CHANGES IN BACKGROUND CONCENTRATIONS OF METALS IN THE SEDIMENTS OF MARSH-LAGOON LANDSCAPES OF THE WESTERN CASPIAN

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The last 1978-1995 transgression of the Caspian Sea caused the development of marsh-lagoon system along the Western Caspian seashore. Due to salt marshes are very vulnerable to sea-level fluctuations, complex and dynamic system, they may be considered as a regional model of rapid environmental transformation.
Changing conditions of migration in the soils of marsh-lagoon landscapes during the sea-level rise influenced on the migration of elements of variable valency, primarily Fe and Mn, but also Zn, Cu, Pb, Ni, Co, leading to their mobilization in slightly alkaline and neutral reducing conditions and subsequent deposition on the geochemical barriers.
That led to the emergence of landscape-geochemical anomalies of Fe and heavy metals in the soils of salt marshes with a characteristic time of formation of any persistent anomalies during 5-10 years.

Key words: Caspian Sea, fluctuations of the sea level, salt marshes, regional changes, landscape-geochemical anomalies, transport and accumulation of metals

I. INTRODUCTION

Recent climate changes have had widespread impacts on human and natural systems [9]. The rise of the world ocean's level is among the most important present-day environmental problem. Many coastal areas experience inundation and waterlogging by sea-water. Global mean sea level rose by 0.19 m over the period 1901 to 2010. The rate of sea level rise since the mid-19th century has been larger than the mean rate during the previous two millennia [9].

Coastal areas are very dynamic regions and they are of immense ecological and economic importance. Coastal wetlands, which are comprised of marshes, swamps, mangroves and other coastal plant communities, provide a large number of goods and services . Nowadays they face a number of hazards including rise in sea-level, increased atmospheric concentration of carbon dioxide, rise in air and water temperature, and changes in the frequency and the intensity of precipitation and storm patterns [2]. Sea-level rise can disrupt wetlands in three significant ways: inundation, erosion, and salt water intrusion. By the 2080s, sea-level rise could cause the loss of up to 22% of the world's coastal wetlands [18]. The threat posed by the rise in sea level has received increased attention [2, 3,18, 19].

The Caspian Sea is well known for large and rapid sea-level fluctuations. The most recent cycle lasted only 65 years [10,13]. Sea-level fell by over 3 m between 1929 and 1977 and rose again

by 2,4 m until 1995, when it started falling again [5,21]. Today it is stable at – 27.74 m below global sea-level [4]. The new method of forecasting the Caspian sea level shows, that in the coming years the sea level will rise again [17].

The Caspian Sea shores are perhaps the best sites to study the effect of sea-level changes on coasts [6,8,10, 11,12,15]. Understanding the consequences of Caspian sea-level changes is very important as they threat large areas with inundation, pollution and environmental changes [11,22].

Conducted researches have shown that different types of the Caspian Sea shores had various reactions on sea-level changes [6,8,11,12]. During transgression the intensity of coastal processes depend on the steepness of the coastal slope. The most dramatic consequences of the influence of rapid transgression were experienced by accumulative coasts [8].

Along accumulative shores transgression increases the geomorphological, lithological, soil, biotic, as well as geochemical diversity of the coastal landscapes. This is caused by the formation and landwards movement of a barrier-lagoon system, with a corresponding rise of the groundwater table, and also simultaneous vigorous development of vegetation in newly-formed hydromorphic and semi-hydromorphic areas.

The formation of the barrier-lagoon system during the last transgressive coastal cycle is typically for different regions of the Caspian shore [8,14]. Lagoon coasts occupy about 32% of the world ocean accumulative shores [20]. The domination of accumulative coasts reflects the eustatic sea-level rise in postglacial period [16]. Thus, the evolution of the Caspian coasts under the sea-level changes serves as natural model that can be used for understanding the general features of development of the world ocean coasts. Our local study of geochemical changes of the Caspian marsh-lagoon landscapes describes the regional environmental changes of the coastal zone.

The most contrasting landscape-geochemical changes of the coastal zone of the Caspian sea occurred within the lagoon shores, where a marine terrace has a small width (a few hundred meters), being replaced New-Caspian Holocene terrace outside the zone of influence of the modern sea level fluctuations. Within the modern marine terraces during transgression occurred contrasting changes in alkaline-acid and redox conditions and salinity of soils [6,11,12]. The fluctuation of the sea-level caused changes of the natural background concentrations of chemical elements in the coastal soils. The studying of such natural changes of the local geochemical background may help correctly to estimate the real level of the human-induced contamination of the coastal zone.

Our previous investigation showed that during the transgressive phase many heavy metals (Cu, Co, Zn, Ni, Cr, Fe, Pb) accumulated at geochemical barriers in the marsh-lagoon landscapes of Central Dagestan [11,12]. Their concentrations in the marsh zone became higher than in the soils of the adjoining territory. So the natural background concentrations of the heavy metals in the coastal soils were lower during the regression period and it has increased after the beginning of the Caspian sea-level rise.

In this paper we describe the changes of background concentrations of metals in the sediments of marsh-lagoon landscapes along the western coast of the Caspian sea. Our study shows that the intensity of geochemical processes, accumulation and transport of metals in soils and bottom sediments of marsh-lagoon landscapes has differences in the variety of key sites.

II. MATERIALS AND METHODS

Geochemical studies of marsh-lagoon landscapes were conducted on the 4 sites located on the west coast of the Caspian Sea. The first site is located on the coastal plain of Dagestan, the second - the north shore of the Apsheron peninsula, the third site was on Kur-Araz lowland and the fourth site - Lenkoran lowland. Landscape-geochemical catenas, crossed the main elements of the relief from the New-Caspian terrace through modern terrace to the beach, were studied using the profiling method.

Field works on the first site were conducted near the Turali research and training station, which belongs to the Moscow State University and is located 30 km to the south of Makhachkala, the capital of Dagestan. The investigations were carried out in 1995-1996 when the sea-level rose [6,11,12] and they were continued in 2001-2005 when it became stable.

The *Turali key site* stretches from the waterline across a modern constructional plain to the scarp of the New-Caspian Holocene terrace. The New-Caspian terrace is separated from the modern terrace by a relatively low scarp (up to 2 m high). The level of the terrace is 3.5 m higher than the sea level now.

The modern constructional plain varies in width from 100 to 500 m; a series of low bars of 1929, 1941, and 1956 can be distinguished within this plain. They were formed during different stages of the Caspian Sea retreating that started in 1929 (when the waterline was at 25.5 m below sea level) and continued until 1978. From 1978 till 1995 a considerable part of the 1956 terrace was inundated. At the present time, this part is occupied by 0.8-1.0 m deep and several hundreds of meters wide lagoon separated from the sea by a modern barrier beach with a height of 1.0-1.2 m and a width of 10-30 m.

The field work was carried out at a cross-section (150×400 m) stretched from the New-Caspian terrace to the sea shore through the modern strand flat. The landscape-geochemical, geomorphological, soil and geobotanical investigations were fulfilled at four parallel transects (T, 2D, 2N, 2M) located across the coastal plain (perpendicular to the shoreline).

The main transect is “T”. The study of soil pits along this transect was carried out in 1995-1996 and 2001-2005. During the fieldworks about 500 soil samples, 100 samples of bottom sediments, 100 samples of natural waters were collected.

The other key sites along the western coast of the Caspian Sea have been studied once in 1999.

The *Apsheron key site* is located near Gaia village that is 2 km to the north-north-west from the port of Apsheron. The main transect here is “Ar” (7 soil profiles), crossing the main forms of relief from the edge of the sea of modern marine terrace to the New-Caspian terrace at a distance of about 300 m.

The *Kura key site* is located on the left bank of the Kura river, 8 km from its bed, and 5 km to the north of the Bund village. Landscape and geochemical studies were conducted on the profile “K” (7 soil profiles), that intersects a system of "modern barrier beach - coastal lagoon".

The *Lenkoran key site* is located 5 km to the north of the city of Lankaran near the village Olkhovka. The length of the profile L (13 soil profiles) is about 700 meters. It crosses the main elements of relief: New-Caspian terrace - modern constructional plain - lagoon - modern barrier beach.

During the fieldworks along the Azerbaijani coast of the Caspian Sea about 160 soil samples and 24 samples of bottom sediments were collected.

The most important physical and chemical parameters of surface and ground waters and of each selected soil horizons were defined immediately at the sampling points: pH, Eh, total dissolved salts (TDS), the sodium content. The measurements were made with the help of portable devices (HANNA Instruments, Italy), providing the automatic temperature corrections of parameters. For bottom sediments and soil horizons below the ground water table the measurements were done directly and under their natural moisture. For determination of physical-chemical parameters in the soil horizons above the groundwater table, distilled water was added to each soil sample with 1:1 ratio, the mixture was stirred by plastic stick, and measurements were made in the obtained suspension.

The bulk content of chemical elements was determined by quantitative spectral method in Bronnitskaya geological and geochemical expedition.

The cation content analysis of water samples and mobile forms of chemical elements in soils were done by the atomic-absorption method using the spectrophotometer Hitachi 180 (Japan). The content of sodium, potassium, calcium, and manganese were defined without background correction, and the content of Fe, Mn, Ni, Cr, Co, Zn, Pb, Cd, Mo were defined with correction based on the Zeeman effect. For analysis of mobile forms of elements in soils and bottom sediments 1N (2N) HCl was used as the extraction agent. Water-soluble, exchangeable and amorphous forms of elements passes are extracted in this way, and also, in part, organic-mineral connections.

III. Results and discussion

Background content of trace elements in the beach sediments

Average contents of trace elements in the beach sediments change significantly along the coastal zone of the Caspian sea. The coast of Azerbaijan is characterized by a high geochemical background in comparison with the Russian coast of the Caspian sea (Table 1).

Minimal values of elements are observed in the beach sediments of the Turali key site [1], that folded by the material of Sulak river, with the participation of scattered Terek material (hornblende, pyroxene, mica).

The deposits of the modern barrier beach of the Turali site (Fig.1) are depleted in most elements in comparison to Clark [24], except for Sr that is participating in the evaporatortive concentration in the steppe and desert landscapes.

When moving to the south in areas of Apsheron and Kura there is a slight increase in the content of chemical elements, which is associated with erosion of the deluvial sediments of the Caucasus mountains with a predominance of augite, epidote, micas, pyroxenes, in co-organizing the contents of Sr, Pb, Co, Cu and Ni exceed the Clark values.

The contents of almost all trace elements (except Sr) show the maximal values in the beach sediments of Lankaran key site, due to their high content in mafic minerals (augite and titan-augite, ilmenite, magnetite, etc.) in the deluvial sediments of the Talish mountains [1].

Table 1. Average contents of trace elements in the beach sediments of West coast of the Caspian sea (mg/kg)

Key site (n-number of samples)		Fe	V	Cr	Co	Ni	Cu	Zn	As	Pb	Sr
Turali (6)	1*	5895	13,9	21,9	3,0	5,6	5,8	18,8	--	7,5	1159
	2	1382	--	0,7	0,5	0,3	1,1	4,6	--	2,6	225
Apsheron (3)	1	27000	22,9	55,3	31,6	39,7	64,9	48,9	9,3	24,8	838,7
	2	5527	--	1,3	3,1	5,3	0,9	15,1	--	4,6	351
Kura (2)	1	33000	37,9	73,2	33,3	54,5	84,7	73,2	15,1	62,0	1472,8
	2	6176	--	3,2	4,4	9,3	6,1	15,8	--	4,2	436
Lenkoran (3)	1	80000	205,9	414,4	76,2	102,6	117,7	90,4	13,0	55,3	763,4
	2	19670	--	8,1	7,0	28,1	32,0	61,3	--	11,2	96
[1] Vinogradov, 1962	1	46500	90	83	18	58	47	83	1,7	16	340
[2]Turekian, Wedepohl, (1961)	1	9800	20	35	0,3	2	X	16	1	7	20

*1-bulk content, 2- mobile forms (2нHCl).

[1] – Clark of the element in the earth's crust; [2]- the average content of chemical elements in sandstones.

The beach sediments of Turali key site are depleted in Fe, V and Cr in comparison with the average content of chemical elements in sandstones [23]. The contents of Co, Ni, Zn, Pb, Sr are higher than the average content in the sandstones. In the beach sediments of other key sites the background content of elements are above the average contents in the sandstones, while the Sr content is more in 38-74 times, Ni – 20-51 times, and Co – 100 - 250 times.

Thus, the average contents of most trace elements in the beach sediments of the coastal zone generally increase in the direction from the North to the South. The high content of Sr in the sediments of Turali and Kura key sites is due to the evaporative concentration and a large proportion of shell detritus. Sometimes it exceeds 1100 mg/kg, which is 3-4 times higher than the Clark value and its content in coastal sediments of the Lankaran key site is only 763,4 mg/kg, which is associated with a predominance of pebble material.

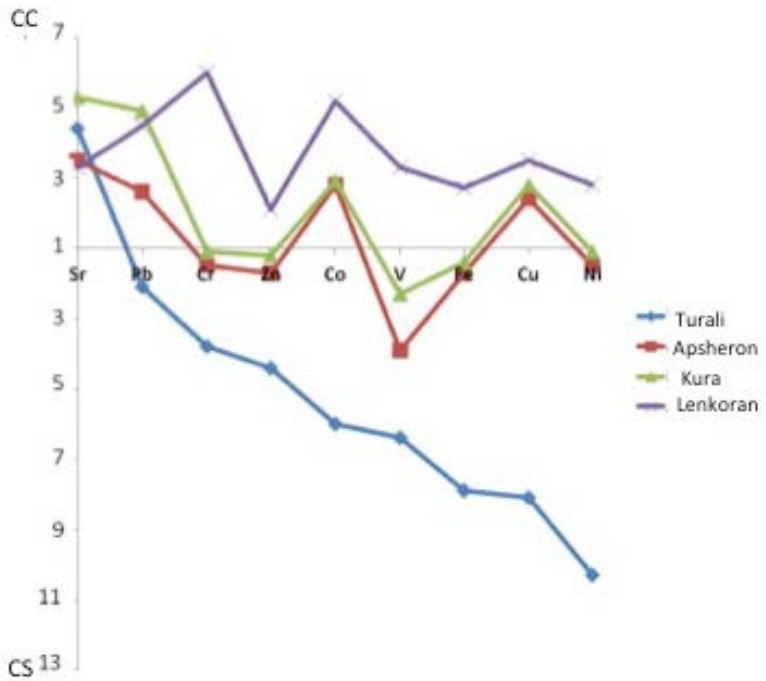

Fig. 3.4 Geochemical spectra of beach sediments along the Western coast of the Caspian sea (CC- Clark of concentration; CS - Clark of scattering)

Oxidative alkaline environment in beach sediments determines the low mobility of many cationogenic elements in soils and waters (Fig.2).

The portion of mobile forms of chemical elements does not exceed 40% in these sediments in different parts of the west coast. The portion of mobile forms of Zn (up to 67%), Cu and Ni (27 %) increases in the sediments of the Lenkoran lowland that is associated apparently with the increase in the proportion of organo-mineral complexes of these elements in the soils of variable-humid subtropics.

Thus, the migration and accumulation of chemical elements in the coastal zone occur in different geochemical background, which is determined by lithological and geochemical specialization of supply provinces.

Radial geochemical differentiation of coastal landscapes

Sea-level rise caused the transformation of migration flows. Landscape-geochemical processes in the marsh-lagoon landscapes led to the redistribution of chemical elements in coastal soils with the accumulation of certain associations of elements on geochemical barriers.

The geochemical transformation of coastal soils is related to a complex combination of landscape-geochemical processes, such as sulfidogenesis, gleyzation, iron accumulation (ferrugination), accumulation of humus and peat, halogenesis, and changes in redox conditions [11,12].

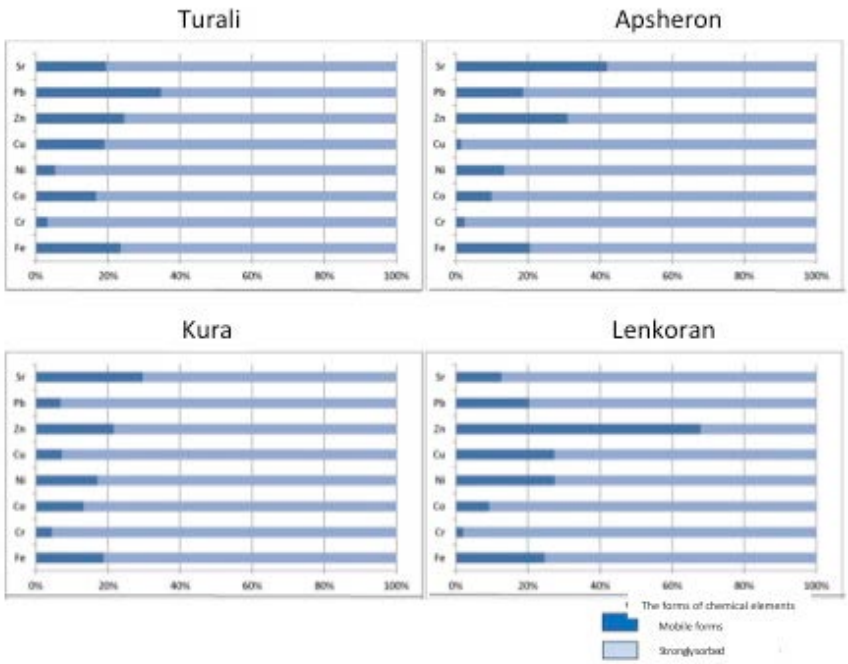

Fig. 2. The forms of chemical elements in the beach sediments of the west coast of the Caspian sea

A set of radial geochemical barriers, as well as their capacity differ in different parts of the western coast of the Caspian sea, which is associated with the heterogeneity of the migration conditions due to lithological and granulometric composition of rocks, as well as differences in bioclimatic conditions.

The main geochemical barriers in coastal landscapes with the accumulation of heavy metals are: oxygen − Fe, Mn, Co, biogeochemical − Zn, Cu, Cr, Ni, Cr, Cd, and sulfide − Fe, Mn, Zn, Cu, Co, Mo. The intensity of the oxygen barrier (accumulation ratio Fe) decreases along the west coast from north to south. Biogeochemical barriers most pronounced in soils of the Lenkoran, due to the great biological productivity of plant communities and nutrient accumulation of trace elements. The degree of appearance of sulfide barrier is the greatest in marsh soils and bottom sediments of the lagoon area of the Turali key site, the lowest –in layered marsh soils of Kura key site.

Gley, alkaline, acidic and evaporative barriers are common locally in meadow, marsh and saline landscapes. On Turali key site the contents of Mo and Cu increase on the gley barrier; of Mn, Co, Ni - on alkaline; of Mo – on acidic; of Sr - on evaporative.

Lateral differentiation of coastal landscapes

Lateral differentiation of marsh-lagoon landscapes of the Caspian sea is determined by hydrogeochemical features of groundwater flow with the chloride-sulphate-sodium composition.

There are two zones of the lateral differentiation of chemical elements within modern marine terrace. In meadow landscapes with poorly developed hydromorphic soils as the result of nutrient absorption, the mobility of cationogenic and anionic elements increases. In alkaline conditions the cationogenic elements don’t migrate, so the lateral migration which is typical only for anionic elements.

Active migration of anionic elements promotes the soda geochemical environment in the soil on the coastal shafts. The contrasting geochemical anomalies of Mo and Cr form in the wet-meadow and marsh soils.

The transformation of redox and alkali-acid conditions leads to a redistribution of cationogenic elements in the marsh zone. The mobility of Fe, Mn and Co increases in the reducing conditions that lead to their migration and accumulation on the geochemical barriers with the formation of the geochemical anomalies of these elements.

Thus, the two paragenetic associations of migration elements distinguish in the coastal landscapes, the first – the mobile forms of anionic elements (Mo and Cr) and the second – cationogenic elements (Fe, Mn, Co, Zn, Cu, Ni).

The contrast of lateral differentiation of mobile forms of Fe, Mn, Zn, Cu, Ni, Cr and Pb in soils and sediments of coastal landscapes is higher on the Lenkoran key site than in areas of Apsheron and Kura.

On the Lenkoran key site in subordinate positions of the marsh-lagoon landscapes the geochemical anomalies of Mn (up to 3.6 L), Pb and Ni (L to 3.1) are formed. In organogenic horizons of wet-meadow and marsh soils the contents of Cu, Ni, Zn increase because of biogenic accumulation. Accumulation of heavy metals and Fe also occurs in sulfide and gley barriers in marsh zone.

The coefficients of the lateral differentiation of Fe, Cr, Cu, Ni and Zn increases to 2-2,5 in the soils and sediments of the marsh zone in the Apsheron and Kura key sites.

IV. Conclusion

Geochemical features of migration and concentration of mobile forms of heavy metals and Fe in the coastal landscapes of the western Caspian region have much in common, due to the uniformity of the geochemical conditions of migration and the similar system of geochemical barriers formed in subordinate landscapes. The intensity of mobilization of cationogenic elements is determined by nutrient absorption, especially in Turali and Lenkoran key sites.

The changing conditions of migration in the marsh zone under the sea level rise significantly affected the migration of elements with variable valence, primarily Fe and Mn, but also Zn, Cu, Pb, Ni, Co, leading to their mobilization in slightly alkaline and neutral reducing conditions and subsequent deposition on a number of geochemical barriers. The geochemical anomalies of several elements formed in the marsh zone as the result of their radial and lateral migration. So, in bottom sediments of lagoons the contents of the Fe and Co increased from 1.5 times on the Lenkoran key site up to 4-5 times on the Turali key site; the content of Zn is more average in 1.5 times on all sites, and the content of Cu increased from 1.5 times at the site of Turali up to 5 times on the Apsheron key site.

Due to the sea level rise the geochemical structure of the coastal area complicated because of the formation of the marsh-lagoon landscapes that led to the emergence of landscape-geochemical anomalies of Fe and heavy metals in the soils of the marsh zone with a characteristic time of formation of any persistent anomalies of approximately 5-10 years.

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