Розгляд завдання моделювання проникнення важких металів, що викидаються з відпрацьованими газами автомобільних двигунів, проводилося для ґрунту з коефіцієнтом фільтрації $к_ф$ та коефіцієнтом дифузії D. В результаті математичного моделювання отримано експоненціальне рівняння, вхідними змінними для якого є поверхнева концентрація шкідливих компонентів с, коефіцієнт фільтрації $к_ф$, коефіцієнт дифузії D та глибина ґрунту l. Вихідними змінними для отриманого експоненціального рівняння є концентрація шкідливих компонентів $с_1$ на глибині l.

За отриманим рівнянням теоретично досліджено глибину проникнення важких металів у ґрунт – l, в залежності від поверхневої концентрації $с_1<с_2$ і незмінному відношенні $к_ф/D$. В результаті глибина проникнення важких металів зростає, що пояснюється зростанням рушійної сили процесу дифузії. Дослідивши вплив зростання відношення $к_ф/D$ на глибину проникнення важких металів у ґрунт при незмінних поверхневих концентраціях $с_1$ та $с_2$, встановлено зменшення їх глибини проникнення, що пояснюється зниженням процесу дифузії.

Отримані теоретичні результати підтверджені експериментальними дослідженнями глибини проникнення важких металів – відпрацьованих газів бензинового двигуна ЗМЗ-511.10 в ґрунт. Встановлено, що вміст важких металів в ґрунті на довільній глибині відповідає теоретичним розрахункам, а розбіжність знаходиться в межах похибки вимірювання приладів, що під час вимірювання концентрації свинцю знаходиться у межах 12,5–15 %, цинку 5,5–7,5 % і марганцю 8,5–11 %. Так, концентрації важких металів, виміряні на довільних глибинах, сягають для свинцю 0,1 та 0,2 м, для цинку 0,1; 0,2 та 0,3 м, для марганцю 0,1; 0,2 та 0,25 м. Це свідчить про достовірність результатів, одержаних за експоненціальним рівнянням. Отже, запропонована модель забезпечує високу точність визначення концентрації важких металів в ґрунті і може бути використана для прогнозування їх глибини проникнення, якщо відома поверхнева концентрація

Ключові слова: автомобільний транспорт, паливо, бензин, відпрацьовані гази, важкі метали, ґрунт, прогнозування забруднення

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IMPROVEMENT OF THE MODEL OF FORECASTING HEAVY METALS OF EXHAUST GASES OF MOTOR VEHICLES IN THE SOIL

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1. Introduction

Road transport is one of the main sources of environmental pollution, and also a major source of noise and heat pollution in cities.

Today, the following main sources of environmental pollution by road transport are distinguished:

1) exhaust gases of internal combustion engines;

2) waste motor and gear oils, coolants (glycols), brake fluids, batteries, etc.;

3) mechanical wear products of tires and brake system (pads);

4) noise, heat pollution of the environment.

Compared to other pollutants, waste operational materials are not spread in the environment and are disposed centrally. In this group of pollutants, exhaust gases are the main and most dangerous source of pollution, since gases are toxic, accumulate in the lower atmosphere and contain carcinogens.

So, the issue of environmental pollution by emissions from mobile sources today is rather acute in the world. In general, pollution by mobile sources is quite a complex issue, and the study of it is costly. Therefore, the problem of forecasting the distribution of harmful components – exhaust gases of motor vehicles in the environment using mathematical models is relevant.

2. Literature review and problem statement

The concentration of harmful substances in ICE exhaust gases depends on a number of factors: driving mode, road relief, vehicle condition and fuel type. The work [1] proposes to use biomass energy to improve the environment, preserve conventional fuel and energy resources, diversify energy sources through the introduction of torrefaction technology.

In [2], the analysis of biological resources for biofuel production is carried out. The study shows that the use of alternative fuels solves the problem of environmental pollution and leads to a decrease in the concentration of harmful components in ICE exhaust gases.

In view of increasing environmental requirements for the composition of ICE exhaust gases, every year more and more attention is paid to the problems of reducing the influence of these factors on ICE exhaust gas composition. The importance and severity of this problem grow due to the annual increase in vehicle emissions polluting the atmosphere and soil (by an average of 3–5 %) [3].

According to [4], the surface concentration for a stationary point source under the condition of normal distribution of the concentration of substances in the atmosphere is calculated by the formula:

$$C(x,y,z)=\frac{Q\cdot K\cdot V}{2\pi\cdot u_S\cdot\sigma_Y\cdot\sigma_Z}\cdot\exp\left(-0{,}5\frac{y^2}{\sigma_Y^2}\right), \tag{1}$$

where $C(x, y, z)$ is the concentration of the pollutant emitted at the point x, y, z, μg/m^3; Q is the volume of emission, g/s; K is the conversion factor – $1\cdot 10^6$; V is the vertical dispersion conditions; u_S is the wind speed at the effective height of the emission source, m/s; σ_y is the standard deviation of horizontal dispersion, m; σ_z is the standard deviation of vertical dispersion, m; y is the lateral deviation from the axis, m.

For mobile sources, the problem of forecasting the distribution of harmful components of exhaust gases can be solved by [5–7].

In [5], the basic principle of studies on air pollution forecasting takes into account the nature of the physical process of impurity propagation in the atmosphere and the special effects of meteorological conditions on impurity concentrations in the air. The research does not take into account anthropogenic factors, probably having a high impact on pollution propagation in the atmosphere.

The idea of the method proposed in [6] is to first perform an analysis of meteorological conditions and other parameters with the help of an unmanned aerial vehicle. The conditions of the problem and the analytical expression of the model equation and ratios for all its parameters, calculated by different methods, are specified. This method is difficult to use because it contains many variables that are complex and cumbersome to define.

In [7], an inexpensive and low-power system based on air quality monitoring sensors is proposed. Unlike traditional air pollution monitoring stations, this system is portable and is based on low-cost sensors and microcontrollers. However, the use of this system is difficult in metropolitan areas, since it does not take into account the peculiarities of air flows, so its readings will contain a significant measurement error.

In [8], it is proposed to reduce harmful emissions of engines using alternative fuels based on blends of commercial fuels with fusel oils. However, this technique can be used only for petrol engines, and fusel oils are quite toxic because they contain a number of carcinogens, such as methyl alcohol.

The problem of mathematical description of the distribution of harmful components emitted into the air is currently largely solved, and a number of experimental studies have been carried out directly for road transport.

It is known that cars are also a source of soil contamination with heavy metals [9]. During fuel combustion in internal combustion engines (ICE), lead, manganese, cadmium, zinc, etc., enter the soil together with exhaust gases. Since, according to DSTU 7687: 2015, petrol is allowed to contain lead up to 5 mg/dm^3, manganese up to 6 mg/dm^3, cadmium and zinc are emitted as a result of high temperature of fuel combustion in ICE and industrial facilities.

The problem of experimental study of harmful emissions of exhaust gases is solved in [10]. But the authors only considered nitrogen oxide emissions.

Emissions of harmful components not only of fuels but also lubricants are investigated in [11]. The disadvantage of this work is that the authors limited themselves to freight vehicles.

The issue of changes in the concentration of harmful components on the soil depending on mixture composition and engine structure is considered in [12]. But the authors do not take into account all the design features of modern automotive engines that affect the concentrations of toxic components in the soil.

Soil composition and type of components determined by the authors have a significant influence on heavy metal distribution in the soil [13]. According to the studies, manganese migrates most readily in all soil types, and forest soils are the most resistant to penetration of heavy metals. However, the authors did not determine patterns of heavy metal penetration and therefore did not propose a methodology for predicting their migration.

In [14], the factors influencing the migration of heavy metals in soils are analyzed. The authors found that the main factor is soil type. However, the mathematical dependence of the depth of penetration of heavy metals on soil parameters is not determined by the authors.

Large-scale studies of heavy metal migration in the soil-plant system are performed in [15]. According to the results, concentrations of Cr, Pb and Zn in the soil-wheat system are obtained and their corresponding migration models are developed. The authors revealed the nonlinear nature of the dependence of heavy metal concentration on soil depth, but did not provide an analytical equation for forecasting the penetration of heavy metals into the soil.

Atmospheric sediments and further deposition of heavy metals on soils are investigated in [16], where the focus is on the territory of Germany. The authors propose to determine the concentration of components using numerical models, technical devices and biomonitors. However, all attention is focused on forecasting the concentration of heavy metals in the atmosphere and plants.

The study of heavy metal concentration in soils at the site of large-scale mining operations related to lead and zinc extraction in the mountainous areas of Missouri, Kansas, and Oklahoma (USA) is performed in [17]. The uneven distribution of lead, cadmium and zinc contamination around the mining site is found, and mapping of heavy metal contamination in these soils is performed. However, the issue of forecasting the contamination of these territories is not addressed in the work.

In [18], a method of forecasting the levels of heavy metals in soils of different genesis to evaluate their environmental and productive functions is developed. However, the proposed method is based on the linear dependence of heavy metal concentration in soils, and the above works [13–15] found that the nature of the concentration curves is nonlinear.

The thermal state of the engine exerts a significant influence on the propagation of harmful components of ICE exhaust gases in the soil. The authors of [19, 20] propose measures to accelerate the engine warm-up after start-up and investigate the dynamics of emission reduction. However, the system proposed in [19] is somewhat complicated, and the country driving cycles chosen in [20] significantly underestimate real emissions of harmful components.

The authors of [21] investigated the emissions of toxic components not only of traditional types of cars, but also hybrid ones. The disadvantage of this paper is that the authors limited themselves to considering large-sized hybrid buses.

One of the ways to reduce emissions of harmful components of ICE exhaust gases is to use alternative fuels.

Thus, in [22], to improve the environmental performance of diesel engines, it is proposed to use a hydrogen-diesel mixture as fuel, which reduces emissions by 30 %.

High environmental performance of the diesel engine is obtained in [23] when converting it to biogas, which, as a result, reduces its toxicity by 65 %.

In [24], it is proposed to reduce the negative impact of engines on the environment using innovative fuel production technologies, which reduce toxicity by 15–20 %.

The use of mineral fuels for jet engines [25] has a positive effect on environmental performance and reduces the level of environmental pollution by 25–30 %.

An important role in reducing harmful emissions of engines into the environment is played by the rational choice of fuel type [26], which will contribute to the reduction of engine toxicity by 5–10 %.

The authors of [27] propose to reduce the negative impact of road transport on cities by improving urban public transport routes.

Therefore, the problem of forecasting the propagation of harmful components of exhaust gases of motor vehicles in the soil is not sufficiently investigated, and therefore requires further study to ensure sufficient accuracy in forecasting the depth concentrations of harmful components in soils, since previous studies did not address the effects of permeability and diffusion coefficients of the soil on the depth of heavy metals penetration and did not provide an analytical equation for forecasting the depth of their penetration into the soil.

3. The aim and objectives of the study

The aim of the study is to improve the model of heavy metals penetration into the soil. This will allow forecasting the distribution of lead, zinc and manganese into the soil from emissions of exhaust gases of automobile engines.

To achieve the aim, the following objectives were set:

– to determine the effect of permeability and diffusion coefficients on the penetration of heavy metals into the soil;

– to obtain an analytical equation for forecasting the penetration depth of lead, zinc and manganese from exhaust emissions of motor vehicles, depending on soil type;

– to determine the accuracy of forecasting the heavy metals concentration in the experimental site by the developed analytical method.

4. Materials and methods for studying the concentration of heavy metals in soil

For experimental research, a laboratory pilot plant is developed (Fig. 1), including a pipeline (1), exhaust gas splitter (2) and testing platform (3).

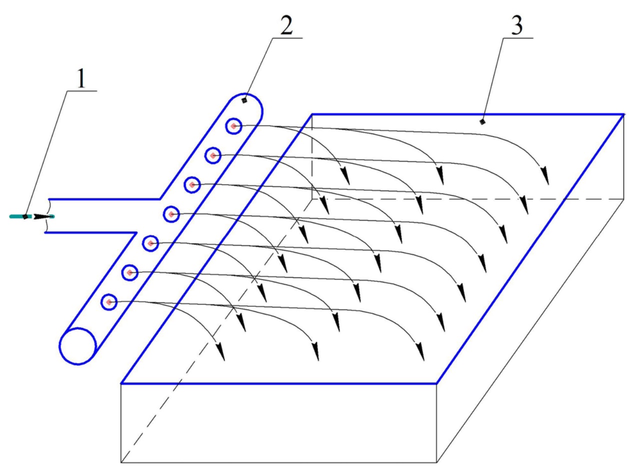

Fig. 1. Installation for experimental studies of changes in the concentration of heavy metals in the experimental plot of soil, depending on depth: 1 – exhaust pipeline of the ZMZ-511.10 engine; 2 – exhaust gas splitter; 3 – 1 m^2 platform for soil studies for heavy metals

In order to identify the effect of ICE exhaust gases on the content of heavy metals in the soil, the scheme of the pilot plant includes the testing platform (3), where the soil is semi-solid, yellow-gray loam, which is quite common in Eastern Europe.

In the process of studying the heavy metals content in soil and plants under the influence of exhaust gases of the ZMZ-511.10 engine, the testing platform with a plant top layer (Fig. 1) of 1 m^2 is used. For this platform, the soil is loam with permeability coefficient c_p=5.75·10^{-7} m/s and diffusion coefficient D=4.4.10^{-8} m^2/s at a distance of 30 m from the road with average traffic of 6,880 vehicles/day. After the soil was brought to the testing platform (Fig. 1) near the laboratory with the pilot plant, at the rate of two testing platforms, it was under the influence of environmental factors for 30 days. Next, soil samples were taken from the testing platform using the point method to determine the background content of heavy metals.

The testing platform was saturated with exhaust gases of the ZMZ-511.10 engine, which operated for 40 hours (four days) with a constant engine load of 37 kW. The velocity of the exhaust gases above the platform, provided by two VO 13-284 fans (Russia), was about υ_{eg}=0.3 m/s. The exhaust gas velocity was measured using a U5 vane anemometer (Russia). The uniformity of exhaust gas distribution on the surface of the testing platform was ensured by means of the exhaust gas splitter 2 (Fig. 1), made in the form of a 1 m long steel pipe with seven holes of 0.015 m in diameter.

Determination of heavy metals content in the soil was carried out in the laboratory of the Ivano-Frankivsk Regional State Design and Technological Center for Soil Fertility and Product Quality Protection, which is certified by Ukrspozhivstandard (Ukraine) for technical completeness by the method of atomic absorption spectrometry. The method involves extracting the studied metal from the soil with nitric acid, filtering the resulting extract through a dry folded filter and determining the optical density of the acid solution of the metal in the filtrate on the C-115 atomic absorption spectrophotometer (Russia) in the acetylene-air flame. At the same time, a blank analysis was performed for the purity of the reagents used, i. e. all stages were repeated, but without sampling. The graph of the optical density of standard acid solutions of heavy metal against its concentrations in the solution is preliminarily constructed. It is used to find the concentration of heavy metals in the studied acid solution of soil extract A_{s1}, mg/dm^3 and the concentration of metals in the acid solution A_{s0}, mg/dm^3.

The weight content of heavy metals in soil C_s, mg/kg was determined by the formula:

$$C_s = \frac{V_s \cdot \left(A_{s1} - A_{s0}\right)}{m_s}, \qquad (2)$$

where V_s is the volume of the studied acid solution of the soil extract, cm^3; m_s is the mass of the dry soil sample, g.

Indirect error of determining the mass concentration of heavy metals in the soil ΔC_s,% was determined by the expression:

$$\Delta C_S = \frac{\partial C_S}{\partial V_S}\Delta V_S + \frac{\partial C_S}{\partial A_{S1}}\Delta A_{S1} + \frac{\partial C_S}{\partial A_{S0}}\Delta A_{S0} + \frac{\partial C_S}{\partial m_S}\Delta m_S, \qquad (3)$$

where ΔV_s is the absolute error of determining the volume of the acid solution of the soil extract, %;

ΔA_{s1}, ΔA_{s0} are the absolute error of measuring the concentration of heavy metals in the studied acid solution of the soil extract and error of measuring the concentration of heavy metals in the acid solution, %;

Δm_s is the absolute error of determining the mass of the dry soil sample, %.

The relative error of determining the mass concentration of harmful components in the soil δC_s, % was calculated by the formula:

$$\delta C_S = \frac{\Delta C_S}{C_S}. \qquad (4)$$

The study of the effect of ICE exhaust gases on the concentration of heavy metals in the soil was carried out in the following sequence:

1) determination of heavy metals in the background soil;
2) saturation of soil surface with exhaust gases of the engine during its operation on commercial petrol;
3) determination of heavy metals content in the experimental soil.

5. Improvement of the model of forecasting the distribution of harmful components of exhaust gases of motor vehicles in the soil

Consider the problem of modeling the penetration of harmful components of exhaust gases of automobile engines in the soil. For this purpose, as a physical model, we choose an elementary area on the soil surface on the roadside with a constant surface concentration of the harmful component.

In an arbitrary plane that is perpendicular to the direction of diffusion of harmful components into the soil (Fig. 2), where the conditions of the diffusion process in the x-axis direction are the same, we select the element dx in the soil layer bounded by the planes parallel to the surface plane and located at distances x and x+dx.

For the study, we use semi-solid, yellow-gray, low-moisture loam with permeability coefficient c_p and diffusion coefficient D.

It is necessary to find the functional dependence of changes in the concentration of harmful components on the soil thickness, considering the process stationary.

Make a material balance for the selected element. According to Fick's first law [28], the amount of harmful components passing through the elementary plane dS in the diffusion direction over time dτ is:

$$\mathrm{d}M = -D\frac{\mathrm{d}c}{\mathrm{d}x}\mathrm{d}S\mathrm{d}\tau, \qquad (5)$$

where dM is the amount of harmful components diffusing in the x direction; c is the concentration of harmful components at a certain depth; D is the diffusion coefficient.

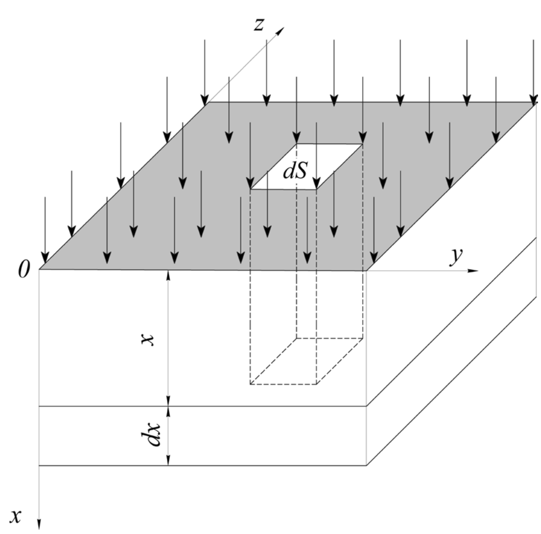

Fig. 2. Physical model of penetration of dangerous substances into the soil

The material balance equation for the considered elementary area is as follows:

$$-D\frac{\mathrm{d}c}{\mathrm{d}x}\mathrm{d}S\mathrm{d}\tau+D\left[\frac{\mathrm{d}c}{\mathrm{d}x}+\mathrm{d}\left(\frac{\mathrm{d}c}{\mathrm{d}x}\right)\right]\mathrm{d}S\mathrm{d}\tau-$$
$$-\frac{c_p\mathrm{d}c}{\mathrm{d}x}\mathrm{d}S\mathrm{d}\tau=0, \qquad (6)$$

where c_p is the permeability coefficient. Denoting $c_p/D=\omega$ and simplifying, the material balance equation (6) is reduced to the second-order linear differential equation:

$$\frac{\mathrm{d}^2c}{\mathrm{d}x^2}-\omega\frac{\mathrm{d}c}{\mathrm{d}x}=0. \qquad (7)$$

Given the known concentrations of harmful components at some depth l_1 and l_2, $c(l_1)=c_1$, $c(l_2)=c_2$ and provided the diffusion process is stationary, the solution of the differential equation (7) is as follows:

$$c(x)=\frac{c_2-c_1e^{\omega(l_2-l_1)}}{1-e^{\omega(l_2-l_1)}}+\frac{c_1-c_2}{e^{l_1\omega}\left(1-e^{\omega(l_2-l_1)}\right)}\cdot e^{\omega x}. \qquad (8)$$

In terms of the curvature nature, the graphs of changes in the concentration of harmful components over the soil depth, constructed according to equation (8), correspond to the data of [18], which testifies in favor of correctness of the obtained results.

The obtained equation (8) allows determining the distribution of harmful components of exhaust gases – heavy metals in the soil depth with known values of surface concentrations of these components.

Perform an analysis of the effect of ω on the penetration depth of lead l (Fig. 3) by the obtained equation (8). Since the decrease in ω is due to an increase in the diffusion coefficient, this contributes to an increase in the depth of lead penetration into the soil (Fig. 3).

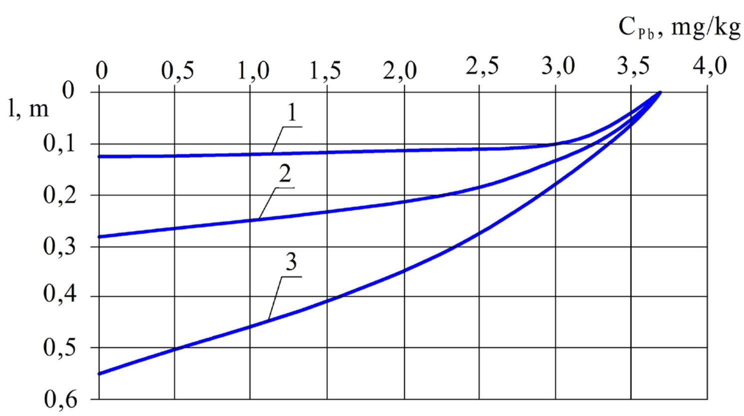

Fig. 3. Effect of ω on the depth of lead penetration into the soil / for constant concentrations c_1 and c_2: l_1=0 m; l_2=0.1 m; ω is: 1 – 71.1; 2 – 13.1; 3 – 2.6

Fig. 4 shows the results of theoretical studies of the depth of lead penetration into the soil – l, depending on the surface concentration c_1 and c_2 and constant ω. An increase in lead concentration at depths l_1 and l_2 for ω=const (Fig. 4) leads to an increase in the depth of lead penetration into the soil, as the driving force of the diffusion process grows.

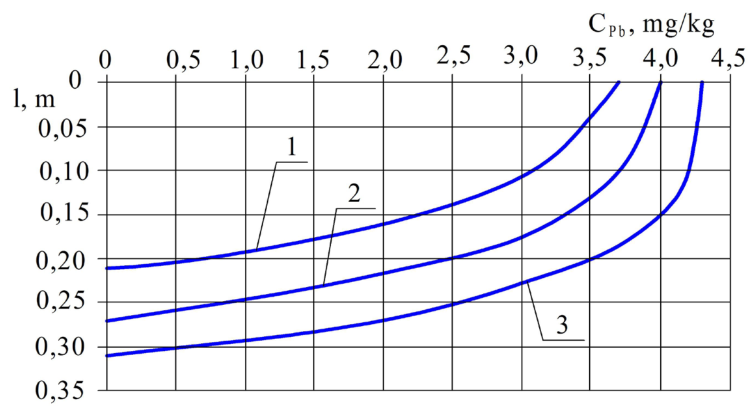

Fig. 4. Effect of surface concentration of lead on the depth of its penetration into the soil / for ω=const: l_1=0 m; l_2=0.1 m; ω=13.1 for all curves; lead concentration c_1 and c_2 mg/m^3: 1 – 3.7 and 3.05; 2 – 4 and 3.7; 3 – 5 and 4.9

In contrast to the works [18, 19], the obtained equation (8) allows to analytically trace changes in the concentration of harmful components – heavy metals, in depth, provided the stationarity of the considered process. The dependencies shown in Fig. 3, 4 indicate that the assumption [19] about the invariability of lead concentration over the height of the root system of the plant cover – 20 cm is false.

6. Results of experimental study of the effect of ICE exhaust gases on the concentration of heavy metals in the soil

The study of the effect of exhaust gases of the ZMZ-511.10 engine on the concentration of heavy metals in the soil was carried out in the following sequence:

1) determination of heavy metals in the background soil;

2) saturation of the soil surface with exhaust gases of the engine during its operation on A-92 commercial petrol, determination of heavy metals content in the soil.

The results of the study of the soil samples on the surface and at different depths for lead, zinc and manganese are shown in Fig. 5–7.

According to the results of the studies, the relative error of measuring the lead concentration in the soil is within 12.5–15 %, zinc 5.5–7.5 % and manganese 8.5–11 %. The solid curves shown in Fig. 5–7 are constructed based on the obtained exponential equation (8), where the surface concentration c and the ratio c_p/D=ω are used as input data.

The points in Fig. 5–7 indicate experimental concentrations of heavy metals measured at arbitrary depths for lead – 0.1 and 0.2 m, zinc – 0.1; 0.2 and 0.3 m and manganese – 0.1; 0.2 and 0.25 m. The deviations of the experimental concentrations at the above depths from those predicted by the exponential equation (8) are explained by the error of the method of measuring the concentration of these components in the soil and determination error ω.

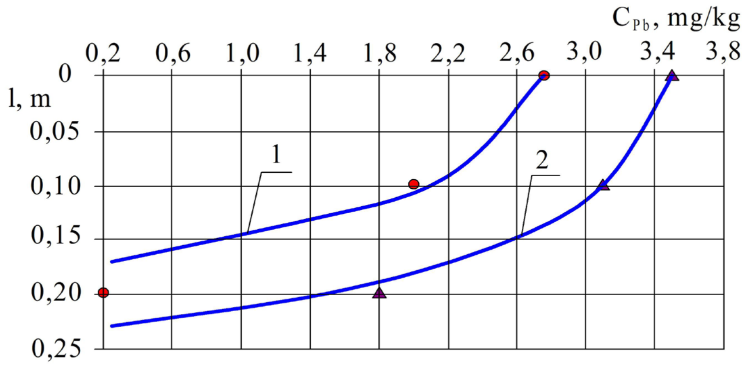

Fig. 5. Experimental depth of lead penetration into the soil: lead content in the soil: 1 — background; 2 —A-92 commercial petrol; — curve constructed by the exponential equation (8) for ω=13.1

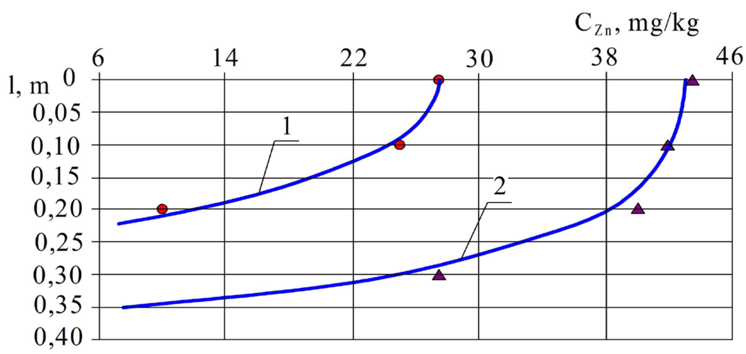

Fig. 6. Experimental depth of zinc penetration into the soil: zinc content in the soil: 1 — background; 2 — A-92 commercial petrol; — curve constructed by the exponential equation (8) for ω=13.1

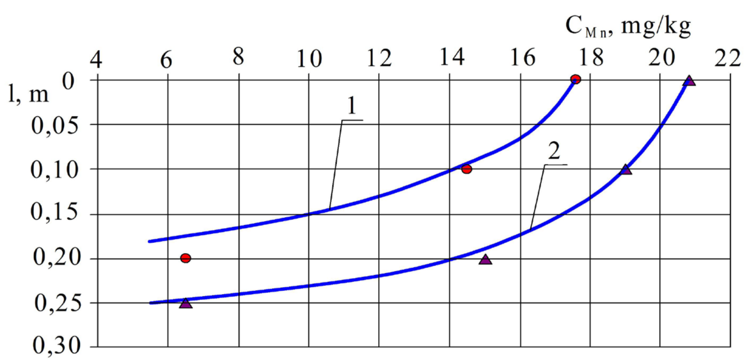

Fig. 7. Experimental depth of manganese penetration in the soil: manganese content in the soil: 1 — background; 2 — A-92 commercial petrol; — curve constructed by the exponential equation (8) for ω=13.1

7. Discussion of the results of the study of the model of forecasting the distribution of heavy metals of exhaust gases of motor vehicles in the soil

Having determined the decisive influence of permeability and diffusion coefficients on the penetration of heavy metals into the soil, the modeling produced an exponential equation for forecasting the depth of penetration of lead, zinc and manganese into the soil at a known c_p/D ratio, surface concentration of components c_1 and under the condition of the stationary process. In the available models [13, 18], molecular diffusion and convection transfer methods are considered to predict the propagation of harmful components in the soil. It is proposed to use diffusion transfer since the fraction of convection transfer in this case is insignificant, which greatly simplifies the model and provides accuracy within 5.5–15 %.

It is confirmed that the experimental concentration of heavy metals at an arbitrary depth (points in Fig. 5–7) and theoretically calculated by the obtained exponential equation (8) (lines in Fig. 5–7) showed error variations for lead within 12.5–15 %, zinc 5.5–7.5 % and manganese 8.5–11 %. This confirms the adequacy of the obtained equation (8) and the possibility to use it for forecasting the distribution of heavy metals in soils. However, for the effective application of the proposed model, the c_p/D ratio should not exceed the limit of 10 to 15 units, which is characteristic of loam.

8. Conclusions

1. The relationship between the depth of penetration of heavy metals into the soil and permeability and diffusion coefficients is determined, which according to the modeling results, is presented in the form of an exponential equation. The obtained equation allows determining the concentration of harmful components of exhaust gases – heavy metals in the soil at the required depth with known values of surface concentrations of these components and c_p/D=ω ratio.

By means of the exponential equation, the effect of ω on the depth of lead penetration is analyzed and it is found that a decrease in ω contributes to an increase in the depth of lead penetration into the soil. This is explained by the increase in the diffusion coefficient.

2. With increasing surface concentration c and constant ω=const, the depth of lead penetration into the soil increases as the driving force of the diffusion process grows.

3. At the experimental site, the concentrations of heavy metals at arbitrary depths for lead – 0.1 and 0.2 m, zinc – 0.1; 0.2 and 0.3 m and manganese – 0.1; 0.2 and 0.25 m are experimentally investigated. The results of the studies and theoretical calculations by the obtained exponential equation showed error variations for lead within 12.5–15 %, zinc 5.5–7.5 % and manganese 8.5–11 %. This confirms the adequacy of the obtained exponential equation and allows it to be used for forecasting the distribution of heavy metals in soils.

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