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Heavy metal contents in the Tyumen city residential area soils

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Abstract: The present paper examines the state of pollution of soils in the city of Tyumen regarding heavy metals contained therein: nickel (Ni), cobalt (Co), manganese (Mn), copper (Cu), cadmium (Cd), lead (Pb) and chromium (Cr). Soil sampling was carried out in autumn 2021 within the city residential areas. The sampling points were chosen in the sites of increased anthropogenic load – near highways and industrial enterprises. In soil samples, the content of acid-soluble and mobile fractions of heavy metals and organic matter was determined, and the pH factor was also measured. The analysis showed that significant excesses, from 3.2 to 14.3 MPC level, were found on nickel in 11 soil samples, and all the soil samples belong to the zones of motor transport impact. In one sample, No. 29, which belongs to the impact zone of such large industrial enterprises as the Elektrostal Tyumen Metallurgical Plant (Ural Mining and Metallurgical Company-Steel, UMMC Steel) and the Motor Plant, the MPC for nickel was exceeded by 8.1 times. There were also excesses in the copper contents in 11 samples, from 1.5 to 4.9 MPC, and in both the zones of motor transport impact and the territories affected by the building materials enterprises, railway junction, and UMMC Steel. For lead, there was a two-times excess in two samples in the zone of motor transport impact, 4.4 times – in the impact zone of the Construction Machinery Plant, and 29.7 times – in the zone of impact of Velizhansky Highway. For cobalt, chromium and manganese, the MPC values for the acid-soluble fractions were not exceeded. For the mobile fractions, excesses were also observed for manganese. The highest excesses of the MPC level for nickel and copper were found in the Vostochny (Eastern) and Central districts of the city, in the areas affected by motor transport and the large enterprises.

Keywords: soil mantle; heavy metals; pH of saline extract of soils; soils; pH of aqueous extract of soils; degree of pollution; MPC; environmental monitoring.

Содержание тяжелых металлов в почвах селитебной зоны г. Тюмени

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Аннотация: Исследовано состояние загрязненности почв г. Тюмени на предмет содержания в них тяжелых металлов: никеля (Ni), кобальта (Co), марганца (Mn), меди (Cu), кадмия (Cd), свинца (Pb) и хрома (Cr). Отбор проб почв проводился осенью 2021 г. на селитебных участках в пределах города. Точки отбора выбирались в зонах повышенной антропогенной нагрузки – вблизи автомагистралей и промышленных предприятий. В пробах почв определено содержание кислоторастворимых и подвижных форм тяжелых металлов, и органического вещества, а также измерен водородный показатель (pH). Анализ показал, что значительные превышения выявлены по

никелю в 11 пробах почв от 3,2 до 14,3 ПДК, причем все пробы почв относятся к зонам влияния автотранспорта. В одной пробе № 29, которая относится к зоне влияния таких крупных промышленных предприятий, как Металлургический завод «Электросталь Тюмени» («УГМК-Сталь») и Моторный завод, превышено ПДК по никелю в 8,1 раза. По содержанию меди тоже есть превышения в 11 пробах, от 1,5 до 4,9 ПДК, причем в зонах влияния как автотранспорта, так и на территориях влияния предприятий строительных материалов, железнодорожной развязки, «УГМК Сталь». По свинцу есть превышения в двух пробах в два раза в зоне влияния автотранспорта, в 4,4 раза в зоне влияния Завода строительных машин, в 29,7 раз в зоне влияния автодорог Велижанского тракта. По кобальту, хрому и марганцу значения ПДК для кислоторастворимых форм не превышены. По подвижным формам превышения наблюдаются и по марганцу. Наибольшие превышения ПДК по никелю, меди выявлены в Восточном и Центральном районах города, в зонах влияния автотранспорта и крупных предприятий.

1. Introduction

Human activities to transform the soils of residential areas result in changes in the elemental composition of soils – heavy metals (HMs) enter the environment where they are able to accumulate in the soil, especially in the upper part of the soil. Besides, HMs are actively involved in geochemical cycles, through which they can penetrate into the atmosphere, hydrosphere, lithosphere and biosphere. Anthropogenic impacts on soils have a negative effect on their structure and characteristics: fertility and biomass production, dynamism and sustainability are reduced, which can lead to soil degradation. At the same time, soil is an indicator of the condition of the landscape and the degree of safety for human habitation. It should be noted that HMs have carcinogenic, toxic and mutagenic effects. The penetration of these pollutants into human and animal bodies leads to deterioration of the health of those ones, up to lethal outcome. In soils HMs are found as oxides, sulphides, and also as soluble salts such as chlorides, nitrates and sulphates. When acidic precipitation enters the soil, nitric acid dissolves the oxides and sulphides of the HMs. In the upper horizons of the soil profile, which contains the greatest amount of humus, metals bind with organic ligands, resulting in the formation of low-mobile complex compounds. Then, they accumulate in the upper horizons of the soil profile, but are not transported by downward water flow to the lower horizons. However, if the concentration of humus is low, the bulk of the HMs will be in a free state and transferred to the deeper horizons and layers under the influence of soil moisture [1].

In this regard, nowadays, the timely assessment of soil contamination with HMs appears to be an urgent task at present. In work [2], the authors establish that more and more attention is given to soil pollution all over the world. This is due to the increasing number of oil and gas processing enterprises that leads to the prevalence of complex pollution from HMs and polycyclic aromatic hydrocarbons (PAHs). Soil co-pollution with the HMs and PAHs poses more serious threats to the environment and human health, such as increased toxicity to microbial activity and diversity, reduced bioavailability, and inhibition of plant growth. Possible ways of purifying soils from such pollutants are represented by electrokinetic remediation and leaching and the use of chelating agents.

Soil monitoring studies that are being conducted determine enrichment factor (EF), environmental risk calculation (ER), bioconcentration factor (BCF), transfer factor (TF), hazard index (HI), and carcinogenic risk (CR). Such studies provide insights into the controls of urbanization in relation to the combined severity of pollution and potential health risk [3].

The main source of HM contamination of soils is dust pollution. At the same time, the concentration of HMs is highest in the fractions having dust particle sizes of < 0.63 μm. The penetration of such particles into the human body can cause a variety of diseases, including cancer [4].

The city of Tyumen is located in the southwest of the West Siberian Plain within the sub-taiga zone. Zonal soils are sod-podzolic and gray forest, black earth occurs closer to the forest-steppe. Soils are formed on covered loams, with the lower part of the profile predominantly of loamy granulometric composition, while the upper part of the profile is loamy-sandy. The soils are slightly alkaline and neutral.

The aim of the present work was to assess the pollution of soils of Tyumen city with the most common HMs (Ni, Co, Mn, Cu, Cd, Pb, Cr), organic matter (OM), as well as to determine the hydrogen index (pH).

2. Materials and Methods

In this study, soils contaminated with HMs in residential areas of Tyumen, as well as adjacent territories, were chosen as analysis objects.

At present, the following industries are being dynamically developing in the city: fuel industry (oil and gas processing), machine building, forestry, etc. There are large industrial facilities in and around Tyumen such as the Tyumen Battery Plant, the Antipinsky Oil Refinery, UMMC-Steel, and the Tyumen Plywood Plant. Moreover, Tyumen is a major transportation hub: The Trans-Siberian Railway, major highways and interchanges pass through its territory. Industrial and transport facilities are the sources of HM entering the environment and have a significant impact on its ecological situation. Soil sampling was conducted in urban and suburban areas. Samples were taken from the upper (0–10 cm) organo-mineral horizon that adsorbs a significant part of dust emissions due to its peculiar structure and large OM amount. Therefore, this soil layer was selected for the study. Characteristics of soil sampling points are presented in Table 1.

Table 1. Characteristics of Soil Samples

Sample No.	Sampling point	Possible impact
1	Pchyolka rural district	Bypass road, Salair Highway
2	Mezhdurechenskaya Street	Salair Highway
3	Tsimlyan Lake green area	Battery Plant
4	Plekhanova village	Bypass road, Plekhanovo Airport
5	Dudareva village	Moscow Highway
6	Paderina village	Moscow Highway, Chervishevsky Highway
7	City forest area	Motor transport
8	Salair Highway, roadside	Motor transport
9	Komunisticheskaya Street	Motor transport
10	Mira Street	Motor transport
11	Komarovo village	Bypass road, Chervishevsky Highway
12	Chervishevsky Highway, roadside	Motor transport
13	Salair Highway, roadside	Motor transport
14	Kazarovo village	Construction Machinery Plant
15	Druzhby Street, city park	Motor transport
16	Kharkovskaya Street	Motor transport
17	Shirotnaya Street	Motor transport
18	Patrusheva village	Motor transport
19	Yasny Horticultural Cooperative	Velizhansky Highway
20	Velizhansky Highway, roadside	Construction Machinery Plant, Motor transport
21	Malinovskogo Street	Motor transport
22	Gilyovskaya grove	Motor transport
23	Stantsionnaya Street	UMMC-Steel, Railroad junction, Motor transport
24	Fedyuninskogo Street, roadside	Motor transport
25	Sadovoye Horticultural Cooperative	Velizhansky Highway
26	Druzhby Street	Bypas road, Plywood Plant
27	Tura River bank	Motor transport
28	Antipino	Starotobolsky Highway, Antipinsky Oil Refinery
29	Andreyevskoye Lake	Motor plant, UMMC-Steel, Motor transport

The pH of aqueous and saline extracts of the selected soils was determined through the method according to Russian Standard 26423-85. The OM content was assessed through gravimetry in accordance with Russian Standard 26213-91. The mass fraction of mobile and acid soluble forms of the metals (copper, lead, zinc, nickel, cadmium, cobalt, chrome, and manganese) in the soil samples was measured by atomic absorption method according to Guidance Document 52.18.289-90 and Guidance Document 52.18.191-89 respectively. The atomic-absorption method realized on a ContrAA700 spectrophotometer (AnalytikJena™,

Jena, Germany) using xenon lamp of continuous spectrum was used to quantify HM contents in acid and acetate-ammonium soil extracts.

3. Results and Discussion

3.1. Determination of pH and organic matter of soil samples

The results of determining the pH of aqueous and saline extracts of soils are shown in Figs. 1 and 2. From Fig. 1, it can be seen that the pH of the soil
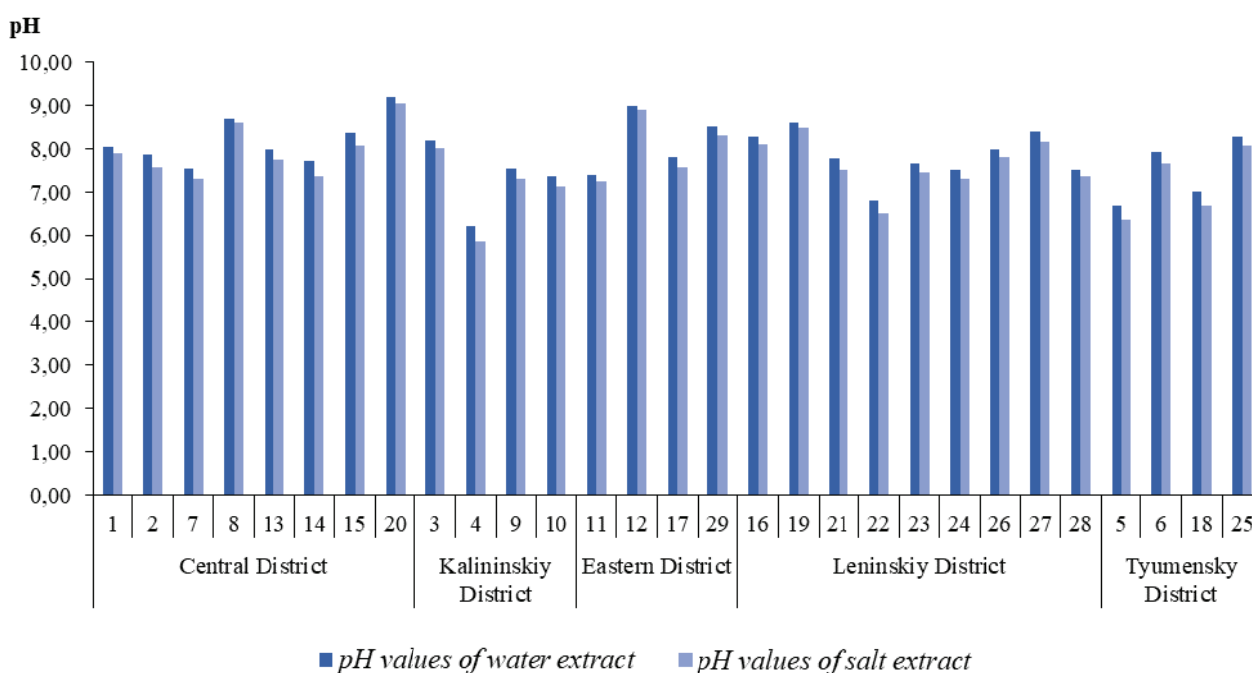

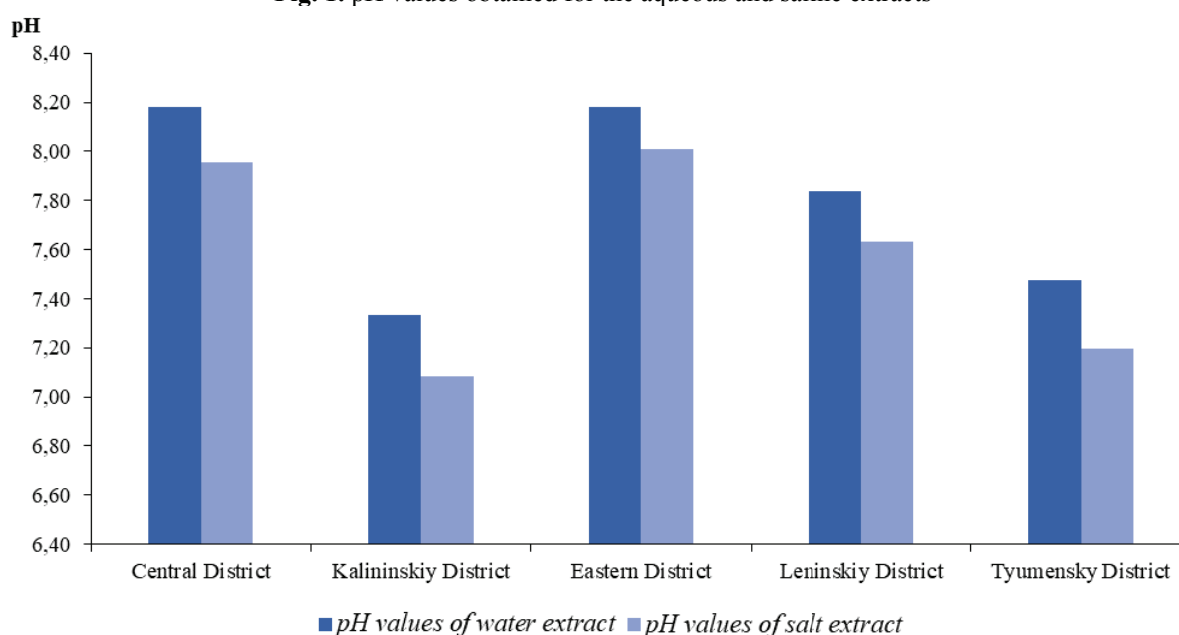**Fig. 1.** pH values obtained for the aqueous and saline extracts

Fig. 2. Average pH values obtained for the aqueous and saline extracts for different districts

solutions is predominantly alkaline. This fact can be explained by the contents of magnesium and calcium carbonates coming from construction and household wastes from industrial enterprises. Furthermore, transport can be an additional source of pollution source, especially, in areas with heavy traffic (*e.g.*, near highways which give HMs in the form of dust particles [5]. High pH values are probably associated with an increase in the mobility of HM compounds that may accumulate in acidic soils due to the presence of humic acids [6].

The pH values of aqueous and saline extracts were found to lie in the ranges of 6.22–9.20 and 5.87–9.06, respectively and refer to neutral, low-alkaline and alkaline media.

The investigated soils belong to the objects with low resistance to acids and high sensitivity in relation to the HMs. Since the upper parts of the soil profiles have a sandy loam granulometric composition, the corresponding maximum permissible concentrations (MPCs) [Sanitary Rules and Regulations 1.2.3685-2] were taken when assessing the HM content.

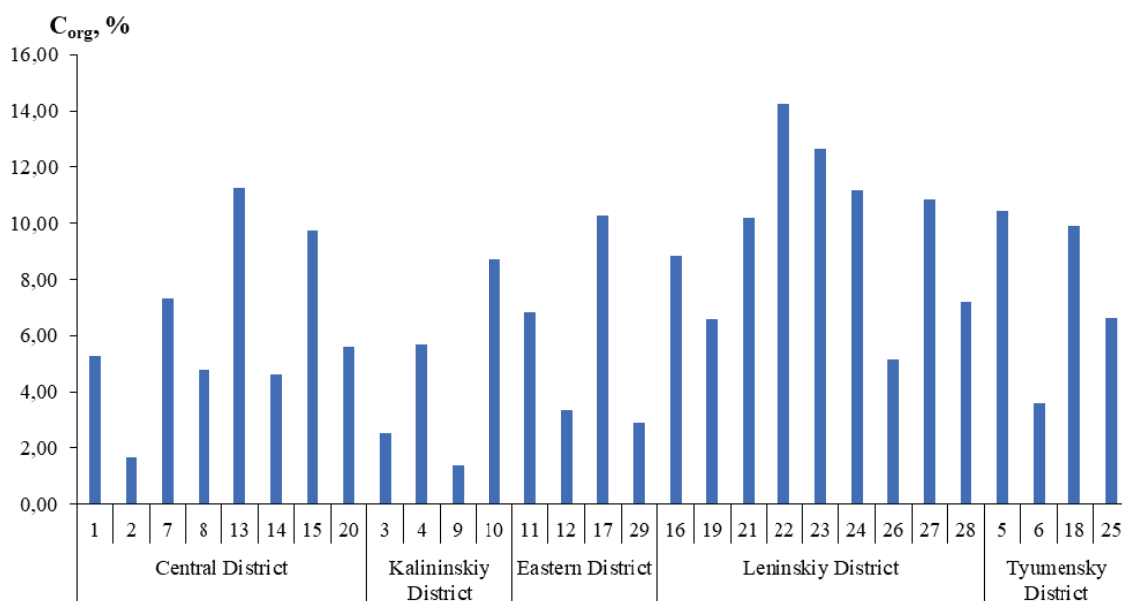The results on the OM determination are presented in Figs. 3 and 4 and Table 2.

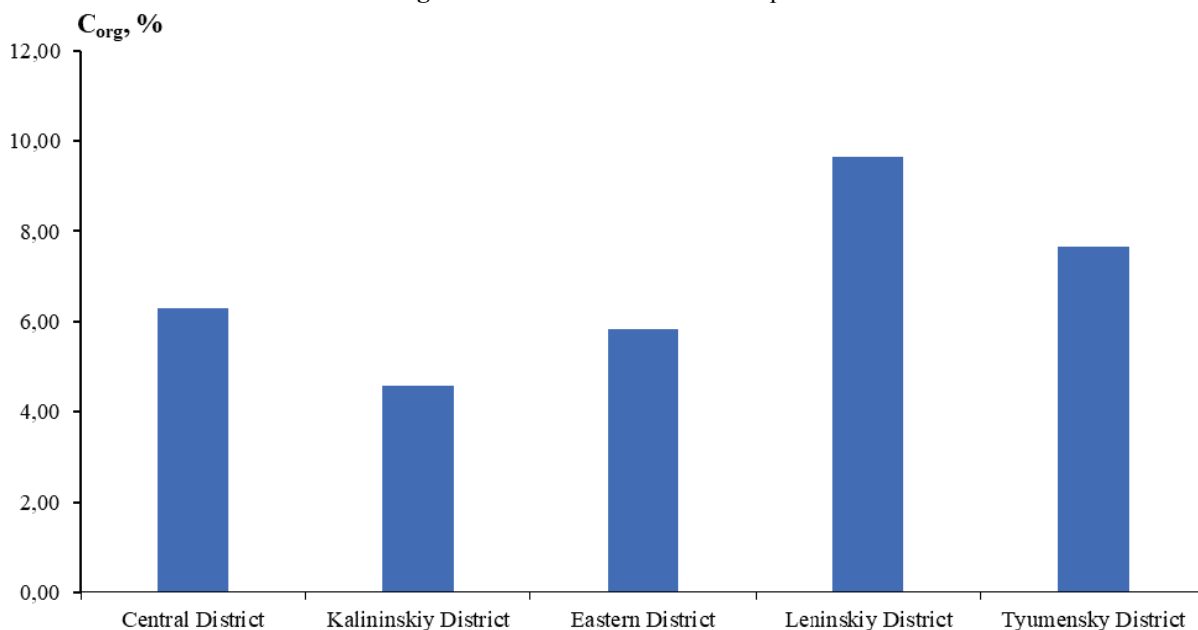**Fig. 3.** OM contents in the soil samples

Fig. 4. Average OM contents in the soil samples

Table 2. OM contents, pH of aqueous
and saline extracts

Sample No.	pH of aqueous extract	pH of saline extract	OM contents C_{org}, %
1	8.05	7.89	5.26
2	7.87	7.56	1.65
3	8.20	8.02	2.52
4	6.22	5.87	5.69
5	6.68	6.36	10.46
6	7.92	7.65	3.58
7	7.54	7.31	7.34
8	8.70	8.60	4.79
9	7.54	7.31	1.39
10	7.38	7.13	8.73
11	7.41	7.24	6.85
12	8.99	8.89	3.34
13	7.99	7.76	11.25
14	7.71	7.37	4.64
15	8.37	8.09	9.76
16	8.28	8.10	8.85
17	7.82	7.58	10.29
18	7.02	6.70	9.92
19	8.62	8.48	6.57
20	9.20	9.06	5.59
21	7.77	7.53	10.19
22	6.80	6.51	14.24
23	7.66	7.45	12.66
24	7.51	7.30	11.18
25	8.29	8.08	6.65
26	8.00	7.81	5.15
27	8.40	8.16	10.86
28	7.52	7.37	7.19
29	8.51	8.32	2.90

The OM percentage in the upper soil horizon is 1.39–14.24 %. The soil sample with the highest OM amount was taken in the Gilyovskaya grove area. High OM contents were also observed in the soils sampled outside the Tyumen city limits and in the Leninsky administrative district of Tyumen city.

3.2. Determination of acid-soluble and mobile fraction of HM

The HM fraction extracted from the soil using ammonium acetate buffer (pH = 4.8) represents the mobile form of HM compounds. At this pH value, the most efficient uptake of trace elements by plants from the soil solution occurs. The mobile HM fraction is associated with its most transportable part. It determines the availability of mineral components to plants and soil toxicity. This fraction is found in the form, in which the HMs are integrated into geochemical cycles and food chains.

The results of determining the HM mobile fraction content of the of HM in the soil are presented in Table 3.

The HMs are extracted from the soil solution using ammonium acetate buffer through ion exchange and complexation reactions. The predominance of one or the other process depends on the nature of the metal to be extracted. For instance, for cobalt and zinc, the extraction is caused to a greater extent by the complexation reaction, whereas for chromium and cadmium, it is caused by the ion exchange reaction [7].

The gross HM content in the soils is determined when the soil samples are exposed to strong acids ($5n \cdot HNO_3$). The value of this indicator makes it possible to judge on the total contamination of soils with the HMs, however, it should be noted that this indicator does not provide information on the element availability of elements [8]. High values of the gross HM content indicate a potential environmentally unfavourable situation of the territory; that is, if the water and plants are not polluted at the moment, the ecological situation may change for the worse if external factors change.

Table 3. Contents of the HM mobile fractions, mg·kg^{-1}

Sample No.	Ni	Co	Mn	Cu	Cd	Pb	Cr
1	19.3±5.8	–	76±23	0.53±0.16	–	–	5.50±1.70
2	–	–	35±10	0.87±0.26	–	5.90±1.80	1.73±0.50
3	–	–	41±12	0.68±0.20	–	–	1.70±0.52
4	1.40±0.43	–	54±16	0.45±0.14	–	0.33±0.10	2.50±0.76
5	–	–	70±21	0.39±0.12	–	–	2.01±0.60
6	2.40±0.71	–	52±16	1.02±0.30	–	0.47±0.14	2.42±0.73

Sample No.	Ni	Co	Mn	Cu	Cd	Pb	Cr
7	–	–	301±90	0.41±0.12	–	–	2.12±0.63
8	21.1±6.2	–	89±27	1.83±0.55	–	42±13	4.30±1.30
9	–	–	43±13	0.97±0.29	–	1.94±0.56	2.44±0.72
10	8.9±2.7	–	171±51	0.92±0.28	–	1.91±0.58	2.81±0.85
11	–	–	77±23	0.37±0.11	–	–	1.50±0.46
12	31.2±9.4	0.34±0.10	88±26	3.01±0.89	–	6.8±2,0	4.00±1.20
13	5.8±1.8	0.15±0.04	103±31	0.67±0.20	–	20.0±6.1	2.02±0.60
14	1.81±0.55	–	65.±20	0.60±0.18	–	–	4.90±1.50
15	0.140±0.043	–	149±45	0.44±0.13	–	–	0.91±0.27
16	–	–	143±43	4.60±1.40	–	–	1.21±0.37
17	–	–	148±44	0.52±0.16	–	–	1.41±0.42
18	–	–	174±52	1.40±0.41	–	9.7±2.9	0.84±0.25
19	30.1±9.1	–	84±25	1.82±0.55	–	18.0±5.4	3.23±0.95
20	27.2±8.2	–	101±30	5.60±1.70	–	80±24	3.90±1.20
21	–	–	90±27	0.65±0.20	–	2.90±0.88	0.87±0.26
22	–	–	228±68	0.80±0.24	–	3.31±0.99	1.13±0.34
23	–	–	136±41	0.50±0.15	–	7.3±2.1	1.13±0.33
24	3.30±0.99	–	147±44	0.68±0.20	–	–	2.51±0.74
25	19.0±5.6	1.10±0.19	287±86	9.20±2.80	2.60±0.77	2076±622	8.20±2.50
26	–	–	72±22	1.01±0.30	–	0.36±0.11	0.96±0.29
27	0.62±0.19	–	332±100	1.01±0.30	–	2.08±0.62	1.41±0.42
28	22.3±6.7	0.62±0.19	95±28	2.44±0.73	–	2.63±0.77	4.20±1.30
29	–	–	92±27	1.12±0.33	–	–	1.60±0.49
MPC	**4**	**5**	**140**	**3**		**6**	**6**

Table 4. Contents of the HM acid-soluble fractions, mg·kg^{-1}

Sample No.	Ni	Co	Mn	Cu	Cd	Pb	Cr
1	160±48	8.8±2.6	267±80	15.3±4.4	–	0.88±0.26	71±21
2	4.8±1.4	3.01±0.91	165±50	71±21	–	16.00±4.90	4.1±1.1
3	28.0±8.4	9.4±2.8	487±146	62±19	–	3.31±0.10	21.1±6.2
4	26.1±7.9	13.1±3.8	604±181	67±20	–	0.96±0.29	21.2±6.2
5	36±11	14.0±4.2	549±165	47±14	–	0.84±0.25	21.4±6.4
6	36±11	3.9±1.2	165±49	34±10	–	14.00±4.10	18.0±5.5
7	3.5±1.1	3.4±1.0	366±110	163±49	–	–	3.3±1.0
8	189±57	11.1±3.2	362±109	39±12	–	61±19	65±20
9	14.0±4.1	6.1±1.8	267±80	50±15	–	–	9.1±2.6
10	133±40	12.1±3.6	407±122	18.1±5.3	–	3.6±1.1	50±15
11	21.1±6.3	8.9±2.7	401±120	25.3±7.6	–	–	15±4.4
12	238±72	14.1±4.3	273±82	26.2±7.9	–	–	82±24
13	114±34	8.5±2.5	264±79	114±34	–	22.1±6.6	34±10

Continue Table 4

Sample No.	Ni	Co	Mn	Cu	Cd	Pb	Cr
14	42±13	7.2±2.2	199±60	38±11	–	–	102±31
15	44±13	3.30±0.99	407±122	43±13	–	–	17.4±5.1
16	67±20	12.0±3.5	449±135	20.0±5.9	–	–	34±10
17	63±19	7.5±2.3	398±119	51±15	–	–	31±9,2
18	33±9.8	6.1±1.8	360±108	158±47	–	–	16.4±4.8
19	286±86	17.2±5.1	266±80	15.2±4.4	–	32.3±9.7	71±21
20	228±68	12.0±3.7	298±89	62±18	–	140±42	65±19
21	42±13	7.8±2.3	579±174	10.4±3.0	–	8.2±2.5	26.2±7.9
22	35±10	8.6±2.6	812±243	30.2±8.9	–	16.0±4.9	16.1±4.9
23	37±11	5.6±1.7	325±97	61±18	–	11.0±3.2	12.1±3.7
24	72±22	3.6±1.1	319±96	37±11	–	–	24±7.3
25	199±60	11.0±3.4	798±239	13.1±3.8	4.8±1.4	951±285	87±26
26	33±10	6.6±2.0	496±149	33.0±9.9	–	3.4±1.0	16.0±4.7
27	74±22	7.1±2.1	688±207	27.2±8.1	–	10.0±3.1	22.3±6.7
28	23.4±7.0	7.7±2.3	510±153	79±24	–	18.4±5.3	17.1±5.0
29	161±48	9.1±2.7	218±65	49±15	–	15.3±4.5	64±19
MPC	**20**	**20**	**1500**	**33**	**0.5**	**32**	**100**

The results on the content of HM acid-soluble forms in the soil are presented in Table 4.

The HM content in sample No. 25 significantly exceeded the MPC values; that sample was taken from the territory of Sadovoye Horticultural Cooperative, where agrarian works have been carried out for several years. A large HM amount could come into the soil from phosphate fertilizers, in which the HM contents can reach 220 mg·kg^{-1} [9]. On this basis, the authors of this study assumed that a large fertilizer amount was entering the soil, or that the site was used as a landfill. Therefore, in further consideration of the data obtained, the values for sample No. 25 were excluded from the total set.

Nickel. The MPC of nickel in the soils of residential areas is 20 mg·kg^{-1} for acid soluble fractions and 4 mg·kg^{-1} for its mobile fractions. The most common are Ni^{2+} compounds. Ni^{3+} exists in an alkaline environment as well as under harsh oxidizing conditions, but such conditions are rare in the natural environment [10, 11]. Nickel is a moderate complexing agent capable of forming predominantly fulvate complexes with organic or inorganic ligands. Besides, it can also be found in soils as carbonate or hydrocarbonate complexes, with the ratio of one or the other complex form depending on the acidity of the medium [12]. Compounds of this element can be adsorbed by fine-grained clay particles as well as by iron, manganese and aluminum hydroxides [13].

Nickel sources may include a variety of industrial emissions, vehicle fuel emissions, and parts of rubber tyres. At different sampling points, the levels of the nickel contents exceeding the MPC were observed, suggesting that the contamination with this metal is not local but extensive, covering the whole area (see Figs. 5, 6).

This contamination may be caused by roads connecting different parts of the city. The high content of the nickel acid-soluble fractions in many samples exceeded the MPC by a factor of 2 to 14, thereby indicating its accumulation in the soils of these districts. The excess levels of the nickel contents in the samples taken near the roadsides (bypass road, as well as the highways: Salair, Chervishevsky, Moscow and Velizhansky) allow concluding about the transport impact.

Cobalt. The MPC level for its acid-soluble fractions is 20 mg·kg^{-1}, whereas for its mobile fractions of cobalt in the case of the soils of residential areas, it is 5 mg·kg^{-1}. In most cases the cobalt contents in soils depend on the parent rock composition. Considerable quantities of cobalt are identified in soils formed from basic rocks and clay sediments. It should be taken into account that the pattern of the cobalt distribution and behavior in soils is much affected by humus contents in the soil horizon.
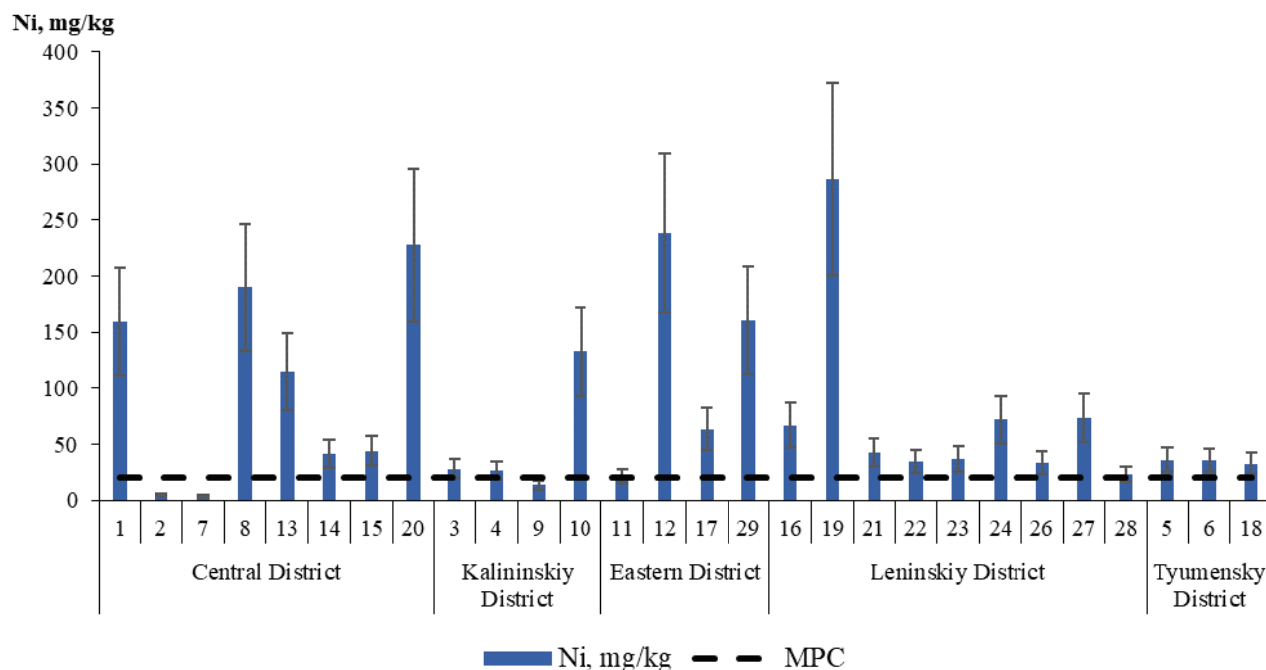
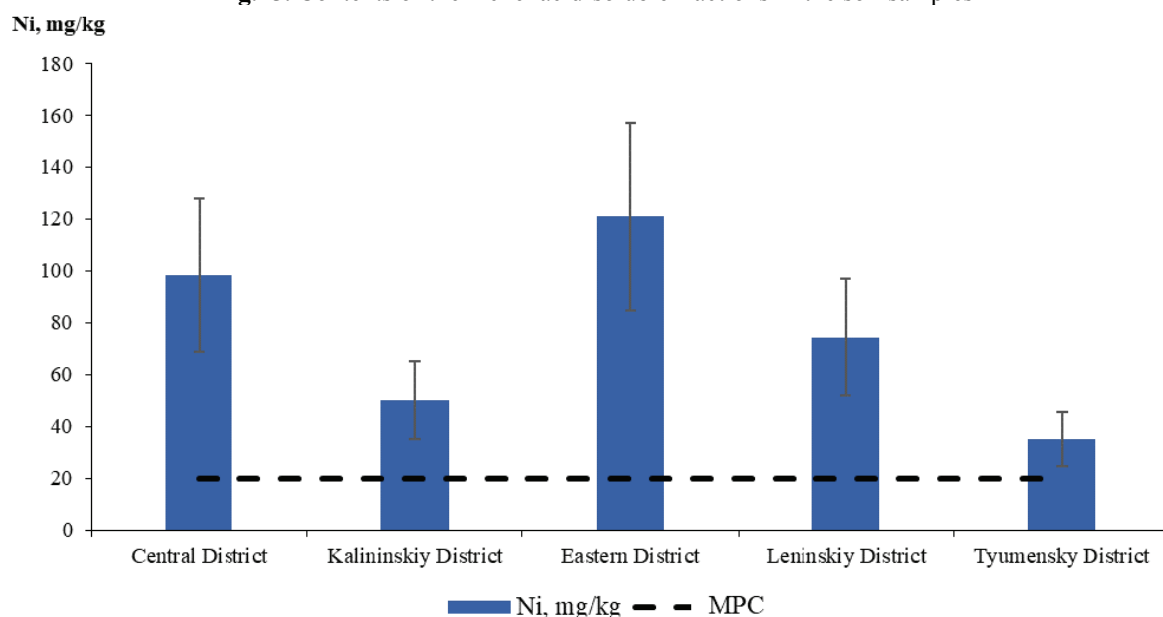**Fig. 5.** Contents of the nickel acid-soluble fractions in the soil samples

Fig. 6. Average contents of the nickel acid-soluble fractions in the soil samples

Cobalt takes different forms depending on pH of the environment and is found as Co^{2+} and Co^{3+}, or as the complex anion $Co(OH)_3^-$, i.e. in the mobile form.

The results on the cobalt contents show that none of the Tyumen districts exceeded the MPC level established for both acid-soluble and mobile fractions of this element (Figs. 7, 8).

Manganese. The manganese MPC level is as follows: for its mobile fractions, it is 140 mg·kg^{-1}, whereas for its acid-soluble fractions, it is 1500 mg·kg^{-1}. This metal is found in soils more often than other elements. The main place of its accumulation

is the top soil layer, since it actively interacts there with the OM. In nature, manganese occurs mainly as Mn^{4+}, Mn^{3+}, Mn^{2+}, or as minerals. Manganese (as Mn^{2+}) can replace divalent cations of some elements (Fe^{2+}, Mg^{2+}) in silicates and oxides, thereby forming ferromanganese nodules, so it is the most common one in the environment.

Slightly excessive levels of manganese MPC for the mobile fractions were observed in samples No. 17, 16 and 26, and in samples Nos. 7, 10, 18, 22, 25 and 27 (Table 3), a significant MPC excess was fixed.
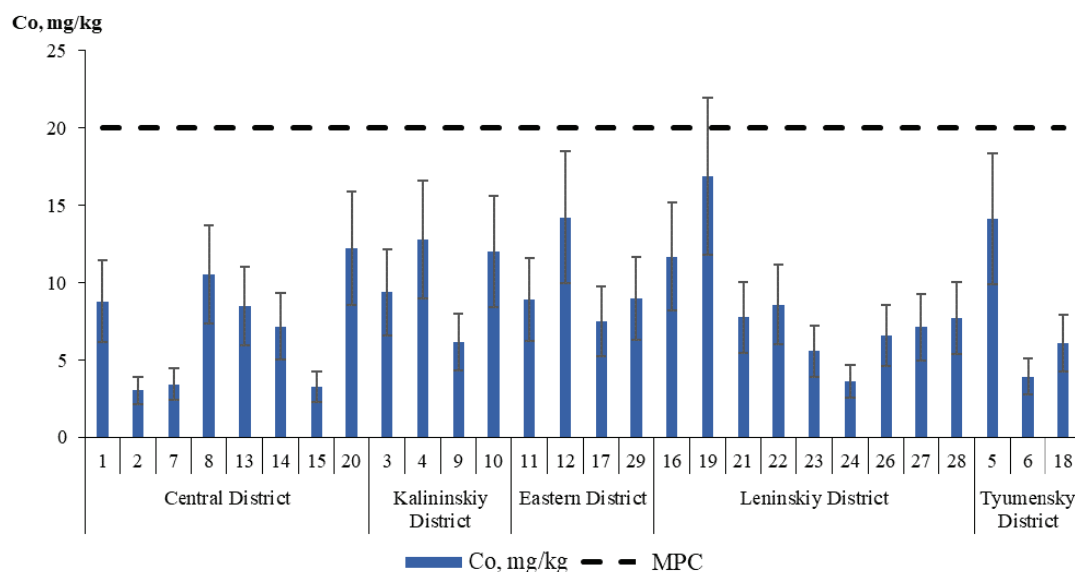
Fig. 7. Contents of the cobalt acid-soluble fractions in the soil samples
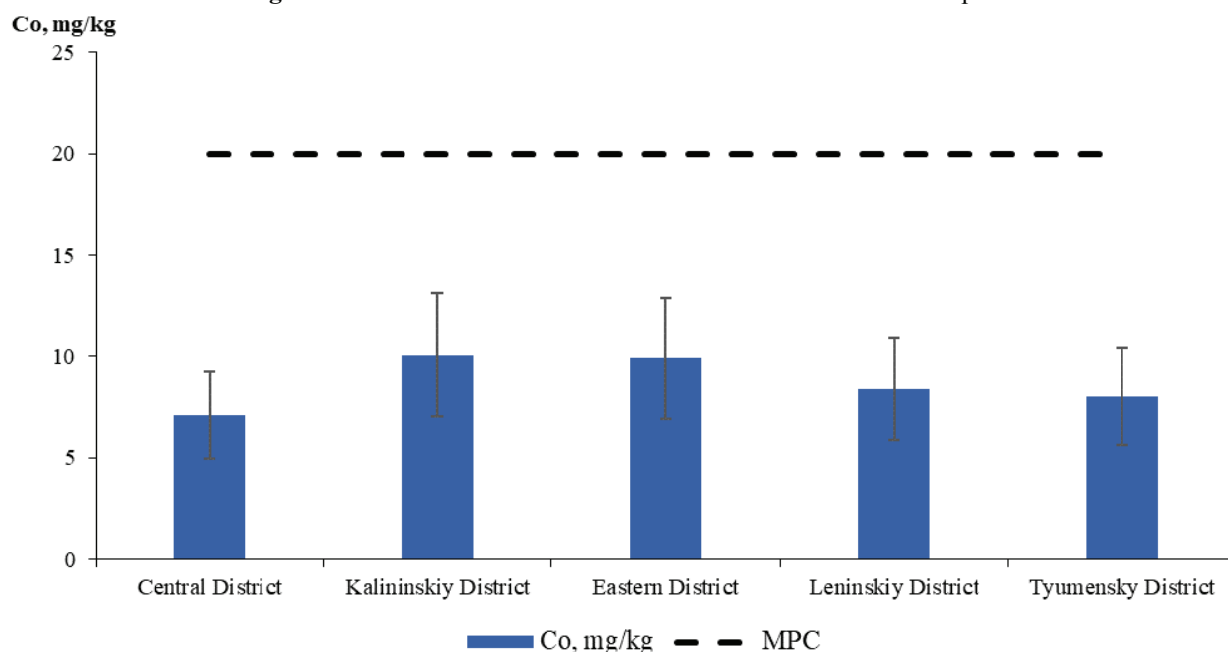

Fig. 8. Average contents of the cobalt acid-soluble fractions in the soil samples

A large OM amount is available in the inspected territories, since the above-mentioned samples were taken in landscaped urban areas (city forest and parks, riverbank, roadside forest belt, and green area near houses). The OM enters the soil with fallen leaves and grass. The disruption of the system of fallen leaves removal at urban sites results in large OM quantities [14]. Manganese accumulates in the upper soil horizons and is not leached to the lower horizons, since it forms insoluble complex compounds with the OM. The activities of ferrous and non-ferrous metallurgy, metal processing and machine building industries result in manganese entering the soil horizons. The soil samples from the area of UMMC-Steel (samples No. 22, 24, 27)

possess have high content of mobile fractions, which may indicate its recent entry.

The contents of the manganese acid-soluble fractions in all samples lied within normal limits, indicating the leaching of this element from the soils in the form of mobile Mn^{2+} (Figs. 9, 10).

Copper. The MPC level for the copper acid-soluble fractions is 33 $mg \cdot kg^{-1}$, and for its mobile fractions in the soils of residential areas is 3 $mg \cdot kg^{-1}$. Copper is a highly toxic element and is most commonly found as Cu^{2+} compounds. At the same time, it is one of the least mobile HMs, because in nature, due to good complexing properties, it forms complexes mainly with organic ligands.
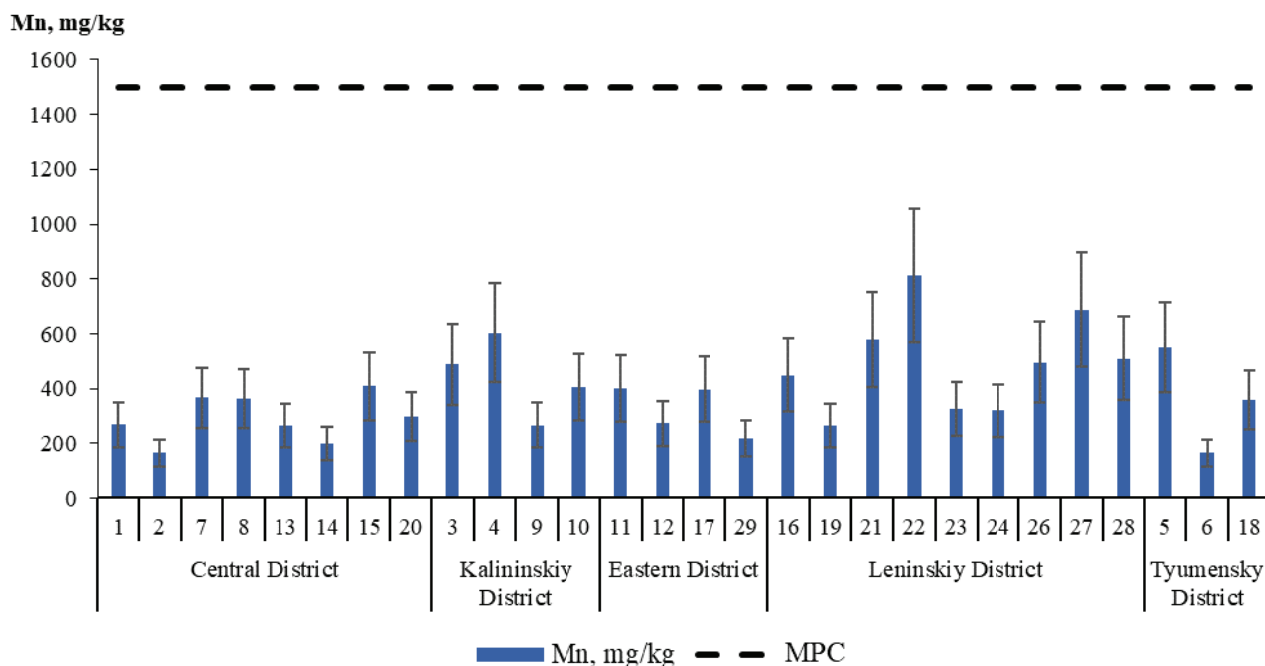
Fig. 9. Contents of the manganese acid-soluble fractions in the soil samples
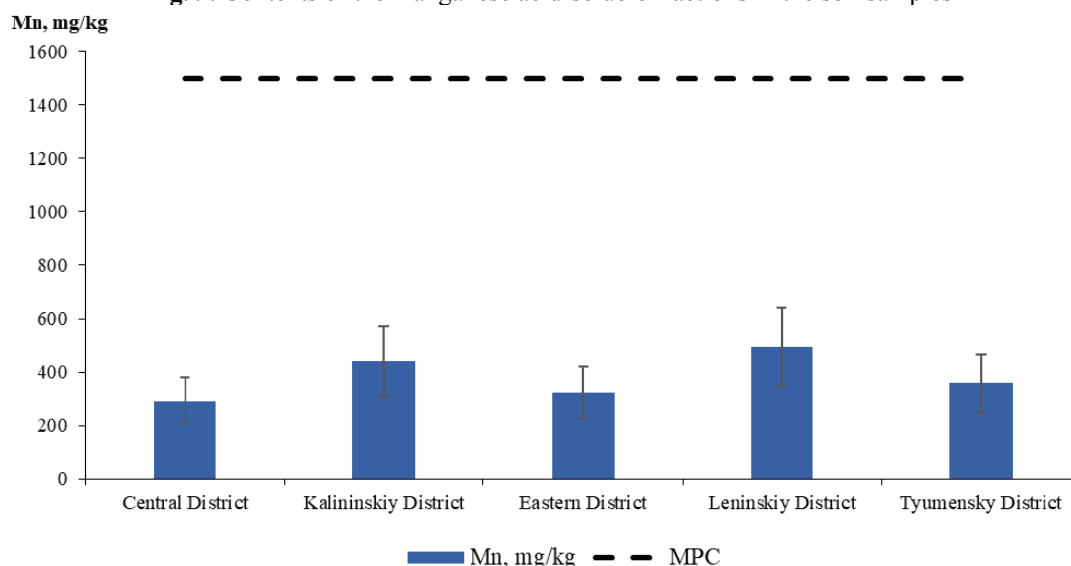

Fig. 10. Average contents of the manganese acid-soluble fractions in the soil samples

Copper becomes most toxic at pH values of 5.5 to 6.5 as it is dissolved as divalent copper ions. In more acidic soils, copper is less mobile and, therefore, non-toxic. At pH more than 9.0, complexes with inorganic ligands can be formed. Also, adsorption on suspended clay particles decreases its mobility. The excess of the content of the copper mobile fractions was found in samples No. 20 and 26, although these values do not exceed the MPC more than twice (Table 3). The accumulation of copper in soils in the form of complex compounds with fulvic acids is evidenced by exceeding of the MPC on average from 2 to 5 times for the copper acid-soluble fractions (Figs. 11, 12).

Cadmium. The MPC level for the cadmium acid-soluble fractions is 0.5 mg·kg^{-1}, and no standard value has been established for its mobile fractions.

Cadmium is mainly accumulated in the form of complexes with humic acids. It is a rarely dispersed element and is considered to be one of the most toxic metals, since its rates exceed permissible levels even at the minimum soil contamination value. The background cadmium content in soils is mainly determined by the composition of its parent rock. Cadmium is most mobile in soil solution media at pH 4.5–5.5. In alkaline conditions, it is low-mobile, therefore, its mobility values correlate with the acidity of the soil solution medium.
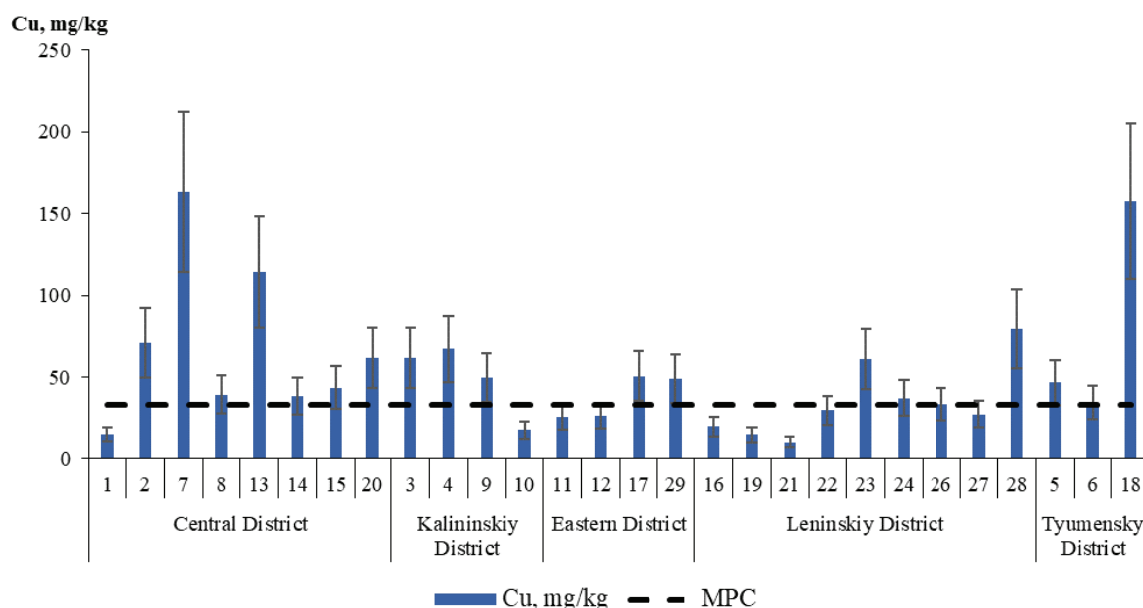
Cu, mg/kg

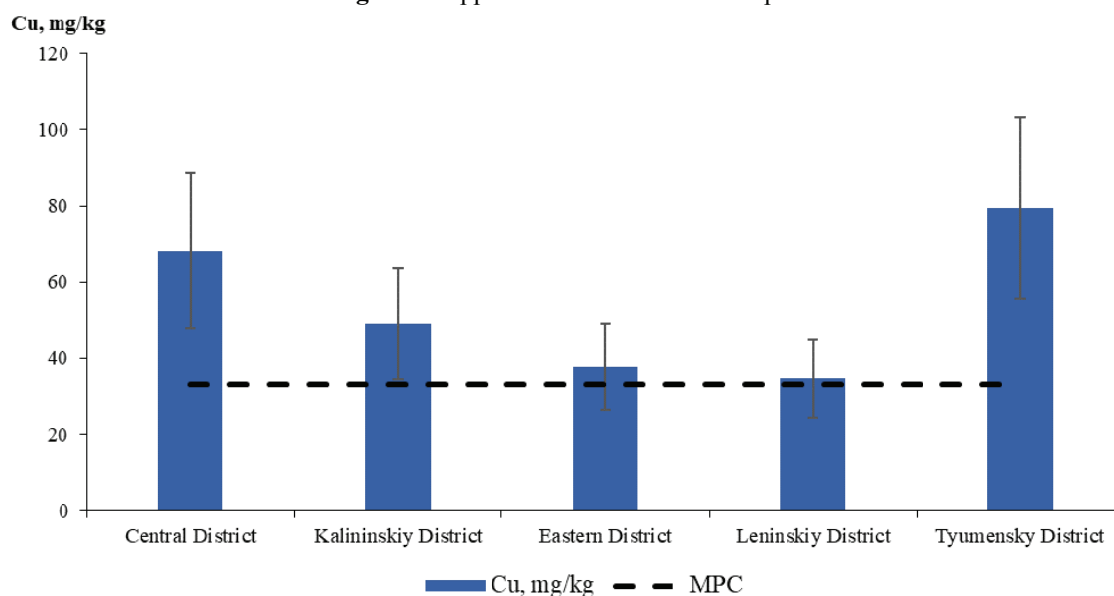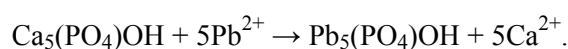**Fig. 11.** Copper contents in the soil samples

Cu, mg/kg

Fig. 12. Average copper contents in the soil samples

When considering the data of the analyzed samples of Tyumen city, no excess of the MPC for this element was noted (see Tables 3, 4).

Lead. The MPC level for the lead mobile fractions in the case of soils from residential areas is 6 mg·kg^{-1}, for its acid-soluble fractions, it is 32 mg·kg^{-1}. Lead compounds accumulate in soils as a result of sorption on oxides and hydroxides of manganese and iron. Moreover, lead forms part of easily degradable minerals – PbO, PbCO$_3$, and PbSO$_4$. Degradability makes these forms of lead in soils the most dangerous. At the same time, the phosphate mineral [Pb$_5$(PO$_4$)$_3$Cl] is the least toxic as it has low solubility and stability in a wide pH range. The mobility and bioavailability of lead without its

removal from the medium can be achieved by applying phosphate to contaminated soils. This reaction can be represented as follows:

$$Ca_5(PO_4)OH + 5Pb^{2+} \rightarrow Pb_5(PO_4)OH + 5Ca^{2+}.$$

A significant excess of the MPC level for lead both in the mobile and the acid-soluble form was observed in samples No. 8 and 20 taken at roadsides (Tables 3, 4). For these soils, 7- and 13-fold excesses of the MPC level for its mobile fractions, and 2- and 4-fold excesses of the MPC for the acid-soluble fractions were observed, respectively (Figs. 13, 14).

Possible sources of lead pollution are wastes from metallurgical plants, landfills of used electric batteries, paints, and metal alloys. In addition, lead
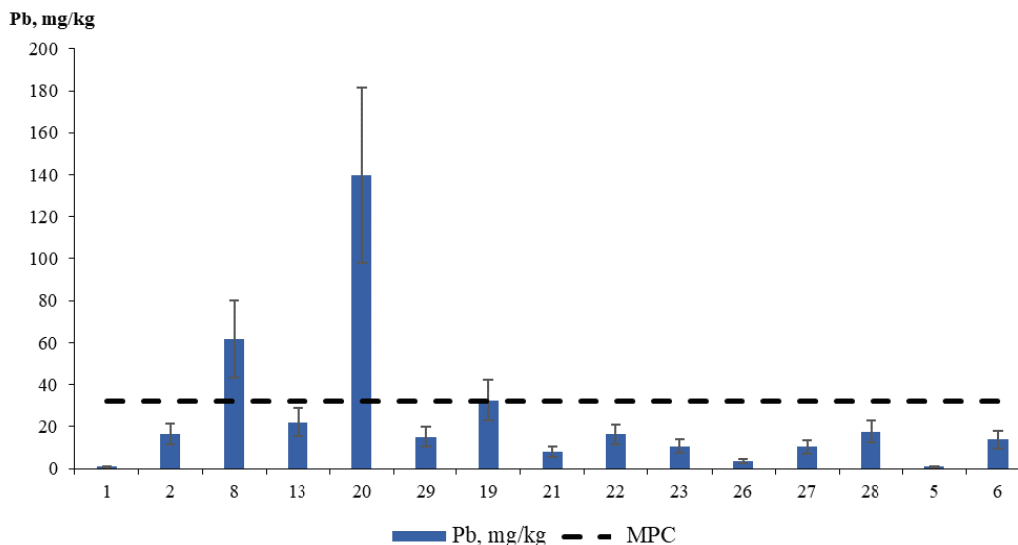
Fig. 13. Contents of the lead acid-soluble fractions in the soil samples
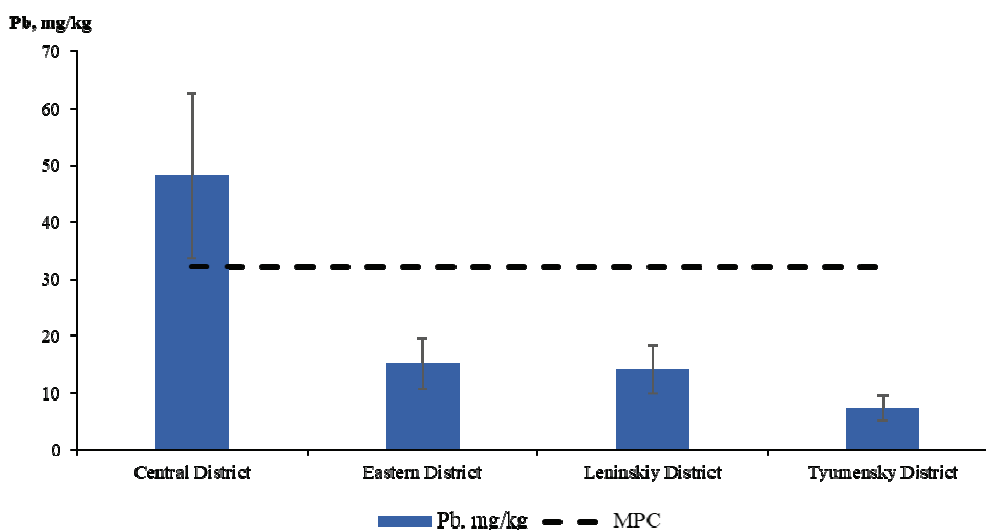

Fig. 14. Average contents of the lead acid-soluble fractions in the soil samples

may enter soils from exhaust gases of vehicles running on petrol with lead additive. Its excessive concentrations were observed in the Central district, which can be explained by the increased traffic load in this part of the city.

Chromium. The MPC level established for its mobile fractions in case of soils of residential areas is 6 $mg \cdot kg^{-1}$, and for the acid-soluble fractions, it is 100 $mg \cdot kg^{-1}$. Chromium exists in several forms, the most stable of which are compounds with oxidation degrees of +6 and +3. The form, in which chromium is found in soils, depends not only on the acidity of the medium [15], but also on its redox potential [16].

Thus, +6 oxidation degree chromium possesses low complexing ability, and is available in soils as $HCrO_4^-$ and CrO_4^{2-}. +3 degree chromium, in its turn, has high complexing properties and, as a result, it is present in soil solution as $[Cr(OH)_2]^+$ and $[Cr(OH)]^{2+}$ (at pH 7.5–8.5) as well as complexes with humus and

fulvic acids. It should be noted that these forms are actively adsorbed by clays, whereas the CrO_4^{2-} chromate anion is adsorbed only in more acidic media.

The presence of chromium in one form or the other also determines its toxicological properties. The most dangerous are the Cr^{+6} compounds, which have toxic, carcinogenic and mutagenic effects. At the same time, Cr^{+3} compounds in acidic media are inert, and at pH 5.5 become almost insoluble, so they do not harmfully affect the organisms.

The main areas of chromium application are metallurgical and chemical industries due to high corrosion resistance and strength of this element [17].

Among the investigated samples, only sample No. 14 exceeded the MPC established for chromium. However, the exceeding of the limits for the contents of the acid-soluble fractions is insignificant.
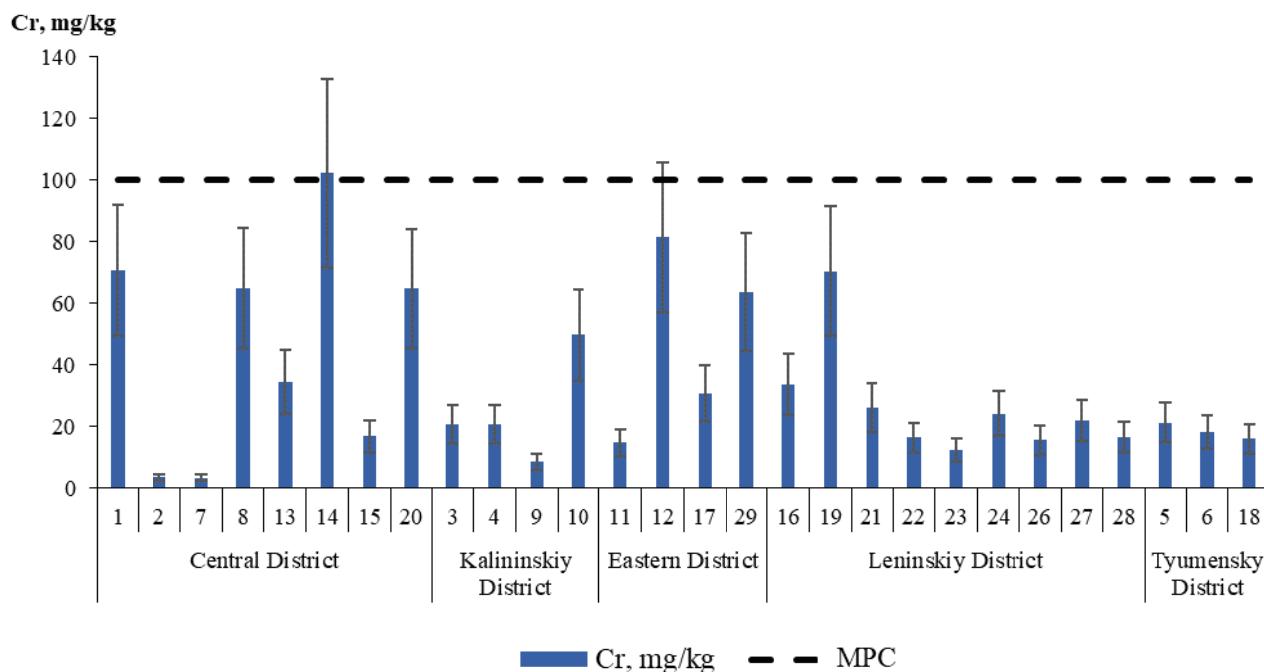
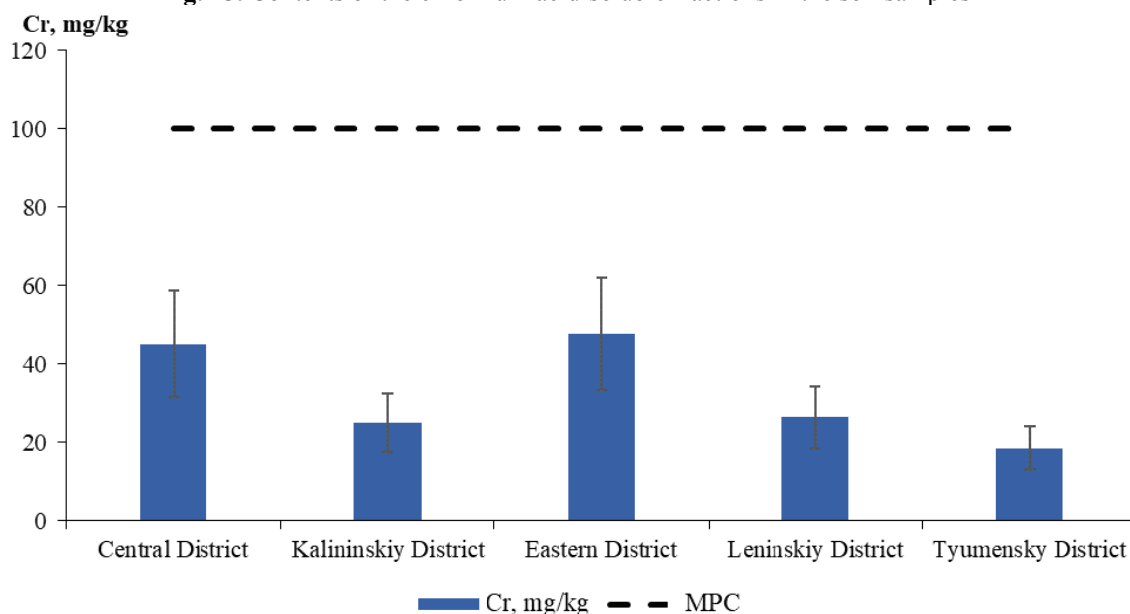**Fig. 15.** Contents of the chromium acid-soluble fractions in the soil samples

Fig. 16. Average contents of the chromium acid-soluble fractions in the soil samples

3.3. Correlation analysis

According to the Goldschmidt classification, all the elements in nature belong to one of the five groups: atmophilic, chalcophilic, lithophilic, siderophilic, as well as rare elements and elements not found in nature [18]. In this paper, a correlation analysis was carried out between the contents of the different element pairs. This type of analysis can reveal the absence or presence of correlation between elements belonging to the same group according to the geochemical classification of Goldschmidt, as well as indicate the possible causes of the HM accumulation.

Within the framework of this classification, matrices of pair wise correlations for the HM and OM contents and pH were constructed using the Microsoft Excel software. Indicators with a correlation coefficient of 0.5 were considered as correlated. The results of the analysis are presented in Table 5.

The highest correlations were found between the pairs of the following metals: Co – Ni, Cr; Pb – Cr; Cr – Ni, Co, Pb. The presence of correlations between nickel and cobalt contents is quite understandable, as they belong to siderophilic group of elements. The correlation between lead and chromium contents, different in nature, indicates the

Table 5. Matrices of pairwise correlations of the HM acid-soluble fractions in the soils

	Ni, mg·kg^{-1}	Co, mg·kg^{-1}	Mn, mg·kg^{-1}	Cu, mg·kg^{-1}	Pb, mg·kg^{-1}	Cr, mg·kg^{-1}	pH	C$_{org}$, %
Ni, mg·kg^{-1}	1.00	**0.67**	–0.16	–0.34	0.36	**0.80**	**0.65**	–0.15
Co, mg·kg^{-1}	**0.67**	1.00	0.22	–0.38	0.17	**0.54**	0.15	–0.06
Mn, mg·kg^{-1}	–0.16	0.22	1.00	–0.21	0.39	–0.17	–0.30	**0.48**
Cu, mg·kg^{-1}	–0.34	–0.38	–0.21	1.00	–0.26	–0.41	–0.28	0.08
Pb, mg·kg^{-1}	0.36	0.17	0.39	–0.26	1.00	**0.54**	0.21	–0.06
Cr, mg·kg^{-1}	**0.80**	**0.54**	–0.17	–0.41	**0.54**	1.00	**0.52**	–0.28
pH	**0.65**	0.15	–0.30	–0.28	0.21	**0.52**	1.00	–0.35
C$_{org}$, %	–0.15	–0.06	**0.48**	0.08	–0.06	–0.28	–0.35	1.00

anthropogenic nature of their entry into the environment.

A correlation between the chemical element content in the soil and the pH of the aqueous extract for Cu, Cr, Ni was also been detected. This information can be interpreted as a confirmation of the effect of metal accumulation effect during the soil alkalinization, since in the samples studied, there was a shift to the alkaline pH region. The observed correlation between the soil OM content and the manganese concentration is related to the formation of strong complexes with the soil organic component.

4. Conclusion

Thus, in the present work, the pH values of saline and aqueous soil extracts were determined to be 5.87 to 9.06 and 6.22 to 9.20, respectively. A comparison of the obtained results on the HM content in the soils with Sanitary Rules and Regulations normative values showed that the contents of both mobile and acid-soluble fractions exceed the MPC values for copper, lead, nickel and manganese. The concentrations of cobalt, cadmium and chromium are not exceeded. Based on the correlation analysis of these results, it can be concluded that there is a significant anthropogenic load on the soils of Tyumen city, especially for the Vostochny (Eastern) and Central districts, where the main transport routes and industrial enterprises (UMMC-Steel, Construction Machinery Plant) are located.

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7. Conflict of interests

The authors declare no conflict of interest.

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