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PHYSICO-CHEMICAL PROCESSES IN ICE AND FROZEN GROUND

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THE GEOCHEMISTRY OF ANTHROPOGENIC DEPOSITS IN YAKUTSK

V.N. Makarov, N.V. Torgovkin

Melnikov Permafrost Institute, SB RAS, 36, Merzlotnaya str., Yakutsk, 677010, Russia; vnmakarov@mpi.ysn.ru

The geochemical nature of the anthropogenic deposits (the cultural layer) in the urban area of Yakutsk is described. The presence of permafrost has determined the geodynamic and geochemical stability of the anthropogenic deposits, which vary in their chemical and mineral composition, structure, and physical and mechanical properties, as well as in the mode of chemical migration and concentration. It has been shown that the occurrence of anomalous concentrations of microelements in the urban soils is due to anthropogenic processes and the chemistry of Quaternary alluvial deposits. Human-induced salinization and contrasting anomalies of toxic elements in the older parts of the city occur throughout the cultural layer and extend to the upper layers of the alluvium. The thickness of the human-induced geochemical haloes in the cultural layer depends on the age of urban development, reaching 8 to 10 m.

Geochemistry, anthropogenic deposits, urbanization, cultural layer, permafrost

INTRODUCTION

The geological activity of the man has resulted in emergence of a new type of soils – anthropogenic deposits, including "cultural urban deposits" [*Paffengolts et al., 1973, p. 59*]. From the archeological viewpoint, anthropogenic deposits indicate a cultural layer (not of natural origin), a term for indicating a layer of ground containing traces of human activity, "deposits gradually forming as a result of interaction between the soil formation processes and various human activities" [*Lesman, 1998, p. 30*]. The authors consider the terms "anthropogenic deposits" and "cultural layer" (CL) as regarding the territory of Yakutsk as synonyms.

The natural conditions of the territory, the geological and geochemical processes occurring there, the history of the city's development and the character of the economic activity of humans determine formation of anthropogenic deposits.

Currently anthropogenic accumulation of micro- and macro- elements in the cultural layers of the cities is being intensely investigated. A number of studies have been devoted to accumulation of chemical elements in the cultural layers of large cities aged 1000 years or less [*Dobrovolsky, 1997; Kazdym, 2002; Gerasimova, 2003; Kasimov, 2004*]. Meanwhile, there are practically no data relating to the geochemical characteristics of the cultural layer of the cities located in the permafrost zone.

FORMATION OF A CULTURAL LAYER IN A CITY

The relation between natural (climate, permafrost, landscapes, and geological characteristics) and anthropogenic (the city infrastructure, the amount and composition of contaminants) factors determined the existing environmental and geochemical situation in the city of Yakutsk.

The CL in the permafrost zone was first characterized by N.I. Saltykov in his paper "On building foundations in Yakutsk" [*1946*]. The thickness of this layer, consisting of "...humus, construction rubbish and human garbage, which have accumulated over three hundred years of the city's existence and which have mixed with natural dusty-loamy cover,.. varies depending on the age of individual zones of the city. It is the largest (up to 1.50–1.75 m) in the district ... populated already at the end of the XVII century" [*Saltykov, 1946, p. 102*]. It is interesting that «in the "cultural" layer, rich in humus, the supra-permafrost waters of the city contain significant amounts of admixtures of Cl, SO_4 salts and other salts, which sometimes remain in a liquid state at the temperature of –3°–4°» [*Ibid., p. 103*].

The anthropogenic deposits in the territory of Yakutsk consist of multiple components. These are natural alluvial formations, moved in the process of urban construction and waste of various origin (production and construction waste, common household waste, etc.). Characteristic of the CL of the central streets of the city are the buried remains of pavements made of larch bars put on a layer of sand about 0.5 m thick delivered there from other places.

The conditions of forming the cultural layer in the territory of Yakutsk are quite specific: in its upper part manifestation of the seasonal freezing and thawing processes of the ground and of the suprapermafrost waters varies. As the depth of the active layer is often less than the thickness of the cultural layer of

Table 1. **Changes in the thickness of the active layer of the ground during a period of 48 years (1963–2011) in the districts of Yakutsk with different period of anthropogenic impact [*Makarov and Sedelnikova, 2016*]**

Period of anthropogenic impact on the city territories, year	Year	Active layer thickness, m			Changes in the AL thickness		Trend, m/year	The number of boreholes
		min	max	average	m	%		
320–370	1963	1.10	1.82	1.42	+0.96	+68	0.023	4
	2011	1.63	2.92	2.38				
220–270	1963	1.13	2.10	1.75	+0.84	+48	0.20	5
	2011	1.96	3.73	2.59				
120–170	1963	1.10	1.90	1.40	+1.04	+74	0.025	3
	2011	2.25	2.89	2.59				
20–70	1963	1.20	2.10	1.84	+0.07	+4	0.002	7
	2011	1.53	>10	1.91				
The average figure for 48 years	1963	1.10	2.10	1.66	+0.64	+30	0.015	19
	2011	1.53	>10	2.30				

the soils, underground ice is formed in the frozen part of the layer (cement ice, ice interlayers, lenses, veins), which is an integral part of the anthropogenic deposits, primarily in the old part of the city.

Over the recent 30–40 years, amid the relative stability of the temperature of permafrost soils on the natural landscapes, which have preserved in the outskirts of Yakutsk, their temperature in the central part of the city has drastically changed. The vector of the variations in the temperature field of the soils is positive [*Dorofeev and Syromyatnikov, 2013*].

The lower boundary of the layer of annual soil temperature cycles in the territory of Yakutsk is recorded at the depths of 10–12 m and sometimes it lowers to the depths of 15–16 m.

When analyzing the material [*Makarov and Sedelnikova, 2016*] obtained in the course of geocryological monitoring conducted in 2010–2012 by the researchers of the Permafrost Institute, SB RAS, headed by V.V. Kunitsky [*Dorofeev and Syromyatnikov, 2013*], the researchers recorded an increase in the depth of the active layer on the territory of Yakutsk. In the period of 1963–2011, the depth of the active layer in the territory of the city increased on average by 60–65 cm. In old districts, where the duration of the anthropogenic impact equals 150–350 years, the depth of the active layer rose even more – by 0.84–1.07 m. In the districts developed for less than 50 years, the character of the active layer has practically not changed (Table 1).

The growing relation is observed between the depth of the active layer in the period of intense development of the city infrastructure (the middle of the XX–beginning of the XXI century) and the number of residents of the administrative districts of Yakutsk, i.e., in fact, the intensity of the anthropogenic impact (Fig. 1).

The presence of permafrost determines the geodynamic and geochemical stability of the stratum of the anthropogenic deposits differing for their chemical and mineral compositions, structure, physical and mechanical properties and the specific migration of chemical elements.

The thickness of the CL in Yakutsk varies from the center of the city to its outskirts. The average thickness of deposits in the old districts of the city is 4 m and in the 'young' districts (in the outskirts) – less than 2.5 m (Fig. 2).

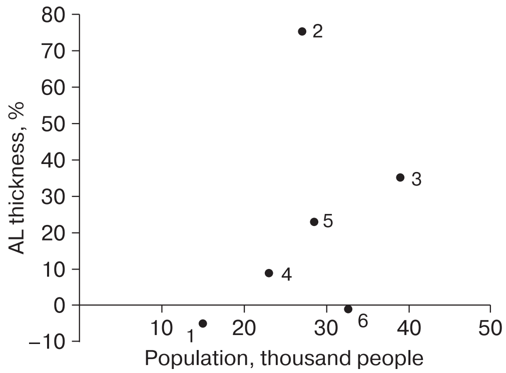

Fig. 1. Dependence of the thickness of the active layer on the population of the administrative districts of Yakutsk (middle of the XX–beginning of the XXI century).

Administrative district: 1 – Avtodorozhny, 2 – Gubinsky, 3 – Oktyabrsky, 4 – Saisarsky, 5 – Stroitelny, 6 – Tsentralny.

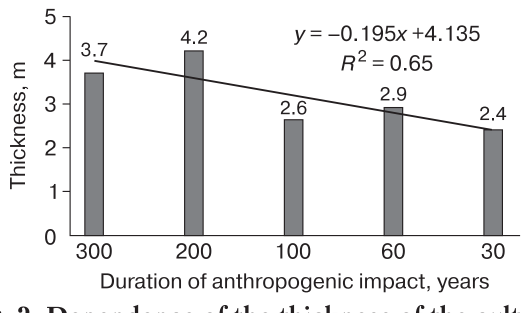

Fig. 2. Dependence of the thickness of the cultural layer on the duration of the anthropogenic impact.


Fig. 3. "Sunk" houses of Yakutsk.

Over 300 years, before the beginning of the 1950s of the XX century, Yakutsk was, in fact, a large village. "From an outsider's viewpoint, you will see large backyards with various facilities and appliances. Nearly in every backyard, you will see sheds for the cattle, paddocks for horses, vegetable gardens, etc." [quoted from *Popov, 2007, p. 102*]. This is how this witness describes the city's sanitary condition [quoted from *Popov, 2007*]: «The city and its suburbs are contaminated by waste of all sorts. This picture may be without exaggeration referred to Yakutsk of the beginning of the XIX century till the very last time. In summer, the city streets are filled with lots of dust, and sometimes dust envelopes the entire city. As one approaches the city, especially in the evening, one can almost always see the dusty mist over it. In the rain period and spring, when snow melts, the city gets drowned in mud. Bogs in the streets are a common sight. Lakes in the city have long been polluted, and water in them is extremely dirty... Lakes have been filled with garbage and feces more than once. ...The city is encircled by dumps, and a citizen going to "breeze in some fresh air", will first wander through the paths laid by the dump trenches. In summer, the dumps get burnt, and the smoke coming from them often envelopes the city. All this environment creates unhealthy conditions for the city. Gastric diseases, especially in July and August, primarily affecting children, are common. Typhus is always there, sometimes taking an epidemic character. Malaria also occurs. To be certain, these diseases are related to the general anti-sanitary condition of the city and of its suburbs» [*Ibid., p. 152*].

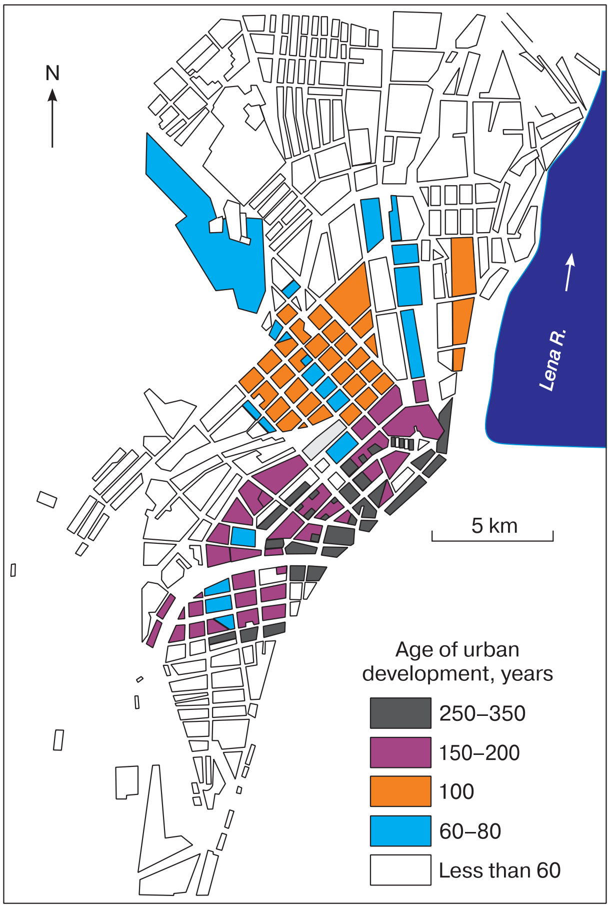

Fig. 4. The age of urban development of Yakutsk (according to the plans and maps of the city from the beginning of the XVIII century to the present time).

Until the middle of the XX century, there was neither centralized and permanent removal of all the waste, nor washdown of minor rubbish, and waste buildup far exceeded waste removal from the territory of the city.

A good example of a formed CL is the level of the modern surface in the old part of Yakutsk, which often exceeds the level of the foundations of the ground floors of many buildings. It seems that the buildings are "ingrown" into the ground. In fact, the CL built up around them (Fig. 3).

Resulting from more than three centuries' settlement of the city territory of Yakutsk, the local bioanthroposphere formed. However, formation of modern anthropogenic deposits in the territory of the city started from the middle of the 1950s, when the character of the economic life of the city changed.

The geochemical characteristic of the CL deposits was made by the authors as a result of long-time lithochemical monitoring of the "city soils" of investigating borehole cores. Borehole profiles of different ages were found in different districts of the city, from modern ones aged 50 years and less to old ones aged 300–350. Their comparison allows scientists to judge about the chemical composition of the CL in each of the five areas of urbanization, which differ by the age of urban development, and, hence, of anthropogenic impact (Fig. 4).

THE CHEMICAL COMPOSITION OF ANTHROPOGENIC DEPOSITS

Formation of CL consisting of humus, construction and household waste resulted from keeping a large number of horses and cows in the territory of the city, oven heating, and the lack of sewage, which contributed to accumulation of organic matter. Organic matter (feces, dung) is well-preserved under conditions of the cryolithozone in the anaerobic medium. Specific putrid odor could be smelt when frozen ground thawed usually at the depth of 2–4 m, sometimes as deep as 6–8 m. Dung was an essential component of the CL of Yakutsk and accumulated in its territory from the date of the city's foundation for nearly 300 years. It was only in the middle of the XX when the city's economy essentially changed (a sewage collector was put into operation, horses were replaced with motor vehicles, cattle was no longer pastured in the city, etc.), that feces and dung stopped coming to the city soils. As a result, the chemical composition of the CL in the city changed, which could be well noticed by the sharp reduction of the concentration of nitrogen compounds in the deposits aged less than 50 years (Table 2).

The depth of penetration of the anomalous amount of nitrogen (>0.01 mg-eq/100 g) grows as the age of the urban development rises: while in the younger 50-year soils it is not more than 3 m, in 100-year soils it is already 6.5 m, and in the oldest soils aged 200–300 years, it reaches 8.5 m (Table 3).

The intensity of accumulation of the anomalous amount of nitrogen compounds decreases in the following series: $NO_3^- > NH_4^+ > NO_2^-$. The prevalence of the NO_3^- end product of nitrogen oxidation indicates the long history of soil contamination.

The cultural layer is distinguished by the high content of phosphates, sodium, potassium, calcium, and magnesium. The high concentrations of phosphates are mainly related to the processes of decomposition of organic matter and of household waste. Concentration of phosphates in the CL soils reaches its maximum in its upper part within the limits of the active layer soils – 850–1125 mg/kg to reduce to 775–925 mg/kg in the permafrost strata of the CL. In the lower alluvial permafrost deposits, the content of phosphates reduced to the background values – 625 mg/kg.

In the "old" CL soils aged 100–350, the depth of penetration of the anomalous phosphate concentrations is practically the same (5–6 m) and reduces in younger soils aged 70 to 2–4 m, and no anomalies of phosphates are observed in the modern urban development areas.

Calcium and magnesium penetrate the CL soils normally from different construction materials (limestone, mortar, cement, concrete). Biophile elements (potassium and sodium) become accumulated due to decomposition of organic matter, mainly of timber; in addition, ash is the source of potassium. The anomalous content of potassium of 0.2–0.6 mg-eq/100 g is observed only in the upper part of the CL in the zone of the active layer with maximum duration of anthropogenic impact (over 200 years).

Table 2. **The concentration of nitrogen in soils in the territory of Yakutsk of different development age, mg-eq/100 g**

Depth, m	300 years	100 years	50 years
	Borehole # 3	Borehole # 14	Borehole # 4
1	**0.010**	0.008	0.008
2	**0.015**	**0.010**	0.006
3	**0.016**	**0.060**	**0.015**
4	**0.032**	0.009	0.005
5	**0.117**	**0.011**	0.004
6	**0.079**	**0.042**	0.005
7	**0.152**	0.009	0.005
8	**0.047**	0.007	0.004
9	0.007	0.009	0.007

Note. The sum of NO_3^-, NO_2^-, NH_4^+ calculated per the amount of N.

The bold type indicates the anomalous values of N.

Table 3. **The depth of penetration of nitrogen* compounds into the grounds of Yakutsk, m**

Nitrogen compounds	Age of the cultural layer, years				
	300	200	100	70	<50
NH_4^+	8.5	5.5	7.0	1.5	2.7
NO_2^-	6.5	6.5	6.5	8.5	1.5
NO_3^-	10.0	10.0	5.5	3.5	2.2
ΣN	8.3	7.3	6.3	4.5	3.0

* The chemical tests were conducted in the geochemistry laboratory of the Permafrost Institute SB RAS (accreditation certificate ROSS RU. 0001.518584, as of 05.06.2011), chemical analysts L. Boitsova and O. Shepeleva.

Table 4. **Concentration of cations in active and frozen soils of the cultural layer**

Ions	Concentration, mg-eq/100 g				CL_{AL}/CL_{pf}	CL_{pf}/Q_{al}	CL/Q_{al}
	CL_{AL}	CL_{pf}	CL	Q_{al}			
Ca^{2+}	0.340	0.190	0.270	0.130	1.8	1.5	2.1
Mg^{2+}	0.170	0.160	0.165	0.070	1.1	2.3	2.4
K^{+}	0.035	0.020	0.030	0.020	1.8	1.0	1.5
Na^{+}	0.520	0.240	0.380	0.110	2.2	2.2	3.4

Note. CL_{AL} – cations in active soils of the cultural layer; CL_{pf} – cations in frozen soils of the cultural layer; CL – cations in active and frozen soils of the cultural layer; Q_{al} – cations in alluvial deposits.

Comparison of the content of cations in the active layer and frozen soils of the CL and in alluvial deposits is shown in Table 4.

Maximum contrast in the accumulation of cations in CL soils compared to alluvial deposits is characteristic of Na^+, while the minimum contrast is observed for – K^+ and may be represented next to (CL/Q_{al}): $Na^+ > Mg^{2+}$, $Ca^{2+} > K^+$.

The most uniform ratio of the cultural layer (CL_{AL}/CL_{pf}) of cations in the active layer (CL_{AL}) and permafrost grounds (CL_{pf}) is characteristic of Mg^{2+} ions. The maximum reduction – 2.2 times – of cations in the CL_{pf} compared to CL_{AL} is observed in Na^+ ions. By decrease in the concentration of cations in CL_{pf} compared to CL_{AL}, cations are grouped into the following series: $Na^+ > K^+$, $Ca^{2+} > Mg^{2+}$.

Comparison of the content of anions in the active layer and frozen grounds of the cultural layer and in alluvial deposits is shown in Table 5.

Maximum contrast in the accumulation of anions in CL soils compared to alluvial deposits is characteristic of Cl^-, minimum contrast is observed in HPO_4^{2-} and may be presented next to (CL/Q_{al}): $Cl^- > NO_3^-$, $SO_4^{2-} > HCO_3^- > HPO_4^{2-}$.

The proportion of anions in the active layer and frozen soils of the cultural layer (CL_{AL}/CL_{pf}): SO_4^{2-}, $HCO_3^- > Cl^- > NO_3^- > HPO_4^{2-}$ indicates maximum mobility of nitrates and chlorides in the soils of the CL_{pf}.

Similar series of migration of cations and anions, which have different mobility in frozen soils at the temperature of –6 °C, were experimentally established previously by *Yu.P. Lebedenko* [*1988*]: cations – $Na^+ > Mg^{2+} > K^+$, anions – $Cl^- > SO_4^{2-} > NO_3^-$.

In the frozen soils of the CL of the city, the most favorable conditions for migration of salts seem to exist at negative temperatures (–3...–5 °C), when a large amount of water is contained in the films of pore solutions but is little related to the mineral part, and the water conductivity of frozen soils is maximum.

Alluvial permafrost deposits are characterized by the weakly acidic reaction of the medium, on average pH = 6.81. The weakly acidic, close to neutral, value of pH continues to be recorded also in the above frozen ground of the CL in the interval of depths 3–6 m. The reaction of the active layer medium in the upper part of the CL is weakly alkaline, also in the range of pH = 7.18–7.73.

Increased alkalinity of the urban environment in active CL ground and especially in the urban soils (pH sometimes rose to 9) makes the existence of weakly alkaline and strongly alkaline (sodic) classes of geochemical barriers possible.

A number of studies on the chemistry of big cities are devoted to accumulation of microelements in the cultural layer, where the focus is made on toxic heavy metals – Pb, Cd, As, Hg [*Nezhdanova et al., 1984; Makarov, 1985; Sadovnikova, 1989; Dobrovolsky, 1997; Gerasimova, 2003; Kasimov, 2004*]. However, there is practically no information on the geochemical structure of the CL of the cities located in the permafrost zone.

Table 5. **Concentration of anions in active and frozen soils of the cultural layer**

Ions	Concentration, mg-eq/100 g				CL_{AL}/CL_{pf}	CL_{pf}/Q_{al}	CL/Q_{al}
	CL_{AL}	CL_{pf}	CL	Q_{al}			
HCO_3^-	0.45	0.21	0.33	0.18	2.1	1.2	1.8
SO_4^{2-}	0.40	0.18	0.29	0.09	2.2	2.0	3.2
Cl^-	0.27	0.16	0.26	0.06	1.7	2.7	4.3
NO_3^-	0.03	0.021	0.024	0.007	1.4	3.0	3.4
HPO_4^{2-}	850	775	813	625	1.1	1.2	1.3

Note. CL_{AL} – anions in active soils of the cultural layer; CL_{pf} – anions in frozen soils of the cultural layer; CL – anions in active and frozen soils of the cultural layer; Q_{al} – anions in alluvial deposits. Concentration of HPO_4^{2-} is expressed in mg/kg.

Table 6. **Comparison of the concentration of macro elements** in alluvial deposits (Q_{al}) with abundance of the element (AE) in the Earth's crust*, mg/kg**

Chemical element	Q_{al}	AE	Q_{al}/AE	Chemical element	Q_{al}	AE	Q_{al}/AE
Li	22	32	0.7	Ge	1.2	1.4	0.9
Be	1	3.8	0.3	As	0.96	1.7	0.6
B	21	12	1.8	Y	17	20	0.8
P	800	930	0.9	Nb	15	20	0.8
Sc	10	10	1.0	Mo	1.6	1.1	1.4
Ti	5000	4500	1.1	Ag	0.08	0.07	1.1
V	36	90	0.4	Cd	0.65	0.13	5.0
Cr	59	83	0.7	Sn	2.7	2.5	1.1
Mn	550	1000	0.6	Yb	0.80	0.33	2.4
Co	6	18	0.3	W	2	1.3	1.5
Ni	24	58	0.4	La	1.8	29	0.1
Cu	20	47	0.4	Pb	24	16	1.5
Zn	65	83	0.8	Bi	1	0.009	100
Ga	14	19	0.7	Hg	30	83	0.4

Note. The content of Hg is expressed in mg/t. The number of boreholes is 71.

* Abundance of the element in the Earth's crust, according to: [*Vinogradov, 1962*].

** Atomic emission analysis was performed in the Central Geological Laboratory of Yakutskgeologia (accreditation certificate # ROSS RU.0001.511039).

Accumulation of microelements in the anthropogenic urban deposits may be related not only to human activity but also to the high content of the elements in the natural rocks on which the CL was formed.

Modern (Holocene) alluvial deposits in the valley of the Lena River, which represent soil-forming substrate, serve as the original supplier of products of hypergene weathering and play an exclusive role in forming modern residuum and soils. Alluvial deposits of the Quaternary Age have in many ways determined the mineralogical and chemical composition of the CL.

The chemical composition of the alluvial deposits (in the depth range of 10–20 m) in the area of Yakutsk and its comparison of the chemical composition with the abundance of elements in the Earth's crust is shown in Table 6.

For their chemical composition, the alluvial deposits are weakly acidic, close to neutral (pH = 6.81), weakly mineralized (the average salinity is 0.025 %), sulfate-carbonate, mixed for cations, and with a relatively high content of ammonium.

The results of comparison of the chemical composition with the abundance of elements in the Earth's crust demonstrate that the alluvial deposits of the Quaternary Age in the territory of the city are geochemically focused around litho- and chalcophile elements: B, W, Pb, Ti, Sn, Mo, Ag, the content of which exceeds the abundance of elements in the Earth's crust by a factor of 1.2–2 (Table 7). P and Ge follow them, quantitatively close to the normal abundance of elements in the Earth's crust.

Essential reduction in concentration is observed in sandy-clayey and sandy alluvial soils, primarily in relation to the lithophile elements: V, Co, Ni, Cu, La, Be, Hg, the fraction of which is lower than the abundance of elements in the Earth's crust, less than 0.5 of the abundance of elements in the Earth's crust. Concentration of most microelements of this group grows in the anthropogenic deposits but remains at the level of the negative anomaly.

Maximum geochemical transformation is observed in the upper layer of the urban soils (0–0.2 m), where in the process of the anthropogenic impact the degree of contrast significantly increases compared to the normal abundance of elements in the Earth's crust, of the group of chalcophile (Hg, Zn, Pb, Ag, Tl) and some lithophile (B, Mn, Y) chemical elements.

Table 7. **Coefficient of concentration of chemical elements in alluvial deposits in the area of Yakutsk**

Soils	Concentration coefficient (in relation to the abundance of the element in the Earth's crust, AE)				The number of samples
	<0.5	0.7–1.0	1.0–1.5	1.5–2.0	
Alluvial deposits	V, Co, Ni, Cu, La, Be, Hg	P, Cr, Mn, Y, Zn, Ga, Ge, Nb, Yb, Sc, Li	Ti, Mo, Sn, Ag	B, Pb,W	190

Note. The table was composed according to: [*Makarov, 1985; Podyachev, 2009; Makarov and Sedelnikova, 2016*].

Table 8. **Contrast of anthropogenic geochemical anomalies (CL) in relation to Q_{al}**

CL/Q_{al}	Chemical element
>10	Cl, NO_3, K, Na, NO_2
5–10	Hg, S
3–5	Mg, Ag, C, Ca
2–3	Li, V, Co, Zn, W, Pb
1.5–2	P, Cr, Ni, Cu, Ge, NH_4, Sn
~1	Ti, Mn, Ga, Y, Mo, Bi, Nb, B; pH

The value of the contrast of anthropogenic geochemical anomalies consists in the ratio between the average concentration of microelements in the CL grounds of different ages and in alluvial deposits; it is shown in Table 8.

Maximum contrast of the anthropogenic geochemical anomalies in relation to the chemical composition of alluvial deposits (>5) is characteristic of ions (macro components) of the saline composition of the cultural layer grounds: Cl^-, NO_3^-, K^+, Na^+, NO_2^-, SO_4^{2-} and lithochemical anomalies Hg and Ag.

The series of decreasing contrast of macro components in anthropogenic deposits compared to the chemical composition of alluvial deposits are as follows:

anions: $Cl > NO_3 > NO_2 > SO_4 > HCO_3$;
cations: K > Na > Mg > Ca.

The "ancient" grounds of the cultural layer aged about 300 years were uncovered with a borehole in the territory of the city district Old Town. According to the map "The Plan of the Town of Yakutsk of 1770" [*Popov, 2007*], the borehole was drilled in the area of the shopping arcade. By the end of the XVIII century, this territory had already been well-developed. There was the Transfiguration church, the shopping arcade, houses with barns, sheds, etc.

The permafrost-lithological and geochemical characteristic of the "ancient" grounds of the CL is shown in Table 9.

The cross section of the deposits uncovered with the borehole is represented by a soil-vegetation layer about 0.5 m thick; in the range of 0.5–1.5 m – by active soils of the CL – black loam containing organic matter and wood chips; in the CL soils is estimated as 4.0 m, corresponding to the averaged data on the thickness of the CL in the city districts with duration of the anthropogenic impact of about 300 years (Fig. 2). From 4 m to the borehole bottom (12 m), there are alluvial deposits of the Quaternary Age: gray medium-grain, frozen and icy sand.

Chemically, the CL grounds are distinguished by the following: 1) primarily alkaline reaction of the medium (on average pH = 7.26); 2) increased salinity (on average 0.075–0.35 %) due to the presence of chlorides; 3) the anomalous concentration of heavy

Table 9. **The lithological and geochemical characteristic of "old" soils of the cultural layer**

Depth, m	Brief description of the soil	pH	Salinity, %	Cl^-	Zn	Pb	Mn	Ag
				mg-eq/100 g	mg/kg			
Active soil of the cultural layer								
0.0–0.5	Soil and vegetation layer	**7.76**	**0.075**	**0.24**	**150**	**85**	**1500**	**0.15**
0.5–1.0	Black loam with organic matter and wood chips, thawed	6.80	**0.13**	**0.37**	**150**	**100**	**1100**	**5.00**
1.0–1.5	Brown loam with organic matter, moist, thawed	7.15	**0.12**	**0.31**	**150**	**60**	**970**	**2.40**
Frozen soil of the cultural layer								
1.5–1.8	Brown medium-grain sand with inclusions of organic matter	**7.50**	**0.11**	**0.29**	**150**	25	**1100**	**2.60**
1.8–2.7	Brown clay with inclusions of organic matter	7.50	**0.11**	**1.25**	**150**	20	**700**	**0.12**
2.7–4.0	Light yellow loam with inclusions of organic matter	6.86	**0.35**	**2.38**	**125**	17	**800**	**0.30**
Permafrost alluvium								
4.0	Gray medium-grain sand, frozen, icy	7.35	**0.32**	**2.32**	**100**	20	**700**	0.05
5.0		7.45	**0.30**	**2.43**	85	20	600	0.10
6.0		7.60	**0.28**	**2.54**	50	20	500	0.10
7.0		7.25	**0.14**	**0.99**	50	20	500	0.15
8.0		7.62	**0.12**	**0.91**	70	20	500	0.10
9.0		7.26	**0.06**	**0.34**	70	20	500	0.15
10.0		7.00	0.05	**0.20**	70	20	500	0.10
11.0		7.00	0.03	0.08	70	20	500	0.10
12.0		7.10	0.02	0.11	70	20	500	0.15

Note. The district "Old Town" of Yakutsk, 18A, Chernyshevsky Street. The lithological description of the soils was made by I.V. Dorofeev and I.I. Syromyatnikov. The bold type indicates anomalous values of the components.

metals (Zn, Pb, Mn, Ag), which is 2–5 times (up to 50 for silver) than in alluvial deposits not affected by anthropogenic impact. The active and frozen grounds of the CL are practically uniform geochemically. However, in frozen grounds of the CL deeper than 1.5 m anomalous concentrations of Pb, characteristic of active grounds, are absent, and sharp increase in the concentration of chlorides in the lower horizons in the depth range of 1.8–4.0 m is observed.

The upper part of the permafrost alluvial deposits uncovered with the borehole was exposed to essential anthropogenic impact. The indication of this is the alkaline values of the grounds, increased salinity and the high concentration of Cl^- in the grounds recorded to the depth of 9 m. At the same time, in frozen alluvium the spectrum of heavy metals has decreased, and weakly contrasting anomalies of Zn and Mn are observed only in the upper part of the alluvial sands to the depth of about 5 m (Table 9).

A characteristic of the chemical composition of younger grounds of the cultural layer with anthropogenic impact lasting 80–100 years, uncovered during construction of a building foundation, is shown in Fig. 5 and in Table 10.

Thickness of the grounds of the cultural layer (B, C and D in Fig. 5) is 4.2 m. They are characterized by the weakly alkaline reaction, increased salinity due to the growing concentration of hydro carbonates, sulfates and nitrates, by the weakly contrasting anomaly of heavy metals (Zn, Pb, Hg), the concentration of which is 2–3 times higher than in the underlying alluvial deposits (A). Active (D) and frozen (B and C) grounds of the cultural layer are practically uniform in the geochemical respect. However, in the CL_{AL} insignificant increase in the concentration of practically all the chemical elements is observed versus the CL_{pf} (the maximum concentration was recorded for mercury – 1.8 times). Essential accumulation of nitrates in the frozen grounds of the CL (0.027–0.071 mg-eq/100 g), indicating the presence of "old" organic matter, whereas in the active layer grounds the concentration of NO_3^- is only 0.003 mg-eq/100 g (Table 10).

The permafrost-lithological and geochemical characteristic of the youngest grounds was based on

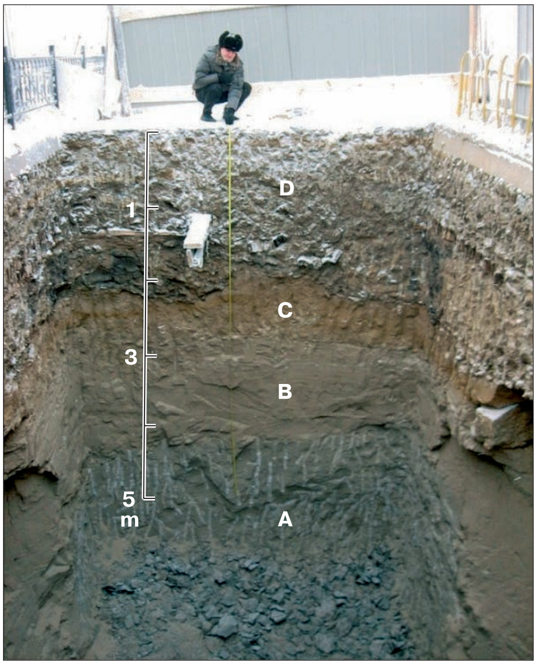

Fig. 5. The cultural layer (the age of 80–100 years) and the underlying grounds in Yakutsk, uncovered by construction of a building foundation:

A – alluvium; B–D – grounds of the cultural layer (B – frozen grounds, the lower part; C – frozen grounds, the middle part; D– active grounds, the upper part). Photo courtesy of I.V. Dorofeev.

the data from borehole # 6 (Table 11). The borehole was drilled in community 202 of Yakutsk, developed on artificially created alluvial soils. The first experimental buildings made of reinforced-concrete panels were completed in 1985. This is one of the youngest districts of the city with the duration of anthropogenic impact of about 30 years.

The deposits uncovered with the borehole have a structure composed of three layers: 1) thawed alluvial grounds 4.1 m thick (gray-brown sand, fine- and medium-grain); 2) frozen alluvial grounds 3.8 m thick, in the range of depths 4.1–8.0 m (sand similar to the above lying sand with a thin interlayer of sandy

Table 10. **The chemical composition of the cultural layer (the age of 80–100 years)**

Layer (see Fig. 5)		Depth, m	Permafrost	pH	Salinity, %	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	Zn	Pb	Hg
						mg-eq/100 g				mg/kg		mg/t
Cultural layer	D	0–1.4	AL	6.93	**0.050**	**0.49**	**0.34**	**0.06**	0.003	**50**	**20**	**26**
	C	1.4–2.6	Permafrost	7.39	**0.040**	**0.57**	**0.17**	0.04	**0.027**	30	15	14
	B	2.6–4.2		7.44	**0.045**	**0.54**	**0.25**	0.03	**0.071**	**50**	15	15
	C + B	1.4–4.2		7.42	**0.042**	**0.56**	**0.21**	0.03	**0.049**	40	15	14
Alluvium	A	4.2–5.0		6.50	0.020	0.17	0.09	0.03	0.001	20	10	4.8

Note. The bold type indicates anomalous values of components.

Table 11. **The lithological and geological characteristic of the cultural layer (the age of 30 years) (borehole # 6, community 202)**

Depth, m	Brief description of the ground	pH	Salinity, %	Cl^-	Zn	Pb	Mn	Hg
				mg-eq/100 g	mg/kg			mg/t
Active ground of the cultural layer								
0.0–3.8	Fine and medium-grained gray and brown sand, feldspar quartz with inclusions of small pebbles, thawed	**6.87**	**0.018**	**0.025**	**100**	**30**	**700**	**23**
		7.71	0.01	0.02	50	10	500	3
		7.22	0.01	0.02	30	10	500	5
		7.09	0.01	0.02	50	10	300	3
3.8–4.1	Gray and brown sand, similar to the above lying ground, very moist, thawed	7.05	0.02	0.03	**100**	15	200	**7**
Frozen ground of the cultural layer								
4.1–5.75	Fine and medium-grained gray and brown sand, feldspar quartz with inclusions of small pebbles and sandy loam interlayers, frozen	6.59	0.01	0.02	30	10	200	3
5.75–7.2	Yellow-gray sand of varying grains, weakly frozen, with massive cryogenic texture	8.11	0.01	0.02	20	10	200	3
7.2–8.0	Yellow-gray sand with medium-sized grains, with thin (2–3 cm) interlayers of dark-gray sandy loam, weakly frozen, with massive cryogenic texture	7.11	0.02	0.02	30	10	300	6
Alluvial deposits								
8.0–8.4	Fine dark-gray sand, with interlayers of sandy loam and light loam, moist and thawed	7.11	0.02	0.02	30	10	300	6
8.4–9.4	Dark-gray loam, with thin interlayers of peaty loam and sand, thawed	7.41	0.03	0.05	**70**	10	200	9

Note. The bold type indicates anomalous values of components.

clay); 3) alluvial deposits which have thawed after alluvion in the range of depths 8.0–9.4 m (dark-gray sands and loams).

For the chemical composition, the soils in the borehole are primarily of the alkaline, weakly saline (0.01–0.03 %), and hydrocarbonate-calcium type; in alluvial deposits – of the hydrocarbonate-calcium-sodium type.

Weak anomaly of heavy metals (Zn, Mn, Pb, Hg), 2–3 times exceeding the background concentration in the underlying alluvial deposits was observed only in the surface ground horizon (0–0.5 m). It is likely that formation of the weakly contrasting anomaly for Zn, Pb, Hg, Li, Cu at the depth of 3.8–4.1 m in quartz-feldspar sands is related to contamination of the grounds with metal during drilling, to which the high concentration of W (15 mg/kg) points.

The thirty years' anthropogenic impact in the territory of community 202 of Yakutsk did not practically cause any essential change in the chemical composition of alluvial sands and resulted in formation of the weakly contrasting geochemical anomaly of heavy metals only in the surface frozen soil horizon (0–0.5 m).

Table 12. **Dependence of the thickness of anthropogenic geochemical halos on the age of development of the urban territory**

Development age	Thickness of anthropogenic halos, m					
	10–8	8–6	6–5	5–3	3–2	2–1
350	Hg, NO_3, NH_4	Na, S, Cl, NO_2	Ca, Mg, C, Ti, V, Mn, Co, Zn, Y	Ag, Ni, Sn, Cu	P, Cr, Ge, B, K	Pb, Mo
200	Hg, NO_3	Zn, NO_2	Mo, Ag, Sn, NH_4	Ti, V, Cr, Na, S, Cl, Ca, Mg, C, K	Li, Co, Cu, Y	Ga, Pb
100	Zn	C, NH_4, Ag, Co, NO_2	Cl, P, Ti, NO_3	Ca, Na, V, Mg, Li, Mo, Hg	Mn, Cr, Ni, Zn, Ag	Co, Cu, Pb
⩽70	–	NO_2	Ti, NO_3	Mn, Co, Pb	Cl, Na, S, Cl, Ca, Mg, C, Ni	P, V, Cr, Cu, Zn, Ga, Ge, Ag, Sn, Hg, NH_4

Table 13. **The chemical composition of alluvial deposits (Q_{al}) and the cultural layer soils (CL)**

Soils	Chemical composition ($C-HCO_3^-$; $S-SO_4^{2-}$)	Anomalous components*
CL_{AL}	$0.096 \dfrac{C\,39\,S\,35\,Cl\,23}{Na\,48\,Ca\,32\,Mg\,16}$ pH 7.4	Hg (7), NO_3, Ag (3), P, Zn, Pb, Sn (1.5)
CL_{pf}	$0.078 \dfrac{C\,37\,S\,32\,Cl\,28}{Na\,39\,Ca\,31\,Mg\,26}$ pH 7.0	NO_3 (6), Ag (2), Hg, P, Zn, Pb, Sn (1.5)
Q_{al}	$0.025 \dfrac{C\,52\,S\,32\,Cl\,16}{Ca\,33\,Na\,31\,Mg\,23\,NH_4\,10}$ pH 6.8	W, Pb, B (1.5–2.0), Ag, Sn, Mo, Ti (1.1–1.5)

* In brackets – the ratios of CL/Q_{al} and Q_{al}/abundance of elements in the Earth's crust, AE (last line).

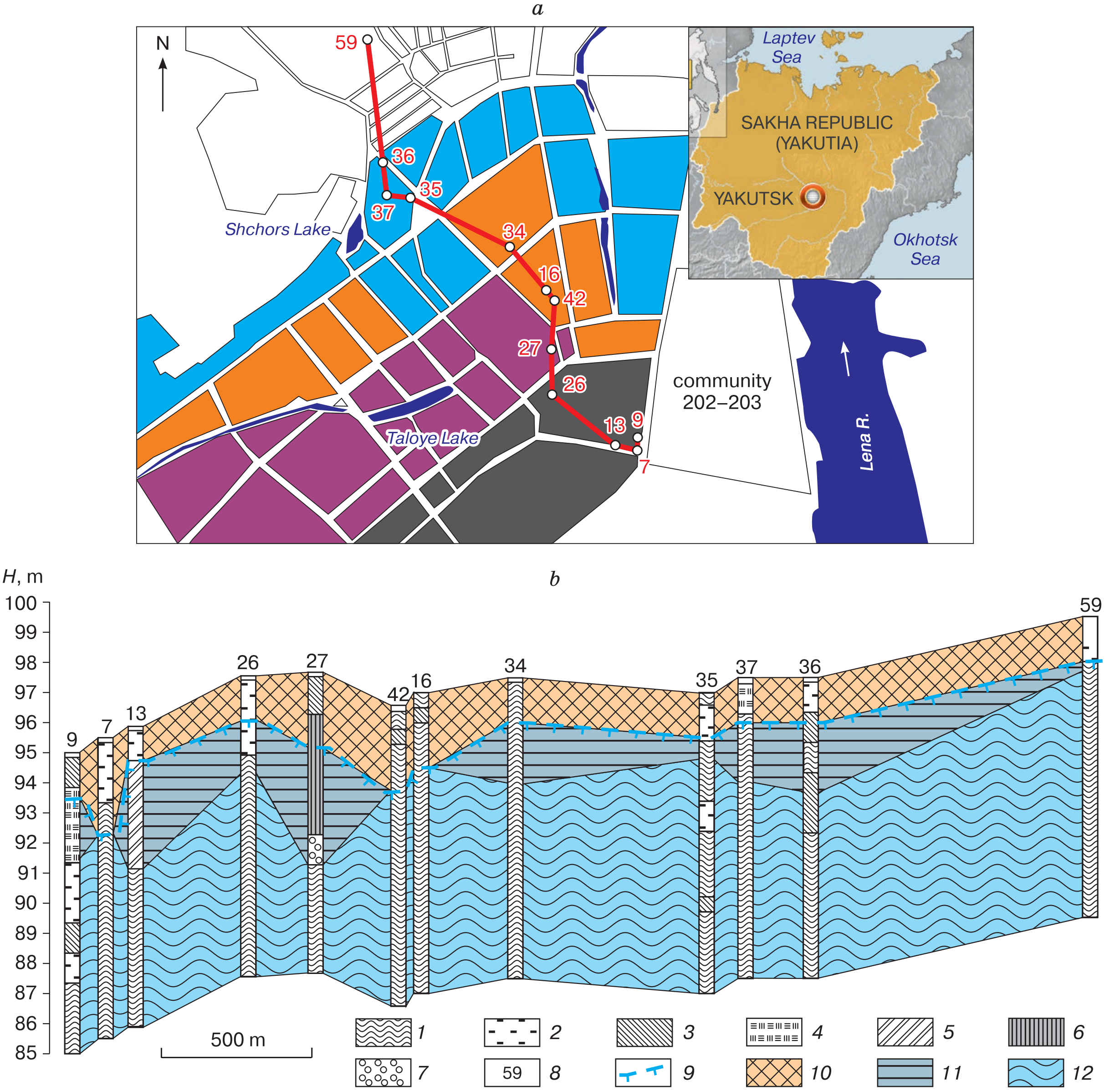

Fig. 6. The age of the urban development (*a*) and the permafrost-geochemical cross section of the anthropogenic deposits (*b*).

a – the enlarged fragment of Fig. 4. The red line – the line of location of the permafrost-geochemical cross section in the territory of the city; figures – borehole numbers at the cross section; see the other notifications in Fig. 4; *b* – cultural layer; *1* – sand; *2* – sandy loam; *3* – loam; *4* – peat; *5* – ice; *6* – reinforced concrete; *7* – wood; *8* – borehole number; *9* – permafrost top; *10*, *11* – anthropogenic deposits (*10* – active, *11* – frozen); *12* – frozen alluvium.

The anthropogenic geochemical anomalies in active layer (CL_{AL}) and frozen (CL_{pf}) ground of the cultural layer of Yakutsk differ for the level of concentration of chemical elements. The contrasting intensity of the anomalies in the CL grounds in relation to the concentration in alluvial deposits varies in CL_{AL} from 1.09 (pH) to 7.18 (Hg) and is on average 3.05, and in CL_{pf} – from 1.01 (Mn) to 5.43 (Cl^-), on average 2.10, less by approximately one-third.

The highest contrast intensity of migration in CL_{AL}/CL_{pf} is characteristic of mercury, the concentration of which in CL_{pf} is 5 times less than in CL_{AL}, which may be explained by reduction of the migration ability of Hg as the ground temperature is decreased.

Dependence of the thickness and composition of the chemical elements of anthropogenic geochemical halos in the CL on the age of developing the urban territory has been determined. In the old districts of the city, where the duration of the anthropogenic impact exceeds 200 years, geochemical anomalies, the thickness of which exceeds 5 m, are formed by a large complex of micro components (Table 12).

The chemical composition of the alluvial deposits and the character of transformation of the mineral composition and of the spectrum of anomalous elements in active layer and frozen ground of the cultural layer are shown in Table 13 and in the permafrost-geochemical cross-section (Fig. 6).

CONCLUSIONS

• A geochemical study of the cultural layer deposits of the urbanized territory of Yakutsk has been first conducted.

• Resulting from more than 300-years-long development of the urban territory of Yakutsk, a local cryo-bio-anthroposphere has been formed, the qualitative and quantitative geochemical characteristics of which depend on the duration and intensity of the anthropogenic impact.

• Formation of the lithological and geochemical parameters of the cultural layer of Yakutsk took place in two historical steps: the first step ("rural") lasted over 300 years, from the date of the beginning of development of the territory of Yakutsk (1642) to the mid 1950s; the second step ("urban"), when over the recent 60–70 years the urbanized territory of Yakutsk as such has been formed. The many years' freezing of the ground determined the specific conditions of forming the mass of the anthropogenic deposits with different chemical and mineral composition, different structure, physical and mechanical properties and the specifics of migration of the chemical elements.

• Concentration of micro elements in the urban grounds is caused by their penetration into the ground due to anthropogenic impact and the geochemical properties of alluvial Quaternary deposits, enriched with W, B, Pb, Ti, Sn, Mo, Ag and having deficit of V, Co, Ni, Cu, La, Be, Hg, the percentage of which is recorded at the level of 0.5 (<abundance of elements in the Earth's crust).

• The geocryological conditions in the territory of Yakutsk (thickness of permafrost is 250–450 m, thickness of the active layer is 1.5–2.5 m, the ground temperature at the depth of 10 m is equal to −2...−6 °C) account for formation of a double CL: in the active layer and in the permafrost, differing by their geochemical parameters.

• Maximum contrast of anthropogenic geochemical anomalies in relation to the chemical composition of alluvial deposits is observed in ions – macro components of the salt composition, Cl^- (29), NO_3^- (18), K^+ (16), Na^+ (14), NO_2^- (12), SO_4^{2-} (5), Hg (5) (the contrast factor is indicated in brackets).

• The anthropogenic salination and the contrast anomalies of macro- and microelements in the old districts of the city encompass the grounds of the cultural layer and the upper horizons of alluvial deposits (sometimes reaching 5–6 m). Thickness of anthropogenic geochemical anomalies in the grounds of the cultural layer and in the top of the alluvial deposits depends on the age of development of the urban territory and reaches 9–10 m.

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