Загальна екологія та радіоекологія

УДК 631.4:502.7:577.4

Yu. A. Bilyavskyj
Cand. of Agr. Sc.
T. M. Myslyva
Cand. of Agr. Sc.
Zhytomyr National Agroecological University

HEAVY METALS IN SOILS OF 20-KILOMETRE SUBURBAN ZONE OF ZHYTOMYR

The level of maintenance of heavy metals in soils on the territory of rural settlements of the 20-km suburban zone of Zhytomyr has been investigated. It has been established that the principal pollutants of soil are fixed forms of copper (coefficient of concentration K_p = 1,6–6,1), lead (K_p = 5,8–20,1) and zinc (K_p = 17,0–73,0) .

Key words: *soil, heavy metals, contaminations, fixed forms, gross forms, coefficient of concentration, total index of contamination.*

A problem statement

Because of unsuccessful land reform and practical elimination of large collective agricultural enterprises and replacing of them by shallow farmer economies, the problem of soil contamination in rural locality has sharpened. It is related to the fact that as a rule the specialists on ecologically safe and scientifically grounded application of pesticides and agrochemicals are absent in farmer economies, that results in contamination of soils and water sources of rural territories [10, 13]. Taking into consideration that the state kept oneself aloof from the control after the use of land in private sector and that the monitoring supervisions on the state of soils within the limits of rural territories are not practically conducted, the ecological problems will be urgent here in future, that is why researches of causes and effects of their display are actual.

The analysis of recent publications

The heavy metals and their connections are characterized with considerable stability, high toxic properties, expressed cumulative properties and negative influence on man's health and acquire the most priority value among the numerous anthropogenic pollutants of biosphere [3, 5, 8]. Soils are the natural stores of heavy metals in the environment and the basic source of contamination of contiguous environments, including higher plants. Almost 90 % of heavy metals are accumulated by soil, and then migrate into natural water and absorbed by plants and penetrates into trophic chains the eventual link of which is a human organism [9]. The ground cover in the conditions of strengthening of processes of technogenesis feels considerable

anthropogenic influence not only within the limits of the urbanized territories but also on the territory of rural settlements. It is necessary to say that there are a number of factors that draw the origin of ecological problems within the limits of rural territories. In particular, through the sharp diminishing of total number of cattle and pigs the amount of wastes of stock-raising – the basic source of organic fertilizers - went down perceptibly. The last resulted in wide uncontrolled and scientifically not grounded application of mineral fertilizers by the private landowners on the small landed holdings, as a result, except the nourishing elements, a lot of toxic elements which are contained in composition mineral fertilizers as a ballast matters are brought into soil [12, 13].

Purpose, objects and methods of research

The purpose of research is to estimate the levels of contamination of soil with the gross and fixed forms of heavy metals (Cu, Pb, Cd and Zn) on the territory of rural settlements of 20-km suburban zone of Zhytomyr, and the establishment of features of accumulation of heavy metals in the components of agrolandscapes.

The researches were conducted during 2009-2013 within the limits of such rural settlements: Luka, Pryazhiv, Kalynivka, Bystri, Ivanivka, Novoselytsya, Pischanka, Perlyavka, Pisky, Gadzynka. The settlements were selected to cover all suburban zones with the radius of 20-km. The probed territory is presented mainly by soddy-podzolic and grey podzolic soils, the profile of which was partly or fully broken to the depth of 50 cm as a result of anthropogenic influence and their physical and chemical and agricultural properties were changed. The amount of samples of soil from every private holding was determined by its general area. The samples were selected from the layer of soil in depth of 0-20 sm [7].

The content of mobile nitrogen in soil was determined according to Kornfild (ГОСТ 26211-84); mobile phosphorus and exchange potassium – according to the method of Kirsanova in modification of NSCISA (ДСТУ 4405:2005); the content of humus – according to the ДСТУ 4286:2004; pH_{KC1} – according to the ГОСТ 26483-85. Extracting of gross forms of heavy metals has been carried out with concentrated HNO_3 according to the requirements [6], and the extracting of fixed forms of heavy metals – with 1н of HNO_3. For elemental analysis, an atomic absorption spectrometer (С 115-1М) was used. Pb and Cd levels in the samples were determined by HGA graphite furnace, using argon as inert gas. Other measurements were carried out in the air/acetylene flame. All the experimental data have been reported in mg/kg. The technogenic of part of heavy metals was determined after the method that has been described in [1]. The estimation of the content of Cu, Pb, Cd and Zn in soil was based on determination of such geochemical coefficients, as a coefficient of concentration of element (K_p) [11] and index of saturation of soil by the element (s) I_{el} [4]. The total index of contamination of soil Z_c was determined for the estimation of multielements anomalies that characterize the presence of various pollutants in soil and the average

exceeding of their concentration in relation to the background [2]. The statistical processing of experimental data has been carried out with the application of Microsoft Excel and Statistica 6.0.

Results and discussion. It has been determined that the soils within the limits of 20-km suburban zone of Zhytomyr are mainly presented by the soddy-podzolic varieties of different particle-size, which have been formed on water-glacial deposits, rarer – by the gray-podzolic varieties of loamy and sandy loam particle-size soils (v. Pisky, v. Pryazhiv), on occasion – by chornozems and turf soils (v. Perlyavka, v. Luka). Agricultural chemistry properties of arable layer of the soil vary dependence on the degree of cultivation of the soil (tab. 1).

The average content of humus in soils is at the level of 1,8–4,0 %, on occasion arriving at 4,5–5,1 %, pH of the ground solution hesitates from weak acid to neutral (pH = 5,1–7,5). Urbosoils have high and ever-higher content of mobile phosphorus and potassium that varies within the limits of 239–1081 мg/kg and 124–1000 мg/kg accordingly. In general the soil on the territory of suburban rural settlements is characterized by favourable agricultural chemistry indices for growing vegetables and potato and is well cultivated in the process of individual market-gardening.

Table 1. **Agrochemical and physical and chemical indices of soils of rural settlements within the limits of 20-km suburban zone of Zhytomyr, 2009–2013, topsoil 0–20 cm, n=152**

Inspected area, ha	**Content of humus, %**				
	1,5–2,0	**2,0–2,5**	**2,5–3,0**	**3,0–3,5**	**3,5–4,0**
152 ha	22,8 15,0	31,2 20,5	49,8 32,8	23,4 15,4	24,8 16,3
	pH of soil solution				
	5,0–5,5	5,5–6,0	6,0–6,5	6,5–7,0*	7,0*–7,5*
	25,3 16,7	15,2 10,0	30,4 20,0	45,6 30,0	35,5 23,3
	Content of mobile nitrogen, mg/kg of soil				
	60–70	70–80	80–90	90–100	100–120
	30,4 20,0	22,8 15,0	25,4 16,7	32,9 21,7	40,5 26,6
	Content of mobile phosphorus, mg/kg of soil				
	200–400	400–600	600–800	800–1000	1000–1100
	30,4 20,0	35,5 23,3	27,8 18,3	43,1 28,4	15,2 10,0
	Content of exchange potassium, mg/kg of soil				
	100–200	200–400	400–600	600–800	800–1000
	17,7 11,7	40,5 26,6	50,7 33,3	25,3 16,7	17,7 11,7

Note:: 1) numerator – ha; denominator – % percents from the inspected area; 2) * – pH_{H2O}

Gross content of Cu, Pb, Cd and Zn in the soil differs in dependence on type of the rock on which the soils within the limits of settlements have been formed. The content of gross forms of copper varies from 12,4 to 28,2 mg/kg that corresponds to average content of this element according to the classification for acid and weak acid soils [2]. Exceeding of maximum amount concentration of gross copper in soil has not been fixed. The content of gross forms of zinc in soils of rural territories hesitated from 14,7 to 82,6 mg/kg, that corresponds to the average and enhanceable content of this element according to the classification for acid and weak acid soils [2]. Exceeding of maximum amount concentration of gross zinc in soil has not been fixed. The content of gross forms of lead in soils of rural territories hesitated from 2,8 до 22,7 mg/kg, that corresponds to low and middle content of this element according to the classification for acid and weak acid soils [2]. Exceeding of maximum amount concentration of gross lead in soil was not been fixed. The content of gross forms of cadmium in soils of rural territories hesitated from 0,12 to 0,96 mg/kg, that correspond to enhanceable and high maintenance of this element according to the classification for acid and weak acid soils [2]. Exceeding of maximum amount concentration of gross cadmium in soil has not been fixed.

It is very important to have information about technogenic constituent in total content of gross form of heavy metal in soil for the ecological estimation of contamination. The technogenic part of heavy metals can be used for this purpose because this index characterizes the part of technogenic element in its total gross content in soil. The results of calculation of this index are presented at tabl. 2.

Table 2. **Technogenic part of heavy metals in soils of rural settlements within the limits of 20-km suburban zone of Zhytomyr, %**

Place of selection of soil samples	Cu	Pb	Cd	Zn
Pischanka, n = 10	н	н	н	73
Pryazhiv, n = 20	50	52	78	51
Kalynivka, n = 16	53	56	н	74
Bystri, n = 12	52	57	61	69
Ivanivka, n = 24	н	н	н	60
Novoselytsya, n = 8	51	н	н	52
Perlyavka, n = 8	52	н	н	62
Pisky, n = 20	67	н	51	58
Luka, n = 20	н	н	63	н
Gadzynka, n = 14	69	71	62	75

Note: н – low (unreliable) technogenic orientation of element.

The high and medium technogenic orientation of copper has been set for soils of all settlements, with the exception of Luka, Pischanka and Ivanivka, where it has been low. The medium technogenic orientation of lead characterizes the soils on the territory of Kalynivka, Pryazhiv and Bystri, the high technogenic orientation – the soils on the territory of Gadzynka. The medium technogenic orientation of cadmium is

characteristic for the territory of Bystri, Pisky, Luka and Gadzynka, the medium technogenic orientation of zinc is characteristic for the territory of all villages with the exception of Luka where it has been low. It is necessary to say that only the soils of Pryazhiv are marked by medium technogenic orientation of cadmium. The technogenic orientation of investigational heavy metals in soils of rural territories forms a range like: Zn > Cu > Cd > Pb.

As for the content of fixed forms of heavy metals, it is set that on the territory of rural settlements copper, lead and zinc are the priority pollutants of the soil because their concentration exceed the background content considerably.

The soil within the limits of Gadzynka is characterize by the maximal amounts of fixed copper because Kr makes on the average 6,1. High concentration of copper is characteristic for the soil within the limits of agrosettlements landscapes on the territory of Pisky, where Kr of fixed forms makes on the average 5,7. The minimum values of K_p of fixed forms of Cu that hesitate from 0,6 to 3,3 have been indicated in the soil on the territory of Luka. As copper is an essential trace element, the level of soils provision with this element within the limits of the probed territory is high even for the cultures of high accumulation.

The maximal amounts of fixed forms of zinc are concentrated in soils on the territory of Kalynivka and Pischanka (K_p = 73,0 – 76,2 accordingly). The high K_p of fixed forms of zinc is indicated in the soils on the territory of Perlyavka, Bystri and Gadzynka where the mid-coefficient of concentration of this element arrived at 60,2 – 69,5. The soils on the territory of Luka contain the least amounts of fixed zinc. The coefficient of concentration of this element in soil does not exceed 17,0. As zinc is an essential trace element, as well as copper, the level of soils provision with this element within the limits of the probed territory is high even for the cultures of high accumulation.

As for lead, the high concentrations of its fixed forms contained in the soils on the territory of Kalynivka, Bystri and Pryazhiv, where K_p of lead arrives at 17,2–20,1 on the average. The minimum concentrations of fixed lead is contained in the soils on the territory of Luka and Pischanka, where the coefficient of its concentration does not exceed 6,0–6,2.

The concentrations of fixed forms of cadmium appeared the least in soils. The indices hesitates from 0,60 (Pischanka) to 0,86 (Pisky). It is necessary to mark that the content of cadmium in soil exceeded background (K_p = 1,02–1,84) on the territory of Pryazhiv, Bystri and Luka, while in the soils of other probed rural settlements the coefficient of its concentration was < 1.

It is possible to estimate the general ecological state of the probed territory as for its contamination by heavy metals using the total index of contamination by heavy metals. We can also use the index of saturation by heavy metals of 0 – 20 cm topsoil for description of accumulation of elements (tabl. 3).

Table 3. **Coefficient of concentration, total index of contamination and index of saturation by heavy metals of soils of rural settlements within the limits of 20-km suburban zone of Zhytomyr**

Place of selection of soil samples	Coefficient of concentration, K_p				Total index of contamination, Zc	Index of saturation of soil by heavy metals, $I_{elCu\ Pb\ Cd\ Zn}$
	Cu	Pb	Cd	Zn		
Pischanka	3,3 1,8-5,7	6,2 1,5-10,4	0,60 0,18-1,05	76,2 26,5-127,3	66,9 26,9-144,8	5,1 1,9-10,2
Pryazhiv	3,7 1,8-6,1	17,2 12,1-20,0	1,75 0,75-2,91	39,3 14,3-65,8	61,7 25,9-95,1	8,1 3,9-12,6
Kalynivka	3,8 1,9-6,0	20,1 14,9-26,0	0,81 0,29-1,20	73,0 41,8-99,3	97,6 55,0-132,8	8,2 4,3-12,5
Bystri	3,9 2,3-5,9	19,4 14,6-24,9	1,84 0,65-2,71	65,8 30,8-83,8	90,8 45,3-117,5	9,7 5,1-13,8
Ivanivka	3,2 1,7-5,3	5,8 1,4-10,2	0,76 0,36-1,35	47,2 21,8-73,2	56,7 22,1-89,8	5,1 2,1-8,4
Novoselytsya	3,5 2,0-6,1	7,2 1,8-11,6	0,72 0,28-1,15	44,0 18,5-71,7	55,4 19,5-91,3	5,3 2,2-9,8
Perlyavka	3,9 1,9-6,0	7,4 3,5-12,9	0,78 0,31-1,30	69,5 25,7-125,5	74,0 28,2-146,1	6,0 2,7-11,2
Pisky	5,7 3,0-7,2	7,6 3,8-13,4	0,86 0,30-1,40	51,3 22,8-116,3	65,4 26,2-139,7	6,6 2,9-12,4
Luka	1,6 0,6-3,3	6,0 1,5-10,4	1,05 0,50-2,05	17,0 6,6-39,2	25,7 6,2-55,0	3,6 1,3-7,4
Gadzynka	6,1 3,6-8,7	11,8 5,2-15,7	1,02 0,45-1,50	60,2 23,4-122,4	79,2 29,6-147,3	8,2 3,8-12,7

Note: numerator – average value of index, denominator – the limits of changeability of index.

In obedience to the comparative evaluation scale of soil contamination hazard the soils within the limits of all of the probed rural settlements of 20-km of suburban area after the total index of contamination of Zc fall into the category of dangerous contamination and are useless for growing potato and vegetables. An exception makes only the soil on the territory of Luka, where the situation is characterized as moderato dangerous. It is necessary to add that only the soils on the territory of Luka is suitable for growing any culture without limitations, however undercontrol of their quality. The most dangerous situation with contamination of soil by heavy metals has been formed on the territory of Kalynivka (Z_c = 97,6) and Bystri (Z_c = 90,8). The indices of saturation by heavy metals 0 – 20 cm of topsoil, which considerably exceed unit and on the average hesitate from 3,6 to 9,7 testify the predominance of processes of accumulation of pollutants in soil. According to the intensity of contamination of soil of agrosettle landscapes, the probed heavy metals form such range: Zn > Pb > Cu > Cd.

Conclusion: 1) The soils within the limits of rural settlements of 20-km suburban zone of Zhytomyr is well-cultivated in the process of individual market-gardening and characterized favourable agrochemical and physical and chemical properties for growing potato and vegetables. 2) The priority pollutants of soil of agrosettle landscapes are fixed forms of copper (coefficient of concentration K_p = 1,6–6,1), lead (K_p = 5,8–20,1) and zinc (K_p = 17,0–73,0). 3) The character of pollutants distribution in soil has the mosaic character, because the area of contamination point makes from 32 to 65 % of inspected territory, and the area of the most intensive contamination makes from 7 to 18 % of inspected territory. 4) The processes of accumulation of pollutants in agrosettle landscapes considerably exceed the processes of their dispersion (index of saturation of soil by heavy metals $I_{elCu\ Pb\ Cd\ Zn}$ = 3,6–9,7). 5) The territory within the limits of Bystri and Kalynivka is the most dangerous as for geoecology of contamination of the soil by heavy metals (Zc = 90,8–97,6).

Subsequent researches should be concentrated on more detailed inspection of the territory of agrosettle landscapes of suburban area of Zhytomyr as for the contamination of soil and plant cover by heavy metals and creation of raster map of contamination of this territory.

References

1. *Baron S.* Dispersion of heavy metals (metalloids) in soils from 800-year-old pollution (Mont-Lozere, France) / *S. Baron, J. Carignan, A. Ploquin* // Environ. Sci. Technol. – 2006. – V. 40. – P. 5319–5326.
2. *Балюк С. А.* Проведення грунтово-геохімічного обстеження урбанізованих територій / *С. А. Балюк, А. І. Фатєєв, М. М. Мірошниченко*. – Харків: ННЦ «ІГА ім. О. Н. Соколовського» УААН, 2004. – 62 с.
3. *Валерко Р. А.* Особливості акумуляції свинцю у едафотопах і фітоценозах Житомира / *Р. А. Валерко, Т. М. Мислива, Л. О. Герасимчук* // Вісн. ЖНАЕУ. – 2011. – № 1. – С. 179–189.
4. *Дмитрук Ю. М.* Оцінка вмісту нікелю в ґрунтах Покутсько-Буковинських Карпат на основі геохімічних коефіцієнтів / *Ю. М. Дмитрук* // Ґрунтознавство. – 2003. – Т. 4, № 1–2. – С. 78–83.
5. Екологічні та гігієнічні проблеми забруднення рухомими формами важких металів ґрунту промислових агломерацій Придніпров'я / *С. М. Крамарьов, Е. А. Деркачов, О. М. Колодочка* [та ін.] // Довкілля та здоров'я. – 2004. – № 2 (29). – С. 24–28.
6. Методические указания по определению тяжелых металлов в почвах сельхозугодий и продукции растениеводства / ЦИНАО. – М. : ЦИНАО, 1991. – 58 с.
7. Методичні рекомендації з агроекологічного моніторингу селітебних територій / за ред. *Н. А. Макаренко*. – К., 2005. – 26 с.
8. *Мислива Т. М.* Важкі метали в урбогрунтах приміської зони м. Житомир / *Т. М. Мислива* // Наукові пр. Ін-ту біоенергетичних культур і цукрових буряків. – 2013. – Вип. 17, т. ІІ. – С. 75–81.

9. *Мыслыва Т. Н.* Загрязнение тяжелыми металлами овощных культур, выращиваемых в пределах 15-км пригородной зоны г. Житомир / *Т. Н. Мыслыва* // Молодежь и инновации – 2013 : материалы Междунар. науч.-практ. конф. молодых ученых, (Горки, Республика Беларусь, 29–31 мая 2013 г.) / Белорусская гос. с.-х. акад. – Горки, 2013. – С. 201–204.

10. Особливості накопичення важких металів в урбаноземах м. Житомир та його приміської зони / [*Ю. А. Камінський, Я. М. Ярошенко, О. А. Харусь, Т. М. Мислива*] // Наука. Молодь. Екологія – 2012 : зб. матеріалів VIII наук.-практ. конф. студ., аспірантів та молодих вчених, 25–26 квіт. 2012 р. – Житомир, 2012. – С. 176–180.

11. Охрана природы. Почвы. Общие требования к классификации почв по влиянию на них химических загрязняющих веществ [Электронный ресурс] : ГОСТ 17.4.3.06–86 [Действителен от 1986-10-03]. – Госстандарт СССР, 1986. – Режим доступа: www.leonorm.com.ua.

12. *Палапа Н. В.* Ароекологічні проблеми сільських селітебних територій та шляхи їх розв'язання / *Н. В. Палапа, Ю. П. Колесник* // Агроекологічний журнал. – 2009. – № 1. – С. 30–36.

13. Санітарно-гігієнічна оцінка сільських селітебних територій / *М. П. Вашкулат, О. М. Черевко, Є. В. Лівінська* [та ін.] // Агроекол. журн. – 2009. – № 1. – С. 36–40.

М. : Изд-во стандартов. 1985. – 7 с.