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ENVIRONMENTAL MONITORING OF THE CASPIAN SEA OFFSHORE AND COASTAL AREAS WITHIN THE SUBURBS OF AKTAU CITY

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Abstract

Growth of city population and migration of communities lead to higher accumulation of heavy metals in coastal areas of the Caspian Sea suburbs. In the present study there are represented geographical and ecological locations and environmental monitoring results of the Caspian Sea offshore and coastal area near Akshukyr (Aktau suburbs). The shallow offshore near Aktau city and adjacent areas were monitored in cooperation with the Institute of Ocean Sciences. Sea water analysis carried out special measurements as Expert-003 Photoelectric Colorimeter, Fluid Analyzer, pH-meters 1 and 5 ml LABMATE syringes. Near Aktau city it was selected four hydrologic stations (HS) for analysis of water and soil surface. Pollution of the Caspian Sea with heavy metals has been observed, since greater portion of metals comes from river flow. The content of heavy metals in the Northern Caspian is 2-7 times higher than in the Volga River, which may be attributed to an increased levels of dissolved forms of metals in comparison to the suspended form as a result of mixing of river and sea waters. Soils are not contaminated with heavy metals as the distance from the testing site, TS-2. The highest rank amounts of copper and cadmium content are characterized by TS-2 (33.5) and (29.0) series accordingly.

Key words: coastal area, heavy metals, hydrocarbons, monitoring, sea area, soils

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1. Introduction

Nowadays environmental contamination such as of the Caspian Sea area has a negative effect on health of the humans, because people has already interfered and continue to interfere into some important environment processes associated with their existence during their economic activities (Agca et al., 2014). Complex and contradictory relations of humans with the environment, incremental urbanization, high rates of offshore oil production development, consumer and inconsiderate use of subsoil mineral resources within the series of country regions including the Mangistau, a province of Kazakhstan can cause some extreme environmental situations resulting in ecological crises. In general, the Caspian Sea ecosystem is considered as pre-crisis one and can deteriorate as a result of the large-sale encroachment

in the environment due to the planned production development in the north-east shallow part (Bastami et al., 2015). Some sea areas are characterized by poor degrees of studies and direct observations data in spite of numerous studies of the Caspian Sea. Series of fundamental and applied issues requiring a regional approach to study the conditions of the Caspian Sea coastal area arise within these regions. This situation had extremely aggravated over the last three decades when the number of scientific studies of this problem reduced dramatically (Liu et al., 2015; Syrylbekkyzy et al., 2014). The east part of the Middle Caspian Sea coast and the sea area of the Mangistau, Aktau and its suburban areas, in particular is one of such regions. Moreover, the Aktau is the single port of the Kazakhstan used for international transportation of petroleum products. In view of the above, studying of the Caspian Sea areas and region center coastal areas

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is considered as an actual and current issue. These studies can assist in the environment quality management actions. The aim of the survey is an evaluation of the pollution level of the sea side and shore of the Caspian Sea in the region center area of Mangistau (Alexeyenko et al., 2013; Chicherina et al., 2004; Kostianoy and Kosarev, 2005; Kroshenko et al., 2018; Kenzhetaev, 2013; Rasuly et al., 2010; Semidyayeva et al., 2015; Vieira et al., 2018; Wen et al., 2019; Zhao et al., 2018).

2. Material and methods

2.1. Material

The study materials of the Yessenov University in cooperation with the Institute of Ocean Sciences named after P.P. Shirshov (Russia) are the principal source of the actual information (Kenzhetaev, 2013). The shallow offshore near Aktau and adjacent areas were monitored in cooperation with the Institute of Ocean Sciences on April, 2018. The geophysical measurements were conducted from the beam position of the catamaran being on the driftways, only station in Aktau 3 section has been anchored. There were 4 sections, each of them was composed of four hydrologic stations (HS), samples were taken at the water surface conditions from four spot stations (14, 15 16 and 17). A mobile weather station had been installed at a height of 5 m above sea level at the yacht club mooring northwards of Aktau.

A number of 4 testing sites (TS), TS-1, TS-2, TS-3 and TS-4 (background) were staked for monitoring of soil condition within the Aktau suburban areas opposite hydrological stations HS-14 - HS-17 (Fig.1). TS-1 was staked 20 km away of Aktau in Akshukyr settlement at the distance of 303.65 m of the coastal sea line. TS-2 is located near the Aktau - Fort Shevchenko road at the distance of 1635.1 m from TS-1 located near the open storage of fertilizers and storage of road construction materials. TS-3 is located within the area of private buildings at the distance of 2135 m from TS-2. TS-4 (background) at the distance of 9578 m from TS-3 where almost no pollutant emissions caused by construction and industrial operations are observed.

2.2. Hydrophysical and hydrochemical measurements

Hydrophysical and hydrochemical measurements were performed at each hydrologic station including water sampling and laboratory analyses. A temporary laboratory was organized and equipped at the Faculty of Engineering for water samples analyses and conservation. Sea water samples were processed on the same day of their sampling. The following equipment was used for the analytical studies: Expert-003 Photoelectric Colorimeter, Fluid Analyzer, pH-meter channel meter for ions, 1 and 5 mL LABMATE syringes (Chicherina et al., 2004).

2.3. Sea water sampling

The water samples were taken in compliance with governmental- standards No. 17.1.5.05-85. General requirements for surface and sea water sampling. The water sample was transferred to the dishes for samples immediately after sampling according to government standards 17.1.5.04-81. Hydro Bios type plastic bathometer was used for water sampling (Semidyayeva et al., 2015).

2.4. Hydrochemical parameters determination

The specified parameters were determined in accordance with the standard methods accepted by the field practices. The pH value was determined by the potentiometer method according to guidance document No. 52.10.243-92 in the National Bureau of Standards practical scale. Unfiltered samples were used for determination. Total alkalinity was determined by the direct titration method with a color termination. Unfiltered samples were used for determination. Content of dissolved inorganic phosphorus and phosphates were determined colorimetrically in compliance with guidance document No. 52.24.382-2006. Hydrochemical analyses were performed in total including determination of pH - 12, dissolved inorganic phosphorus - 12, nitrite nitrogen - 12, nitrate nitrogen - 14, ammonium nitrogen - 12, total nitrogen - 12 and dissolved oxygen - 12. Sea water temperature and salinity values were registered by means of the flowing sounding system using the YSI 6600 sounder. The sounding system is composed of a pump with a capacity of about 1 L/s supplying the outside water to the special container with a capacity of 30 liters (M.P., 2018).

The sea current rate is measured by the (ADCP) RDI Work Horse 600 kHz Doppler acoustic current meter hung out overboard and kept in the surface layer of water within 10 minutes. Content of oil product phenols and synthetic surfactants in water samples was analyzed by the Environment and Chemical Engineering laboratory using a gas chromatograph AGILENT 6890 with mass selective detector (USA).

2.5. Hydrochemical parameters determination

Soil samples were taken at the depth of 0-20 cm by means of the sampler in compliance with the five spot pattern method at Testing Sites TS-1, 2, 3 and 4 (background). The method is represented by taking a mixed sample on the basis of 1 sample per 100 m² (10×10 m each site). The mixed sample is composed of 5 soil samples taken from 5 spots by the five-spot pattern method. An average weight of samples was 300-400 g. Samples are represented by mixed samples taken from 20 spots, i.e. 5 spots per 4 TS.



Fig. 1. Outline map of testing sites for monitoring of soil condition performed in the SAS Planet environment

2.6. Determination of heavy metals

Heavy metals in soil were determined by the atomic absorption spectrometry with plasma atomization in compliance with the method No. M-MVI-80-80-2008. Due to high bulk content of determined heavy metals (HM) in soil the mobile forms of the following elements Pb, Ni, Cr, Hg, V, Cu, Fe, Zn were determined. The certain concentrations of heavy metals (HM) were compared with the maximum allowable concentration (MAC).

Heavy metals in water was determined by Expert-003 Photoelectric Colorimeter (Russian Federation), Fluid Analyzer, pH-meter-4 for metal ions, 1 and 5 ml LABMATE syringes (Poland).

The acquired data was processed in the environment of Statistica 10 analytic software interface. The analysis method was selected by the Kruskal-Wallis ANOVA criteria statistics with a small scope of survey samples with different statistical laws. The Kruskal-Wallis ANOVA criteria statistics is similar with parametric one factor dispersion analysis but these criteria are based on ranks and not on the mean values.

3. Results and discussion

The sampling stations were located in the offshore near Akshukur and S. Shapagatov settlements being suburban settlements of the region center and 13 km and 21 km away from Aktau accordingly. The operations were conducted from the catamaran board (Fig. 1) and four one-day sea passages have been done.

A number of 4 sections including 17 stations were performed in total. In case of the north-southwards reading then section 1 included stations (14, 15, 16 and 17), section 2 included stations (4, 5, 6 and 7), section 3 (3, 8, 2 and 1) and an anchored station), section 4 (9, 10, 11 and 12). The first section with hydrological stations HS-14, HS-15, HS-16 and HS-17 was considered in this paper. Station HS-14 was located 1153.85 m away of the coast near private buildings in Akshukyr settlement.

Station HS-15 was at the distance of 3627.17 m away of the coast and at the distance of 2180 m away of station HS-14. Station HS-16 was located at the distance of 6406.71 m from the coast and 2500 m away of station HS-15. Station HS-17 was 8745.93 m away of the coast and 2300 m away of station HS-16. Table 1 shall specify hydrological stations (HS), their location, coordinates, depth and distance from the coast. Fig. 2 shows the outline map of four Hydrological Station location.

3.1. Sea water physical and chemical characteristics

Water depth at the hydrological stations HS-14 - HS-17 varied within the range from 11.9 to 19.8 m. Water transparency varied within the range of 9-13.6 m and in April the water transparency slightly differed from the same in May. A slight increase of water turbidity in May was caused by increase of the mixed layer thickness under the wind effect. Table 1 shows hydrological and hydrochemical conditions of sea water at the studied HS in April and May. The water temperature in the surface layer was 13.8-15.3°C. It should be noted that increase of water temperature in May at the studied stations (HS-14 - HS-17) is observed in the subsurface layer to 15.3°C due to intensive warming up caused by solar radiation and also by low intensity of wind load effect on these days. Dissolved oxygen concentration varied from 10.57 to 10.63. Sea water pH values were within the range of 8.27-8.49 and a decreased value for April was observed. The water salinity average is 9.8 ‰ and more or less the same for 2 months of studies. The water electric conductivity varied within close limits of 18.3-18.5 mS/cm.

3.2. Content of biogenic elements in water

Table 2 represents results of content of biogenic elements in water at the HS. In May content of ammonium nitrogen varied within the limits of 0.043-0.109 -, and these values exceeded the values recorded in April.

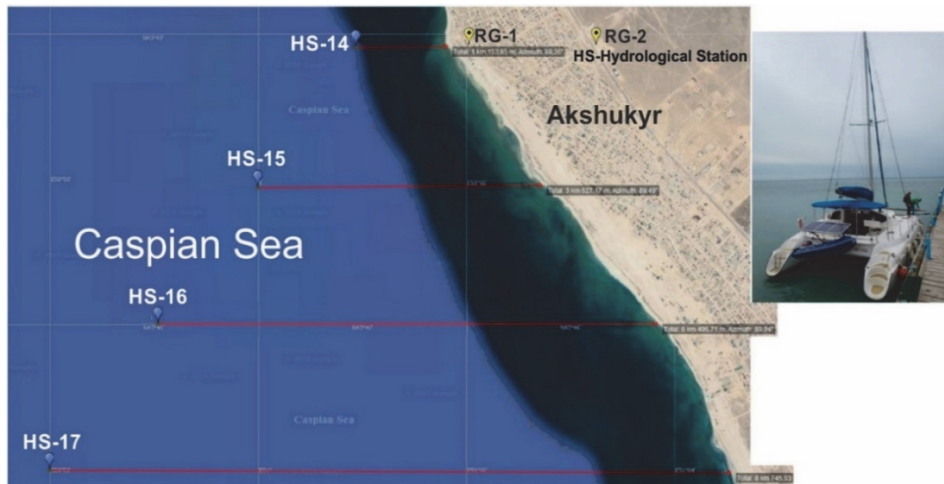


Fig. 2. On the left: outline map made under the SAS Planet environment, on the right: catamaran used for the Caspian Sea hydrological studies

Table 1. Sea water hydrological and hydrochemical conditions at hydrological station

Station	HS-14	HS-15	HS-16	HS-17
Depth of water, m	11.9	17.8	18.5	19.8
Transparency of water, cm	9.0*(9.3**)	10.8*(10.9**)	11.3*(11.7**)	12.5*(13.6)
Turbidity of water, NTU	4.2*(4.5**)	3.5*(3.7**)	4.9*(5.1**)	5.5*(5.6**)
Temperature of water, °C	13.9*(15.3**)	14.1*(14.8**)	14.3*(14.9**)	13.9*(14.9**)
Dissolved oxygen, wt. %	10.62	10.57	10.63	10.41
pH of water	8.3*(8.4**)	8.4*(8.5**)	8.27*(8.3**)	8.49*(8.5**)
Salt content of water, ‰	10.43	10.57	10.61	10.63
Elasticity, mS/cm	18.3	18.4	18.5	18.5

* Study results, April 2019; ** Study results, May 2019

Table 2. Concentration of biogenic elements at hydrological station

Station	HS-14	HS-15	HS-16	HS-17
Ammonium nitrogen, mg/L	0.087*(0.096**)	0.026*(0.043**)	0.064*(0.081**)	0.085*(0.109**)
Nitrite nitrogen, mg/L	0.047*(0.0084**)	0.026*(0.0088**)	0.063*(0.0092**)	0.079***(0.001**)
Nitrate nitrogen, mg/L	0.083*(0.092**)	0.085*(0.097**)	0.089*(0.101**)	0.091*(0.103**)
Total nitrogen, mg/L	1.63	1.55	1.58	1.60
Phosphates, mg/L	0.067*(0.005**)	0.053***(0.047**)	0.052*(0.049**)	0.051*(0.049**)

* Study results, April 2019; ** Study results, May 2019

In April, the content of nitrate nitrogen in water was low, 0.026-0.087 mg/L and varied within the limits of 0.092-0.103 mg/L in May. In April, the content of nitrate nitrogen was also low compared with the results registered in May. Average content of total nitrogen both in April and May was 1.63 mg/L. In April the concentration of phosphates in water was slightly elevated compared with the results registered in May.

High water flow rates of up to 22 m/s were observed in the sea surface layer within the studied section 1 (HS-14 - HS-17) in April. The water current rates decreased to 3-4 cm/s and 4-5 cm/s depending on the sea depth and distance from the coast. The direction of the Caspian Sea surface layer is prevailingly westward and north-westward and the direction of the deep sea layers is southward and westward (Fig. 3). Table 3 shows the content of synthetic surfactants in water. Recorded concentration of phenols in water at Hydrological Station exceeded maximum allowable concentration (MAC).

Concentration of oil products in water is registered within the limits of 0.005-0.008 mg/L.

The sea water at hydrological station was analyzed for content of arsenic metalloid (As) and barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), nickel (Ni), lead (Pb), vanadium (V), aluminum (Al) and zinc (Zn) metals. Results of analysis represents in Table 4. On the basis of the water samples analyses the content of arsenic, iron, mercury, vanadium and aluminum was lower than the detection level.

It has been recorded that the maximum allowable concentration is exceeded on the average as follows: cadmium (by 2.1 times), chromium (by 4.0 times), copper (by 3.7 times), nickel (by 5.2 times) and lead (by 4.6 times). Content of barium and zinc is normal. It should be noted that the heavy metals concentration in sea water has random distribution. Such random distribution is due to high current rates in the surface layer and distance to the navigable waterways.

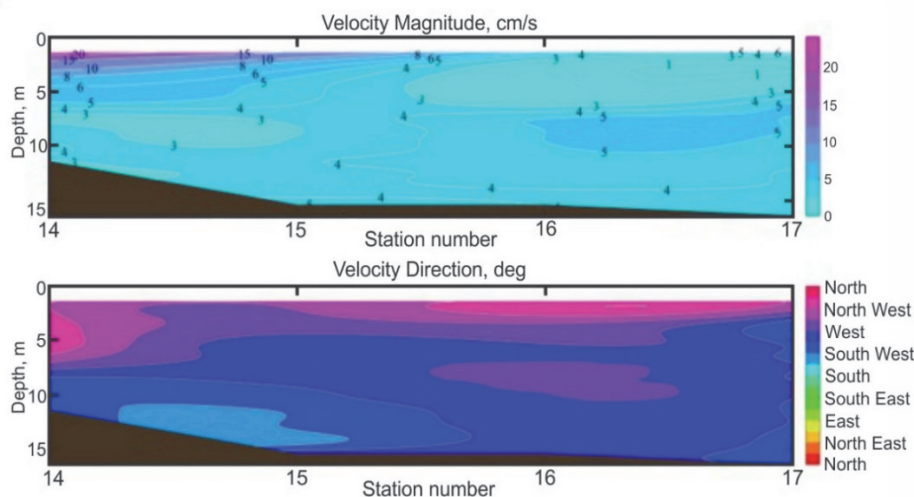


Fig. 3. Variation of rate (the upper plot) and direction (the lower plot) of the Caspian Sea water currents on section 1

Table 3. Concentration of phenols and oil products in water at hydrological station

Station	mg/L		
	Phenols	Oil products	Synthetic Surfactants
HS-14	0.0082	0.007	< 0.05
HS-15	0.0075	0.008	< 0.05
HS-16	0.0093	0.006	< 0.05
HS-17	0.0012	0.005	< 0.05
Maximum allowable concentration	0.001	0.05	0.5

Table 4. Concentration of heavy metals and metalloids in water

Heavy metals, mg/L	Stations					
	HS-14	HS-15	HS-16	HS-17	MAC*	MAC**
As	< 0.005	< 0.005	< 0.005	< 0.005	0.01	0.05
Ba	0.008	0.007	0.008	0.007	2.0	0.1
Cd	0.017	0.015	0.021	0.019	0.01	0.01
Cr	0.11	0.20	0.13	0.18	0.001	0.05
Cu	1.9	2.3	3.7	1.85	0.005	1.0
Fe	< 0.1	< 0.1	< 0.1	< 0.1	0.05	0.3
Hg	< 0.0002	< 0.0002	< 0.0002	< 0.0002	0.0001	0.0005
Ni	0.37	0.51	0.45	0.39	0.01	0.1
Pb	0.092	0.097	0.138	0.117	0.01	0.03
Zn	0.03	0.03	0.02	0.03	0.05	5.0
V	< 0.001	< 0.001	< 0.001	< 0.001	0.001	0.1
Al	< 0.04	< 0.04	< 0.04	< 0.04	0.04	0.1

*Summary list of MAC and Safe Reference Levels of Impact for the hazardous substances in the fish farm water bodies **Sanitary requirements to potable water safety (No. 147.229.506)

Thus the minimum concentration of cadmium is 0.015 mg/L at HS-15 (3627 m away from the coast and 17.8 m deep), while the maximum concentration is about 0.021 mgCd/L at HS-16 (6407 m away from the coast and 18.5 m deep) within the area of the navigable water ways. The lower content of chromium is 0.11 mg/L within the coastal area and a maximum of 0.20 mg/L is registered at HS-15, at the distance of 3627 m. The concentration of copper is lower, about 1.85 mg/L MAC at the distance of 8.74 km from the coast compared with HS-16 located 6.4 km away of the Caspian Sea coastal line. The high concentration of nickel of 0.51 mg/L is registered at HS-15 and it is

lower, namely 0.37 mg/L and 0.39 mg/L at HS-14 and HS-17 accordingly. At HS-16, the concentration of lead is observed as 0.138 mg/L (navigable ways) and at HS-14 low content of lead is recorded 0.092 mg/L (1.15 km away of the coast).

3.3. Physical and chemical characteristics of soil

Table 5 presents physical and chemical properties of the monitoring results. Brown desert soil is widely spread within the top soil of Akshukyr settlement. The soils are associated with saline or slightly saline at the depth of the upper saline horizon.

Table 5. Physical and chemical properties of soil at the testing sites

<i>Physical and chemical characteristics of soil</i>	<i>Testing sites (soil condition monitoring)</i>			
	<i>TS-1</i>	<i>TS-2</i>	<i>TS-3</i>	<i>TS-4 (background)</i>
Humus, wt. %	1.18	1.39	1.47	2.62
Total nitrogen, wt. %	0.26	0.34	0.39	0.27
Phosphorus (bulk), mg/kg	1660.30	472.5	515.17	2004.0
Carbonates, wt. %	3.11	1.77	1.82	2.75
Exchange capacity, mg eq/100 g of soil	9.62	22.85	24.15	32.15
Exchange calcium, mg eq/100 g of soil	1.5	4.0	5.0	1.3
Exchange magnesium, mg eq/100 g of soil	7.11	17.0	18.45	11.7
Exchange sodium, mg eq/100 g of soil	0.61	0.93	0.97	16.13
Total salts, ‰	0.57	1.06	1.30	0.2
pH	7.39	7.10	7.41	6.85

The content of humus in the upper horizon of these soils varies from 1.18 to 2.62 %. It decreases to 0.42-0.97 % downwards along the profile. The content of biogenic elements is low. The bulk phosphorus in the surface horizons amounts to 515.17-2004 mg/kg. The content of carbonates is within the limits of 1.77-3.11 %. The total nitrogen varied within the limits of 0.26-0.39 %.

In general, the heavier granulometric composition the higher the exchange capacity. The exchange capacity value varies from 9.62 to 32.15 mg-eq/100 g of soil. It is observed that the exchange of magnesium prevails in the soil absorption complex (40-80% of the exchange capacity). The water suspension in soils reaction is slightly alkaline or close to neutral (pH 6.85-7.41).

The chloride-sulfate for anions and calcium-sodium for cations are widely spread among the salt formation by chemical mechanism type. The testing area soils differ by low content of organic matter, alkaline reaction of soil solutions, salinity and poor anthropogenic effect resistance.

The topsoil at all TS, except for TS-4 (background) is exposed to heavy disturbances immediately within the territory of private buildings and adjacent areas.

3.4. Content of heavy metals in the testing site (TS) soils

Fig. 4 shows that soils are not contaminated with heavy metals as the distance from TS-2 contaminated soils increases to 9.5 km relative to TS-4 (background), except for arsenic metalloid and such exceeding is naturally occurring.

If the content of copper in soils of TS-1 exceeds (1.06 mg/L MAC), TS-2 (1.56 mg/L MAC), TS-3 (1.2 mg/L MAC), then its content at TS-4 is less than 0.7 mg/L. The exceeding content of copper in soils of TS-1, TS-2 and TS-3 is substantially due to emissions of transport engaged in construction of the private sector and materials transportation (Fig. 4A). The content of nickel at TS-2 (1.32 mg/L MAC) exceeds due to effect of various paint containers and transport operated on tars (tractor machines) (Fig. 4B). Exceeding value of arsenic metalloid (Fig. 4C) is observed at TS-1 (1.45 mg/L MAC), at TS-2 (2.45

mg/L MAC), at TS-3 (2.1 mg/L MAC), and the highest value is observed at background TS-4 (3.65 mg/L MAC). This situation is due to the fact that the elevated content of arsenic in the Aktau region is natural and also associated with the natural processes of accumulation and migration. Exceeding cadmium is registered only at TS-2 (1.88 mg/L MAC) due to operation of diesel transport within the storage area and transportation of construction and road materials (Fig. 4D).

Chrome concentration does not exceed the MAC values at all TS. MAC exceeding concentration of lead was registered also at TS-2 due to the effect of exhaust gases of transport and tractor machinery and motor graders. The contents of copper, nickel, zinc, arsenic, cadmium, chrome and lead show that soils of TS-2 (open storage of road construction materials and near roads) are exposed to maximum contamination and soils of background TS-4 are exposed to minimum contamination (Fig. 4E).

3.5. Statistic processing of the study's results

Table 6 shows results of survey data analysis in Statistica. Processing of heavy metals and arsenic metalloid content in surveyed TS soils data analysis in Statistica shows that the Kruskal-Wallis criteria are statistically significant for Cu (0.047) and As (0.042). The highest rank amounts of content of copper and cadmium is characterized by series of data of TS-2 (33.5) and (29.0) accordingly. These substances make a maximum input in deference in content of these elements among all groups.

4. Conclusions

The present work represents the detailed study of the monitoring of the Caspian Sea offshore and coastal areas within the suburbs of Aktau city with various technical methods. Now, natural submarine oil seeps, exploration and drilling activities generally cause low contamination though most of the Caspian Sea. The most widespread and most hazardous pollution for the Caspian Sea is petrochemicals products. At present an average concentration of oil hydrocarbons in the Caspian exceeds 1.5-2 times the norm for fishery water bodies.

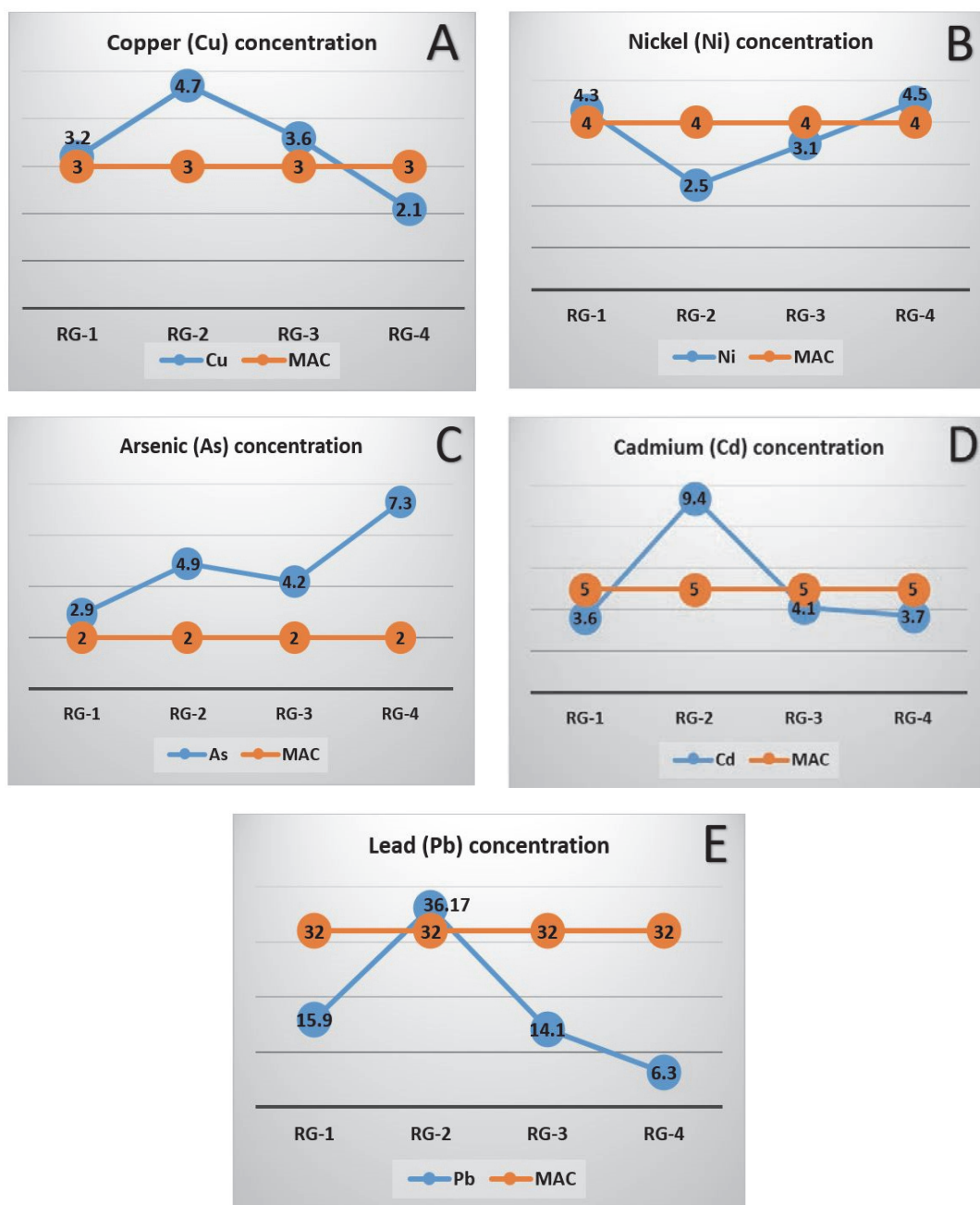


Fig. 4. Diagrams of heavy metal concentration in soils near Akshukyr settlement (Aktau suburb) at TS-1, TS-2, TS-3 and TS-4 (background): (A) Cu concentration with its MAC, (B) Ni concentration with its MAC, (C) As concentration with its MAC, (D) represent Cd concentration with its MAC, (E) Pb concentration with its MAC

Table 6. Average content of heavy metals, arsenic for 0-20 cm layer in soils of the surveyed area at TS-1, TS-2, TS-3 and TS-4 (background) and results of statistic processing in Statistica

Matter	Testing sites within the soil monitoring area				Criterion Kruskal-Wallis	Total ranks (mean rank)
	TS-1 (n = 4)	TS-2 (n = 4)	TS-3 (n = 4)	TS-4 (Background)		
Cu	2.96±0.51	4.16±1.04	2.93±0.10	1.83±1.09	0.047	33.5 (11.1)
Ni	3.72±4.36	5.11±3.27	2.56±3.16	2.45±1.50	0.084	25.5 (8.5)
Zn	11.3±2.71	16.1±3.73	6.13±4.49	7.86±5.19	0.256	27.0 (9.0)
As	2.11±0.41	3.60±0.73	3.69±0.85	7.11±0.97	0.042	22.0 (7.5)
Cd	2.54±1.75	8.45±2.05	2.81±3.65	2.91±3.81	0.842	29.0 (8.33)
Cr	3.85±0.71	5.11±1.03	2.99±1.78	2.41±1.93	0.135	23.5 (9.83)
Pb	15.1±13.7	34.9±10.2	12.7±11.6	6.15±13.1	0.532	22.0 (7.33)

Fortunately, concentrations of other hazardous pollutants do not exceed the maximum admissible levels for fishery in the Caspian Sea, if the incidents connected with local pollution and also with volley emissions and different technogenic accidents (the number of which is steadily growing). As concerns volley emissions, it should be stressed that every year approximately 20-30 such cases are recorded.

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