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Analysis of the content of heavy metal ions in the coastal zones of the northern part of the Apsheron peninsula

The article is devoted to studies of heavy metal pollution of the soil cover of the coastal zones of the northern part of the Apsheron Peninsula. Pollution of the coastal zones of the Caspian Sea, serving to a greater extent as a recreational area for the population, by toxic substances is of great concern and to solve this problem, periodic studies of these zones for the presence of heavy metals are necessary. For the first time, a comparative analysis of the content of heavy metals in different areas (Buzovna, Sumgait, Novkhany) of the northern part of the Apsheron peninsula was carried out and the presumable causes of their accumulation were outlined. The researched soils in the northwestern and northeastern part of the peninsula were grouped according to the degree of concentration of heavy metals depending on the depth of the researched soils. Zinc (77.0 mg/kg, at 0–16 cm depth, transect № 03), copper, and cadmium (88 mg/kg and 0.36 mg/kg at 0–20 cm depth, transect № 05) had the highest concentrations relative to other trace elements. Concentrations of zinc and copper in the northwestern direction of the peninsula increase by 1.5 and 3–3.5 times, respectively, as compared with the generally accepted norms. Average content of heavy metals, especially Ni, Cd, Pb in flooded soils at the depth of 0–100 cm increased 2.7 times on average as a result of coastal flooding by waters of Caspian Sea. The value of total heavy metals reaches a maximum in the northwestern direction.

Keywords: environmental pollution, heavy metals, Caspian ecosystems, sea level fluctuations, coastal soils, consequences of soil flooding, shoreline ecology, toxic components.

Introduction

Pollution of soils by heavy metals has different sources, the main ones in urban areas are: transport-road complex, industrial enterprises, unrecycled industrial and municipal wastes. The distribution of heavy metals on the soil surface in Baku and Apsheron is uneven and is determined by many factors and, first of all, by the density of the population. It also depends on the characteristics of pollution sources, meteorological features of the region, geochemical factors and landscape conditions of the peninsula as a whole and many scientific works of both foreign and Azerbaijani scientists are devoted to these studies [1–3].

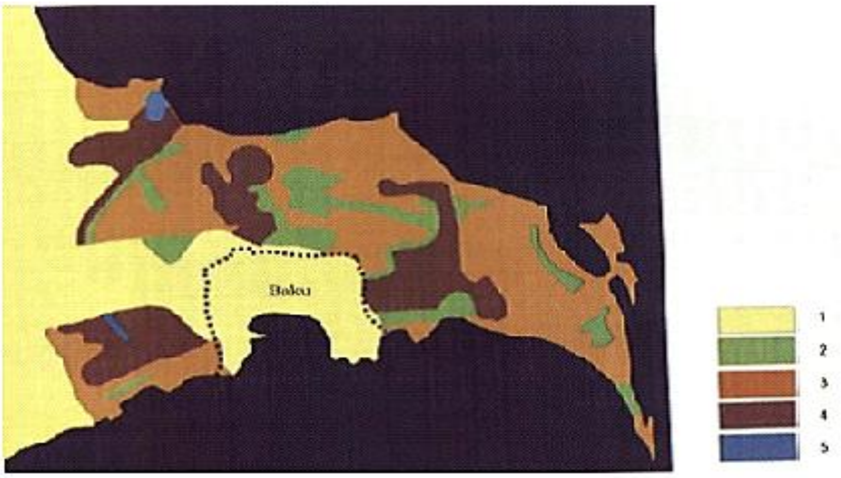
Figure 1 presents a scheme of soil contamination of the Apsheron peninsula with heavy metals.

According to literary sources, character of migration of elements in soils depends on dynamic chemical equilibrium between components of soil, physical and chemical properties of natural and anthropogenic waters draining landscapes and on a parity of water and biogenic migration of heavy metals [4].

Getting into the soil, heavy metals migrate, overcoming the geochemical barriers of both natural and anthropogenic nature. The character of migration of heavy metals is influenced by many factors. For example, on fixation of heavy metals influence solid-phase barriers: aluminosilicate (Zn, Ni), ferrous (Cr), manganese (Zn, Ni, Co, Cd, Pb) and carbonate (Cd, Cu) [5].

However, pollution of the coastal soils of the Apsheron peninsula with heavy metals also occurs due to changes in the level of the Caspian Sea. The results of studies of scientists on the modeling of the Caspian

Sea level for the period 2001–2050 for 12 variants differing by scenarios of climatic conditions and dynamics of water consumption in the basin show that, despite a very wide range of possible climatic conditions by mid-century and corresponding estimates of river flow, values of mathematical expectations of the levels even by 2050 do not differ very significantly and do not exceed 1.0 m [6].



1 — uncontaminated lands; *2* — minimal pollution; *3* — weak pollution; *4* — medium pollution; *5* — heavy pollution

Figure 1. Scheme of soil contamination of the Apsheron peninsula with heavy metals
(according to the Ministry of Ecology of Azerbaijan, 2000)

The anomalously long sea-level fall from 1930 to 1977, followed by the anomalously long rise from 1978 to 1995, which occurred in the twentieth century and had dramatic consequences for the coastal populations, led to changes in coastlines and had a considerable impact on soil properties. Because of the 10–15-year rise in the sea level, accompanied by the impact of oil drilling effluents, the groundwater table has risen markedly up to 0.5–1.0 m from the soil surface and this, in turn, has led to severe ecological consequences for some areas [7].

To date, waters containing a variety of harmful toxic substances resulting from anthropogenic activities are discharged into the Caspian Sea [8].

Pollutants affect biological objects, vital functions and reproduction of hydrobionts, numbers of which have significantly decreased in the last 20 years.

For many decades, scientists have been studying the role of anthropogenic and technogenic factors in the formation of river flow and the causes of fluctuations in the level of the Caspian Sea. Entry of toxic substances into the sea (over 5 tons of compounds of heavy metals, about 145 thousand tons of oil products, about 4.4 thousand tons of biogenic pollutants) with the river runoff is one of the main factors having a negative impact on dynamics of the Caspian Sea ecosystem. Changes in the level of pollutants in the waters of the Caspian Sea should also be attributed to the sources of an increase in the level of pollutants in the Caspian Sea, which are flowing with flooding of coastal territories and at the same time of toxic substances. Such a confluence of circumstances has its negative impact on the health of the population. It is known that due to the mild climate the coastal areas of the Apsheron peninsula are used by the population both for recreation and for cultivation of various crops, especially gourds [9].

An important role in the saturation of the Caspian Sea waters with toxic components is played by the atmospheric transfer of harmful exhaust gases from motor vehicles and industrial gas emissions, as well as transport traffic in the Caspian Sea. In addition, during the modern period in the Caspian Sea, which is rich in hydrocarbon reserves, works on the exploration and development of oil and gas fields are carried out [10]. This, in turn, will increase the number of tanker traffic in the future and serve as a potential source of pollution of surface waters with heavy metals, accompanying the processes of oil and gas production. Heavy metals are among the group of the highest priority harmful pollutants present in the waters of the Caspian Sea. Such substances as manganese, nickel, zinc, iron, cadmium, lead, copper and their compounds have a feature of long-term preservation and accumulation in water and in bottom sediments. Their danger is exacerbated by the fact that they do not undergo chemical biodegradation, but only redistribute between abiotic and biotic components and interact with them. On the one hand, the presence in moderate doses of heavy metals in fish organisms is necessary, because they participate in biochemical processes and are a necessary source of energy for aquatic organisms. But on the other hand, if their concentration is higher than the maximum allowable, they have an antibiotic effect on the manifestation of life processes and cause genetic changes. In this connection information about forms of existence, migration, and bioaccumulation of heavy metals in links of ecosystems becomes especially urgent. Taking into account the urgency of solving the problem of pollution of the environment with heavy metals, the purpose of studying the background content and migration of heavy metals in the soil cover of the coastal zones of the northern coast of the Republic of Azerbaijan was set.

Experimental

The sources of factual information were the materials of our own field studies on the presence of heavy metals in the coastal zone of the Caspian Sea in the northern direction of the Apsheron Peninsula, which were carried out........ 2021–2022 with...... Samples were taken from 0–20 cm, 20–50 cm and 50–100 cm depths. Soil samples were packed in polyethylene bags and appropriate labels were attached.

The soil sampling technique for detecting the content of heavy metal ions and their analysis corresponded to GOST 17.4.4.02–2017; GOST R 53218–2008; GOST R 50683–94 [11–13].

Experimental studies were performed on the AAS vario 6 instrument of "Analytik Jena AG". To reduce the influence of background at ETA and the level of errors due to multiple sample dilutions, we decided to reduce the sample weight from 0.5 to 0.1 g (for Cu, Zn, Pb, Cd, Cr, Ni, Co) and to increase the sample solution volume. The sample suspension was preliminarily calcined in order to decompose the organic basis of the sample. Treatment of the sample with hydrofluoric acid provides removal of silicon from the solution. Next, the sample was treated twice with a mixture of acids HNO_3: HCl (1:3) when heated to wet salts. The wet salts were transferred to V = 50 ml of 0.2 % HNO_3. The sample solution thus obtained was ready for measurement in ETA. Absorption was carried out in a graphite cuvette heated with an electric current, in which sample atomization and formation of atomic vapor occur. The spectrometer uses a transverse-heated graphite furnace, which is the main unit of the electro thermal atomizer. Monochromatic radiation of the element being determined (in this case Cu) from a selective light source (hollow cathode lamp) with narrow spectral lines is focused by the lighting system and passes through the atomic vapor. The atoms of the element being detected absorb part of the intensity of the light from the selective source. The conditions for determining metals from the obtained solutions are as follows. Slit width of the monochromator was 0.8 nm. The supply voltage of the photomultiplier tube was 362 V, the lamp current was 3.0 mA. Measurements were performed in an argon atmosphere; a deuterium background corrector was used. The resonance line of 324.8 nm was used. To determine the elemental composition we used the method of calibration graph and as a reference solution — an aqueous solution of Cu (II) ions in sulfuric acid. Graduated solutions of known concentration were prepared and their absorbance was measured, by the results of these measurements the graduation diagram was made. Correctness of definitions was checked with the help of the reference sample taken from territory of the Botanical garden of Baku city. Analyzed 5 samples SDPS-1, for each sample performed series n = 4, the error in the range ± 10 %, with confidence probability P = 0.95. The results correspond to the certified values.

Results and Discussion

Studies of the concentration levels of heavy metals (Cu, Zn, Pb, Cd, Cr, Ni, Co) in the soils of flooded areas of the northwest (N-W) and northeast (N-E) directions of the Apsheron peninsula were conducted at a depth of 0–100 cm in the Buzovna, Sumgait, Novkhana areas and the data are summarized in Tables 1–3.

Table 1

Content of heavy metals in soils of the N-W direction (Novkhany) of the coastal zone of the Apsheron Peninsula

Land Cut №	Depth of sampling, cm	Content of heavy metals, mg/kg						
		Cu	Zn	Pb	Cd	Cr	Ni	Co
1	2	3	4	5	6	7	8	9
Clarks		20	50	10	0.1–1.0	70	40	8
№ 01	0–20	18.9	78.6	12.6	0.9	44.8	29	2,7
	20–50	19.0	78.6	12.6	0.9	44.8	29.3	2,72
	50–100	23.6	78.6	12.5	0.9	44.8	29.2	2,7
Average data		20,5±0,1	78.6±0.1	12.6±0.1	0.9±0.1	44.8±0.1	29.2±0.1	2.7±0.1

Continuation of Table 1

1	2	3	4	5	6	7	8	9
№ 02	0–20	19.6	69.3	13.9	1.0	51.1	33	5,6
	20–50	19.7	69.02	13.7	0.98	50.4	30	5,4
	50–100	19.7	69.3	13.6	0.99	50.4	31	5,4
Average data		19,7±0,1	69.2±0.1	13.7±0.1	1.0±0.1	50.6±0.1	31±0.1	5.5±0.1
№ 03	0–20	21.6	73.4	11.6	1.0	43.4	26.7	4,7
	20–50	21.1	73.0	11.5	0.9	42.7	26.5	4,4
	50–100	20.0	73.1	11.5	0.7	42.7	26.4	4,3
Average data		21,2±0,1	73.2±0.1	11.5±0.1	0.8±0.1	42.9±0.1	26.5±0.1	4.5±0.1
№ 04	0–20	28.7	74.9	13.8	1.1	65.8	37.0	7,4
	20–50	28.4	74.7	13.7	1.1	65.45	36.9	7,4
	50–100	28.3	74.3	13.5	0.98	64.75	36.9	7,3
Average data		28,5±0,1	74.6±0.1	13.7±0.1	1.1±0.1	65.3±0.1	36.9±0.1	7.4±0.1
№ 05	0–20	26.0	62.9	12.8	1.3	59.2	38.3	7,3
	20–50	25.7	62.5	12.7	1.2	58.4	38.0	7,1
	50–100	25.6	62.6	12.7	0.9	58.4	38.1	7,0
Average data		25,7±0,1	62.7±0.1	12.7±0.1	1.1±0.1	58.7±0.1	38.2±0.1	7.2±0.1

Table 2

Content of heavy metals in soils of N-W direction (Sumgait) of the coastal zone of the Apsheron Peninsula

Land Cut №	Depth of sampling, cm	Content of heavy metals, mg/kg						
		Cu	Zn	Pb	Cd	Cr	Ni	Co
Clarks		20	50	10	0.1–1.0	70	40	8
№ 6	0–20	28.9	89.9	17.4	0.15	49.0	13.9	3,5
	20–50	28.7	90.0	17.4	0.12	48.6	13.7	3,1
	50–100	28.6	90.0	17.2	0.11	47.9	13.7	3,1
Average data		28.7±0.1	89.9±0.1	17.3±0.1	0.13±0.1	48.5±0.1	13.7±0.1	3.2±0.1
№ 7	0–20	32.9	93.9	13.5	1.4	80.2	44.8	8,8
	20–50	32.7	93.4	13.3	1.3	79.4	44.5	8,6
	50–100	32.6	93.4	13.2	1.2	79.1	44.3	8,6
Average data		32.7±0.1	93.6±0.1	13.3±0.1	1.3±0.1	79.6±0.1	44.5±0.1	8.7±0.1
№ 8	0–20	30.5	92.7	15.8	1.3	103.25	53.0	9,4
	20–50	30.3	92.5	15.4	1.1	102.6	49.8	9,3
	50–100	30.2	92.1	15.2	1.1	102.6	50.0	9,1
Average data		30.3±0.1	92.4±0.1	15.5±0.1	1.2±0.1	102.9±0.1	50.9±0.1	9.3±0.1
№ 9	0–20	36.9	89.5	16.8	1.5	112.0	39.1	76,7
	20–50	36.7	89.4	16.1	1.3	111.3	38.6	76,5
	50–100	36.5	89.2	16.1	1.2	110.6	38.3	76,2
Average data		36.7±0.1	89.4±0.1	16.3±0.1	1.3±0.1	111.3±0.1	38.7±0.1	76.5±0.1
№ 10	0–20	26.7	72.9	12.5	1.3	79.1	29.8	53,6
	20–50	26.5	72.8	12.6	1.2	78.4	29.7	53,5
	50–100	26.3	72.6	12.0	1.2	78.1	29.6	53,4
Average data		26.5±0.1	72.7±0.1	12.4±0.1	1.2±0.1	78.5±0.1	29.7±0.1	53.5±0.1

Table 3

The content of heavy metals in the soils of the N-E direction (Buzovna) of the coastal zone of the Apsheron peninsula

Land Cut №	Depth of sampling, cm	Content of heavy metals, mg/kg						
		Cu	Zn	Pb	Cd	Cr	Ni	Co
1	2	3	4	5	6	7	8	9
Clarks		20	50	10	0.1–1.0	70	40	8
№ 11	0–20	16.2	8.6	9.5	0.9	65.4	39	4,6
	20–50	16.1	8.4	9.3	0.8	64.4	37	4,1
	50–100	16.1	8.3	9.3	0.6	63.4	38	4,4
Average data		16,1±0,1	8.4±0.1	9.4±0.1	0.7±0.1	64.4±0.1	38±0.1	4.4±0.1

Continuation of Table 3

1	2	3	4	5	6	7	8	9
№ 12	0–20	18.7	39.7	8.5	0.9	58.8	36.8	4,7
	20–50	18.4	39.4	8.2	0.7	58.4	36.5	4,5
	50–100	18.3	39.2	8.3	0.6	57.7	36.7	4,1
Average data		18,5±0,1	39.4±0.1	8.3±0.1	0.7±0.1	58.3±0.1	36.7±0.1	4.4±0.1
№ 13	0–20	16.7	36.9	10.9	0.7	63.7	41.6	5,9
	20–50	16.5	36.6	10.7	0.4	62.6	41.3	5,7
	50–100	16.5	36.2	10.8	0.5	61.6	41.2	5,6
Average data		16,6±0,1	36.6±0.1	10.8±0.1	0.5±0.1	62.6±0.1	41.4±0.1	5.7±0.1
№ 14	0–20	20.8	55.5	10.0	1.2	66.1	28.8	7,4
	20–50	20.4	55.3	9.7	1.1	66.5	28.7	7,3
	50–100	20.4	52.2	9.6	1.1	65.1	28.5	7,1
Average data		20,5±0,1	55.3±0.1	9.7±0.1	1.1±0.1	65.9±0.1	28.7±0.1	7.3±0.1
№ 15	0–20	13.9	44.3	8.9	0.6	48.3	29.9	5,7
	20–50	13.4	44.7	8.5	0.4	47.2	29.5	5,6
	50–100	13.6	44.2	8.1	0.4	46.2	29.6	5,1
Average data		13,6±0,1	44.4±0.1	8.5±0.1	0.5±0.1	47.2±0.1	29.7±0.1	5.4±0.1

These parameters show the levels of heavy metals content, but do not give an answer about the degree of relative enrichment of soils with certain trace elements in comparison with clarks of soils. According to the data on the content of heavy metals the researched soils of the coastal territories of the Caspian Sea N-W and N-E directions of the Apsheron peninsula can be grouped according to the degree of concentration. The content of heavy metals (averaged over depth) in the soils of the N-W and N-W directions of the Apsheron peninsula coastal zone is reflected in Figures 2 and 3.

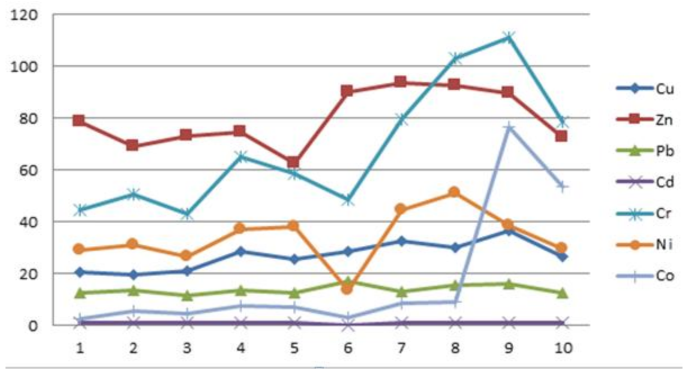


Figure 2. Content of heavy metals (averaged over depth) in soils of the N-W direction of the coastal zone of the Apsheron Peninsula

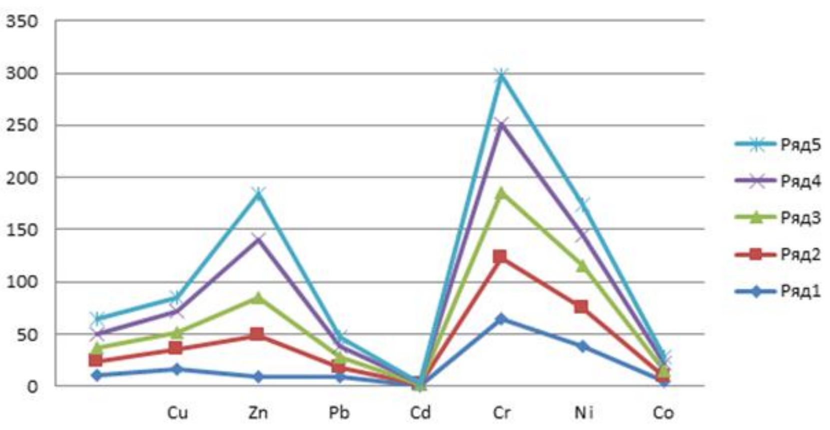


Figure 3. Content of heavy metals (averaged over depth) in soils of the N-E direction of the coastal zone of the Apsheron Peninsula

Zinc, copper, and cobalt have the highest concentrations compared to other trace elements. Presumably, among the reasons mentioned above, the content of heavy metals in soils also varies depending on the location of key areas from sources of technogenic release. Thus, deepening to the N-W direction of coastal zones of the peninsula concentration of copper and zinc in 1.8 times, and cobalt in 9.5 times exceeds the really permissible concentration according to clarks, generally accepted MAC.

Farther to the north at 500 meters their concentration is by order of magnitude higher: zinc — 93.4÷72.6, cadmium — 1.3÷0.12 (mg/kg). In the north-western direction, the concentration of copper is markedly high, amounting in the upper part of the soil (0–20 cm) — 36.9 mg/kg, which exceeds the permissible standard of 1.8 times. Along the eastern direction along the coastal zone, the concentration of heavy elements decreases, being: zinc — 55.3÷8.4, cadmium — 1.1÷0.5, copper — 20.5÷13.6 (mg/kg). Probably, the excess of the concentration of elements in the soils, located in the western direction compared with a point on the eastern direction (section number 15), is associated with an increase in the number of sources of man-made pollution. To date, the prevailing power of industrial potential (over 70 %), which covers about 2.5 % of the total area of Azerbaijan, is located mainly in the territory of two cities — Baku and Sumgayit. The concentration of such a large number of oil refining, petrochemical, oil production, metallurgy and petroleum engineering enterprises in a limited territory has had a negative impact on the ecology of this region [14].

Many heavy elements tend to be washed off the soil surface and accumulate in the lower layers, and cadmium tends to accumulate in the upper soil layer and is poorly degradable in the natural environment, which makes it very difficult to clean up [15].

The next group should include lead, indicators of which are close to clark units. This element has rather high values in sediments, in some cases exceeding the geochemical background.

Lead concentration, which requires only strongly humusified soil to be fixed, is close to clark units in Novkhana and Buzovna area (13.7÷11.5 mg/kg and 10.8÷8.3 mg/kg, respectively), exceeding MPC almost 1.7 in the western direction. The slightly increased lead content towards the direction of Sumgait is probably due to the impact of the rise of highly saline chloride waters to the surface.

Chromium, copper, cobalt and nickel have higher content of elements in soils. The chromium content in the Sumgait area is almost 1.6 times and cobalt 9.5 times higher than the permissible norms in all directions of the superphosphate plant close to the Sumgait city.

Conclusions

Based on an analysis of the literature and factual data obtained, we can judge that the geochemical situation of the studied semi-desert coastal areas Absheron peninsula in general is unfavorable for the migration of most trace elements, especially heavy metals deposited here, mainly in the form of insoluble hydroxides and carbonates.

Under the influence of flooding, the average content of heavy metals (Cu, Zn, Pb, Cd, Cr, Ni, Co) in the soil profile (0–100 cm depth) of flooded soils increased on average 2.7 times, with Cu, Zn, and Co predominantly accumulated here.

The soil cover of the coastal zone of the NW direction of the Apsheron peninsula is characterized by increased concentrations (compared with previous years) of heavy metals, especially Cu, Zn, Pb [16, 17].

Changes in the level of the Caspian Sea and, as a consequence, periodic flooding of the coastal area by sea water contributes to an increase in the concentration of heavy metals in the soil of coastal areas and this increase, although not critically negative, but requires specific measures to eliminate the effects of heavy metals in the coastal zones of the Absheron peninsula.

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Апшерон түбегінің солтүстік бөлігіндегі жағалау аймақтарындағы ауыр металл иондарының құрамын талдау

Мақала Апшерон түбегінің солтүстік бөлігіндегі жағалау аймақтарының ауыр металдармен жер жамылғысының ластануын зерттеуге арналған. Халық үшін демалыс аймағы ретінде қызмет ететін Каспий теңізінің жағалау аймақтарының улы заттармен ластануы үлкен алаңдаушылық туғызады және бұл мәселені шешу үшін осы аймақтарды ауыр металдарға мерзімді зерттеу қажет. Алғаш рет Апшерон түбегінің солтүстік бөлігіндегі әртүрлі аудандардағы (Бузовна, Сумгаит, Новхана) ауыр металдардың құрамына салыстырмалы талдау жүргізілді және олардың жиналуының болжамды себептері анықталды. Түбектің солтүстік-батыс және солтүстік-шығыс бөліктеріндегі зерттелген топырақтар зерттелетін топырақтың тереңдігіне байланысты ауыр металдардың концентрация дәрежесіне қарай топтастырылды. Мырыш (77,0 мг/кг, 0–16 см тереңдікте, № 03 кесу), мыс және кадмий (88 мг/кг және 0–20 см тереңдікте 0,36 мг/кг, № 05 кесу) басқа микроэлементтермен салыстырғанда ең жоғары концентрацияға ие болды. Түбектің солтүстік-батыс бағытындағы мырыш пен мыс концентрациясы жалпы қабылданған нормалармен салыстырғанда сәйкесінше 1,5 және 3–3,5 есе артады. 0–100 см тереңдіктегі су басқан топырақтардағы ауыр металдардың, әсіресе Ni, Cd, Pb орташа мөлшері Каспий теңізінің суларымен жағалау аудандарын су басу нәтижесінде орта есеппен 2,7 есе өсті. Ауыр металдардың жалпы құрамының мәні солтүстік-батыс бағытта максимумға жетеді.

Кілт сөздер: ластану, ауыр металдар, Каспий теңізінің экожүйелері, теңіз деңгейінің ауытқуы, жағалаудағы топырақтар, топырақ су басуының салдары, жағалау экологиясы, улы компоненттер.

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Анализ содержания ионов тяжелых металлов в прибрежных зонах северной части Апшеронского полуострова

Статья посвящена исследованиям загрязнения тяжелым металлом почвенного покрова прибрежных зон северной части Апшеронского полуострова. Загрязнение прибрежных зон Каспийского моря, служащих в большей степени рекреационной зоной для населения, токсичными веществами вызывает большую озабоченность, и для решения этой проблемы необходимы периодические исследования этих зон на наличие тяжелых металлов. Впервые был проведен сравнительный анализ содержания тяжелых металлов в разных районах (Бузовна, Сумгаит, Новханы) северной части Апшеронского полуострова и намечены предполагаемые причины их накопления. Исследуемые почвы в северо-западной и северо-восточной частях полуострова сгруппированы по степени концентрации тяжелых металлов в зависимости от глубины исследуемых почв. Цинк (77,0 мг/кг, при глубине 0–16 см, пересечение # 03), медь и кадмий (88 мг/кг и 0,36 мг/кг при глубине 0–20 см, пересечение # 05) имели самые высокие концентрации по сравнению с другими микроэлементами. Концентрации цинка и меди в северо-западном направлении полуострова увеличиваются в 1,5 и 3–3,5 раза соответственно по сравнению с общепринятыми нормами. Среднее содержание тяжелых металлов, особенно Ni, Cd, Pb в затопленных почвах на глубине 0–100 см, увеличилось в среднем в 2,7 раза в результате затопления прибрежных районов водами Каспийского моря. Значение общего количества тяжелых металлов достигает максимума в северо-западном направлении.

Ключевые слова: загрязнение, тяжелые металлы, экосистемы Каспийского моря, колебания уровня моря, прибрежные почвы, последствия затопления почв, экология береговой линии, токсичные компоненты.

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