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Toxicological state and chemical properties of soils in urbanized ecosystems of Murmansk

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Abstract
Nowadays, active urbanization directly affects to the transformation of natural ecosystems in all natural zones of Russian Federation. First of all, soils of the cities are exposed to undergoing to intensive transformation. With this transformation, natural soils change to urban and "urbo-natural soils". Arctic ecosystems are most susceptible to anthropogenic influence because they have a low regeneration and restoration ability. Urban soils demonstrate numerous and various processes of transformation and migration of substances, which are the most important links in the biogeochemical cycles, linking the various structural components of ecosystems and the biosphere as a whole. In this context the processes of soils transformation under the influence of the urbanization has been considered. Soils of residential, recreational (park), industrial and non-developed urban zones were studied on example of Murmansk city as one on the northernmost city in European part of Russia. Microbiological activities, toxicological state (heavy metals, Zc), and content of carbon in soils were revealed.

Key words: Arctic landscapes, urbanization, soils, anthropogenic impact, ecosystems

Abreviations: Zc - polluton saets coefficient, HM - heavy metals, TOC - total organic carbon, BR - basal respiration

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Introduction

Urbanization radically changed the native ecosystem and indigenous people inhabitation in the Arctic zone, which until recently were isolated from humans (Stroganova 1998, Zemlyanitsky et al. 1962, Lehmann et Stahr 2007, [1] - WRB, FAO 2014). The process of urbanization of the Arctic regions is about 300 years old (Shiklomanov et al. 2017, Dybbroe 2008). In fact, the whole circumpolar region of the North

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is vulnerable to urbanization (Jull 2016, Jull et Cho 2013). Intensive growth of cities facilities the resettlement of people from their native habitats settlements to large urban agglomerates (Nyseth 2017). There is no single methodology developed to address the problem of urban sustainability in the fast-growing urban zone (Shiklomanov et al. 2017). As a result of urbanization, a number of problems arise that affect the stability of natural ecosystems and the stability of urban systems. Most of the problems are related to the natural environment of the Arctic, due primarily to the climatic features of the region (Dybbroe 2008).

It is expected that the impact of climate change on human development will be more pronounced in the permafrost-affected soils and related environments. Permafrost-affected soils are very sensitive to climate change and anthropogenic activities, they serve as the basis for human infrastructure and affect social and economic development (Streletskiy et Shiklomanov 2013). Thus, soils can be considered as one of the important integrative accumulator of negative environmental risks. Investigation of ecotoxicological state of soils is necessary for understanding the sustainability of the urban environment in the Arctic. The interrelation between urban infrastructure and permafrost-affected soils is especially pronounced in the Russian Arctic, where the population is concentrated mainly in urban centers located in areas prone to the permafrost-affected soils (for example, Murmansk, Vorkuta, Salekhard, Nadym, Novy Urengoy, Norilsk, Magadan, Yakutsk). About 89% of the population of the Russian Arctic live in cities (Streletskiy et Shiklomanov 2013, Fossland 2012).

The development of soils in the urban environment depends on natural (climate, geology) and socio-economic (population density, city planning, land use) factors (Nyseth 2017, Dybbroe et al. 2010). Regardless of this, the development of previously mature areas is always accompanied by the removal of vegetation, redistribution of snow, changes in hydrological regimes, which in turn changes the heat exchange between the atmosphere and the soil. Anthropogenic influence is characterized by intensification of negative, cryogenic processes, soil sealing and soil cover consumption by antropogenic activity (Streletskiy et Shiklomanov 2013). Permafrost-affected soils are usually used as a reliable support in building construction. They are protected from thawing during construction and throughout the life of the structure. Even with very expensive periodic maintenance, the life expectancy of buildings in the areas of distribution of permafrost-affected soils is on average 30 to 50 years (Shiklomanov et al. 2017). However, structures are usually exploited for a much longer period. The increase in near-surface temperature contributes to the degradation of permafrost-affected soils at which the construction of urban structures occurs, which leads to their destruction and, as a consequence, causes socio-economic damage to the region (Dybbroe 2008). The degradation of the permafrost in soils also affects the transport and communication arteries of cities, the roads and railways are destroyed, and there are disruptions in the centralized heating and water supply system of the population (Carbone et al. 2014). In addition to the degradation of permafrost-affected soils in the urban environment, there is also a removal of the vegetation cover, which is a key factor in the wind propagation of snow, the hydrological regime, and the stability of the slopes. In urban areas, the removal of vegetation increases the temperature of the soil, which again leads to the degradation of the permafrost-affected soils and the destruction of engineering structures (Shiklomanov et al. 2017, Jull 2016). The topic of investigation of soil ecosystem services transformation become more and more required for further understanding of urban ecosystems development. One of the key ecosystem functions of soils is self remediation and detoxication of the whole environment. This function is considered as under investigated, especially for polar environments.

The thirty seven cities are located in the Russian Arctic (Loginov 2017). The territory of the Arctic zone is 4386.6 thousand km^2 or 25.7% of the country's total area in Russia. The population of people lived in Russian Arctic is more than 2.5 million, which is less than 2% of the country's population and about 40% of the population of the entire Arctic. The Arctic is extremely heterogeneous not only in terms of population concentration, but also in terms of intensity of economic activity and infrastructure development in this regard, the urban environment is divided into functional zones (Dobretsov et Pokhilenko 2010). The Arctic zone of the Russian Federation is characterized by the highest urbanization: more than 80% of the population is concentrated in cities and towns with a population of more than five thousand people.

Soil formation in urban ecosystems is caused by morphological changes and physico-chemical properties (Lebedeva et Tonkonogov 1993). In urban soil, unlike natural analogues, new components appear new energy and material connections inherent in urban ecosystems. It must be taken into account that anthropogenic transformed soils are an important component of urban ecosystems and have a significant impact on the quality of human life.

The climate of Arctic cities differs significantly from the natural zones. The difference in the climate of the city and the outskirts is sometimes equivalent to latitudinal movement up to 250 km to the south (Gerasimova et al. 2003). The air temperature within cities is affected by numerous industrial sources (dust from enterprises, feature of urban development, transport, heating mains). Average daily temperature deviations in cities have a smaller amplitude than in the vicinity. In the summer, increasing density of construction and asphalt from 20 to 50% increases the difference in maximum temperatures in the center and the outskirts of the city from 5 to 14°C. Due to the isolated surface by asphalt, most of the precipitation does not enter the soil. In connection with the increased heating of asphalt and urban structures, relative to natural ecosystems, there is overheating of the soil. Increased convection in the atmosphere of megacities, as well as technogenic dustiness contribute to an increase in the number of thunderstorms over the city, an increase in the intensity of showers and the total amount of precipitation. Precipitation in winter can reach 150%, summer - 115% of the norm in 481 mm (for Murmansk). Annual precipitation increased in Moscow by 25% exhaust gases and building dust, which is equivalent to the effect of clouds (Gerasimova et al. 2003).

The landforms has been largely modified by a variety of human activities: leveling the surface; terracing or cutting off the soil surface layer in cities. The relief of the city affects not only the water (preferential flow), but also the air migration of pollutants. In the cities of Central Russia karst-suffosion depressions are often observed, sedimentation of the soil layer as a result of an increasing consumption of underground artesian waters, a decrease in the volume of soil mass caused by leaching of soluble salts and lime. The soil-vegetation complex often degrades under the influence of karst-suffosion processes (Gerasimova et al. 2003).

Pollution of soils with heavy metals (HM) become a global environmental problem due to the diversity of anthropogenic sources, the active insertion of metals in the processes of biochemical migration and their toxicity to living organisms. Urban soils are formed under conditions of large anthropogenic loads, and therefore significantly differ from natural analogues. As the result of anthropogenic activity, the quantity of many elements, in comparison with natural levels enters the environment, often in compounds and forms not characteristic of the natural environment (Dymov et al. 2013, Alekseev et al. 2017, Legostayeva et al. 2017, Ji et al. 2019).

Soils play a key role in the functioning of polar terrestrial ecosystems. However, the soil cover of the polar regions remains practically unexplored by now. Soils of such a large polar city as Murmansk have not been investigated before. In this connection, the study of anthropogenic transformation of the soil cover under polar conditions is of particular interest.

The research is focused on describing the morphological features, physical and chemical properties of urban soils in Murmansk.

Material and Methods

Study area

The city of Murmansk - the administrative center of the Murmansk region is in the north-west of Russia. Murmansk is the largest city located beyond the Arctic Circle. The total area of the city is about 150 km^2. The population for 2016 is 301,572 people.

The city of Murmansk is located on the eastern coast of the Kolskiy Bay of the Barents sea. The Kolskiy Peninsula is situated on the north-eastern extremity of the Baltic crystalline shield, composed mainly of the massive-crystallic granites and gneisses. The main features of the peninsula's relief are due to numerous faults and cracks in the crystal shield, and also have traces of the powerful impact of glaciers that have smoothed out mountain peaks and left a large number of moraine deposits (Rodoman 2001).

The city is located in the Arctic zone of temperate climate. The climate of the city is intensively influenced by the proximity of the Barents Sea, in which the warm North Atlantic Current flows appears. In this regard, the climate of Murmansk is significantly different from the climate of the Kolskiy Peninsula as a whole. Unlike many northern cities, in Murmansk there are high winter temperatures for the North. The average temperature in January-February in Murmansk is about -10 to -11°C. The average July temperature is about +12 to +13°C. Most of the precipitation in Murmansk about 500 mm per year falls from June to September, the peak of cloudy days and days with precipitation falls in August. Snow lies in the city on average 210 days and completely descends to May (in the vicinity of the city snow can lie until June).

The territory of the Murmansk region is located in two geographical areas - the northern taiga and the tundra, between which a narrow ecotone of forest-tundra is situated. The forest zone occupies slightly less than 80% of the peninsula's area. Forests here are rare, light, the height of the trees does not exceed 10-12 m. Pine, spruce and birch are dominated. Spruce is concentrated mainly in the east and in the north, the pine in the west and in the south. On richer, moderately moist soils, green-pine forests grow, with a surface cover dominated by of green mosses.

Soil cover survey and sampling

In the city of Murmansk, the study of the soil cover was carried out in September 2015 and July 2016. Within the city, four functional zone were selected: industrial, residential (living sector), recreational (park) zones and non-developed urban area (Fig. 1). The reference soil for the city is Podzol (zonal type) (Goryachkin 2010). The profile of Podzol is represented by a humus stratified thickness of more than 40 cm, which is conditionally regarded as a stratified gray, dark or light-yellow horizon. Soil samples were different for various purposes. Individual soil samples were taken from each generic soil horizons for analytical specification of the soil type. Bulk samples, combined form 5 replication, were collected from organo-mineral topsoil from the depth 0-5 cm for determination of the heavy metals in the fine earth at the same time. Zc indexes were calculated only for theses samples of topsoils, because they are most important for human health risk ([2] - SanPIN 1987).

Fig. 1. The investigation sites of the Murmansk, Russian Arctic. Functional zones within investigation area: 1) Non-developed urban area (Podzol); 2) Industrial zone (Technosols); 3) Recreational (Podzol); 4) Residential (Podzol).

Chemical, physical and microbial analysis

Soil samples were selected for each horizon to analyze physical and chemical properties. The air-dried soil samples were grounded passed through a 1 mm sieve. Analyses were conducted in the certified laboratory of St. Petersburg State University at the Department of Applied Ecology, Russia. Soils were analyzed according to the following methods: determination of actual acidity (pH_{H2O}) and potential soil acidity ($CaCl_2$). Soil microbial respiration was determined using incubation chambers (Kimble et Follett 2001). To evaluate the gravimetric content of carbon in the fine earth we had used data of "dry combustion" (TOC). The determination of TOC is based on sample direct combustion and further evaluation of emitted CO_2 by chromatography. During oxidation all the organic carbon turns into carbon dioxide. Further on, in resulting products of combustion utilized from chlorides and other halogens, the measurement of carbon dioxide takes place (Abakumov et Popov 2005). The particle-size distribution was determined and classified according classical sedimentation method. The determination of the content of heavy metals in the soil was performed in accordance with the methodology of M-MVI-80-2008 by Quantum 2M Atomic absorption spectrometer ([3] - GOST M-MVI 80-2008). Extraction of acid-soluble forms of metals was carried out in accordance with RD 52.18.191-89 ([3] - GOST M-MVI 80-2008, 2008).

The ecological analysis of the level of danger of contamination of urban soils with a complex of heavy metals was carried out based on the total chemical contamination index (Zc) ([2] - SanPiN 4266-87, 1987). Background level for trace elements were taken from overview, made by Kashulina (2002) in her thesis, devoted to geochemical characterization of this region.

$$Zc = \sum_{i=1}^{n} Kc - (n-1) \qquad \textit{Eqn. } 1$$

where Kc - the concentration coefficient of the i-th chemical element, n - is the number equal to the number of elements entering the geochemical association.

$$Kc = \frac{Ci}{Cback.} \qquad \textit{Eqn. } 2$$

where Ci - the actual content of the element, $C_{back.}$ - geochemical background.

Results and Discussion

The soils were diagnosed according to WRB soil taxonomy, the data of physical and chemical studies are presented in Table 1.

In the city of Murmansk, podzols soils are dominant. The profile of some podzols consists a plaggic horizon, replaced by any natural horizon or directly by the parent rock; the boundary is relatively flat (*see* Fig. 2). Plaggic horizon is formed from several upper horizons of natural soils (organo-accumulative, eluvial and others), or from "remnants" of strongly eroded thick humus horizons. Soils are formed in natural conditions, as showed by the diversity of their mid-horizons. Types are determined by the features of the plaggic horizon and its combinations with the subarable part of the profile, represented by the parent rock or various mid-horizons.

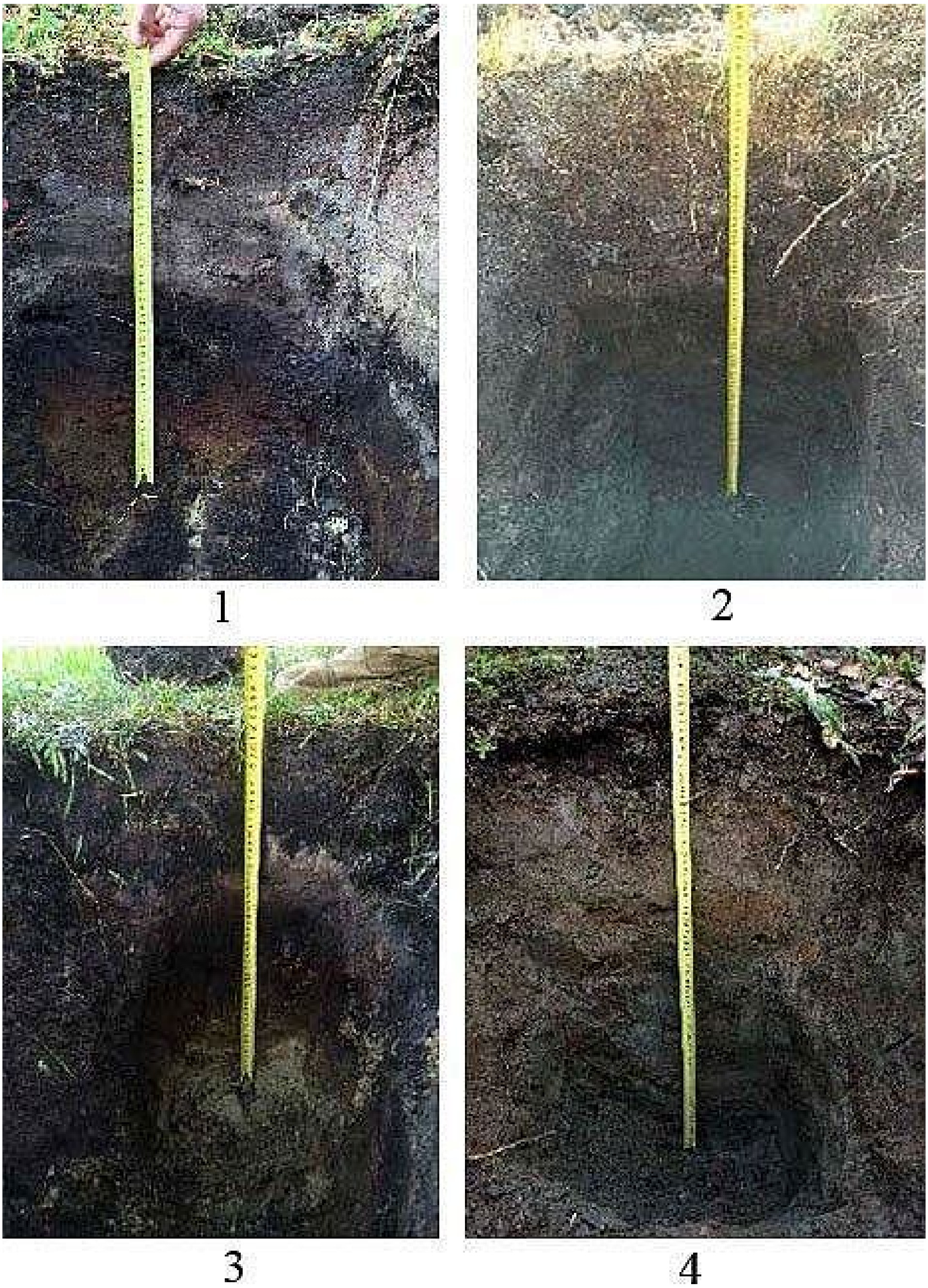

Fig. 2. Soil types in the Murmansk: 1 - Podzol (Non-developed urban area); 2 - Technosol (Industrial zone); 3 - Podzol (Recreational zone); 4 - Podzol (Residential zone).

Soils	Depth (cm)	Hori-zon	pH (H_2O)	pH ($CaCl_2$)	BR mg CO_2 100 g^{-1} d^{-1}	TOC (g/kg)	Particle-size classes (%)		
							sand	silt	clay
Podzols (Non-developed urban area)	0-2	O	4.25	3.08	126	14.1	-	-	-
	2-14	E	4.63	3.15	118	19.0	-	-	-
	14-24	BF	4.80	3.07	101	19.7	85	10	5
	24-36	BC	5.03	3.88	88	18.0	92	2	5
	36-52	BC	5.99	4.27	135	22.1	89	5	6
Technosols (Industrial Zone)	0-2	O	4.85	4.06	132	22.6	-	-	-
	2-32	C	4.15	3.52	57	17.3	-	-	-
	32-49	Ctur	3.58	3.51	30	19.2	95	2	4
	49-90	Ctut	4.12	3.67	85	22.2	88	5	8
Podzols (Recreational zone)	0-5	O	4.41	3.71	142	18.7	-	-	-
	5-16	E	4.51	3.67	78	14.6	89	4	7
	16-24	BF	4.91	3.54	142	21.1	91	4	5
	24-42	BC	4.92	3.91	125	19.1	90	4	7
	42-52	BC	4.93	4.19	145	20.0	91	2	7
Podzols (Residential zone)	0-4	O	4.89	4.24	105	15.5	-	-	-
	4-11	E	4.83	4.18	102	14.3	93	3	5
	11-38	BF	5.82	4.92	142	21,0	87	7	6
	38-84	BC	5.56	4.90	71	21.5	86	9	5

Table 1. Physical properties, total organic carbon (TOC), pH and basal respiration (BR) of different soils of Murmansk.

Acidity of soils in the Murmansk

The main chemical parameters of the soils of four different functional zones were analyzed. The pH value normally increases along soil profile. This is due to the active acidification of soil from the surface (typical for the reference soil), which occurs during anthropogenic activity in the urban environment, this is typical for Podzols of the city (Table 1). The industrial zone is characterized by an increase in acidity in the middle of the profile to 3.6, and then its decrease to 4.1. This distribution is not typical for other soils that form in the urban environment of Murmansk and can be associated with a high anthropogenic influence on this functional zone. Also, the pH increasing at high depths is due to the presence in the soil of anthropogenic artifacts in the form of construction debris it is typical for all presented soils. According to the extracts of pH ($CaCl_2$), we can testify that in the soil there is a low content of exchangeable cations in the composition of the soil absorption complex. This may also be due to the presence in the soil of anthropogenic artifacts.

Many authors note that the pH of urban soils varies widely, but soils with a neutral and slightly alkaline predominate (Lepneva 1987, Syso 2007) and in some cases strong-alkaline values (Naprasnikova 2007). Many studies have shown that the pH of urban soils is higher than that of natural soils (Blume 1989, Hollis 1991), most authors attribute this fact to soil through surface runoff and drainage waters of calcium and sodium chlorides and other salts that are strewn with sidewalks and roads in winter. Another reason is the release of calcium from various debris, construction debris, cement, bricks, giving an alkaline environment. But, in case of Murmansk alkilinization of the urban soil in not so pronounced as in southern cities.

Microbial activity in the soils of the Murmansk

Average values of basal respiration is 106 mg CO_2 100 g^{-1} d^{-1}. In residential and industrial zone there is a decrease of microbial activity along the profile from 105 to 71 mg CO_2 100 g^{-1} d^{-1}, and from 132 to 85 mg CO_2 100 g^{-1} d^{-1} which is a typical for undisturbed ecosystems. For the remaining functional zones (Non-developed urban area, Recreational zone) the microbial respiration increased along the soil profile for the non-developed urban zone from 126 to 135 mg CO_2 100 g^{-1} d^{-1} and the park zone from 142 to 145 mg CO_2 100 g^{-1} d^{-1}. This is primarily due to the presence of buried organic horizons and the introduction of fresh transported soil materials to build up cultural landscapes in the city.

The study of microbial activity in the cities of the Far North has not been studied before, so we can compare the data obtained only with soils that are outside the zone of influence of the city. For natural soils, a similar distribution of values is characteristic, high levels are observed in the surface horizons, as well as on contact with permafrost-affected soils and reach 143 mg CO_2 100 g^{-1} d^{-1} (Polyakov et al. 2017).

Organic carbon content in the soils of the city of Murmansk

Analysis of the organic carbon content shows very high values to 22.6 $g{\cdot}kg^{-1}$. For all functional zones, an increase in the organic carbon content along the profile was found. Such distribution of TOC is untypical for natural environments and can be primarily associated with anthropogenic activity. For Podzols, the average TOC content varied from 16 to 20 $g{\cdot}kg^{-1}$ along profile. In the upper layers, due to active microbial processes and anthropogenic influence (collecting of grass and leaf), this leads to a decrease in the content of organic carbon. High values in the lower layers can be associated with the burial of organic horizons. In the industrial zone, high levels of organic carbon content throughout the profile are associated with the suppression of microbial communities in this functional zone. TOC content is high in the soils studied due to low decomposition rate of raw moor type of humus, accumulated in profiles in cold conditions.

The content of organic carbon in urban soils varies and on its content in the original substrate, as well as on the use of fertilizers, organic debris applying. For example, in the soils of St. Petersburg (Bakhmatova et Matinyan 2016) and Moscow, the average humus content for upper layer is 0.4-0.6 $g{\cdot}kg^{-1}$, in Vladivostok 0.5-1.1 $g{\cdot}kg^{-1}$, in Nizhny Novgorod 0.3-1.0 $g{\cdot}kg^{-1}$. The range of variation in the amount of organic carbon in the studied cities is quite wide (in the upper layer from 0.18 to 0.5 g·kg^{-1}), which is a characteristic feature of urban soils (Bakhmatova et Matinyan 2016). The highest content of organic carbon is typical for the upper organogenic horizons for most of samples.

Thus, the results of the studies show that in soils having different degrees of anthropogenic transformation, both an increase and decrease in the content of organic matter can be observed, the direction of the process being determined by plant cover and intensity of anthropogenic impact.

Soil texture of the Murmansk city

According to the soil texture, the high sand content (up to 93%) and low contents of silt and clay were found. There were no significant differences in soil texture between functional zones. The high content of sand indicates that the soil has a low cation exchange capacity. In these conditions most of the nutrients are not easily accessible to plants. The soil texture affects the intensity of development of water and wind erosion (Shein et al. 2001). In this context, sandy textured soils can be considered as vulnerable and low resistant to anthropogenic impact.

Toxicological state

The highest content of HM are observed in soils confined to the industrial zone of the city, this is due to the high anthropogenic load on this sector. In the residential zone, there is also a small contamination of nickel and zinc, that is comparable with urban soils from Yamal region (Alekseev et al. 2016). In all functional zones, cadmium accumulation in soils has not been detected. High concentration of nickel are associated with an increased content of nickel in the parent material, the natural level is 36 mg·kg^{-1} (Fig. 3).

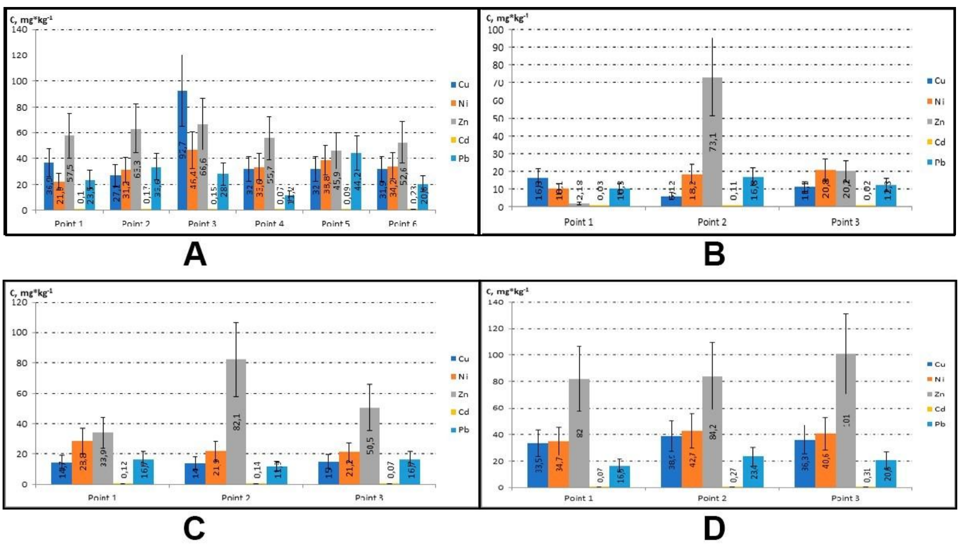

Fig. 3. The content of heavy metals in the soils of the Murmansk. (mg·kg^{-1} ± SD). *Notes*: A - Industrial zone; B - Non-developed area; C - Residential zone; D - Park zone.

From the data on the total soil contamination index, all values are low (not dangerous, index < 16) (Fig. 4). The indicator more fully characterizes the state of the environment than the indicator of maximum permissible concentrations, because takes into account regional features of the sites of concentrations of elements in the soil (Alekseev et al. 2016).

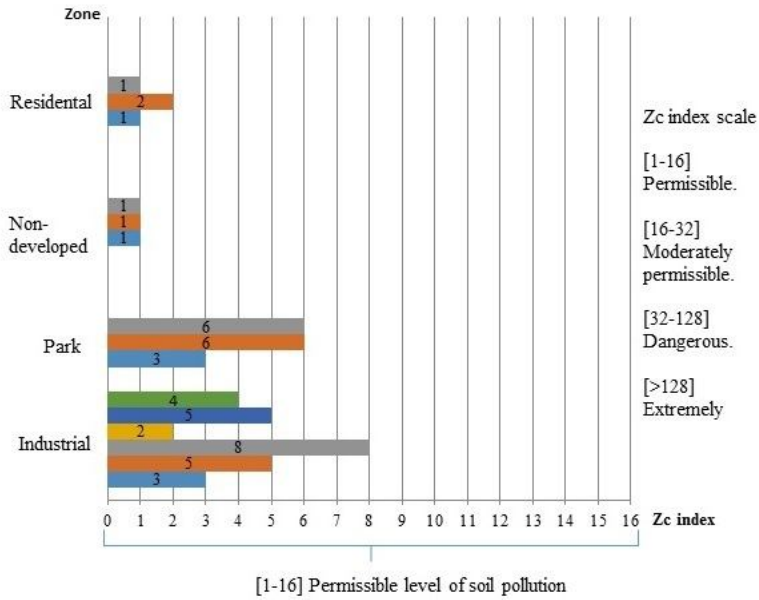

Fig. 4. Total soil contamination index of the Murmansk.

Conclusions

Data obtained showed the serious differences between residential, non-developed and industrial soils by Zc index. High acidity and low biological activity contribute to the accumulation of organic carbon in soils. Anthropogenic activity in cities leads to a change in the biological productivity of the soil, which is expressed in the extension of the growing season in plants caused by an increase in the average value temperature and the entry of additional moisture into the soil. In this regard, there is an additional accumulation of organic carbon in the city soils. All soils investigated are characterized by increased organic carbon content in comparison with mature soils of this region. The risk of contamination of the soil cover of the city of Murmansk and the surrounding areas is very high in comparison with more southern cities. In conditions of permafrost, the migration of substances in the soil is very difficult and their gradual accumulation takes place with possible formations of geochemical barriers not specific of the investigated area. More, over low cation exchange capacity in conditions of low content of the fine earth may result in low resistivity of soils to inorganic contamination. Increased anthropogenic pressure in Arctic ecosystems and urbanized areas leads to intensive degradation of the soil cover and the ecosystem in general.

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