen leaves to the body of the Californian worm and removing them as insoluble components in the lower compass. In addition, it has been experimentally established that during the composting period various heavy metals showed uneven migration and transformation in a soluble form. The most active was adsorption and removal of zinc compost. It was found that humic water-soluble compounds convert more than 78% of the total zinc that was contained in the composted substrate. The least mobile compound was lead. However, even such a metal, as lead, during 150 days of composting by the California worm, turned into 40% soluble form and migrated to the lower layers of humic liquids. Thus, the processing of vegetable waste from cities (fallen leaves, lawn grass, garbage disposal, etc.) by composting using growing worms will not only solve the social problem of utilization, but will also contribute to increasing environmental safety and economic efficiency.

Key words: heavy metals, transformation, California worms, compost, vegetable waste, utilization.

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Introduction. The problem of utilization of plant waste today is acutely concerned by the municipal services of many cities in the world [1, 15]. Dry leaves, waste from green farms, greenery businesses, accumulate in garbage, and dump gases or burn. The ecological consequences of the inefficient disposal of such waste are obvious: littering the territories of cities, increasing the use of raw materials, pollution of soil and air by toxic products of combustion and heavy metals. In particular, when burning one ton of plant residues in air, up to 9 kg of micro particles of smoke is discharged into the air. These include dust, nitrogen oxides, carbon monoxide, heavy metals and a number of carcinogenic compounds, as well as dioxin and dioxin – one of the most toxic substances for humans. Getting into the human body, they suppress the immune system, destroy hormones and vitamins, and create favorable conditions for the formation of malignant neoplasms. Particularly dangerous the autumn burning of smoke leaves for children with a sensitive immune system, elderly people with cardiovascular, allergic diseases and respiratory problems, especially asthmatics [11].

Studies show that in areas where burning dry leaves in the last 20 years, soil fertility has decreased by 4 times. In addition, with dry leaves, we destroy biological enemies of aphids and other pests of trees. However, larvae of pests remain in the cortex until a new vegetation of trees emerges [13].

In addition, it is noted that in most cases, autumn leaves very can quickly become a mixture of leaves and various household rubbish, which during the winter actively accumulate, mixing with leaves and creating a favorable place for rats and dangerous infections, which they spread. As for the methods of using fallen leaves, the views of ecologists can diverge. Some people are advised to leave leaves in parks at all to rot and feed the soil; others suggest collecting in special compost pits, although in this case, heavy metals will still remain in the soil [9].

Analysis of recent publications. According to the definitions of the data of the Law of Ukraine "On Waste", household waste is waste that is formed during the life and activity of man in residential and non-residential buildings (solid, large-sized, repair, liquid, in addition to waste associated with the production activities of enterprises), and not used at the place of their accumulation; solid waste - residues of substances, materials, objects, products that cannot be used for future purposes, such as food, household goods, packaging materials [16]. Dry leaves, branches, weeds are not the part of household waste and are not the subject for collection, storage, removal and burial with household waste. Therefore, utilization of vegetable waste has its own specifics.

Foreign experience shows that leaves and trees that lean from the lawn can be left on the soil for natural biofermentation. For example, treatment of fallen leaves in the USA. Polish experience shows that the most effective is the collection and evacuation of plant waste to landfills and composting in the city in composters. In Germany, for example, from dry leaves the briquettes for biofuelsare produced, which is three times cheaper than methane. In the UK, they have learned how to produce environmentally friendly fuel based on dry fallen leaves and wax [2, 9, 14, 17].

The first experience of environmentally friendly recycling of plant waste is in separate cities of Ukraine. In particular, in 2007, a "Program for the recycling of vegetable waste" was developed in Kyiv. Now in all districts of the capital, only one method of "struggle" with leaves - composting is distributed. The significance of compost contains the chemical compounds required for plants. For composting the leaves are in a heap width of 2 meters and a height of 1,7 m, the basis of this mass is enclosed almost 25 centimeters of soil layer. All subsequent layers of leaves should not exceed 30 cm. They are sprinkled with earth and, at certain intervals, are pushed. Compost is considered to be ready if it has turned into a homogeneous dark lump mass [3, 5].

The Dnieper authorities offered their idea of solving the problem of fallen leaves: squeeze to briquettes and use them to heat the premises. In Cherkassy people start to process leaves on briquettes [4]. A similar program operates in Ivano-Frankovsk [8]. To do this, special containers have been installed in urban parks, in which organic rubbish turns into fertilizer. Now, leaves, flowers, remains of food and other organic waste in Cherkassy parks do not need to be burned or taken to the landfill. All organic waste is sent to special containers in which they are converted into organic fertilizers. A year later, this fertilizer is planned to be used for plant nutrition in parks and squares [10].

The "test" compost appeared in StryiPark in Lvov, 18, where the site for collecting large and small waste is located. The Lvov Communal Enterprise «Lviv-spec-communtrans» has installed three-section compost for use in farms. The created reservoir must be completely filled with leaves. And to accelerate the processes of decomposition of compost add a preparation of effective microorganisms [6].

Consequently, the basis for the effective utilization of waste of Ukrainian cities, both legislative and technical, is laid. However, some ecological aspects of the processing of fallen leaves remain unexplored. First of all it concerns the conversion of heavy metals. Therefore, the **purpose** of our research was to determine how the concentration of individual minerals for the processing of fallen leaves on compost with the use of the California worm changes. To do this we set the **task**: to study the chemical composition of fallen leaves and the content of heavy metals in it, to compost with breeding of worms, to study the dynamics of the concentration of heavy metals in the finished compost, compare the obtained data with the compost characteristics of different species.

Materials and methods of research. The experimental part of the work was carried out at the laboratory of the animal feeding and water biological resources department of VinnitsaNationalAgrarianUniversity. Samples of plant waste (fallen leaves) were selected for experiment from different sites. They were crushed, dampened to 60-80% moisture, mixed with sand and soil in a ratio of 3:1:2. The mixture contains with breeding of worms in the amount of 10 pieces per 1 kg. Composting was carried out for 150 days. The subject of the study was compost, obtained for utilization of plant waste, and object - the content and transformation of heavy metals. The chemical composition and properties of the material were carried out at the ZNPP of Soil Productivity of NAAS of Ukraine (village Agronomic Vinnitsa district of Vinnitsa region). In the samples, the lead, cadmium, copper, zinc and manganese content were determined according to the current standard (GOST 7670: 2014).

The digital material was processed statistically for N. A. Plohinsky (1969). The resulting digital data was processed using the MS EXEL 98 and Windows program, statistically processed by Student.

The results were considered statistically significant at p <0.05, p <0.01, p <0.001. In the table material of the work the following symbols are taken: * p <0.05, ** p <0.01, *** p <0.001.

Research results. Conditional for a group of heavy metals are metals with a specific gravity of more than 4.5 g/cm^3. It is lead, cadmium, mercury, chromium, copper. Metals, and among them heavy metals are widespread in nature, where they are usually in the form of ores, less often - elements. Metals in the form of pure elements, most likely, do not determine the toxic effect, since they are practically insoluble. The exception is volatile metals, for example, the evaporation of mercury, which can penetrate the body through the respiratory apparatus or skin. Toxic properties detect metal compounds that are readily soluble and strongly dissociate. Dissolution and dissociation facilitate the penetration of toxins through the tissue into the body [11].

Like dioxins, which will be discussed below, almost 70 % of toxic metals enters the body along with food. Today, foodstuffs are the subject of intensive international trade, the FAO (Food Organization) and the World Health Organization's Food Code (Codex Alimentarius) have incorporated some heavy metals into the food component. They are under control in international trade. These are the eight most dangerous toxic elements: mercury, cadmium, lead, arsenic, copper, tin, zinc, iron. In Russia, they added seven more: antimony, nickel, chromium, aluminum, selenium, fluorine, iodine (although the last three are not metal at all) [16].

The values of concentrations in excess of the background indicate pollution of the environment. The main source of environmental pollution of heavy metals are various industries. Consequently, the chemical industry (the production of dyes, plant protection products, plastics, dyes) is a source of contamination of arsenic, barium, cadmium, chromium, copper, iron, mercury [11, 14].

Lead, selenium, strontium, tin, titanium, zinc produce various types of industry in the environment. For example, the pulp and paper industry supplies the environment with such metals as chrome, copper, mercury, nickel, lead; electrochemical industry - cadmium, cobalt, chromium, copper, mercury, molybdenum, nickel, selenium, titanium, vanadium, tungsten, zinc; metallurgy industry - iron, cadmium, chromium, copper, mercury, nickel, lead, zinc; ceramic industry - chrome, nickel, copper, cobalt, lead, strontium. Significant sources of heavy metals are power stations and thermal power plants. In the latter case, the complex of heavy metals entering the environment with sewage, with the release of gases and dust, with solid waste, to a large extent depends on the type of processed fuel, coal, oil, gas [12].

In cities, the sources of heavy metals are industrial enterprises and transport. Accumulation of heavy metals on the streets of cities is carried out by air, water, soil and vegetation. For example, the background in the soil of lead is 20,0-40,0, copper - 5,0-15,0, cadmium - 0,05 - 0,7, and zinc - 10,0-125,0 mg/kg depending on the type of soil. Our experiments studied the accumulation of some heavy metals in plant waste (dry leaf, grass of other plant waste) in the city of Vinnitsa. The results of these studies are shown in Table 1. As shown by the results of studies on the background of heavy metals in the investigated substrate did not exceed the maximum allowable standards.

Table 1 – **The content of heavy metals in vegetable waste**, mg / kg *(M±m, n=3)*

№ п/п	Indicator	Concentration in recalculation:	
		on a completely dry substance	on natural matter
1	Pb	2,37 ± 0,07	1,48 ± 0,03
2	Cd	0,45 ± 0,02	0,07 ± 0,02
3	Cu	4,34 ± 0,27	2,17 ± 0,12
4	Zn	81,38 ± 0,57	40,70 ± 0,29

One of the types of organic waste utilization of plants is composting. It is known that heavy metals in water, soil and plant residues are in various forms and have different physical and chemical properties. For example, pollution in the form of heavy metals in the aqueous medium serves as solutions, colloids and suspensions. In dissolved form, free ions of hydrate, simple inorganic and organic complexes operate. The diameter of these forms does not exceed 0.001 mg. The ions of metals associated with the complex, a multitude of molecular organic legends’ having a particle size in the range of 0.001-0.01 mg, form colloidal forms. Ions of metals are adsorbed on particles of colloidal micelle or organic particles in the size of 0.01-0.1 mg in the form of suspensions. Sedimentation suspensions are part of the precipitate. The forms of the existence of heavy metals in the aquatic environment depend on the physical and chemical equilibrium, among which the following should be distinguished: reaction formation of complexes, hydrolysis reaction, oxidation and reduction reaction and adsorption and desorption processes, displacement and dissolution reactions. [11].

There are two types of heavy metals in the soil: lithogenic, that is, associated with the material of the parent rock, anthropogenic, that is, those that enter the soil as a result of human activity. In the second case, the adsorption properties of the soil are very significant. They are due to its specific structure: it contains micelles of mineral or organic colloids and soil solution. Soil colloids usually have a negative charge, which facilitates the exchange adsorption of deposition of heavy metal ions from the soil solution to the diffusion layer of the micelle. The adsorption properties of the micelle depend on both the type and the structure of the colloid, and the nature of the cation. The greatest adsorption capacity, which is determined by the so-called adsorption capacity, is characterized by organic colloids. Therefore, for the composting of fallen leaves and other vegetable household wastes, it is necessary to control the contamination of components of the compost mixture with the content of heavy metals. According to our studies, the conversion of heavy metals into compost depended on the composting period and the type of heavy metal (Fig. 1, 2).

Thus, the content of lead in compost with a significant difference decreased after 4 months of composting (the difference was 0.23 mg/kg,). In the 5 months of composting, the pig's level in the mixture increased to 0.94 kg/kg. In our opinion, due to the formation of colloidal micelles and the loss of insoluble forms in the lower layers of the mixture (Fig. 1).

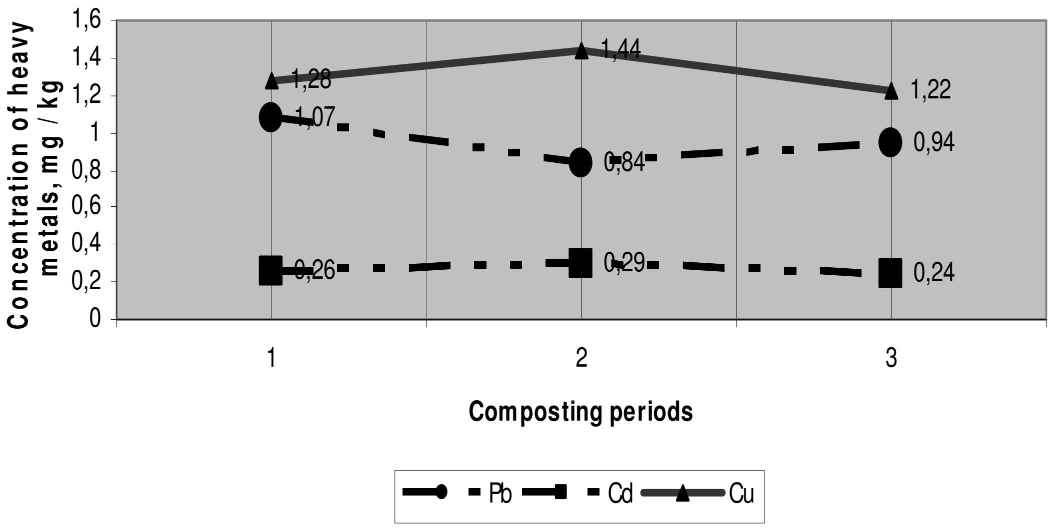

Figure 1. **Concentration of lead, cadmium and copper in compost in different periods, mg / kg 1kg of absolutely dry mass** (1 to 100 days of composting, 2 to 120 days of composting, 3 to 150 days of composting).

Another was the picture of the migration of cadmium, copper and zinc. These heavy metals accumulated in the compost mass up to 120 days. The difference between copper content in the substrate in 3 months composting and 4 months was 0.16 mg / kg ($p < 0.01$). At the end of composting, the content of cadmium and copper in the substrate was lower compared to the initial level. However, we found that zinc content in the finished compost was greater than in the control sample (Figure 2).

Salt of manganese in the composting of fallen leaves turns gradually into a soluble state. Thus, compared with the initial state of compost for 120 days, the level of manganese has decreased by 0,71 times, and in the finished compost - by 0,66 times.

Migration of heavy metals into compost is determined by adsorption and precipitation of their constituent substrates. We calculated that the largest conversion of heavy metals into the soluble state is 78.37% zinc and copper (71.89%) (Table 2).

Discussion. The use of fallen leaves as raw material for compost has been known since ancient times. To this day, gardeners use tips for recycling vegetable waste. You can use fallen leaves as a heat-insulating material, mulching material, filler for bulk beds. As fertilizer, it is recommended to use vegetable waste when eating fruit trees. In addition, leaf foliage can be released in composting wells with soil, water and lime, or simply left in special fermentation bags [1, 4, 9]. However, are heavy metals disinfected after composting such waste?

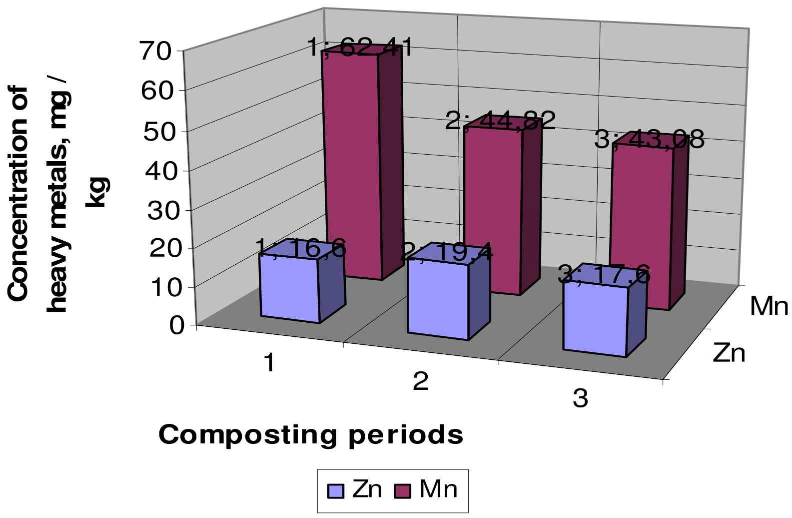

Figure 2. **Concentration of zinc and manganese in compost at different periods, mg / kg 1 kg of absolutely dry mass** (1 - 100 days of composting, 2-120 days of composting, 3-150 days of composting)

Table 2 – **Transformation of heavy metals during the composting of plant wastes using Californian worms** *(M±m, n=3)*

№ п/п	Indicator	Number of transformed into soluble state of metals, mg / kg		Conversion rate of heavy metals,% (to the original content in vegetable waste)
		in dry matter	in the natural substance	
1	Pb	1,43 ± 0,03	0,69 ± 0,03	60,34
2	Cd	0,21 ± 0,01	0,10 ± 0,003	46,67
3	Cu	3,12 ± 0,09	1,51 ± 0,01	71,89
4	Zn	63,78 ± 2,65	30,86 ± 0,89	78,37

Our studies have shown that waste from the city (fallen leaves, vegetable waste, garden waste, etc.) contain heavy metals: lead, cadmium, copper and zinc within acceptable limits. The prohibition of combustion of such wastes on the territory of Ukraine contributed to the reduction of migration in the form of oxides in the air of heavy metals. Therefore, the search for ecological methods of utilization of vegetable waste is urgent. We proposed a biological method for utilizing plant waste using composting using the Californian worm. As a result of semi-annual composting, there is a mixture of fallen leaves with moist soil and sand, which translates a part of heavy metals into a soluble state. It was found that the most mobile were such metals as copper and zinc. An explanation for this can be found in the reports of scientists on the high adsorption capacity of humic acids and fulvic acids [12, 14, 16]. According to scientists, their adsorption capacity is, respectively, 200-300 and 400-500 mill equivalents per 100 g substrate.

The specificity of the conversion of heavy metals from vegetable waste during composting to the substrate is their physical and chemical properties. Therefore, they differed in the level of migration, the transition to a soluble state and differently derived from compost with humic fluid.

Conclusions. Vegetable waste of cities (dry leaves, lawn grasses, waste of landscape firms) is an excellent source for composting, but heavy metals accumulate. It was established that lead, cadmium, copper and zinc in waste products of vegetable origin in the city of Vinnitsa did not exceed norms.

With the use of the progressive method of composting the dry leaf with the aid of the California worm, heterogeneous migration of heavy metals was observed. It was found that compared to leaves the compost contained 78% less zinc, 71% less copper, 60% lead and 47% cadmium.

In the future, our research will focus on the development of optimal waste recycling technology and the development of technological solutions for the use of products for the processing of fallen leaves for greenhouses, boiler houses, public institutions.

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Трансформація важких металів у рослинних відходах міста при вермикомпостуванні

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У статті подано результати досліджень трансформації важких металів у рослинних побутових відходах (опалому листі) в процесі компостування за допомогою каліфорнійського черв'яка. Відомо, що в містах за вегетаційний період накопичується велика кількість опалого листя. Воно є цінною сировиною для виробництва палива, чудовим тепловим ізолятором, добрим сидератом та може підлягати вторинній переробці. Нами була розроблена технологія виробництва гумусу на основі рослинних побутових відходів (опале листя) за допомогою каліфорнійського черв'яка. Перед компостуванням визначали концентрацію важких металів (свинцю, кадмію, міді та цинку) в зібраному з вулиць міста Вінниця листі. Аналізи показали, що фон цих металів у рослинних відходах не перевищував гранично допустимі норми. Експериментально доведено, що за компостування відбувається трансформація важких металів з опалого листя у тіло каліфорнійського черв'яка та виведення їх у вигляді нерозчинних компонентів у нижчих шарах ложа компостера. За періодами компостування різні важкі метали трансформувалися та мігрували по-різному. Про це свідчать результати вивчення вмісту свинцю, кадмію, міді, цинку та марганцю на початку ферментації, після 100, 120 та 150 діб компостування. Достовірне зниження вмісту свинцю в компості на 0,23 мг/кг у субстраті було виявлено на 120-у добу компостування. Наприкінці біоферментації в компості рівень кадмію, міді та марганцю знизився відповідно на 8,5 та 31 %. Крім того, експериментально установлено, що за період компостування різні важкі метали проявляли неоднакову міграційну здатність та трансформацію у розчинні форми. Найбільш активно проходила адсорбція та виведення з компосту цинку. Встановлено, що в гумінові розчинні у воді сполуки трансформувалося більше 78 % усього цинку, який містився в компостованому субстраті. Найменш мобільними виявилися сполуки свинцю. Проте навіть такий метал як свинець, за 150 діб компостування за допомогою каліфорнійського черв'яка, на 40 % переходив у розчинну форму та мігрував у нижні шари ложа з гуміновими рідинами. Тому вторинна переробка рослинних відходів міст (опалого листя, газонної трави, відходів садово-паркового господарства тощо) шляхом компостування з використанням вермікультури дозволить не тільки вирішити соціальну проблему утилізації, але й сприятиме підвищенню екологічної безпеки та економічної ефективності.

Ключові слова: важкі метали, трансформація, каліфорнійські черв'яки, компост, рослинні відходи, компостування.

Трансформация тяжелых металлов в растительных отходах города при вермикомпостировании

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В статье представлены результаты исследований трансформации тяжелых металлов из растительных отходов города (опалые листья) в процессе компостирования при помощи калифорнийского червяка. Известно, что растительные отходы являются ценным сырьем для производства топлива, служат хорошим теплоизолятором, прекрасным сидерантом и могут вторично перерабатываться. Нами была разработана технология производства гумуса на основе растительных отходов города с использованием вермикультуры (разведения калифорнийского червяка). Перед компостированием определяли концентрацию тяжелых металлов (свинца, кадмия, меди и цинка) в собранной с улиц города Винница листве. Анализы показали, что фон этих металлов в растительных отходах не превышал предельно допустимые нормы. Экспериментально установлено, что при компостировании происходит трансформация тяжелых металлов из растительных отходов с последующим выведением в нижние слои ложа в виде растворимых соединений. Кроме того, выявлено, что за период компостирования разные тяжелые металлы проявляли неодинаковую миграцию и трансформацию в растворимые формы. Наиболее активно проходила адсорбция и выведение из компоста цинка. Установлено, что в гуминовые растворимые в воде соединения трансформировалось более 78 % всего цинка, который содержался в компостированном субстрате. Наименее мобильными оказались соединения свинца. Однако даже такой тяжелый метал как свинец, за 150 суток компостирования с использованием калифорнийского червяка, на 40 % перешел в растворимую форму и мигрировал с гуминовой жидкостью. Поэтому вторичная переработка растительных отходов города (опавших листьев, газонной травы, отходов садово-парковой деятельности и др.) путем компостирования с использованием калифорнийского червяка может не только решить социальную проблему утилизации, но и способствовать повышению экологической безопасности и экономической эффективности.

Ключевые слова: тяжелые металлы, трансформация, калифорнийские червяки, компост, растительные отходы города.

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