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EVALUATION OF SOIL CONTAMINATION BY HEAVY METALS IN THE ZONE OF TPP INFLUENCE

Е. Б. Хоботова, В. І. Ларін, І. В. Грайворонська. ОЦІНКА ЗАБРУДНЕННЯ ҐРУНТІВ ВАЖКИМИ МЕТАЛАМИ У ЗОНІ ВПЛИВУ ТЕПЛОВИХ ЕЛЕКТРОСТАНЦІЙ. За масштабами впливу на навколишнє середовище теплова енергетика посідає одне з перших місць. Викиди ТЕС в основному осідають на ґрунт. Сполуки ґрунту на тривалий термін зв'язують іони важких металів (ВМ), перешкоджають їх міграції. Буферна ємність ґрунту щодо металів залежить від багатьох факторів: складу ґрунту, кислотності, процесів комплексоутворення, окиснення–відновлення, сорбції–десорбції та ін. Вивчення вмісту ВМ у ґрунтах необхідне для контролю за станом навколишнього середовища, охорони його від забруднення. Одним з найкрупніших забруднювачів навколишнього середовища в Харківській області є Зміївська ТЕС. Мета роботи – визначення особливостей забруднення ВМ ґрунтів поблизу Зміївської ТЕС та розробка рекомендацій щодо покращення ситуації.

Для досягнення поставленої мети вирішені наступні задачі: встановлення особливостей акумулювання окремих ВМ у ґрунтах; визначення залежності між рН ґрунтів та наявністю в них певних хімічних елементів; вивчення залежності між складом забруднення і утворенням малорозчинних сполук у ґрунтах.

Результати роботи. Встановлено, що найбільш забрудненою є територія, розташована від джерела викиду в радіусі 10 км. Найбільш поширеними забруднювачами є Cu , Sr , Co , V , Cr . Ґрунти басейна р. Сіверський Донець більшою мірою утримують іони Cu , Zn і Pb . Наукова новизна. Метали V , Cr є аніоногенами, кислотні залишки утворюються в слабо лужних ґрунтах і з ВМ утворюють нерозчинні або малорозчинні сполуки, що приводить до їх накопичення. У ґрунтах виявлено сполуки SrCrO_4 , SrCr_2O_7 , $\text{Sr}(\text{VO}_3)_2$, $\text{Zn}_2\text{V}_2\text{O}_7$, $\text{Zn}_3(\text{VO}_4)_2$, $\text{Zn}(\text{VO}_3)_2$. На підставі визначення коефіцієнтів поліелементного забруднення показано, що в ґрунтах з високою гумусністю, буферністю і здатністю утворювати комплекси з іонами металів вище максимальні концентрації ВМ і ширше розкид концентрацій за винятком Pd , Zn і Cd . Визначені кореляційні залежності між рН і вмістом макро- і мікроелементів в різних ґрунтах. Найбільший коефіцієнт кореляції між концентрацією Al і рН (0,6–0,9). Розроблено рекомендації для зниження рівня забруднення ВМ ґрунтів поблизу Зміївської ТЕС: реконструкція котлоагрегату, встановлення електрофільтра для вловлювання золи, використання золошлакових відходів у виробництві портландцементу, ваннування ґрунтів з метою дискримінації ВМ.

Ключові слова: ґрунти, важкі метали, забруднення, викиди, теплові електростанції, рН ґрунтів.

Э. Б. Хоботова, В. И. Ларин, И. В. Грайворонская. ОЦЕНКА ЗАГРЯЗНЕНИЯ ПОЧВ ТЯЖЕЛЫМИ МЕТАЛЛАМИ В ЗОНЕ ВЛИЯНИЯ ТЕПЛОВЫХ ЭЛЕКТРОСТАНЦИЙ. По масштабам воздействия на окружающую среду тепловая энергетика занимает одно из первых мест. Выбросы ТЭС в основном оседают на почву. Соединения почвы на длительный срок связывают ионы тяжелых металлов (ТМ), препятствуют их миграции. Буферная емкость почвы по металлам зависит от многих факторов: состава почвы, кислотности, процессов комплексообразования, окисления-восстановления, сорбции-десорбции и др. Изучение содержания ТМ в почвах необходимо для контроля за состоянием окружающей среды, охраны его от загрязнения. Одним из крупнейших загрязнителей окружающей среды в Харьковской области является Змиевская ТЭС. Цель работы – определение особенностей загрязнения ТМ почв вблизи Змиевской ТЭС и разработка рекомендаций по улучшению ситуации. Для достижения поставленной цели решены следующие задачи: установление особенностей аккумуляции отдельных ТМ в почвах; определение зависимости между рН почв и наличием в них определенных химических элементов; изучение зависимости между составом загрязнения и образованием малорастворимых соединений в почвах. Результаты работы. Установлено, что наиболее загрязнена территория, расположенная от источника выброса в радиусе 10 км. Наиболее распространенными загрязнителями являются Cu , Sr , Co , V , Cr . Почвы бассейна р. Северский Донец в большей степени удерживают ионы Cu , Zn и Pb . Научная новизна. Металлы V , Cr являются анионогенами, кислотные остатки образуются в слабо щелочных почвах и с ТМ образуют нерастворимые или малорастворимые соединения, что приводит к их накоплению. В почвах выявлены соединения SrCrO_4 , SrCr_2O_7 , $\text{Sr}(\text{VO}_3)_2$, $\text{Zn}_2\text{V}_2\text{O}_7$, $\text{Zn}_3(\text{VO}_4)_2$, $\text{Zn}(\text{VO}_3)_2$. На основании определения коэффициентов полиэлементного загрязнения показано, что в почвах с высокой гумусностью, буферностью и способностью образовывать комплексы с ионами металлов выше максимальные концентрации ТМ и шире разброс концентраций за исключением Pd , Zn и Cd . Определены корреляционные зависимости между рН и содержанием макро- и микроэлементов в различных почвах. Наибольший коэффициент корреляции между концентрацией Al и рН (0,6–0,9). Разработаны рекомендации для снижения уровня загрязнения ТМ почв вблизи Змиевской ТЭС: реконструкция котлоагрегата, установление электрофильтра для улавливания золы, использование золошлаковых отходов в производстве портландцемента, известкование почв с целью дискриминации ТМ.

Ключевые слова: почвы, тяжелые металлы, загрязнение, выбросы, тепловые электростанции, рН почв.

Formulation of the problem. By the scale of the impact on the environment thermal power engineering takes one of the first places. Hundreds of thermal power plants (TPP) and central heating-and-power plants burn millions of tons of organic fuels. They account for about 25 % of all harmful emissions. Thermal power engineering is also responsible for 12 % of solid industrial wastes. They are mainly ash and slag. Lately, ash has been used for various purposes. However, one of its disadvantages is available heavy metals (HM) in its composition. TPP emissions are predominantly deposited on the soil. Soil in the urboecosystem performs one of the main roles. It is in it that metals are closed as anthropogenic pollution. The compounds of the soil bind ions of metals for a long time, preventing their migration. The soil buffer capacity for metals depends on many factors: type and composition of the soil, humus content, acidity, complexation processes, oxidation–reduction, sorption–desorption, and others.

Recently, numerous studies have been carried out on the comprehensive assessment of HM contamination of soil urboecosystems taking into account environmental safety standards [1–4]. The method of determining the ecological risk at different levels of soil pollution with lead [2] and manganese [3] has been improved. A biological toxicity test of soils was conducted to determine the degree of soil contamination by metal compounds [4].

Analysis of recent research and publications.

The study [5] shows that thermal power station contaminates the surrounding soil with toxic elements: Cr, Fe and Zn, reduced soil fertility and variety of beneficial soil microorganisms. The chemical composition of soils along the profile near Kolaghat thermal power plant (India) was investigated [6]. For soils near the dump of ash, there is observed a maximum contamination with elements Mo, As, Cr, Mn, Cu, Ni, Co, Pb, Be, V, Zn at a depth of 2–5 cm. The soils near Egbin thermal station (Nigeria) was polluted of Cu and Zn [7]. There were positive correlations between concentrations of HM in the soils and in the plants. In the paper [8] maps of spatial contamination of soils with heavy metals from a source – a coal-fired thermal power plant of high power (Serbia) – were compiled. Concentration coefficients in the soil varied in the range of 0.3–15.5. Soil pollution is studied not only when thermal power plants use black and brown coal, but also other types of fuel, for example, lignite. The work [9] determines the level of soils and water pollution near suchlike power plant in Northern Greece, as well as food produced in the region. The pollution of the soils in Montenegro with heavy metals Pb, Cd, Cu and Zn is mainly due to anthropogenic pol-

lution [10]. The concentrations of lead and cadmium are about twice as high as their background levels.

Studies of Chinese scientists [11–14] are of interest. The authors of [11] showed that a power plant in Guizhou Province contributes to the Hg pollution in nearby soils. The soils in the vicinity of Luohe Power Plant are contaminated by As and Cd. The accumulation index for soil and risk assessment for health were determined [12]. Mercury emission from coal-fired power plants results in the formation of methyl mercury in the environment. The authors [13] discovered its increased content in rice, which is grown on the territory near the coal-fired power station. A number of recommendations have been developed for reducing the emissions of heavy metals from thermal power plants [14].

The source of HM during TPP operation is both fine particles of ash and ash that goes into ash dumps. The highest amount of smoke emissions sedimentates in the area of 2.5–4.0 km from power plants. Ash that is blown from ash dumps can create HM concentrations in the soil several times as high as the emissions from pipes [15]. This is the soil that is in the center of a cross-border transfer, HM migration. Examination of the HM content in the soils is necessary for monitoring the environment, its protection from pollution, the background amount of HM being the starting point [1].

The influx of HM into plant tissues through the root system is influenced by soil pH, redox conditions, competition between cations, hydrolysis, the formation of insoluble salts [16]. Mathematical models that describe the dependence of the yield of vegetable and orchard crops depending on a set of external factors have been created [17].

Identification of previously unsettled parts of the general problem. One of the largest pollutants in Kharkiv region is Zmiiv TPP, situated in the Siverskyi Donetsk Basin. It is included in the system of Production Energy Association "Kharkivenergo" of Ministry of Power Engineering of Ukraine. The share of Zmiiv TPP is about 60 % of the total volume of industrial emissions in Kharkiv region [18]. Zmiiv TPP pollutes the air due to emissions of combustion products. Coal of "ASH" grade is used as the main fuel at TPP, with its average calorific capacity of 4608 kcal/kg, ash content – 31.2 %, humidity level – 8.3 %. For steam generation the power boilers TP–100 are installed. They are equipped with two individual systems of pulverization with an intermediate hopper. The pulverized coal enters the separator where large fractions are separated and returned to the mill. After the separator the pulverized coal enters the cyclone, and then dropped into the furnace. Furnace gas is cleaned from ashes in the blocks of 200 MW in wet ash catchers; in the blocks of 300 MW in electric filters. The efficiency of the

available ash catchers is only 90 %, which does not provide the required degree of purification. The highest non-recurrent concentrations of pollutants in the atmosphere exceed ash maximum permissible concentration (MPC) 5.4 times [18]. Additionally, the air is polluted by the ash dump of the TPP, from the surface of which 104.3 tons of dust, sedimentated in the soil, are blown away per year. HM incoming from the ash dump is also possible with drainage water when leaching HM from slag and washing away fine-grained fractions of ash. The ash dump covers an area of 350 hectares and the volume of the accumulated ash and slag mixture is about 25 million tons. In the ash dump area the slag and ash tank is placed to collect 400 thousand of tons of ash and slag per year [19].

Paper [20] gives field figures and maps of soils contamination by HM in Kharkiv region. But there is a lack of systematized data on HM contamination of soils near Zmiiv TPP, there is almost no data on HM migration in soils, dependence of accumulation of chemical elements on the soil type and acidity and possibility of making compounds of different solubility in water. Obtaining such data may contribute to the development of recommendations for protection of soils against pollution and discrimination of the HM in the ground.

The aim and tasks of the research. The aim of the research is to find out peculiarities of heavy metal contamination of the soil near Zmiiv TTP and to develop recommendations on improving the situation.

To achieve this aim the following tasks have been solved:

- 1) the features of accumulation of various HM in soils have been specified;
- 2) the dependence between the soils pH and presence of certain chemical elements in them has been defined;
- 3) the dependence between the content of contamination and creation of slow soluble compounds in the soil has been studied.

The main principle of control for soil contamination is the checking of concentration compliance with the established MPC and approximate permissible concentration (APC).

Research methodology. HM concentrations in the aqueous extract from the soil were determined by the atomic-emission spectral analysis, atomic absorption analysis and by the method of capillary electrophoresis [21]. To determine the composition of the solid inorganic part of soils X-ray phase analysis was performed. Due to the consistent analysis of soils the following slightly soluble compounds in the samples were identified: $Zn_2V_2O_7$, $Zn_3(VO_4)_2$, $Zn(VO_3)_2$, $Pb(VO_3)_2$, $4PbO \cdot V_2O_5$, $Pb_3(VO_4)_2$,

$PbCrO_4$, $PbCr_2O_7$, $SrCrO_4$, $SrCr_2O_7$, $Sr(VO_3)_2$, $Ni_2V_2O_7$.

Results of research. The content of heavy metals in soils on the territory of TPP emissions.

The area for the study was chosen, taking into account various landscapes, soils and types of their use, as well as the distance from the object of pollution – Zmiiv TPP. As the emissions of TPP which is operated on solid fuel contain various HM, the most harmful of them were chosen for research, which are either biologically active or belong to toxic contaminants of the different hazard class, for example, Pb, Zn, Cd belong to the 1st hazard class [22, 23]. Each element in the certain soil conditions creates specific chemical forms which determine their mobility or accumulation in the soils. Mobile forms facilitate the ingress of contaminants into plants and their further moving along the food chain. Out of the mentioned elements Cr and V are movable as oxygen anions, namely: residuals of chromic acid and dichromate ions, vanadium acids (meta-, ortho- and pyrovanadates) as well as VO^{2+} , which is a form of vanadium ingress into plants [24].

The mobility of metals is defined by the value of pH in any soil, as cationic forms are more mobile in an acidic environment, while anionogenic substances – in soils with a higher pH. Therefore, it is true that in the process of transition from one environment to another during the study of behavior of metals in soils, an important factor is specific chemical properties of the element. Table 1 shows the concentration of certain chemical elements in different areas of the Siverskyi Donets Valley, located within the radius of 10 km from the Zmiiv TPP (Table 1). For the amphoteric metal Al, a direct correlation between the content of the element and the pH is observed, which can be related to the appearance of AlO_2^- anions – in an alkaline medium (Table 1).

The analysis of the received data on HM content in the soils on the territory of impact of emissions from Zmiiv TPP has shown that the most disseminated pollutants in the area are Cu, Br, Co, V, Cr (Table 2). The level of contamination was determined when comparing the obtained results of the chemical elements content with the maximum permissible concentration and clarke content of chemical elements for the soils. Thus, the most polluted areas are located within 10 km from TPP. This coincides with the research of other objects: natural territorial complexes along the river of the Siverskyi Donets, urban landscapes of towns and villages [26, 27].

To determine the degree of contamination there were used the coefficient of the soil pollution concentration [28]:

Content of HM in the soils (mg/kg) with different pH (2017–2019 years)

Number of test section	Place of sampling	pH	Fe	Si	Al	Zr
1	Central floodplains	7.9	3.5	33	7.0	0.20
2	Back marsh	6.6	2.5	30	0.7	0.05
3	Hills of the pine forest terrace	4.97	2.5	28	0.5	0.05
4	Raised sections of the floodplain	7.2	3.5	33	7.0	0.30
5	Low sections of the floodplain	7.8	3.5	33	6.5	0.50
6	Wetlands of the riverbed floodplain	7.6	3.5	33	6.0	0.15
Clarke content of elements in the soils, % [25]			3.8	33	7.13	0.03

$$C_c = \frac{C}{C_f}, \quad (1)$$

and the coefficient of polyelement contamination [4, 28]:

$$C_{el} = \frac{C}{MPC} \quad (2)$$

де C is the actual concentration of the chemical element;

C_f is the background concentration of the chemical element;

MPC is maximum permissible concentration of the chemical element.

According to the obtained results (Table 2) all soils near the TPP can be referred to as very contaminated because, according to classification [27, 28] maximum values of C_{el} are between 1.6–33.3. In the following sequence the spread in values of C_{el} is given, while in brackets there are values of C_{el} within 10 km from Zmiiv TPP: V 0.05–2 (0.13); Co 0.5–6 (1); Cu 2–16.7 (4.7); Ni 1–12.5 (1.5); Pb 0.2–1.6 (0.38); Pb_{mobile} 1–8.3 (2); Cr 1.7–33.3 (0.43); Zn 0.5–6 (0.52). Thus, at the distance of 10 km the soil is heavily polluted by copper and the mobile form of lead. It is average polluted with Co and Ni; the level pollution is even lower with other metals. However, the general level of pollution at the distance of 10 km is very high.

HM concentration depends of the type of soils in the Siverskyi Donets Basin. On the left bank there are soils with high humus content: high buffer soils – ordinary medium-humic black earth, typical medium-humic clayey black earth, deep soil residual salty black earth (on one and two-loess terraces); as well as low buffers – sod, weak and medium podzolic sand and clay sand and sod sand under coniferous forests (on the pine terrace) [29]. Typical black earths are characterized by a high content of organic matter and the degree of humification, low content of free humic acids and high content of acids associated with Ca. In Table 2 test sections 7–14 correspond to the left bank and (15–18) to the right

bank.

On the right bank there are high buffer soils: medium- and heavy-loamy and clayey, dark gray and gray podzolized, ordinary black earth medium-humic (at the watershed), and meadow and meadow-black-earth deep-salted (on the floodplain) [29]. Black-earth-meadow soils differ from typical black-earth by a smaller humus reserve and degree of humification, a higher content of free humic acids and a lower content of humic acids associated with calcium.

The analysis of the obtained data (Table 2) shows that in highly humic soils, able to form complexes with metal ions (test sections 1–8), the maximum values of HM concentrations are higher and the variation of concentrations is wider. This applies to all HM except Pd, Zn and Cd. In the latter case, metal concentrations are very small. Zn is the only metal whose maximum accumulation does not change over the studied territory of the Siverskyi Donets Basin. The maximum concentrations of Pd and Ni depend very little on the soil type.

The patterns of accumulation of chemical elements can be characterized by accumulative series by the maximum values of the element concentration in soil and C_{el} [28, 30]. For the left-bank test sections of the Siverskyi Donets Basin, the accumulative series looks as follows by the maximum metal concentration:

Sr, V > Cr > Zn > Cu, Ni > Pb > Co > Cd;

for the right-bank sections it is:

Zn > Sr > V > Cr > Pb > Ni > Cu > Co > Cd.

Accumulative series by the maximum C_{el} value characterize the ability of soils to deposit metal ions. The coefficient of polyelement contamination can be used not only for HM belonging to hazard class I, but also for HM of hazard classes II and III, since their maximum soil content exceeds the MPC. For the left-bank soils, the accumulative series is as follows:

Cu > Zn, Co > Pb > Ni > Cr > V;

for the right-bank soils it is:

Table 2

HM content in the soils of test sections in the zone of Zmiiv TPP influence, mg/kg (2017–2019 years)

Number of test section	Place of sampling (distance from the source of emission, km)	Cd	Cu	Sr	Co	Zn	V	Ni	Cr	Pb
7	Slobozhanske town (1)	< 5	35	300	8	140	60	4	200	35
8	Section near the TPP (0.3–0.5)	< 3	10	200	30	20	280	30	100	30
9	Gardens around the Slobozhanske town (1.8)	< 3	20	100	30	30	300	40	10	30
10	Field, station of Ovocheva (2)	< 3	20	200	30	30	300	30	80	20
11	Fields, village of Blagodatne (10)	< 3	30	50	30	100	300	50	100	30
12	Fields, farm of Shebelinske (village of Donets) (3.5)	< 3	20	100	30	50	280	30	100	30
13	Resort house (> 8 km):									
	raised sections of the central floodplain	3	14	50	5	12	20	6	14	12
	low sections of the floodplain	4	25	250	16	35	100	30	90	14
14	hills of the pine forest terrace	3	30	100	6	30	50	15	25	10
	village of Hyniivka (> 11km):									
	low sections of the central floodplain	4	30	300	10	27	70	40	100	17
	levelled section of the central floodplain	4	50	50	8	50	70	30	100	10
	wet oxbow on the riverbed floodplain	4	50	80	7	50	32	27	70	14
15	village of Zidky, (15.5)	< 5	6	30	2,5	90	7	4	10	6
16	village of Taranivka, (30)	< 5	16	100	4	50	30	7	30	50
17	town of Zmiiv, (18)	< 5	20	30	2,5	140	10	6	20	9
18	village of Borova (28)	< 5	20	110	8	50	80	12	70	14
Hazard class by impact of living organisms [22]		1	2	3	2	1	3	2	2	1
Maximum permissible concentration (MPC) in the soil, mg/kg [22]		0.5	3	–	5	23	150	4	6	32
Clarke content of elements in the soils [25], mg/kg		0.5	20	300	8	50	500	40	200	10

Cu > Zn > Pb > Co > Ni > Cr > V.

Thus, the soils of the Siverskyi Donets basin retain Cu, Zn and Pb to a large extent.

On the basis of the obtained data, an analysis of the impact of soil pH on the content of macro- and microelements was carried out (Table 3). Depending on the pH (Table 3), the concentration of Al changes the most. There is a steady decrease in its concentration with increasing pH, the correlation coefficient from pH is 0.6–0.9. Previously (Table 1), an increase in the concentration of Al ions in an alkaline medium was determined, assuming the formation of AlO_2^- anions. The apparent contradiction can be explained in terms of Al accumulation in soils of different types and in the form of compounds with different solubility in water. For example, the for-

mation of mixed hydroxides or oxohydroxides of Al and other metals in soils with an alkaline medium will reduce the concentration of ions Al^{3+} .

There is also a tendency of reduced concentration of zink with increased alkalinity of the medium. For the microelements (Sr, Zr, Cr) the correlation was not found. Concentration of Si hardly changes with variable pH.

Decreasing level of soil pollution with heavy metals. There are several approaches to lower the level of soil pollution with HM:

- by reducing amount of emissions;
- by ensuring the use of ash and slag waste;
- by providing HM discrimination in the soil.

Reducing amount of emissions. The biggest amount of HM enters the environment with products

Dynamics of HM concentration in the soils depending on the soil pH change, mg/kg
(Zone of Zmiiv TPP influence, 2017–2019 years)

Number of test section	Place of sampling (distance from the source of emission, km)	pH	Al	Si	Sr	Zr	Cr	Zn
11	Field, the village of Blagodatne (10)	6.06	6.5	32	50	30	100	100
19	Gardens around the Slobozhanske town (2.5)	6.20	2.2	32	100	100	100	30
20	Field, the village of Blagodatne (12)	6.30	6.5	32	50	30	95	100
12	Field, the farm of Shebelinske (3.5)	7.04	3.8	33	100	500	100	50
21	Gardens along the highway near the Slobozhanske town (2)	7.20	2.2	34	200	200	100	20
22	Field, the farm of Shebelinske (3)	7.30	3.8	33	100	30	100	50
10	Field, the station of Ovocheva (2)	7.33	3.8	32	200	300	80	30
23	Field, the station of Ovocheva (3)	7.40	3.8	32	200	300	80	30
24	The centre of the Slobozhanske town (0.8)	7.50	2.2	32	100	100	100	30
8	Area near the TPP (0.3)	7.73	2.2	34	200	200	100	20

of combustion. The planned reconstruction of block number 1 will allow to reduce its environmental impact, increase efficiency and reliability. It is planned to reconstruct the combustion chamber from the open type into the "shoulder" one with gas-tight screens, inflow burners and high-angle cold funnel. In this case the capacity will increase by 14 %, and the steam capacity – by 10 % while ensuring high environmental friendliness of the combustion process. Ash emissions will be reduced 27 times.

Waste gases are cleaned in the Venturi scrubbers, from where they come to the collector of pure gas, exhauster and, finally, to the chimney. This leads to the annual emission of about 84 thousand tons of ash that is ≈ 37 % of the total volume of emissions into the atmosphere. The highest concentration of dust particles in the emissions of the boiler № 1 is 41.8 g/m^3 . To improve the situation it is proposed to replace the Venturi scrubbers by electric filters. Dust particles of combustion products are ionized well and are current-carrying. Efficiency of dusty gas flow purification (η) in the electric filters can be estimated by Deyh formula

$$\eta = 1 - e^{-W_e \cdot F_{\text{specif}}}, \quad (2)$$

where W_e – velocity of particles in the electric field, m/s;

F_{specif} – specific surface of electrodes sedimentation that is equal to the ratio of the surface of the elements sedimentation to the consumption of cleaning gases, $\text{m}^2/\text{s}/\text{m}^3$.

In the general case η of electric filters changes from 95 % to 99 % and for Venturi scrubbers – from 70 % to 99 %. Thus, the electric filter can provide more stable high efficiency of dust particles confinement.

Ensuring the use of ash and slag waste. Ash and slag waste of Zmiiv TPP go to the ash dump, which is filled by 95.8 % to the moment. HM ingress into the soil from the ash dump can be possible with its dust pollution and with the drainage water when leaching of HM from slag and washing away highly refined fractions of ash. The place of ultimate accumulation of HM from ash and slag is the soil.

As the construction of the new ash dump and reconstruction of the old one is not planned in the near future, the problem of waste accumulation should be solved by way of its utilization in other industries. The most appropriate method is ash and slag utilization in production of cement. Ashes of TPP consist mainly of SiO_2 and Al_2O_3 . The content of CaO does not exceed 5 %. Due to similarity of chemical and mineralogical characteristics of the fuel and blast-furnace slag, one should not expect major differences in producing and hardening of the cement which contains ash and slag. Ingredients used in the production of cement slag waste must meet specified requirements [31]. Fuel ash and slag are used as both active additives to cement and as components of the cement raw mixture. Concretes based on ash and slag are characterized by twice reduced cycle of steam curing. Products with the addition of ash are frostproof and resist aggressive environment better. Furnace granulated slag may be considered as a less hygroscopic additive to cement in comparison with the furnace slag. Ash is used as a mineral additive in asphalt and in place of sand in expanded-clay concrete.

Providing HM discrimination in the soil. Discrimination of heavy metals in the soil implies HM inactivating, weakening their attacks on living or-

ganisms, reducing their content in crops. Techniques to detoxify excess of HM in the soil include introduction of lime and application of organic fertilizers.

When liming the soil HM ingress to the plant is reduced. This can be explained by several reasons:

1) due to increasing pH heavy metals sedimentate from interstitial water in the form of hydroxides, carbonates and phosphates;

2) as a result of increasing pH and availability of Ca^{2+} in the soil content, the ability of plant roots to absorb some heavy metals, in particular Pb, decreases;

3) liming promotes the formation of complexes of organic substances of the soil with HM [32].

Conclusions. As a result of studying the level of the soil pollution with heavy metals near Zmiiv TPP it was found that:

– the most polluted area is that within 10 km from the source of emission;

– the most common pollutants are Cu, Sr, Co, V, Cr, which, we think, is quite logical: V, Cr are anionogenics, acid residues are formed in slightly alkaline soils and together with HM they form in-

soluble or slightly soluble compounds, that leads to their accumulation. This concerns Cu, Sr, Co;

– with V and Cr availability in the soil the following compounds are formed: SrCrO_4 , SrCr_2O_7 , $\text{Sr}(\text{VO}_3)_2$, $\text{Zn}_2\text{V}_2\text{O}_7$, $\text{Zn}_3(\text{VO}_4)_2$, $\text{Zn}(\text{VO}_3)_2$;

– correlation between pH and the content of macro- and microelements in different soils is determined. The highest correlation coefficient is between pH and Al concentration (0.6–0.9);

– the soils of the Siverskyi Donets Basin contain Cu, Zn and Pb to a greater extent. In the left-bank soils with high humusness and the ability to form complexes with metal ions, the maximum values of HM concentrations are higher and dispersion of concentrations is wider.

To reduce soil pollution with HM near Zmiiv TPP we propose the following: to reconstruct the boiler unit, that will result in reducing ash dust emissions containing HM 27 times; to set the electric filter for retaining ash from exhaust gases; to use ash slag waste in the production of Portland cement; to carry out periodic liming of soils on the areas near Zmiiv TPP with the purpose of HM discrimination.

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EVALUATION OF SOIL CONTAMINATION BY HEAVY METALS IN THE ZONE OF TPP INFLUENCE

Abstract. Thermal power engineering takes one of the first places by the scale of the impact on the environment. Thermal power plant emissions are mainly deposited on the ground. Soil compounds, binding heavy metal ions (HM) for a long time, prevent their migration. The buffer capacity of the soil for metals depends on many factors: soil composition, acidity, complexity, oxidation–reduction, sorption–desorption, etc. Examination of the HM content in the soils is necessary for monitoring the environment, its protection from pollution. One of the largest pollutants in Kharkiv region is Zmiiv TPP.

The goal of the work is to find out peculiarities of heavy metal contamination of the soil near the Zmiiv TTP and develop recommendations on improving the situation.

In order to reach the goal, the following tasks have been solved: features of accumulation of various heavy metals in the soils have been specified, dependence between the soils pH and presence of certain chemical elements in them has been defined, dependence between the content of contamination and development of slow soluble compounds in the soil has been studied.

Research methodology. The main principle of control for soil contamination is checking of concentration compliance with the established maximum permissible concentration (MPC) and approximate permissible concentration (APC). HM concentrations in the aqueous extract from the soil were determined by the atomic-emission spectral analysis, atomic absorption analysis and by the method of capillary electrophoresis. To determine the composition of the solid inorganic part of soils X-ray phase analysis was performed.

Results of research. It is established that the most polluted areas are located within 10 km from TPP. The most disseminated pollutants in the area are Cu, Br, Co, V, Cr. The soils of the Siverskyi Donets Basin retain Cu, Zn and Pb ions to a large extent.

Scientific novelty. Metals V, Cr are anionogenics, acid residues are formed in slightly alkaline soils and together with HM they form insoluble or slightly soluble compounds leading to their accumulation. Compounds SrCrO_4 , SrCr_2O_7 , $\text{Sr}(\text{VO}_3)_2$, $\text{Zn}_2\text{V}_2\text{O}_7$, $\text{Zn}_3(\text{VO}_4)_2$, $\text{Zn}(\text{VO}_3)_2$ were found in the soils. Based on the determination of the coefficients of poly-elemental contamination, it is shown that maximum concentrations of HM are higher and variations of concentrations are wider except Pd, Zn and Cd in the soils with high humus, buffering and ability to form complexes with metal ions. The correlation relationships between pH, macro- and microelements in various soils are determined. The highest correlation coefficient is between Al concentration and pH (0.6–0.9).

Practical significance. Recommendations have been developed to reduce the level of soil contamination near Zmiiv TPP: reconstruction of the boiler unit, installation of an electrostatic precipitator to collect ash, using ash and slag waste in the production of Portland cement, liming soil for discrimination of HM.

Keywords: soils, heavy metals, pollution, emissions, thermal power plants, pH soils.

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