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Arsenic in the environment of Yakutia - potential health hazard

In view of the toxicological role of arsenic, the distribution of its mineral compounds in the environment of Yakutia is examined. The distribution of arsenic was studied in various components of the Yakutia's environment, including the atmosphere, snow cover, surface water and groundwater, and soils. The need for control of human exposure to arsenic compounds is substantiated.

Keywords: Environment, arsenic, mineral compounds, toxicants, health effects

Introduction. Throughout human history, arsenic has played a dual role. It has been known since ancient times as a strong poison capable of causing lung cancer or other illness on the one hand and as a component of bronze, paints, and remedies on the other. Arsenic minerals (orpiment and realgar) were used for centuries as a basis for medicines used to treat skin and blood diseases, syphilis, malaria, flu, and scarlet fever. Currently, arsenic is added to medical and veterinary drugs, insecticides used in agriculture and wood treatment, and some alloys. It is also used in microelectronics industry and laser optics technologies. Considering the toxicity of arsenic, this paper examines its levels in various components of the Yakutia's environment, including the atmosphere, snow cover, surface waters, ground water, soils and rocks.

Review of medical data. Arsenic is known to be highly toxic [2]. A few hundreds tons of arsenic are enough to poison the majority of the human population. The toxicity of arsenic depends on its valence state, solubility, and speciation. Most cases of toxicity manifestation are associated with the inorganic trivalent arsenic which is much more toxic than the pentavalent form. Inorganic arsenic has been recognized as a poison since ancient times. If consumed in large amounts, arsenic can lead to a death.

According to Avtsyn et al. [11], arsenic deficiency syndromes in humans are not known. The main diseases, syndromes and symptoms of the toxic effects of excess arsenic in humans are given in Table 1.

Table 1

Major diseases, syndromes and symptoms of human overexposure to arsenic [11]

Arsenicosis is characterized by digestive disorders, conjunctivitis, opacity of the vitreous body and cornea, septal ulceration, stomatitis, laryngitis, tracheitis, bronchitis, papular and pustular rash, recurrent eczema, atrophic chronic acrodermatitis, symmetrical punctate palmoplantar hyperkeratosis, nail fragility, premature loss and graying of hair. Neurological disorders in the form of intellectual and memory impairments, depression, polyneuritis with muscle atrophies, as well as in the form of retrobulbar neuritis, smell and taste disorders. Endemic arsenic poisoning from drinking water and food – 'black foot disease' (peripheral vascular changes as in obliterating endarteritis), verrucous keratosis of the palms and soles, anemia, cardiac disorders, peripheral neuropathy. Skin and lung cancers can develop.

Inorganic arsenic is associated with the high mortality rate from ischemic heart disease.

Exposure to arsenic and its methylated metabolites can lead to miscarriage and dead childbirths. Studies have shown a close relationship of arsenic exposure to neurological diseases, and impaired intellectual and physical development in children. Effects of arsenic on the respiratory system can result in lung cancer, diseases of the upper respiratory mucous membrane, lung emphysema, and reduced pulmonary function. Serious effects of arsenic on the endocrine system include pancreatic diabetes and some pathologies of the liver. Arsenic can irritate the gastrointestinal tissues it contacts. Severe arsenic poisoning cases exhibit nausea, vomiting, stomach cramps, and diarrhea. In rare cases, poisoning may lead to acute gastroenteritis resulting in circulatory collapse with kidney injury and death. Cancer of the skin, liver, bladder, and lungs can develop. Respiratory exposure to inorganic arsenic leads to the increased risk of lung cancer. It occurred in the workers exposed to arsenic in mines and chemical plants, as well as in the residents living near these facilities and arsenic waste disposal sites.

Skin ailments are the most common non-cancerous effects of chronic oral exposure to inorganic arsenic. They start with hyperpigmentation spots on the body which can progress into palmar and plantar hyperkeratosis [13, 14]. A major incident of a disease known as “black foot disease” occurred in Taiwan in the 1950s resulting from arsenic contamination of ground water [15]. The inorganic As concentration in ground water was 100 to 1810 $\mu\text{g/L}$, exceeding the admissible limit for drinking water by 2–45 times. The symptoms of the disease, a form of dry gangrene, are changes in color of the extremities to brown or black (**Fig. 1**).

Thickening and cracking of the skin leads to ulceration and eventually to gangrene. If poisoning is untreated, the result may be foot amputation [14]. Black foot disease was also found in China, where its severe form – arsenicosis – may be associated with malnutrition.

The largest mass poisoning with arsenic occurred in Bangladesh where a large number of tube water wells were drilled in the mid 1980s within the areas of elevated arsenic levels. Ironically, the wells were dug to improve drinking water quality. Consumption of drinking water with high arsenic concentrations (approximately 14 mg/L, 300 times over the WHO recommended limit) affected 53 million people – about half of the country’s population [15]. It is believed that certain geological conditions – geochemical arsenic anomalies – contribute to the generation of heavy arsenic concentrations in ground water. Aquifers with high arsenic concentrations have been found to be associated with areas of endemic occurrences of arsenic-related diseases, such as Thailand, Mongolia, Taiwan, China, Mexico, Argentina, Chili, Hungary, and others. Large-scale investigations conducted in West Bengal, Bangladesh and India indicate that the endemic character of some diseases, such as diabetes, is related to the high

levels of arsenic compounds in shales and coals from which arsenic is leached by ground water and migrates to water supplies [8, 9, 10]. Arsenic concentrations in the latter may exceed 50 µg/L, sometimes reaching 3400 µg/L [2, 13, 14].

Results of geochemical investigations. Arsenic is the most abundant element in the ores of Yakutia. It is found in many quartz and quartz-carbonate lodes of the gold, polymetallic, tin ore deposits in the Verkhoyansk-Kolyma Folded Region and the Aldan Shield [6]. Arsenic concentrations in the ores of the Kyuchus, Nezhdaninskoe and Sarylakh are as high as 1-2%. The distribution of the main areas of ore mineralization and large geochemical arsenic anomalies in Yakutia is shown in **Fig. 2**.

Arsenic geochemical anomalies are widespread in the eastern, geosynclinal part of Yakutia (see Fig. 2), where arsenic contents in soils sometimes reach “hurricane” values of up to 1%, 2000 times of the background values and maximum contaminant levels (Table 2).

Table 2

**Arsenic concentrations in ores, host rocks and soils
in gold-antimony and gold ore deposits, eastern Yakutia**

Rocks and Soils	As concentration, mg/kg	
	Avg.	Max.
Sarylakh Au-Sb deposit		
Ore body	100·n	1.6%
Enclosing rocks	55	150
Soils	80	460
Zaderzhnoe Au deposit		
Ore body	100·n	5400
Enclosing rocks	15	40
Soils	32	500
MCC _{soil}	2 – 10	

High arsenic concentrations are observed in rocks as well. For example, terrigenous sandstones and shales in eastern Yakutia contain 3.1 to 7.4 mg/kg arsenic in the South Verkhoyansk Synclinorium and 15 to 48 mg/kg in the Kular District, exceeding the maximum contaminant concentration (MCC) for soils by about an order of magnitude.

In Yakutia, anthropogenic arsenic is released to the atmosphere with gaseous and particulate emissions from smelters, and with fertilizers and pesticides used in agriculture; it is contained in gaseous emissions and effluents from coal-fired cogeneration stations, as well as in non-ferrous sulfide mine tailings. Central Yakutia has a very clean atmosphere with arsenic concentration similar to the maximum value for the South Pole air of 0.05 ng/m³. The areas of anthropogenic activity have considerably higher arsenic concentrations. In Yakutsk, for example, the average As concentration in the air is 5 to 20 times greater than the background values for central Yakutia. Several areas of high atmospheric As levels have been identified in the city whose locations indicate emission sources: the airport, power station, downtown area, and

modular building factory (Fig. 3).

Concentrations of arsenic in natural surface and ground waters of Yakutia are generally about 1 to 2 µg/L, but may be 2 to 3 orders of magnitude higher in contaminated areas or in areas where soils have elevated arsenic levels (Table 3).

Table 3

As concentrations in surface water in Yakutia, µg/L

#	Name	Water	Note
Rivers			
1	Irgichen	1-3	
2	Omchikandya	10	
3	Iekiyes	30	Suspended sediment
4	Bolshoi Kuranakh	4.4	
Lakes			
5	Lakes in Yakutsk	3-60	
6	Sosnovoe Lake (Nizhny Bestiakh)	25.3	
7	Labyntyr Lake	<1	
8	Bolshoe Tokko Lake	<1	
MCC		50	Hygienic Standards ГН 2.1.7.020-94

The ground waters commonly contain higher arsenic concentrations than the surface waters (Table 4). An important ecological process in ground water is methylation of arsenic in anaerobic conditions producing readily soluble ($n \cdot 10 - n \cdot 100$ mg/L) and highly toxic $(CH_3)_3As$.

Table 4

Arsenic concentrations in ground water, µg/L

Location	As, µg/L	Analytical technique
Nezhdaninskoe	<240	Semi-quantitative spectral analysis
Udachnaya diamond pipe	740	Atomic spectrometry
Sarylakh, subpermafrost water, 200 m	9	Semi-quantitative spectral analysis
Sentachan, subpermafrost water, 300 m	300	Semi-quantitative spectral analysis
Yakutsk, subpermafrost water, 260 m	2	Semi-quantitative spectral analysis
Bulus springs	25	Atomic spectrometry
MCC	50	

The most favorable conditions for As migration and accumulation in surface and ground waters exist in the weathering zone of the As-enriched gold-antimony and gold ore deposits hosted in inert terrigenous rocks. The waters in the dispersion halos of these deposits (Malan, Sarylakh, Nezhdaninskoe and others) contain the highest arsenic levels – $10 \cdot n - 100 \cdot n$ µg/L.

Serious health risk is associated with arsenic accumulated in mill tailings. Most of the arsenic (80% or more) contained in the As-rich ores gets into tailings after ore processing. Arsenic concentrations in the solid and liquid waste materials from the mills reach ‘hurricane’ values, sometimes exceeding the standard limits by 2-3 orders of magnitude (Table 5).

Table 5

Arsenic concentrations in mill tailings, mg/kg

Mill	Solid, mg/kg	Liquid, $\mu\text{g/L}$	Note
Allakh-Yunskaya gold mill-50	2000	200	Old tails
Deputatskaya mill	< 1000	< 100	Tailings pond
Duetskaya gold mill	500	n.d.	Gravity tailings
Kularzoloto gold mill	< 700	n.d.	Tailings pond
Kuranakhskaya gold mill	n.d.	< 2 800	Slurry
Nezhdaninskoe	< 970	< 240	Sedimentation pond
Samolazovskoe	< 1.5%	n.d.	Sedimentation pond
Sarylakhskaya mill	2 000	< 2000	Slurry
MCC	2	50	n.d – no data

In 1995, a new standard for As in soil was established in Russia, ranging from 2 mg/kg arsenic in sands to 10 mg/kg arsenic in clays. The standard recognized arsenic in soils as a class I toxic contaminant. In Central Yakutia, natural arsenic concentrations in permafrost-affected soils range from 0.4 to 4.4 mg/kg, i.e., within the acceptable limits. Elevated arsenic levels, 3.9-20 mg/kg, are observed in the soils in the sanitary landfill area near Yakutsk. Arsenic concentrations are even higher in the soils affected by ore mining activities (see Table 2), as well as in the urban areas located within geochemical anomalies [12], such as Aldan (Table 6).

Table 6

Arsenic concentrations in urban soils of Yakutia, mg/kg

City	Average	Minimum	Maximum	Note
Yakutsk	11.4	<1	150	MCC for soil 2-10 mg/kg
Aldan	18.0	<1	300	
Mirny	3.0	<1	200	

The biochemical role of arsenic has received little scientific study, although it is known to accumulate in mature leaves and root crops, with maximum levels found in edible mushrooms and mosses. Significantly elevated concentrations in vegetation occur near the tailings (Table 7).

Table 7

Arsenic concentrations in vegetation, mg/kg

Location	Moss	Lichen	Blueberry	Larch needle
Kuranakh mining district (according to <i>Artamonova</i> , 2000)				
Latyshsky Creek basin	< 0.5	0.69 – 1.4	< 0.5	< 0.5 - 0.63
Kuranakh tailings pond	0.5-4.7	0.57-1.26	До 0.52	0.85-2.5
Kuranakh tailings pond, downstream	14.7	2.8	0.71	No data
Kular mining district (according to <i>Yagnyshev et al.</i> , 2004)				
Kular gold mill tailings area	35.0	34,1	17.1 (mountain cranberry)	35.3 (bark)
Land plants [3, 4]	0.02			
Grasses, USA [3]	0.06-0.7			

Conclusions. Recent medical geology investigations indicate that arsenic has broad



effects on the human body and is associated with both non-cancerous and cancerous pathologies. The main sources of arsenic released to the environment of Yakutia are non-ferrous metals industry, mining activities, geochemical anomalies, some geological units, and active zones of the Earth's crust. High arsenic concentrations are widespread in various components of the Yakutia's environment, including the soils, rocks, air, snow cover, surface and ground waters, and vegetation. In the areas of arsenic-rich mineral deposits, geochemical anomalies and tailings, studies are required to assess possible inputs and health effects of inorganic arsenic into the lakes, streams, and aquifers used for water supply. The majority of the industrial and mining sources have been operating over many decades, significantly affecting the environment and population. It is therefore important to understand the occurrence and distribution of arsenic in the environment and to control human exposure to various forms of this element. Arsenic has a property to accumulate in animals and animal products such as milk and meat, reaching concentrations a few, or even tens or hundreds times greater than in soils, water or plants. In-depth research into relationships between cancer and the environment geochemistry, as well as coupled studies of arsenic occurrence in foods and environmental components are needed. Synergetic effects of arsenic and other toxic metals also deserve attention.

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Fig. 1. Plantar hyperkeratosis induced by arsenic poisoning [14]

Fig. 2. Location of main ore mineralization zones and arsenic geochemical anomalies in Yakutia.

1 – Siberian Platform; 2 – Mesozoic folding region; 3 – ore zones with arsenic occurrence: 1 – South Verkhoyansk, 2 – West Verkhoyansk, 3 – Derbeke-Nelgekhinskaya, 4 – Adycha-Tarynskaya, 5 – Kularskaya, 6 – Polousnenskaya, 7 – Chokhchur-Chokurdakhskaya; 4 – large geochemical anomalies of arsenic.

Fig. 3. Arsenic concentrations in atmospheric aerosols at Yakutsk, ng/m³

1 - <0.5; 2 – 0.5-1.0; 3 – 1.0-2.0; 4 – 2.0-3.0; 5 – 3.0-3.13.