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Research into soil contamination by heavy metals in the northern part of the Klaipėda city, Lithuania

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This article describes researches into contamination of surface soil layer by heavy metals (Ag, Co, Cr, Cu, Mn, Ni, Pb, Zn) in the northern territory of the Klaipėda city.

Sixty four samples were taken from the surface soil layer (according to geochemical screening and cartographic techniques, scale: 1:10 000) for the analysis of soil contamination. Sampling places were selected at equal distances within the study area between Sportininkų, J. Kanto, S. Šimkaus and Naujosios uosto, Švyturio streets. The findings are presented in concentration distribution isoline maps.

Key words: heavy metals, soil, technogenic contamination, Lithuania

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INTRODUCTION

The study site is in the northwestern part of Lithuania (Fig. 1). The northern part of the Klaipėda seaport shows rapid development of companies (JC Klaipėdos Jūrų Krovinių Kompanija, JC Klaipėdos Nafta, JSC Krovinių Terminalas, JC KLASCO and JC Laivitė), but the increasing flow of trans-shipped cargos has a negative effect on the living environment.

Klaipėda is characterized by a plain and hilly relief. Part of the territory lies in the area of light and medium loamy, carbonated gleyic brown soils. In the north-western, northern and southern parts of Klaipėda predominant are saturated soils of neutral and alkaline re-

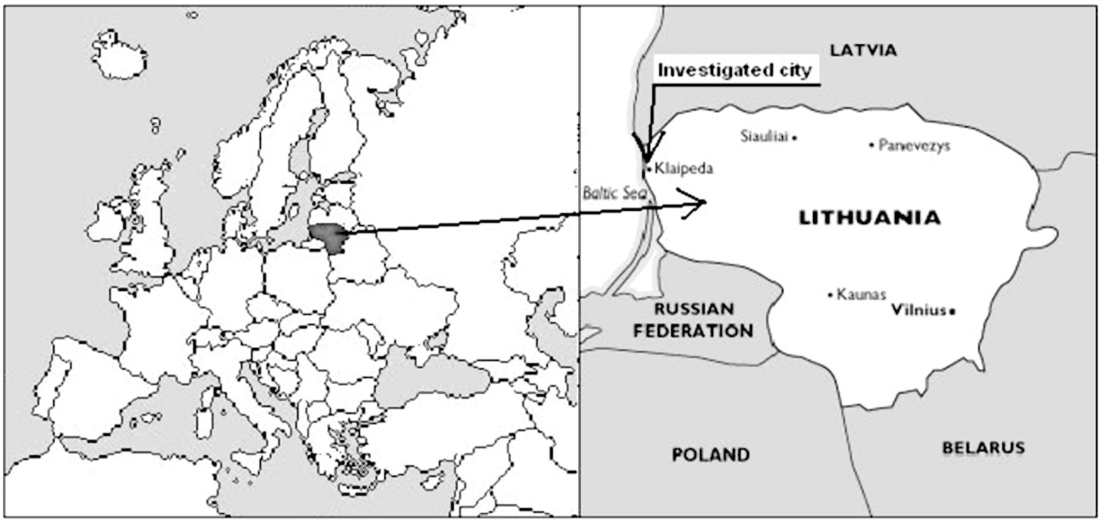

Fig. 1. Location of the Klaipėda city and Lithuania
1 pav. Klaipėdos miesto bei Lietuvos vieta

actions, the north-eastern and eastern parts having more drained soils. Medium acid sandy soils are characteristic of the south-western and south-eastern parts.

Soils in the centre of Klaipėda are sandy and hydrophobic.

Sand or medium and heavy clay soils are in a fairly poor ecological condition. Klaipėda sandy soils are easily drifted, bear a low content of plant nutrition elements and have a poor contaminant sorption capacity (Taraškevičius, Radzevičius, 1998; Taraškevičius et. al., 1999). Hydrophobic sandy soils are evaluated as the worst ones by the condition assessment methods of the urban soil surface horizon. Klaipėda soils have no medium and heavy clay surface horizon.

METHODS

Upon conducting a general survey of the Klaipėda northern district, a precise layout scheme of surface soil sampling points was worked out and the number of soil (surface soil) samples necessary for research was set.

Soil samples were taken in the summer of 2005 by geochemical screening and cartographic techniques (scale 1:10000). To determine the structure of technogenic anomalies, attempts were made to take samples at as equal distances as possible – approximately every 100 m; 64 soil samples were taken for soil contamination analysis (Fig. 2).

Samples were collected according to the "envelope" principle. The sampling depth was up to 0.1 m (Baltrėnas et al., 2002).

Samples placed in special textile bags (around 500 g) were taken to the laboratory of the Vilnius Gediminas Technical University Environmental Protection Department and analysed by the method of atomic absorptive spectroscopy to detect Ag, Cr, Cu, Mn, Ni, Pb, Co and Zn. The extraction of heavy metals was performed with the help of the microwave-accelerated system by the firm ETHOS. A BUCK 210 VPG atomic absorption spectrometer was used for the analysis. The error of the atomic absorption spectroscopy technique is described in Table 1.

The findings were statistically processed with EXCEL software package by calculating the concentration mean and median as well as total and complex contamination values.

The results are presented in isoline maps of concentration distribution. The coordinates are given according to the LKS 94 system.

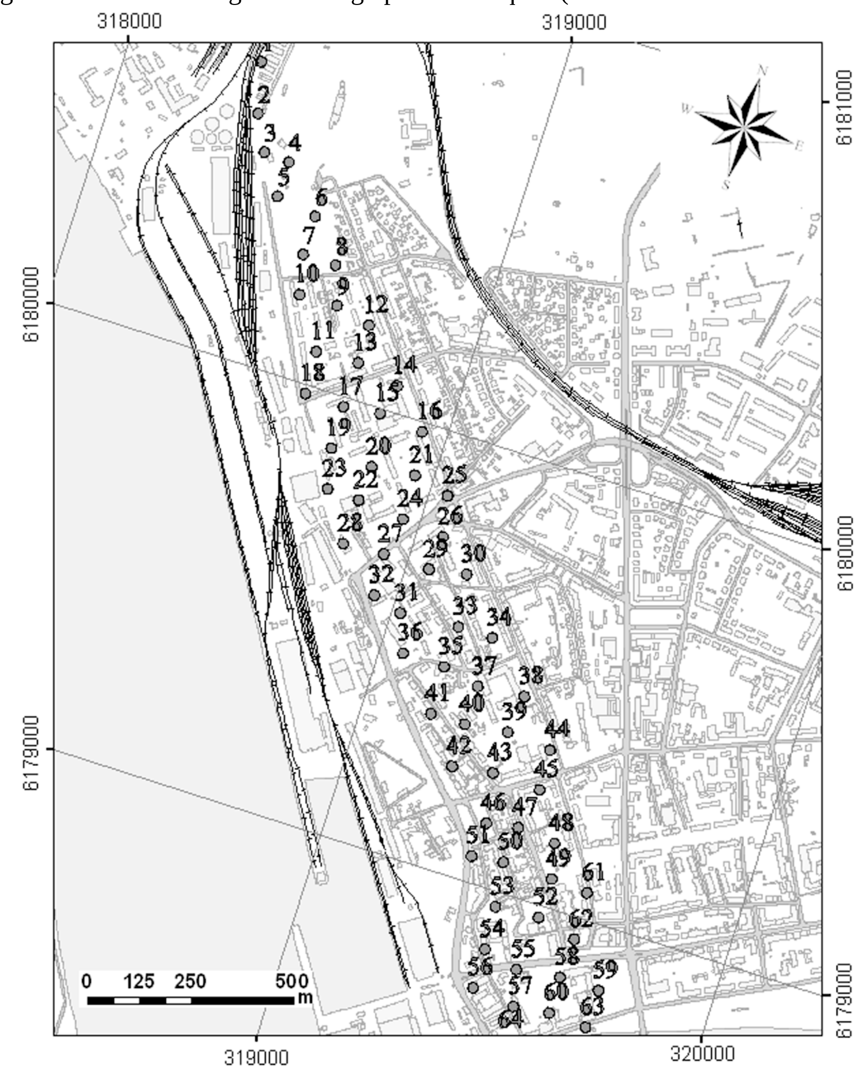

Fig. 2. Soil sampling points
2 pav. Dirvožemio ėminių taškai

RESULTS

The geometric centre of each compound soil sample was recorded on the map. All established data on heavy metals were vectorized and separate basic layers were developed for them. All these layers were transferred to the GIS environment by using Surfer software (Keckler, 1994).

Upon comparing the established concentrations of chemical elements with the background values of heavy metal concentrations we determined their concentration value (K_k), i.e. the indicator describing the level of technogenic contamination. This is the ratio of the chemical element content in a sample to the background content (Taraškevičius, Radzevičius, 1998; Baltrėnas, Kliaugienė, 2003, 2004):

$$K_k = C/C_f, \quad (1)$$

here: C – the established content of the chemical element in a soil sample (mg/kg);

C_f – the background content of the chemical element in the territory (mg/kg).

Table 1. **Data on soil pollution by heavy metals and their concentration coefficient values (K_k)**
1 lentelė. **Dirvožemio ėminių užterštumo sunkiaisiais metalais analizės rezultatai bei koncentracijos koeficientų (K_k) vertės**

Determined value	Mikroelement							
	Cu	Cr	Mn	Zn	Ni	Pb	Ag	Co
Concentration values, mg/m³								
Arithmetical average	27.5	85.6	207.2	72.1	17.9	35.1	0.1032	10.01
Median concentration	26.1	78.3	208.8	41.4	16.7	34.1	0.0908	9.23
Max. value	66.0	182.5	449.1	179.1	41.9	71.6	0.2048	19.89
Min. value	6.7	13.3	43.5	10.3	7.9	10.5	0.0396	2.99
Measurement error, %	10.2	16.9	8.5	8.2	15.9	14.5	22.5	16.2
Beckgraund level*	9.7	37.3	253.0	30.7	14.3	19.8	0.069	4.8
MPC**	100.0	100.0	1500.0	300.0	75.0	100.0	2.0	30.0
Concentration values (K_k)								
Arithmetical average	2.83	2.29	0.82	2.35	1.25	1.77	1.50	2.09
Median value	2.69	2.10	0.83	1.35	1.17	1.72	1.32	1.92
Max. value	6.80	4.89	1.78	5.83	2.93	3.62	2.97	4.14
Min. value	0.69	0.36	0.17	0.33	0.56	0.53	0.57	0.62

* Background content of chemical element in the territory (mg/kg) in the Geochemical Atlas of Lithuania.
** MPC is given from Lithuanian Higiene Norm HN 60:2004.

Fig. 3. Distribution of Ag concentrations in the soil of the northern part of Klaipėda
3 pav. Ag koncentracijų pasiskirstymas Klaipėdos miesto šiaurinės dalies dirvožemyje

By comparing the concentrations with the maximum permissible concentrations (hereinafter MPC) obtained in samples, the complex value of contamination was determined:

$$Ko = C/MPC, \quad (2)$$

here: C – the established content of the chemical element in a soil sample (mg//kg);

MPC – the maximum permissible concentration of the chemical substance in soil (mg/kg).

By summing up *n* of analyzed potentially toxic heavy metals K_k (Table 1) the hazard of contamination was assessed applying the total value of contamination Z_d (Table 2), which was determined by summing up the concentrations of element contaminants in each sample (Kadūnas, 1998; Taraškevičius, Radzevičius, 1998; Baltrėnas, Kliaugienė, 2003, 2004):

$$Z_d = \sum_{i=1}^{n} K_k - (n-1), \quad (3)$$

here: n – the number of chemical elements.

While assessing the contamination of territories according to the total value of contamination, the synergetic effect of chemical elements when the presence of one element together with the other increases the toxicity of the latter was disregarded.

Fig. 4. Distribution of Co concentrations in the soil of the northern part of Klaipėda
4 pav. Co koncentracijų pasiskirstymas Klaipėdos miesto šiaurinės dalies dirvožemyje

The total contamination value is calculated according to the total content of trace elements and the forms of migration thereof are not taken into account. In this case, the values showing a hazardous and especially hazardous level of contamination would be much lower (Taraškevičius, Radzevičius, 1998).

Soil research in the northern part of Klaipėda shows a 0.091 mg/kg median concentration of Ag. The background level in Klaipėda District is 0.069 mg/kg according to the Geochemical Atlas of Lithuania (Kadūnas et al., 1999). The established Ag concentration total value K_k in the territory was 1.5. This shows a low hazardous level of argentic ions in the territory (Fig. 3).

In general, Ag anomalies in Lithuanian soils are present around large industrial cities (Vilnius, Šiauliai, Klaipėda, Kaunas), showing the technogenic contamination of soils (Taraškevičius et al., 1999).

Co median concentration of 9.2 mg/kg was fixed in the soil of the northern part of Klaipėda (background level in Klaipėda District 4.8 mg/kg). The established total Co concentration value K_k in the territory was 1.92, showing a low hazard level of territory contamination by cobalt (Fig. 4).

Cr median concentration of 78.3 mg/kg was fixed in the soil of the Klaipėda City northern part (background level in Klaipėda District 37.3 mg/kg). The fixed total Cr concentration value K_k in the territory was 2.29, showing a low hazard level of territory contamination by chromium. Its increased concentrations are typical of urban soils. The distribution of Cr (like that of Co) is highly dependent on clay content in soil.

The median concentration of Cu was 26.1 mg/kg (background level in Klaipėda district 9.70 mg/kg). The fixed total Cu concentration value K_k in the territory was 2.83, showing an increased contamination by copper (Fig. 5). However, this value still meets the low hazard contamination level.

The median Mn concentration of 208.8 mg/kg was fixed in the northern part of Klaipėda (background level in Klaipėda district 253.0 mg/kg). The established total Mn concentration value K_k in the territory is 0.82, implying an especially low contamination of the territory by manganese.

In the soils of Lithuania, Mn constantly associates with agrogenic P, Ag, Pb, and partially with Zn, Sn, Cu, which, in their turn, are associated with lithogenic elements of clay fraction. In sandy soils, Mn mainly accumulates in clay fraction; in the oxidation barrier it is present in the form of MnO_2 membranes on the surface of minerals (Baltrėnas, Kliaugienė, 2003).

The median concentration of Ni was 16.7 mg/kg (background level in Klaipėda District 14.3 mg/kg). The total Ni concentration value K_k in the territory is 1.25. Contamination by nickel in the territory is at a low level of hazard.

In the soils of Lithuania, the distribution of Ni is similar to that of other lithogenic elements (Li, B, Ga, Co).

The median concentration of Pb in the northern part of Klaipėda was 34.1 mg/kg (background level in Klaipėda District 19.8 mg/kg). The total Pb concentration value K_k in the territory is 1.77 (Fig. 6).

The median concentration of Zn was 41.4 mg/kg (background level in Klaipėda District 30.7 mg/kg).

Fig. 5. Distribution of Cu concentrations in the soil of Klaipėda (northern part)
5 pav. Cr koncentracijų pasiskirstymas Klaipėdos miesto šiaurinės dalies dirvožemyje

The maximum fixed zinc concentration in soil is 179.06 mg/kg. The total Zn technogenic contamination value K_k in the territory is 2.35. The high value of the concentration coefficient shows a high zinc concentration in the territory (Fig. 7).

Due to the fact that Zn has a good sorption capacity with Fe hydroxides, an increase of Zn microelement concentrations was recorded close to the port territory; however, no vivid tendency was observed. This could be predetermined by a high total background level of this element and the mentioned increase in anomalous concentration values around large industrial centres.

Analysis of soil contamination by heavy metals according to the total contamination value (Fig. 8) shows the predominance of permissible soil contamination levels (Z_d < 16). Only four soil samples showed the values of medium hazard ($16 < Z_d < 32$).

DISCUSSION

The association of heavy metals with Fe hydroxides explains the increase of their concentration values in the territory near Švyturio Street. The KLASKO company

Table 2. **Total value of soil contamination Z_d**
2 lentelė. **Dirvožemio suminio užterštumo Z_d rodiklio vertės**

Sample No.	Total value of contamination Z_d	Sample No.	Total value of contamination Z_d	Sample No.	Total value of contamination Z_d	Sample No.	Total value of contamination Z_d
1	-	17	13.80	33	12.32	49	4.93
2	2.89	18	15.25	34	7.33	50	2.08
3	1.10	19	16.08	35	0.82	51	6.30
4	3.32	20	13.86	36	6.49	52	1.45
5	2.82	21	19.90	37	12.02	53	3.77
6	0.55	22	10.56	38	9.49	54	5.62
7	6.15	23	12.67	39	8.42	55	2.58
8	3.47	24	14.18	40	9.02	56	2.07
9	8.94	25	11.76	41	10.86	57	4.20
10	11.13	26	10.10	42	6.51	58	4.51
11	4.39	27	16.61	43	4.46	59	8.23
12	12.62	28	16.47	44	6.14	60	3.26
13	11.50	29	12.63	45	1.45	61	5.29
14	12.04	30	9.42	46	1.78	62	5.46
15	9.35	31	13.19	47	4.03	63	3.46
16	15.09	32	13.43	48	7.37	64	9.51

Fig. 6. Distribution of Pb concentrations in the soil of Klaipėda (northern part)

6 pav. Pb koncentracijų pasiskirstymas Klaipėdos miesto šiaurinės dalies dirvožemyje

undertakes stevedoring of ferro-alloys, and during these operations Fe compound dust gets into the environment.

The increased Co concentration could be predetermined by manganese and iron hydroxides wherewith it got into deposits.

A similar tendency of increased of concentrations of Cr, like in the case of Co, is observed due to sorption with Fe hydroxides.

The highest concentrations of copper were recorded close to crossings and traffic-lights of big motor roads. Most probably this is related to the dust forming during fraying of car break skids (Baltrėnas, Vasarevičius, 2003). Even though Cu concentration in soil surface in this area does not approach MPC, such increase may have a negative impact on the environment.

In all types of soil Cu has positive correlative ties with the P, Zn, Pb (Ag, Sn, Mn) association showing agrichemical contamination. Cu is closely tied with pH (alkaline barrier) only in sand and peat soils. Therefore, the increase of Cu concentration values may be related to ferro-alloy stevedoring operations.

The increase in Ni concentration may be related to the regional load formed by aerosol emissions of power plants.

Hazardous Pb concentrations were detected close to Karo Jūrų Laivynas (Naval Fleet). Contamination in this area could be predetermined by ammunition formerly kept in this territory. In the course of time, storm water flushes lead which while spreading contaminates soil and groundwater.

Pb is well absorbed by carbonates, phosphates, Fe hydroxides and clay minerals, and it precipitates in sulphides and alkaline geochemical barriers. In Lithuanian soils, as a rule, Pb associates with such agrogenic elements as P, Ag, Sn, Mn, Zn, Cu, Mo.

Due to the fact that Zn has a good sorption capacity with Fe hydroxides, an increase of Zn microelement concentrations was recorded close to the port territory; however, no vivid tendency was observed. This could be predetermined by the high total background level of this element and the mentioned increase in anomalous concentration values around large industrial centres.

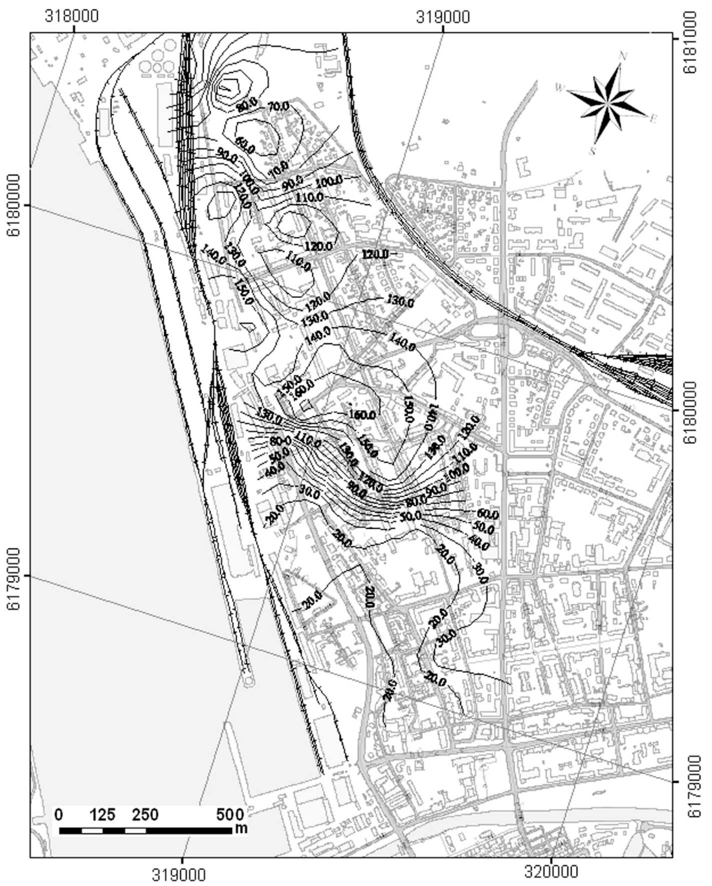

Fig. 7. Distribution of Zn concentrations in the soil of the Klaipėda City (northern part)

7 pav. Zn koncentracijų pasiskirstymas Klaipėdos miesto šiaurinės dalies dirvožemyje

CONCLUSIONS

The increase of Co concentration in the territory of Švyturio Street can be explained by metal association with Fe hydroxides. The KLASCO company carries out ferro-alloy stevedoring operations during which Fe compound dust gets into the environment. Higher concentration of Co could be predetermined by manganese and iron oxides wherewith it got into sediments.

A similar tendency of increased concentrations of Cr, Cu and Zn, like in Co case, is observed due to sorptive properties with Fe hydroxides, which may be related to ferroalloy stevedoring operations.

In the soils of Lithuania, Mn constantly associates with agrogenic elements, therefore the concentration of this metal in urban soils is especially low.

The lowest concentration of Ni is recorded in the coarse fraction of fluvoglacial sand and the highest one in limnoglacial sedimentation moraine clay-loam soils. This distribution results in a low contamination of the territory by Ni microelements.

Pb distribution in the study territory (like in the major part of Lithuanian soils) is mainly predetermined by the high background content of this element and the heavy traffic.

No vivid tendency of increase in Zn microelement concentration was observed around the port territory. This could be predetermined by the total increase in anomalous concentration values around large industrial centres (Vilnius, Šiauliai, Kaunas, Panevėžys, Alytus, Klaipėda).

None of the values of the heavy metal concentrations exceeded the MPC.

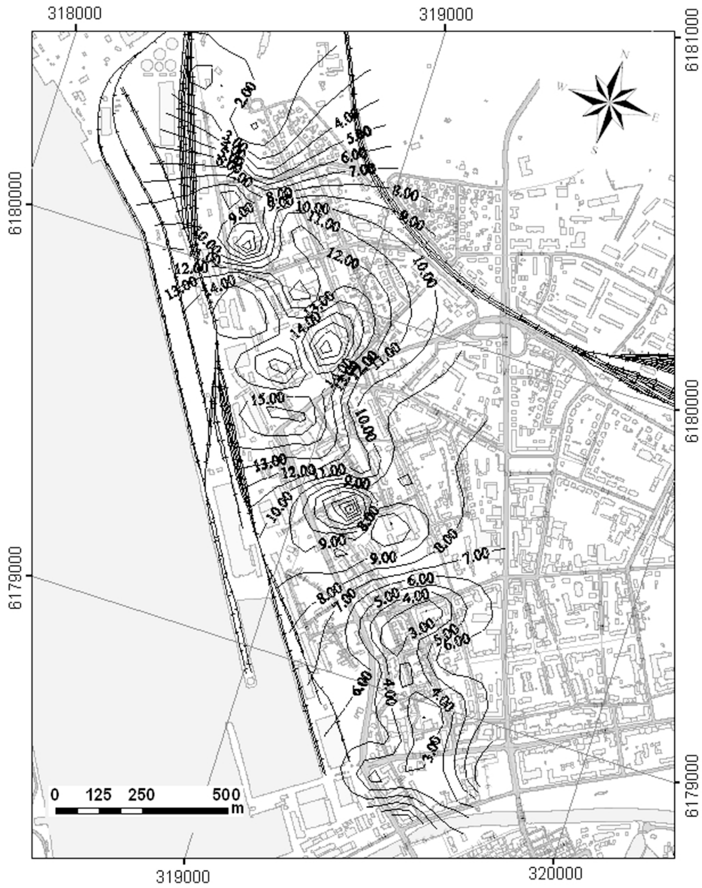

Fig. 8. Distribution of the total contamination value Z_d in the soil of the Klaipėda City (northern part)

8 pav. Suminio užterštumo rodiklio Z_d pasiskirstymas Klaipėdos miesto šiaurinės dalies dirvožemyje

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KLAIPĖDOS MIESTO ŠIAURINĖS DALIES DIRVOŽEMIO UŽTERŠTUMO SUNKIAISIAIS METALAIS TYRIMAI

Santrauka

Šiame straipsnyje aprašomi paviršinio dirvožemio sluoksnio užterštumo sunkiaisiais metalais (Ag, Co, Cr, Cu, Mn, Ni, Pb, Zn) bei naftos produktais tyrimai Klaipėdos miesto šiaurinės dalies teritorijoje.

Dirvožemio užterštumo analizei buvo paimti 64 paviršinio dirvožemio sluoksnio ėminiai (pagal geocheminio profiliavimo ir kartografavimo metodiką, mastelis 1:10 000), kurių paėmimo vietos tolygiai išdėstytos tirtoje teritorijoje tarp Sportininkų, I. Kanto, S. Šimkaus ir Naujosios uosto, Švyturio gatvių. Koncentracijų pasiskirstymas pateiktas izolinijų žemėlapiuose, koordinatės – pagal LKS 94 sistemą.

Nė viena iš analizuotų sunkiųjų metalų koncentracijų verčių neviršijo DLK. Analizuojant dirvožemio užterštumą sunkiaisiais metalais pagal suminio užterštumo rodiklį, vyrauja leistinas dirvožemio užterštumas – Zd < 16. Tik 4 dirvožemio ėminiuose pastebėtos vidutinio pavojingumo koeficiento reikšmės (16 < Zd < 32).

Co, Cr, Cu bei Zn metalų sorbcinės savybės su hidroksidais paaiškina teritorijos prie Švyturio gatvės koncentracijų koeficientų padidėjimą. AB KLASCO vykdo geležies lydinių krovos darbus, kurių metu į aplinką patenka Fe junginių dulkės. Taigi koncentracijų koeficientų padidėjimas gali būti siejamas su minėtų lydinių krovos darbais.

Пранас Балтренас, Вайдотас Вайшис

ИССЛЕДОВАНИЕ ЗАГРЯЗНЕНИЯ ПОВЕРХНОСТНОГО СЛОЯ ПОЧВЫ ТЯЖЕЛЫМИ МЕТАЛЛАМИ В СЕВЕРНОЙ ЧАСТИ Г. КЛАЙПЕДА

Резюме

Описывается исследование загрязнения поверхностного слоя почвы тяжелыми металлами (Ag, Co, Cr, Cu, Mn, Ni, Pb, Zn) и нефтепродуктами в северной части г. Клайпеда.

Для исследования загрязнения были взяты 64 образца поверхностного слоя почвы (на основе методики географического профилирования и картографирования – в масштабе 1:10 000), места которых равномерно распределены по территории между улицами Спортининку, И. Канто, С. Шимкаус, Науйосёс уосто и Швитурио. Результаты эксперимента представлены картами распределения концентрации вышеупомянутых металлов в изолиниях, координаты – по системе ЛКС 94.

По результатам исследования ни один металл не превышал допустимых норм.

Анализируя загрязнения поверхностного слоя почвы тяжелыми металлами, по суммарному показателю загрязнения, доминирует допустимая норма загрязнения – Zd < 16. Лишь в 4 образцах почвы были установлены средние значения коэффициента загрязнения (16 < Zd < 32).

Свойства сорбции металлов Co, Cr, Cu и Zn применяя гидроксид металла (Fe) объясняет повышение коэффициента загрязнения на улице Швитурио. АО KLASCO занимается погрузочными работами сплавов железа, во время которых в окружающую среду выбрасываются частицы железа. Повышение коэффициента загрязнения может быть связано с погрузочными работами.