Chapter 20

Heavy Metal Pollution of Ecosystem in an Industrialized and Urbanized Region of the Republic of Azerbaijan

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Additional information is available at the end of the chapter

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Abstract

Along with other oil-producing regions of the world, environmental pollution is characteristic also for the Absheron Peninsula of Azerbaijan, which has long been subject to the impact of various anthropogenic factors. A large amount of such toxic substances as heavy metals, hydrocarbons and surface-active agents, and so on were released into soil and water basins leading to the change of natural ecosystem throughout the region. A primary goal of this chapter was to study the level of heavy metal pollution in the Absheron industrial region, while evaluating the potential ecological risk posed by each toxic metal including Hg, Cd, As, Cr, Pb, Cu, Ni, and Zn. Analysis of the calculated values of pollution index (PI), enrichment factor (EF), geoaccumulation index (I_{geo}), and ecological risk factor (E_i) indicates the contribution of anthropogenic sources to heavy metal accumulation in soils and sediments of the study area.

Keywords: Absheron Peninsula, heavy metals, ecological risk, soil, sediment

1. Introduction

The Republic of Azerbaijan is located at 38°25′–41°55′ North Latitude and 44°50′–50°51′ East Longitude. It is the largest country among other South Caucasus states according to its territory, number of population, rich fuel energy, and other resources. It occupies an area of 866,000 km^2. The total length of the country's border comes to 2646 km including 390 km with Russian Federation, 480 km with Georgia, 1007 km with Armenia, 756 km with Islamic Republic of Iran, and 13 km with Turkey. The Caspian Sea forms its eastern border.

The Republic of Azerbaijan is characterized by special wonderful nature, climate condition, and physicogeographical features. Its territory is rich in valuable natural resources including oil-gas fields, ore deposits, and mineral waters. The industry is specialized in the development of hydrocarbon and other mineral deposits, oil refining, petrochemical, and chemical industries. Cattle breeding, grain farming, and gardening as well as cotton, tea, and vegetable growing are the main agricultural occupations [1].

In recent years, Azerbaijan has achieved significant economic growth due to its oil and gas resources. A reliable oil-industrial infrastructure has been established in the republic. Along with the strengthening of the social and economic situation in the country, these achievements also contribute to the development of non-oil sector.

Azerbaijan also serves as an important gateway for oil and gas transportation. Construction of the Baku-Tbilisi-Ceyhan (BTC) oil pipeline in 2005 also contributed to the country's economic growth to some extent. A significant increase in the gross domestic production has been observed during the last decades. Most of the national revenue comes from the oil industry.

At the same time, Azerbaijan has serious environmental problems due to the intensive development of the region's hydrocarbon resources, increasing the amount of consumed fossil fuels and greenhouse gas emissions. The major environmental challenges are as follows [1, 2]:

- Pollution of water resources with wastewater, including transboundary pollution
- Inadequate supply of quality water to human settlements, wastage in delivery, and shortage of sewer lines (insufficient quantity of sewerage systems)
- Air pollution by industrial plants and vehicles
- Degradation of fertile soil lands (contamination, erosion, salinity, etc.)
- Improper disposal of solid industrial and municipal wastes including hazardous wastes
- Biodiversity decline including the depletion of forests, flora, and fauna

It is well known that pollution of the environment with toxic compounds causes serious problems due to their negative impact on all the components of ecosystem especially on human health. Unfavorable consequences of ecosystem pollution are appearing more acutely in urbanized territories characterized with a high density of population and industrial enterprises. The Absheron peninsula is the most urbanized territory of the republic of Azerbaijan, where two large industrial cities—Baku and Sumgait—and about 60% of onshore oil production are located.

The Absheron peninsula has about 200,000-ha territory on the coastal line of the Caspian Sea in the southwestern edge of the Great Caucasus Mountain. The region is characterized by a dry semi-desert climate. Strong northern winds are the main distinguishing feature of the peninsula. The average annual air temperature is +14.2°C and the average annual rainfall is about 200–300 mm. The soil cover of the territory mainly consists of gray-brown and coastal sandy soils. The Absheron peninsula is also the location of a great number of oil and gas fields. The region is specialized on the production, initial processing and transportation of crude oil and gas, oil machine building, and fishery. Much of the peninsula is crossed by oil and gas pipelines. Despite the fact that the history of oil production in Absheron dates to ancient times, the industrial development of oil-gas fields has started from the middle of the nineteenth century. About 70% of the republic's industrial potential is concentrated in this territory. Like other industrialized and urbanized regions of the world, the Absheron peninsula could not avoid environmental pollution. There are a number of technogenic-polluted aerials. Oil industry is the main pollution source of the environment. Since the end of the nineteenth century, the peninsula has been subject to intense industrialization and urbanization. Accelerated development of hydrocarbon producing and refining industries has radically changed the historically formed geochemical balance of the environment due to the removal of different chemical elements to the Earth's surface. The territory has over 200 basins of natural and artificial origin. A huge amount of toxic hydrocarbons and heavy metals accumulate in soil and deep sediments, thus leading to the change of the qualities of natural ecosystem. According to its ecological status and climatic landscape character, the Absheron region is categorized to be a territory with the most acute environmental situation in the republic [3, 4].

Currently, environmental pollution is a serious concern worldwide. Oil and oil products contribute significantly to the pollution of environment in oil-bearing regions. The exploration of hydrocarbon deposits, as well as extraction, transportation, storage, and use of oil and gas causes pollution of the environment with hazardous substances. Crude oil includes hydrocarbons such as alkanes, cycloalkanes, unsaturated aliphatic hydrocarbons, and aromatic hydrocarbons, as well as heterocyclic compounds containing nitrogen, oxygen and sulfur, metals, and natural radionuclides.

Past studies have indicated that there are high concentrations of contaminants in soil and water systems of the Absheron peninsula [5–7]. Sometimes, the degree of oil contamination in soil varies from 20 to 30% and more. A large part of the peninsula is occupied by destroyed oil-polluted and bituminous lands. Contaminants accumulated in soils migrate into lakes, reservoirs, surface, and groundwaters throughout the site. Migration of pollutants into deep sections of soil and groundwaters causes serious danger to both local and regional viewpoints.

Today, the pressure on the environment in the peninsula is increasing continuously due to the ever-increasing population, plus industrial and urban growth.

1.1. Heavy metals and their environmental effects

Heavy metals are the most hazardous environmental pollutants due to their toxicity and accumulation ability. According to their classification, heavy metals have a density of more than 5 g/cm^3 (about 6.0 g/cm^3 or more, which is much higher than the average particle density of soils—2.65 g/cm^3) and occur naturally in rocks but concentrations are frequently elevated as a result of contamination. Rare and noble metals are not included in heavy metals category. According to the biological classification of chemical elements, heavy metals belong to a group of micro- and ultra-microelements. In the vast majority of researchers, Pb, Cu, Zn, Ni, Cd, Co, Sb, Sn, Bi, and Hg are considered heavy metals [8–10].

Heavy metals are characterized by two main features—toxic effects on living organisms in relatively low concentrations and bioaccumulative abilities. Being rich in heavy metal soils, plants and bottom sediments become toxic over time, presenting a serious danger to all living things.

Both the accumulation of heavy metals in the environment and their negative impact on the ecosystem are widely studied by scientists from all over the world. The work of many scientists was devoted to the research of heavy metals in biosphere [11–14].

Compared to other ecosystem components, soil accumulates the highest concentration of heavy metals. Being in interaction with other components of ecosystem such as atmosphere, hydrosphere, and plants, soil contributes significantly to the ingress of heavy metals into the human organism. Penetrating into soil, they are accumulated in different parts of agricultural products through root system, and in aquatic organisms and bottom sediments when washed with surface waters. One of the major global problems of the present times—acid rain—is one of the factors increasing heavy metals' level in ecosystem. Washing soil rocks with acid rain increases the amount of metals in lakes and other water basins. Migration of metals in the ecosystem promotes their accumulation in the human body (**Figure 1**).

Heavy metals can be of both native and anthropogenic origins. Their natural sources are rocks and soils, but mainly in the forms inaccessible to wildlife, such as constituents of rocks and soil minerals. When the metal pollution is caused by anthropogenic sources, this can seriously influence all the ecosystem components. Waste disposal, transport emissions, oil-gas and mining industries, atmospheric depositions, and land application of fertilizers are anthropogenic sources of heavy metals [10, 15, 16].

Most oils have certain content of heavy metals. Starting from gasoline, all fractions of oil include metals. The crude oil extracted from the hydrocarbon deposits of Azerbaijan is dominated by iron (up to 0.74%), chrome, and nickel (often more than $n \times 10^{-2}$ ppm). Asphaltene fraction of some oil fields of Absheron peninsula is rich in such microelements as Co, Br, Ag, Au, La, Sb, and Sc (**Table 1**). As a result of neutron activation analysis, 1.2×10^{-3}% Rb, 6.3% $\times 10^{-5}$% Cs, and 2.1% $\times 10^{-5\%}$ Eu were found in the crude oil of the Balakhani oil field [17]. Usually, a majority of heavy metals are found in the asphaltene-tar fractions of oil. They are also found in the composition of oil cuttings and drilling fluids.

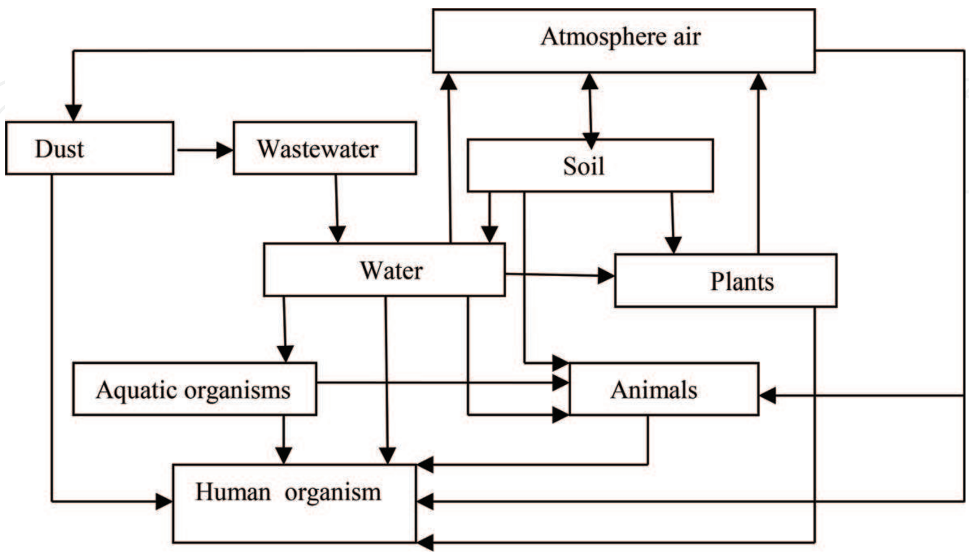

Figure 1. Scheme of heavy metals penetrating into the human organism.

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Oil fields	Metals (%)														
	Fe	**Ni**	**Cr**	**Zn**	**Ba**	**V**	**Co**	**Hg**	**Ag**	**Au**	**La**	**Sb**	**Sc**	**Hf**	**Se**
	$\times 10^{-4}$			**$\times 10^{-5}$**				**$\times 10^{-6}$**					**$\times 10^{-7}$**		
	Asphaltenes														
1.	600	57	96	750	53	151	110	nd*	289	140	87	300	1500	28	47
2.	138	58	174	270	265	260	64	160	nd	8	28	19	20	26	32
3.	400	63	68	110	540	142	35	570	nd	6	nd	4	13	14	nd
	Tars														
4.	170	8	20	80	5	37	2	14	10	150	4	2	10	23	75
5.	34	23	12	3	nd	62	10	nd	2.4	6	nd	nd	2	52	60
6.	110	19	9	8	99	47	4	2250	14	4	nd	9	11	127	46
7.	180	65	27	14	8	53	6	nd	nd	1	nd	1	nd	18	nd

*nd, compound not detected or below instrumental direction limits.

Table 1. Metal content of the Absheron oil fields.

According to the researches of specialists, oil and gas complex creates pedochemical factors of having an impact due to the existing natural technogenic hydrogeological conditions resulting in over-moistening and extent of contamination. There is a potential hazard of washing out of oil and oil products into rivers, bays, ground, and surface waters. Abnormal redistribution of chemical elements forming the secondary lithochemical areas has been recorded in several oil fields of the Absheron peninsula. Thus, some mobile elements including Pb, Zn, Cu, Ni, and Cr are accumulated in soils jointly and form paragenic association. They are able to migrate and accumulate in the appropriate barriers. Their concentrations exceed the normal values typical of the natural landscapes in the Absheron peninsula [5]. There is a tendency of the growth of heavy metals concentration both in the bottom sediments and in some hydrobionts in the Absheron territory. As a result of contamination by wastewater from various anthropogenic sources including offshore oil fields, heavy metals penetrate into the coastal line, natural lakes, and other reservoirs.

Usually, the most commonly encountered metals in polluted areas are lead (Pb), chromium (Cr), mercury (Hg), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), and nickel (Ni). It is well known that heavy metals are nondegradable and persistent pollutants and accumulate in the environment for a long time. In soil, they could be adsorbed and gathered in different parts of plants through root systems. It has been revealed that heavy metal pollution causes adverse effects on the quality and yield of agricultural plants, resulting in the changes of the number, composition, and activity of microorganisms. Practice shows that the geochemical cycle of heavy metals under anthropogenic impacts represents serious, at times unpredictable, environmental effects. As mentioned earlier, due to their migration and accumulation in the environment, most heavy metals can easily enter the food chain and create serious threat to human health. Many heavy metals have a strong affinity for sulfur and disturb the enzyme function forming bonds with sulfur groups. They can get into a food chain and accumulate in an organism reaching toxic levels. These may cause massive mortality of various animal species [18].

In order to find a proper solution to the problem, we studied the level of heavy metal pollution in ecosystem while evaluating the contribution of anthropogenic factors and the potential ecological risk posed by individual elements.

The main purpose of this work was to investigate the heavy metal pollution of

- soils from two types of land uses in the study site, including the areas of oil wells and transport road;
- ground and groundwaters in a zone of influence of the oil-industrial waste;
- waters and sediments of two natural water basins—the Boyuk shore and Bulbula Lakes—that had undergone a long-term impact of anthropogenic sources.

The studies have revealed increased levels of some heavy metals in soils, ground, and surface water basins in the territories subjected to the impact of various anthropogenic sources.

2. The objects and methods of research

The objects of the present research were the territories of oil production enterprises, transport roads, as well as ground and groundwaters around an aeration station and surface water basins in industrial territories (**Figure 2**). The main sources of ecosystem pollution in the study site are the industrial discharges formed during oil fields development and production activities. Along with the produced waters, these discharges also contain drilling solutions and various chemicals used in the drilling and production operations. Thus, the territory is subject to the impact of oil, oil products, heavy metals, and other technogenic waste. The main pollution sources of ground and groundwaters in the territory are the substances characterized with a high migration ability such as crude oil and heavy metals. It should be noted that the atmosphere emissions of oil-gas refineries and petrochemical industries are among the factors contributing to the ecological situation in the study area. In order to evaluate the impact of transport emissions on the heavy metal pollution, soil samples were collected at a 10-m distance of Baku-Mardakan highway.

One of the major objects of the research—Boyuk-shore lake—is located at the center of the Absheron peninsula at an absolute height of 12 m. It is the largest and most polluted lake of the peninsula with a 45-million-m^3 volume, a 15-km^2 surface area, and a 4.2-m maximum depth. Being an enclosed water body, the lake feeds underground and surface waters of water catchment. Starting from 1930s, a huge amount of oil-industrial wastewater has been discharged to this basin (**Picture 1**). According to the information of Ministry of Ecology and Natural Resources, the total daily volume of wastewater released from industrial and communal-domestic objects to the Boyuk-shore lake amounted to 18,000 m^3 [19].

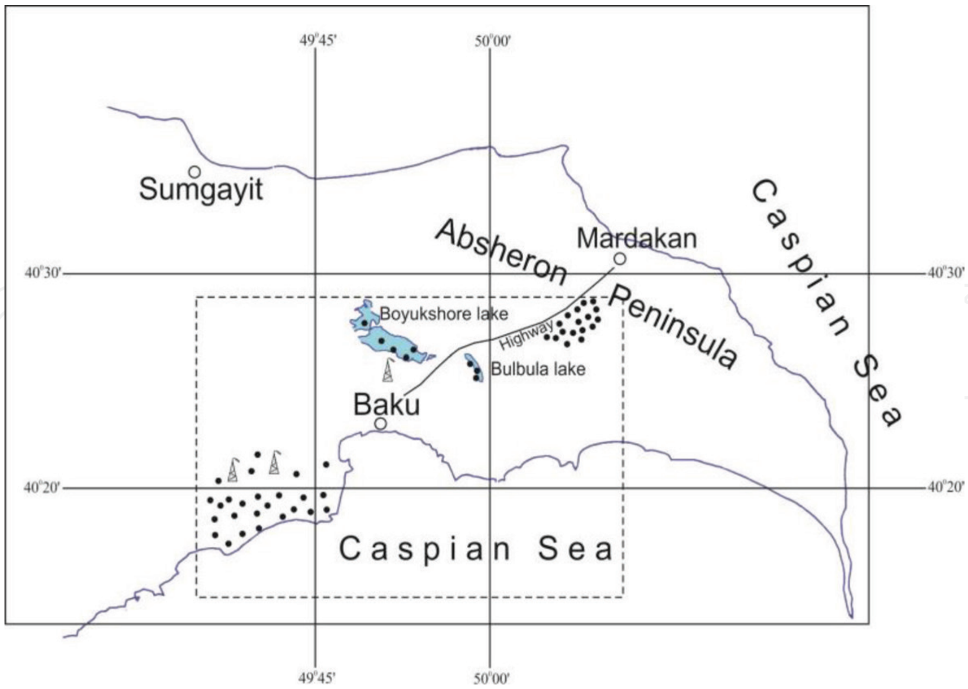

Figure 2. The map of the study area.

Picture 1. Oil-polluted area in the northern part of Boyuk-shore Lake (taken in 2017).

The Bulbula Lake is situated at the center of the Absheron peninsula in the northeastern part of Baku city at 8 m below the ocean level. It is an enclosed saline basin with a 2-km^2 surface area and a 2.05 million m^3 volume. Its maximal depth is 3–4 m. Till the end of the nineteenth century, the water regime of this lake was dependent on seasonal fallings and inflows from adjacent areas. Starting from that time, a large volume of oil-industrial wastewater have been discharged into this basin that resulted in dynamics of its level and flooding the residential buildings, social objects, and infrastructures in the territory (**Picture 2**). In order to lower the lake level, a pumping station with a 60,000-m^3 daily capacity was built for pumping about 30,000-m^3 water to Hovsan treatment plant. The lake is surrounded with five population settlements occupying an area of 122.5 ha with 3690-m length and 320–430 m width and is therefore permanently subject to the impact of domestic waste.

Analysis of water, sediment, and soil samples was carried out according to standard methods [20, 21]. Inductive Coupled Plasma-Optical Emission Spectrometry (ICP-OES) device was used in the analysis of heavy metals (As, Ba, Cd, Cr, Cu, Fe, Mn, Pb, and Zn), except Hg that was analyzed by Cold Vapor Atomic Fluorescence (CVAF) apparatus.

For the first time, the overall pollution status of the study area was evaluated with the calculation of pollution indices of heavy metals.

Various methods have been used to evaluate the heavy metal pollution. The calculation of single pollution index (PI_i), enrichment factor (EF), geoaccumulation index (Igeo), Nemerow pollution index (PI_N), and potential ecological risk index (RI) is widely applied for the assessment of heavy metals' level in soils and sediments [19, 22].

The pollution indexes used during our researches to assess the heavy metal contamination in the study sites are as follows:

2.1. Pollution index

The pollution level of each heavy metal was evaluated using pollution index (PI_i), calculated as the ratio between the metal concentration (C_i) in the sample and its reference value—the national criteria of metal (S_i):

Picture 2. Wastewater flows to Bulbula Lake from its northern side (taken in 2015).

$$\mathrm{PI}_i = \frac{C_i}{S_i} \tag{1}$$

The maximum permissible concentrations (MPCs) of pollutants established by Azerbaijan legislation were taken as S_i values.

2.2. Enrichment factor

Enrichment factor (EF) was initially calculated to identify the origin of elements in atmosphere, precipitation, or seawater, and it was further extended to the study of soils, aquatic sediments, and other components of ecosystem [23]. In this study, the enrichment factors of heavy metals in soils and sediments are calculated to assess the contribution of anthropogenic sources to the natural levels of heavy metals in the Absheron soils and lake sediments. The following formula was used to calculate EF:

$$\mathrm{EF} = \frac{C_i/C_r}{B_i/B_r} \tag{2}$$

where C_i and C_r are the concentrations of the target metal and the reference metal in the sample, while B_i and B_r are the background concentrations (BCs) of the target metal and the reference metal for the natural soils of the Absheron peninsula. Immobile elements such as Al, Fe, Ti, or Mn have been used as the reference metals for EF calculation. EFs for all the heavy metals were calculated using Mn as the reference metal in our study.

2.3. Index of geoaccumulation (I_{geo})

A geoaccumulation index was originally defined by Muller [24] for the evaluation of metal contamination in aquatic sediments, but it was also applied in assessing the metal contamination of soils. The formula used for the calculation of geoaccumulation index soils and sediments is.

$$\mathrm{I}_{\mathrm{geo}} = Log_2\left(\frac{C_n}{1.5\,B_n}\right) \tag{3}$$

where C_n is the measured content of element (n), B_n is the BC of element n, and 1.5 is the background matrix correction factor due to lithogenic effects (the constant 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations in soils).

2.4. Ecological risk factor

The potential ecological risk of heavy metal pollution in the soils and sediments of water basins in the study area was assessed using the ecological risk index (RI) [25]. RI is the comprehensive potential ecological index, which is the sum of individual heavy metals—E_i. It represents the sensitivity of the biological community to the toxic substance and illustrates the potential ecological risk caused by the overall contamination. The RI was calculated as the sum of risk factors of heavy metals:

Metals	Hg	Cd	As	Pb	Cu	Cr	Ni	Zn
MPC (mg/kg)	2.1*	1.0	2.0	32.0	3.0	6.0	4.0	23.0
BC (mg/kg)	0.4	3.0	15	20	100	40	20	70
T_i	40	30	10	5	5	2	5	1

*The value of 2.1 is acceptable only for Hg pollution of soils in nonresidential areas.

Table 2. MPC, BC, and toxic-response factors of heavy metals.

$$\mathrm{RI} = \sum E_i \tag{4}$$

where E_i is the single risk factor for heavy metal i and is defined as.

$$E_i = \mathrm{T}_i f_i = \mathrm{T}_i \frac{C_i}{B_i} \tag{5}$$

where T_i is the toxic-response factor for heavy metal i. The ratio f_i is the metal pollution factor calculated from the measured concentration C_i and the background concentration B_i of metal in soils. MPC and BC, and the T_i values defined by Hakanson for the measured heavy metals that were used during the calculation of pollution indices are given in **Table 2**.

The calculated values of PI_i, E_i, EF, and I_{geo} given in subsequent tables are the means of these indices from at least 10 samples.

3. Results and discussion

Initial studies focused on the assessment of heavy metal pollution in the territory of oil-gas production enterprises. The study was carried out several years ago. Ten soil samples were analyzed for metals including potentially toxic elements—As, Cd, Cr, Hg, Pb, Cu, Zn, and Ba. The values derived from the analyses were compared with both the background concentrations and the maximum permissible concentrations of these elements established by the Cabinet of Ministers of the Republic of Azerbaijan. The results are presented in **Table 3**.

The values in **Table 3** show that the concentrations of the majority of heavy metals, including As, Ba, Cr, Cu, Pb, and Zn, exceed their permissible levels established in the republic. The contents of most toxic metals like As, Pb, and Zn are found to be from 3.4 to 8.2, 14.3 to 42.2 and 11.5 to 105 mg/kg, respectively. Their concentrations were higher than the background levels in some sampling areas. Meanwhile, no exceeding of maximum permissible and background levels on Hg, Cd, and Mn was observed in this area during our researches.

According to their impact on the ecosystem, many of these metals belong to the following categories, with exception of Fe, which is low toxic:

1. As, Hg, Pb, Cd, and Zn—super dangerous
2. Cr and Cu—dangerous
3. Ba and Mn—moderately dangerous

Samples	Heavy metals (mg/kg)									
	As	Ba	Cd	Cr	Cu	Fe	Mn	Hg	Pb	Zn
1	5.8	730	0.28	20.4	67.1	16,500	380	0.04	27.2	60.7
2	7.6	214	0.10	27.1	30.7	30,600	494	0.03	25.3	32.5
3	5.4	1290	0.41	21.6	44.4	28,600	691	0.11	37.3	105
4	8.2	335	0.09	27.7	26.6	15,500	541	0.07	27.2	54.9
5	7.6	330	0.12	14.4	20.8	16,200	294	0.02	26.2	17.1
6	3.4	360	0.15	18.9	57.2	7900	188	0.04	37.1	37.5
7	3.9	45	0.02	6.5	5.0	4500	130	0.01	25.1	11.5
8	4.4	760	0.23	17.7	38.4	13,900	435	0.19	29.8	32.4
9	7.5	570	0.37	16.9	60.0	13,500	474	0.07	42.2	76.2
10	7.8	354	0.08	28.4	29.9	15,600	485	0.03	14.3	52.1
MPC (mg/kg)	2.0	200–350	1.0	6.0	3.0		1500	2.1	6.0	23
BC (mg/kg)	15		3	40	100		250	0.4	20	70

Table 3. The content of heavy metals in oil-contaminated soils.

It is necessary to have knowledge about sediment pollution situation to evaluate the level of heavy metals' impact on water biological system. With this purpose, sediment samples from 12 distinct water bodies (including natural and artificial basins) in the study site were analyzed for heavy metal contamination. It should be noted that along with oil-gas production enterprises, there are some other industrial objects in this area. The results of analyses are presented in **Table 4**. The table indicates that significantly high quantities of heavy metals are accumulated in the bottom sediments of surface waters.

As can be seen from **Table 4**, in many samples, the concentrations of toxic heavy metals, especially Cd, Cr, Cu, and Zn, were found to be greater than their permissible levels accepted in the republic—1, 6, 3, and 23 mg/kg, respectively. In several stations, the contents of most toxic metals like Cd and Zn ranged from 17.8 to 33.0 mg/kg and from 28.3 to 86.8 mg/kg, respectively. The highest concentrations of Cd were recorded in the study sites located closer to cement manufacture and nonferrous metal-processing plants. In a large majority of samples, the values of Cd were higher than its background level (3 mg/kg) to a considerable extent. The content of Cr was significantly higher than its MPC at most of sampling stations. However, no exceeding of the MPC on Pb (32 mg/kg) was detected in the samples during the study period.

Further studies were carried out to assess the potential ecological risk caused by the heavy metal contamination in the Absheron industrial zone through the calculation of single pollution index (PI_i), enrichment factor (EF), geoaccumulation index (Igeo), and potential ecological risk index (RI). The studies focused on the evaluation of the contamination levels of various ecosystem components with toxic metals. At first, the contamination of ground and groundwaters was studied in one of the polluted areas of the Absheron peninsula, in the territory of Hovsan Aerator Station.

Samples	Heavy metals (mg/kg)								
	Ni	Co	Pb	Mn	Cr	Zn	Cu	Cd	V
1	44.7	18.4	18.9	136.4	11.9	20.4	14.9	33.0	3.3
2	3.0	9.6	7.0	155.0	16.1	20.1	12.9	ND	3.0
3	36.4	7.6	6.9	213.4	11.3	16.9	58.9	17.8	1.8
4	15.2	10.9	6.9	162.0	14.9	21.0	14.8	ND	3.2
5	13.2	9.8	6.3	159.1	18.4	20.3	13.6	ND	2.1
6	50.1	19.9	12.1	636.0	23.9	30.0	13.1	29.8	6.9
7	44.6	9.8	9.6	351.0	16.9	86.8	83.1	28.4	4.0
8	52.1	25.0	10.9	546.0	20.6	32.3	11.0	29.4	8.9
9	49.6	24.6	11.3	513.2	23.9	29.6	10.6	1.0	9.3
10	46.8	21.0	11.6	596.0	25.1	28.3	12.9	31.0	5.7
11	15.8	12.1	7.0	169.3	15.9	21.9	16.1	ND	3.4
12	13.4	11.3	6.8	156.8	13.8	19.8	15.4	ND	2.4

Table 4. The content of heavy metals in bottom sediments of surface waters within the Absheron industrial region.

For the evaluation of the pollution level and the potential ecological risk caused by heavy metal pollution in soils, enrichment factor and ecological risk index were calculated for the most important heavy metals with regard to potential hazard such as Cd, Cr, Pb, Zn, and Ni, with contamination values exceeding MPC.

The data derived from heavy metal analysis of ground and groundwaters of the study site are presented in **Tables 5** and **6**. The results indicated that in some groundwater samples, the concentrations of Cd and Zn were found to be higher than their MPC established by the national legislation. No exceeding of MPC was recorded in the values of Pb, Cr, Ni, and Mn during our observations. Overall, the concentrations of the majority of the analyzed heavy

Metals	MPC, mg/l	Sampling stations								
		1	2	3	4	5	6	7	8	9
Cd	0.001	0.010	0.008	0.009	0.009	0.005	0.008	0.014	0.012	0.006
Zn	0.5	0.09	0.09	0.012	0.015	0.014	0.116	0.248	0.190	0.120
Pb	0.03	0.009	0.013	0.006	0.014	0.007	0.012	0.019	0.015	0.008
Cr	0.1	0.007	0.008	0.005	0.012	0.005	0.025	0.040	0.011	0.007
Ni	0.1	0.005	0.018	0.014	0.012	0.006	0.008	0.021	0.010	0.005
Mn	0.05	0.013	0.014	0.016	0.008	0.015	0.027	0.014	0.010	0.008

Table 5. The content of heavy metals in groundwaters (mg/l).

Metals	Sampling stations								
	1	2	3	4	5	6	7	8	9
Cd	3.9	1.4	4.4	6.4	2.2	5.6	3.5	3.3	2.5
Zn	99	140	130	120	110	77	110	80	130
Pb	7	9	8	14	16	9	5	12	14
Cr	30	92	68	55	70	46	130	57	59
Ni	20	30	40	36	25	21	35	53	18
Mn	360	230	270	320	220	320	400	280	260

Table 6. The content of heavy metals in grounds (mg/kg).

metals in groundwaters were at the level of national and international standards. According to the international water-quality standards, the minimal risk concentration of Zn, Cu, Ni, and Pb should be 20, 10, 2, and 10 μq/l, respectively [26, 27].

Analysis of the data presented in **Table 6** shows unequal distribution of heavy metals in the polluted grounds of the territory. The variability in the concentrations of metals may be associated with the origins of their pollution sources. The maximum heavy metal pollution levels observed were 6.4 mg/kg for Cd, 140 mg/kg for Zn, 130 mg/kg for Cr, and 53 mg/kg for Ni. With exception of Mn and Pb, the average concentrations of Cd, Zn, Cr, and Ni in the ground samples were found to be greater than their MPC about 3, 5, 10, and 9 times, respectively.

Figures 3 and **4** show the calculated EF and E_i values of Cd, Zn, Pb, Cr, and Ni. The results of calculation showed that the values of EF of Zn and Cr are 2.18 and 2.50 in the ground from station 2, indicating moderate enrichment by these elements, whereas the EF values of Cd, Pb and Ni were 0.51, 0.49, and 0.71, respectively, exhibiting depletion to mineral enrichment (<2). EF values of all the studied metals in both stations 4 and 8 recorded the values lower than 2, indicating that the grounds of these areas are in the state of depletion to mineral enrichment with respect to these metals. The data presented in **Figure 1** show the same EF values for Pb at all three stations, which can be associated with the composition of the parent materials of soils. A relatively high EF value of Cd (1.67) was observed at sampling station 4.

Comparative analysis of the calculated values of E_i index with the data given in **Table 7** shows that among other elements, Cr and Cd demonstrated a higher ecological risk during the observations, indicating that the site was impacted by the anthropogenic sources of these metals. The calculated E_i values were 46 for Cr at station 2, and 64 for Cd at station 4 exhibiting a moderate potential ecological risk. According to the results of calculations, the area of station 8 can be characterized by a relatively lower enrichment and a potential ecological risk with regard to heavy metal pollution. As can be seen from **Figure 4**, the potential environmental risk of metal in a greater extent depends on its toxicity to the ecosystem, rather than the content of the element in the soil. At station 8, the concentration of Cd exceeded MPC by 3.3 times, and the concentration of Zn exceeded MPC by 3.5 times, whereas according to the calculation results, the values of their ecological risk index E_i were 33 and 1.2, respectively.

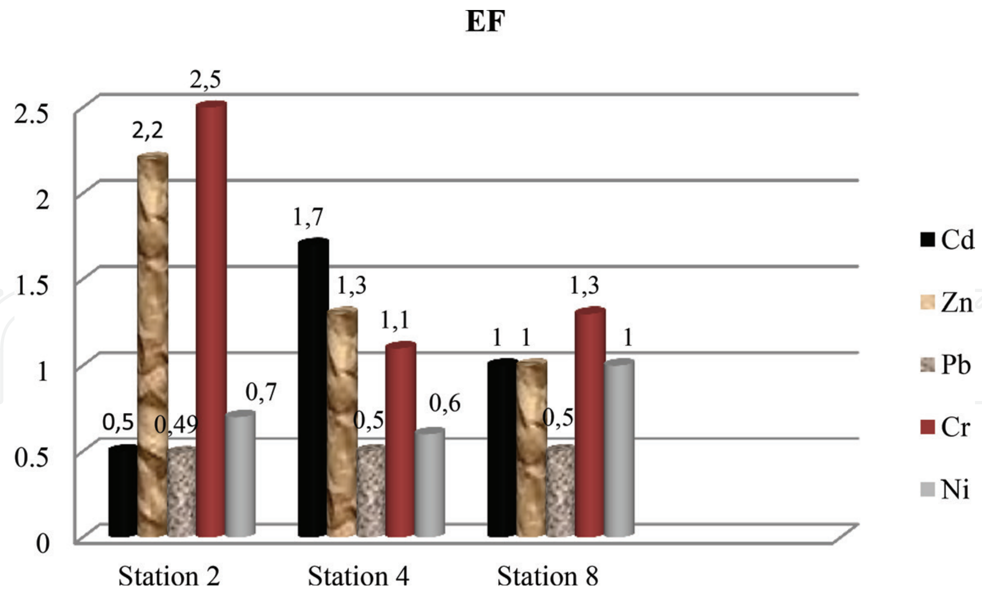

Figure 3. Change of the values of enrichment factor of heavy metals in the grounds of three study stations.

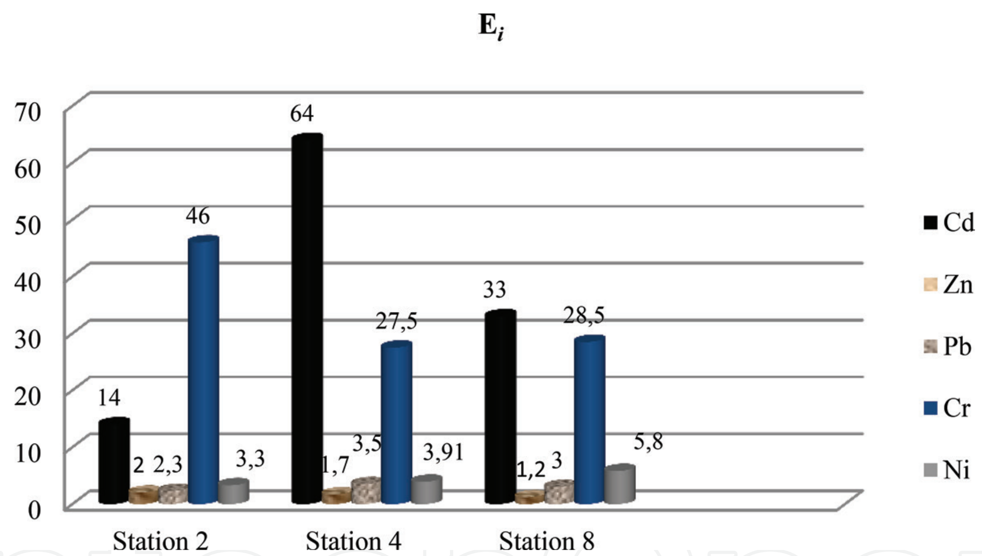

Figure 4. Change of the values of potential ecological risk index of heavy metals in the grounds of three study stations.

Part of the research was carried out to assess the current level of heavy metal pollution of soils and surface water systems in the oil-industrial zone of the Absheron peninsula. The researches focused on the heavy metal pollution of soils from two types of land uses including two natural lakes—Boyuk shore and Bulbula, which have been subject to a long-term impact of various anthropogenic sources. The heavy metal pollution of the study site was assessed through the calculation of the single pollution index (PI_i), geoaccumulation index (I_{geo}), enrichment factor (EF), and ecological risk factor (E_i).

Comparison of the results given in **Table 8** with the pollution classes in **Table 7** shows that oil field area can be categorized as unpolluted by Pb, Cd, Zn, Cu, and Hg, and moderately

Class	I_{geo}		EF		E_i	
1	<0	Unpolluted/slightly polluted	<2	Depletion to mineral enrichment	<40	Low potential ecological risk
2	0–1	Moderately polluted	2–5	Moderate enrichment	40–80	Moderate potential ecological risk
3	1–3	From moderately to strongly polluted	5–20	Significant enrichment	80–160	Considerable potential ecological risk
4	3–5	Strongly polluted	20–40	Very high enrichment	160–320	High potential ecological risk
5	>5	Extremely polluted	>40	Extremely high enrichment	320	Very high potential ecological risk

Table 7. Classification of heavy metal pollution levels in soils and sediments based on I_{geo}, EF, and E_i values.

to strongly polluted by As and Cr, which mean I_{geo} values are higher than 1 to some extent. The mean values of EF are 0.0367 for Cd and 0.8900 for Pb, indicating that the territory can be characterized by the first classification level—depletion to mineral enrichment. According to the mean E*i* values of individual metals within the range of 0.68 (Zn)–7.28 (Pb), the soils of oil field area demonstrate a low potential ecological risk regarding heavy metal contamination.

Figure 5 presents the percentage of individual heavy metals in potential ecological risk index (RI) for the soils of oil field area. It is seen from this figure that the soils from this area had the highest E_i percentage for Pb, Hg, and As compared to other heavy metals.

In order to study the impact of transport emissions on heavy metal contamination of soils, the content of heavy metals was measured in soil samples collected in the vicinity of two main roads. The results are given in **Table 9**.

Elements	Concentration (mg/kg)			PI_i	E_i	EF	$I_{geo.}$
	Min.	Max	Mean	Mean	Mean	Mean	Mean
As	3.4	8.2	4.16	2.8	4.16	0.2683	1.4623
Cd	0.02	0.41	0.18	0.18	1.85	0.0367	−4.5658
Cr	6.5	28.4	19.9	3.36	0.99	0.3000	1.7297
Cu	5.0	67.1	37.1	12.7	1.89	0.2250	−1.9808
Hg	0.01	0.19	0.06	0.03	6.10	0.0912	−3.3219
Pb	14.3	42.2	29.2	0.9	7.28	0.8900	−0.0389
Zn	11.5	105	47.9	2.3	0.68	0.4107	−1.1292
Mn	130	691	410				

Table 8. The content and pollution indices of heavy metals in soils in oil field area.

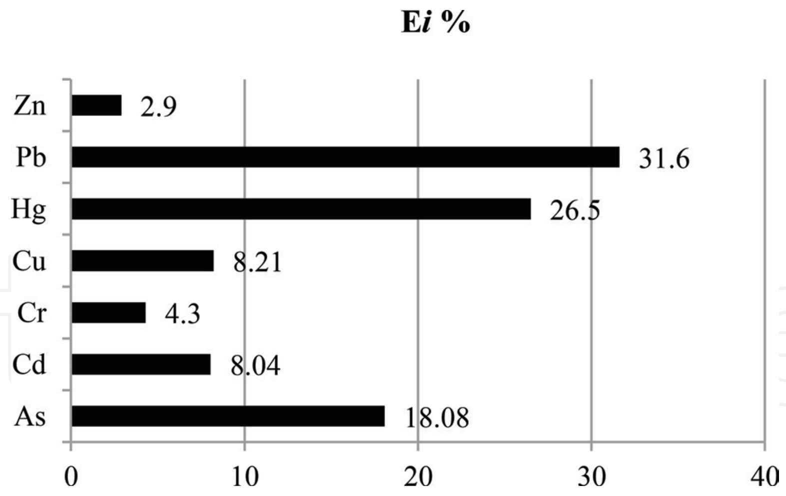

Figure 5. Percentage of heavy metals in potential ecological risk (RI) for the soils of oil fields area.

The calculated values of pollution indices for the soils near to Baku-Mardakan highway that was polluted predominantly by transport emissions (**Table 10**) varied from their values for oil-polluted site. The highest pollution indices in this area were recorded for Pb. The mean values of I_{geo}, EF, and E_i of this metal were 4.1429, 2.1250, and 132.5, respectively, demonstrating strongly polluted, moderate enrichment, and considerable ecological risk levels. The calculated I_{geo} values indicate that the site can be categorized as strongly polluted with respect to Pb and Cr and from moderately to strongly polluted area with respect to Zn and Cu. Relatively low pollution levels were detected for Hg and As in the soils of this area.

Figure 6 indicates that an increasingly high E_i percentage was recorded for Pb, Cd, and Cr in the soils from the area of transport road. Combustion of petroleum products by transport facilities is a major source of environment pollution by these metals.

Initial studies on the ecological situation of the abovementioned lakes were conducted to evaluate the level of contamination of lake waters with oil products and heavy metals. During the studies, the highest levels of heavy metal and oil pollution were recorded in the samples collected from industrial wastewater flow to Boyuk shore Lake (**Table 11**). Among toxic heavy metals, Zn, Pb, and Cd each had the highest concentrations exceeding the MPC by 70, 19, and 44 times, respectively. Increasingly high concentrations of petroleum compounds were observed in the waters of both lakes exceeding the MPC by 10-fold. Elevated levels of Cu contamination were observed at all sampling stations.

The contents and calculated results of pollution indices of heavy metals in the sediments of Boyuk shore and Bulbula Lakes are presented in **Tables 12** and **13**. Minor concentrations of As

Roads	Concentration of metals, mg/kg									
	Pb	Cd	Ni	Zn	Mn	Hg	Cr	As	Co	Cu
Baku-Sumqait	470	4.5	375	430	1950	0.019	860	4.08	52	115
Baku-Mardakan	565	5.8	440	515	2175	0.023	909	5.29	57	150

Table 9. The content of metals along transport roads.

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Elements	Concentration (mg/kg)			PI*i*	E*i*	EF	$I_{geo.}$
	Min.	Max	Mean	Mean	Mean	Mean	Mean
As	1.25	6.17	5.30	2.65	3.5	0.0266	−2.0858
Cd	1.30	5.80	4.50	4.5	45.0	0.1416	0
Cr	215	926	860	143	43.0	1.5000	3.8413
Cu	150	740	575	191	28.7	0.5500	1.9386
Hg	0.007	0.034	0.028	0.013	2.80	0.0219	−7.7433
Pb	75	588	530	16	132.5	2.1250	4.1429
Zn	126	517	435	19	6.20	0.5357	2.0506
Mn	1755	3390	2170				

Table 10. Concentration and mean values of pollution indices of heavy metals in soils in the area of Baku-Mardakan highway.

were detected in the sediments of both lakes during the studies. Consequently, the pollution indices were calculated for six metals including Cd, Cr, Cu, Hg, Pb, and Zn.

It is seen from **Table 12** that the average PI_i values of Cd, Cr, Cu, and Zn in the Boyuk shore Lake sediments showed the mean concentrations to be significantly higher than the MPC of these metals. The maximum concentrations of Cd, Pb, and Zn each were 5, 47.2, and 510 mg/kg, respectively. Laboratory analyses showed that the concentrations of the majority of heavy metals in the sediments of Bulbula Lake were lower than those in Boyuk shore Lake, exclusively Cu which had the highest mean PI_i value of 7.5. The variations in the heavy metals pollution levels can be explained with the origins of their sources.

The results of calculations suggest that in both lakes, the mean values of $I_{geo.}$ and EF for the studied metals represent unpolluted condition, while there are some elevated levels of Cd, Pb, and Zn, especially in the sediments of Boyuk shore Lake. The results showed that the maximum EF value in the sediments of Boyuk shore Lake observed in Zn is greater than 3, indicating that the lake was severely impacted by anthropogenic sources of this metal.

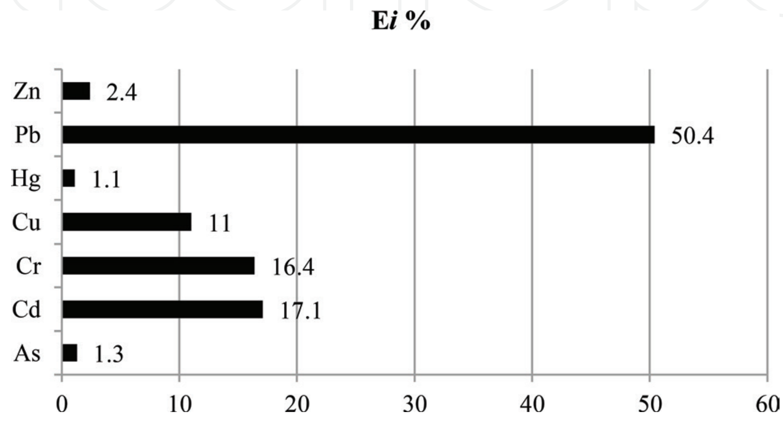

Figure 6. Percentage of heavy metals in potential ecological risk (RI) for the soils of the area close to transport road.

Pollutants (mg/l)	MPC (mg/l)	Boyuk shore Lake	Bulbula Lake
Petroleum compounds	0.05	2.6	2.05
Zn	0.5	35.06	ND
Cu	0.01	1.72	0.37
Ni	0.1	6.07	0.006
Pb	0.03	0.56	0.01
Cd	0.001	0.044	<0.001

Table 11. The content of petroleum compounds and heavy metals in two natural lakes of the Absheron Peninsula.

Elements	Concentration (mg/kg)			PI_i	E_i	EF	$I_{geo.}$
	Min.	**Max**	**Mean**	**Mean**	**Mean**	**Mean**	**Mean**
Cd	1.0	5,0	1.7	1.7	17.0	0.3916	−1.4043
Cr	15.6	59.0	25.1	4.2	1.21	0.4562	−1.2572
Cu	10.6	24.4	14.7	4.9	0.74	0.1125	−3.3510
Hg	0.004	0.063	0.0085	0.04	0.85	0.1500	−6.1413
Pb	16.7	47.2	28.5	0.9	7.12	1.0040	−0.0740
Zn	20.3	510	86.8	3.8	1.24	0.8714	−0.2746
Mn	213.4	546	355				

Table 12. The content and mean values of pollution indices of heavy metals in the sediments of Boyuk shore Lake.

Elements	Concentration (mg/kg)			PI_i	E_i	EF	$I_{geo.}$
	Min.	**Max**	**Mean**	**Mean**	**Mean**	**Mean**	**Mean**
Cd	<0.5	1.4	0.6	0.7	6.00	0.2150	−2.9068
Cr	11.3	28.9	17.7	2.9	0.88	0.2937	−1.7612
Cu	13.1	35.0	22.6	7.5	1.13	0.1475	−2.7305
Hg	0.002	0.029	0.006	0.003	0.60	0.0993	−6.6438
Pb	6.9	30.2	18.4	0.6	4.60	0.6101	−0.7052
Zn	6.6	36.8	20.3	0.9	0.29	0.1928	−2.3708
Mn	179.4	636.0	376.2				

Table 13. The content and mean values of pollution indices of heavy metals in the sediments of Bulbula Lake.

Table 13 shows that the calculated EF values for the studied metals in the sediments of Bulbula Lake are lower than 1, indicating depletion to mineral enrichment. The means of $I_{geo.}$ for all metals were negative in the Bulbula Lake sediments, based on which the lake is categorized with "unpolluted/slightly polluted" class.

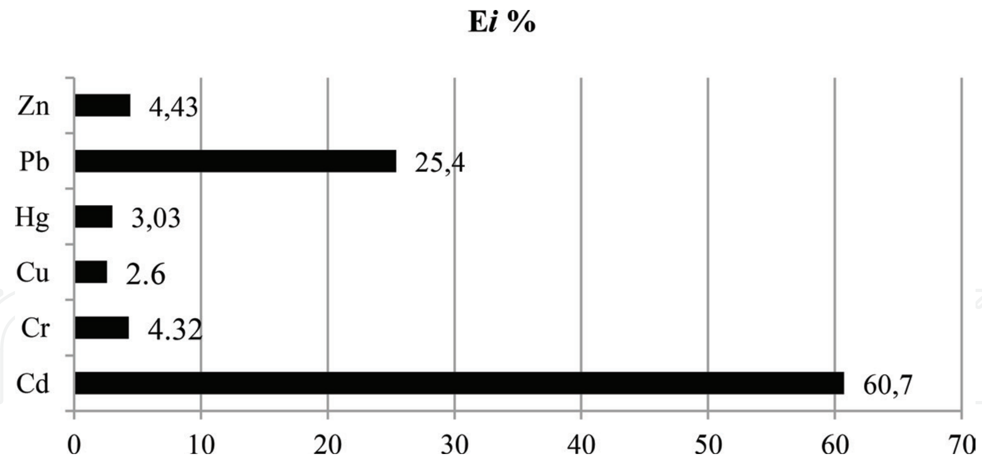

Figure 7. Percentage of heavy metals in potential ecological risk (RI) for the sediments of Boyuk shore Lake.

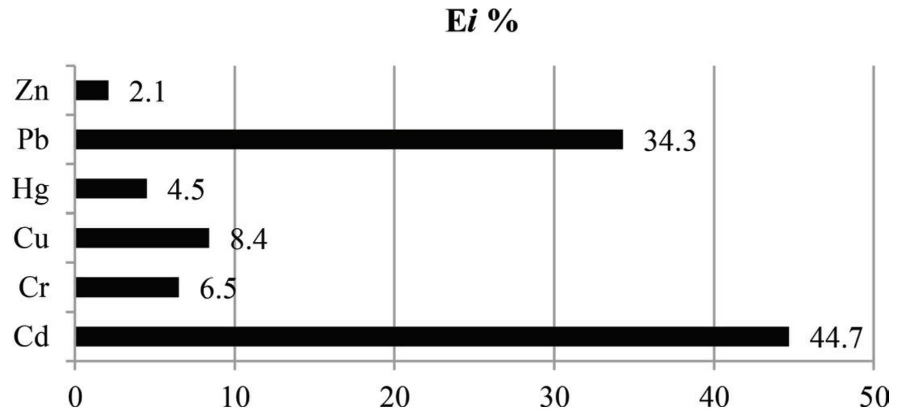

Figure 8. Percentage of heavy metals in potential ecological risk (RI) for the sediments of Bulbula Lake.

The calculated values of E_i indicate that in both lakes, compared to other metals, relatively higher potential risks are related to Pb and Cd (**Figures 7** and **8**). The highest risk was revealed for Cd in Boyuk shore Lake sediments.

4. Conclusions

In summary, the levels of heavy metal contamination of the main ecosystem components including soils, grounds, surface, and groundwaters were assessed in the oil-industrial region of the Absheron peninsula. In order to evaluate the contribution of anthropogenic sources to heavy metal contamination, pollution indexes were calculated for most toxic metals—As, Cd, Cr, Hg, Pb, Cu, Zn, and Ni.

Based on the results of researches, it can be concluded that the long-term impact of anthropogenic discharges has led to the pollution of all ecosystem components in the study site. The majority of the studied metals exceeded their permissible levels. The laboratory analysis revealed high levels of toxic heavy metals in grounds and groundwaters in the territory of aerator station. The studies showed that the concentrations of Cr, Cd, Zn, and Ni in the grounds of this site exceeded their MAC by several times. In order to evaluate the metal pollution status, the EF and E_i indexes of metals were calculated for three areas. Despite the fact that in the majority of samples, the concentrations of heavy metals were higher than their permissible levels, the calculated EF and E_i values suggest that the grounds in the site can be categorized as depletion to mineral enrichment area representing a moderate potential ecological risk with respect to heavy metals. Thus, the grounds in the territory of the aerator station cannot be characterized by a serious potential risk from heavy metals.

Based on the results of the comparative studies carried out in the oil-industrial area and the Baku-Mardakan transport road, we can say that the long-term impact of anthropogenic sources has led to the pollution of ecosystem by heavy metals in this area. The researches have revealed increased levels of heavy metal contamination. High concentrations of Pb, Cr, Zn, and Cu were detected in soils exceeding their permissible limits by several magnitudes that pose serious threat. Both oil industry and transport are the main sources of soil pollution in this site, where transport emission is the dominant factor.

Calculations showed that there is some correlation between the values of EF and $I_{geo.}$ for Boyuk shore and Bulbula Lakes, respectively. The accumulation of metals in the sediments of these lakes was not insignificant, indicating the condition of depletion to mineral enrichment. Analysis of the calculated EF, I_{geo}, and E_i values confirmed that in both lakes, the highest and lowest values of the mentioned indexes were recorded almost in the same metals that can be explained by their lithogenic sources. Higher quantities of heavy metals were detected in the samples from Boyuk shore Lake. This is the evidence of the fact that anthropogenic factors strongly influence the contamination of the lake sediments by heavy metals.

In recent years, according to the Presidential Decree, comprehensive works were implemented on the rehabilitation of nine natural lakes of the Absheron peninsula [28]. The works implemented on the rehabilitation and protection of the Boyuk shore Lake were divided into two phases. The first phase covered a 283-ha lake area and an area of 500 m from the lake. At this stage, the division of the lake into two parts was intended for the eastern part of the lake, adjacent to the Baku Olympic Stadium. The first phase was completed in 2015. However, it is important to have a detailed knowledge on the ecological situation of these lakes and surrounding areas to evaluate the extent of the works to be undertaken for further rehabilitation.

Overall, the potential ecological risk indices indicated a low potential risk (<40) from individual heavy metals, with exception of Pb posing a considerable potential risk level in the territory of Baku-Mardakan highway.

The calculated values suggest that the study area cannot be characterized by a high potential risk from heavy metals but increasing industrial development and urban growth can lead to a higher potential risk in the future years.

In order to prevent pollution and protect the ecosystem from the future disasters, it is possible to recommend

1. development and implementation of complex measures based on a scientifically proven approach to protect the ecosystem from the impact of toxic compounds including heavy metals;

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2. application of ICT systems for the development of an electronic database of the ecosystem pollution including the maps of heavy metals distribution indicating the anthropogenic sources of individual elements;
3. development of a well-rounded program to investigate the heavy metals impact on soil and water ecosystems taking into account their geological transformations, migration, and accumulation conditions including the acidity and alkalinity of soils, oxidation-reductive mode, the content of humus and the presence of readily soluble salts, and so on;
4. development and application of environmental-friendly technologies aimed at the minimization of industrial discharges and heavy metal pollution at all operational stages;
5. development and implementation of an integrated program for the elimination of transport emissions in the Absheron region, mainly in the city of Baku.

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