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Heavy metals in coastal sediments of South Caspian Sea: natural or anthropogenic source?

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ABSTRACT

This paper focuses on heavy metal distribution patterns in sediments of central Guilan (CG) and east Mazandaran (EM) in the south Caspian Sea coasts, north of Iran. Sediment sub-samples were retrieved from core and surficial samples in different environments of marine and coastal lagoons as well as coastal outcrops. Inductively Coupled Plasma Mass Spectrometry and Atomic Emission Spectrometry (ICP-MS and ICP-AES) analysis were used to determine the metal chemistry. Concentration of the selected heavy metals exhibited variations through sediment samples which are partially related to grain size and organic matter content. Geoaccumulation index and statistical procedures have been implemented for analyzing the absolute metal values. Result of the geoaccumulation index demonstrated that the metal distribution reflects the influence of geological background of the watershed area. Some elements including Pb, Ni, Cu, Sr and Ba showed elevated concentration in the CG that could be attributed to development of industrial activities. A comparison of the metal concentration in the marine sediments and the Late Holocene outcrops revealed that the level of the metals concentration at the sea generally corresponds to natural background. The northern part of Iranian multi-lithological catchments basin is the main source for the sediments that drained by the rivers to the South Caspian Sea basin.

Key words: Caspian Sea, Geoaccumulation Index, Heavy Metals, Principal Component Analysis, Sediment

INTRODUCTION

Sediments are the final ambiance for precipitating a wide variety of heavy metals in aquatic environments (Clamano *et al.* 1996; Green - Ruize & Paez - Osuna 2004). Concentration of heavy metals and their distribution in sediments largely depend on the origin of the sediments that could be obtained from natural and / or anthropogenic sources (Bruland *et al.* 1974; Buccolieri *et al.* 2006). Meanwhile, closed and semi-enclosed basins are more susceptible to receive and impound the human-induced source of heavy metals. The Caspian Sea as a land locked basin, receives heavy metals through natural and anthropogenic processes, as well (Klenova 1962; Kholodov & Lisitsina 1989; de Mora *et al.* 2004). Igneous and metamorphic rocks of the catchment basin, sea bottom mud volcanoes, submarine groundwater discharge and wind-blown sediments are amongst the main natural sources of the heavy metals in the Caspian Sea, while sea - based and land -based oil industries, agricultural activities and coastal urban areas are the main anthropogenic sources. Riverine input from north, west and South Caspian Sea accompanied by coastal and sea currents play a major role in distribution of heavy metals in the basin (Klenova *et al.* 1962; Kuprin *et al.* 1974). The East Caspian coast with lack of fluvial discharge and dominant arid climate mainly comprised carbonate sediments (Lebedev *et al.* 1973). High concentrations of some heavy metals in the sediments of the West Caspian coast are attributed to the groundwater discharge (Brusilovskii & Turchkina 1974). Mud volcanoes as natural sources for introducing heavy metals into the sea are more concentrated in South Caspian basin (Glazovskii *et al.* 1976). Anthropogenic activities in and around the Caspian Sea has been accelerated since 1950s and have contaminated coastal sediments in different levels (Zonn 1996; de Mora *et al.* 2004).

To differentiate the natural and human induced parameters on heavy metal concentration and to provide a clear insight to assess the heavy metal background in sediments, geological and geochemical tools have been implemented by several researchers (Freitas *et al.* 1999; Povinec *et al.* 2003). Any difference in heavy metal concentration at top and base of each sediment column offers an opportunity to distinguish the role of human activities in heavy metal contamination (Calmano *et al.* 1996; Freitas, *et al.* 1999; Dassenakis *et al.* 2003).

Previous works on geochemistry of heavy metal concentration in the Caspian Sea have focused on bottom surface sediments, with few data points from southern coast of the Caspian Sea (Kholodov & Lisitsina 1989; de Mora *et al.* 2004). Moreover, the surficial sediments could include both anthropogenic and natural source of heavy metals. Lack of geochemical background value for sediments of the Iranian Caspian coasts is one of constraints to assess the sediment quality and to differentiate natural background of sediments from human - induced impacts. The present study intends to combine records of sedimentological and geochemical proxies retrieved from the surficial sediments, core samples and outcrops along the South Caspian coast in Central Guilan (CG) and East Mazandaran (EM) to present the geochemistry of heavy metals in the South Caspian sediments and to identify major source of heavy metals. The main aim of the present research is to introduce baseline sediment geochemistry to delimit potential contamination and / or pollution source, compared to the natural background of the basin.

Study area

The studied area is located in the South Caspian coast in CG and EM (Fig. 1). The Caspian Sea, the largest land-locked water basin in the world since isolation in the Mid Pliocene (Reynolds *et al.* 1996), is a semi-eclipse basin oriented in N-S direction with a length of about 1200 km and a width of about 400 km. Whereas the northern rivers of the Caspian Sea (Ural, Volga, Terek & Sulak) supply about 90% of fresh water discharge into the sea, the southern rivers including Kura and Sefidrud rivers are the main sources of the sediments (Mikhailov 1997; Voropaev *et al.* 1998).

The Iranian Caspian coast stretches around 820 km in the South Caspian sub-basin (Fig. 1). Due to the sea level rise and strong littoral drifts, coastal lagoons are developed in the CG and EM (Naderi Beni *et al.* 2013). The coastal lagoons receive water and sediment from streams and irrigation waters.

Apart from the southeastern flank of the Caspian Sea that is dominated by detrital carbonates, the Iranian Caspian shore is characterized by dominantly siliciclastic deposits, (Lahijani & Tavakoli 2012). The sediments mainly are supplied by 61 rivers that flow from Iranian coast to the sea (Afshin 1994; Lahijani *et al.* 2007). The area of the catchments basin is about 135000 km^2 which is comprised different geological setting and topography. Surface lithology of the catchments basin with a wide variety of metamorphic, igneous and sedimentary rocks (Aghanabati 2004) controls the composition of the riverine sediment load (Lahijani & Tavakoli 2012). Climatically, most of the Southern Caspian region lies in subtropical climate (Terziyev 1992). Precipitation gradually decreases from 1500 mm/y in the west to 150 mm/y in the eastern coast (Khaleghizavareh 2005). The catchments basin hosts more than 11 million of population. Traditionally, tourism, agriculture and fishery are the main economic activities in the region, while industrial activities get birth in 1960s and developed increasingly since then. The light industries are moderately developed in CG and EM (Lahijani 2001).

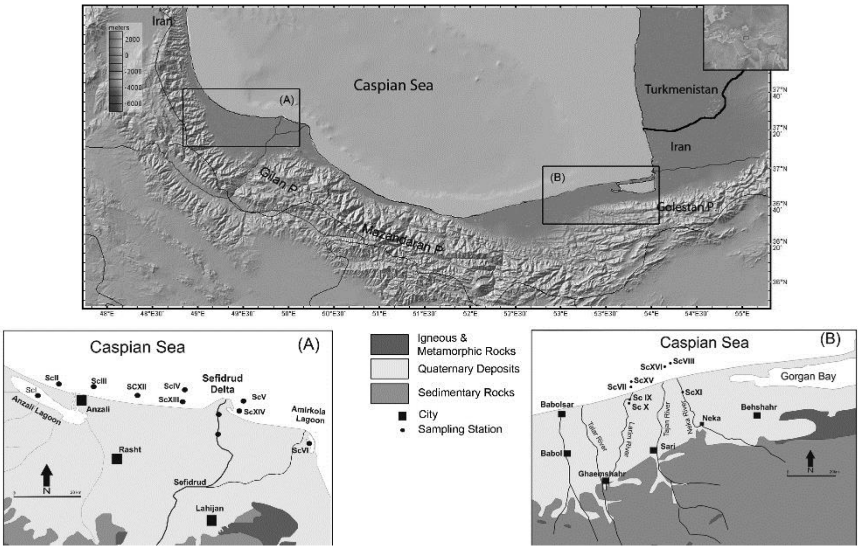

Fig. 1. Iranian coast along South Caspian Sea from GeoMapApp (www.geomapapp.org); The sampling locations and major lithological territories are shown below in A and B windows; (A) Central Guilan, (B) East Mazandaran.

MATERIALS AND METHODS

The sea floor, up to 50 meters of water depth, was cored using a KC gravity corer during two field campaigns in 2002 and 2004. In addition to the cores, the sea-bottom surficial sediments were collected with a Van Veen grab sampler. The Late Holocene outcrops and lagoonal records on land were investigated and sampled, as well (Fig. 1, Table 1). The core samples were preserved in wrapped PVC pipe with a 5.5 cm inner diameter. The disturbed samples (surficial and outcrop samples) were preserved in plastic bags and immediately transferred to laboratory. Subsamples with about 2 cm in thickness were taken from top and base of the cores using throwaway plastic sub-samplers. On the other hand, the disturbed samples were homogenized and a representative subsample was taken for each. Totally, 29 samples (cores, surface and outcrop samples) were treated for the heavy metal geochemistry. A representative portion of each sample was used for grain - size analysis using dry and wet sieving (Folk, 1974) and a "Fritsch Analysette Comfort 22" Laser Particle Sizer (LPS). To prepare the subsamples for geochemical analyses, the subsamples were finely powdered using an agate mill to achieve <63 μm particle sizes, according to several authors (Forstner 1989; Soares *et al.* 1999). Organic matter (OM) was determined by wet digestion (Schumacher 2002) on the bulk sample.

A Bernard calcimeter was used to determine calcium carbonate content, according to the method described by Vatan (1967). Elemental analyses were carried out for a total of 29 samples by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for heavy metals with the exception of cadmium and mercury (Code: ME-MS81, ALS Chemex, Canada), and Atomic Emission Spectrometry (ICP-AES) for main oxides (Code: ME-ICP06, ALS Chemex, Canada) to obtain accurate and precise elemental characteristics of the sediments.

The limit of reporting (LOR) for Cr, Cu, Zn, Ni, Pb, Co, Ga, Sr, Ba and Mn is 0.1 $mg.kg^{-1}$, for V is 1 $mg.kg^{-1}$, for Al is 5 $mg.kg^{-1}$ and for Mg, Fe and Ca is 10 $mg.kg^{-1}$.

Table 1. General characteristics of the sampling stations and the sub-sampling horizons.

Region	***Environment***	***Station No.***	***Sample No.***	***Sampling method***	***Water Depth (m)***	***Sub-sampling Horizon (cm)***	***Sediment Type***	***Fraction for Geochemistry***
Central Guilan	Anzali lagoon	SC I	S-01	Core	3	0	Mud	Clay
		SC I	S-02	Core	3	50	Mud	Clay
	Marine	SC II	S-03	Core	40.1	0	Mud	Clay
		SC II	S-04	Core	40.1	50	Mud	Clay
		SC III	S-05	Core	47.5	0	Mud	Clay
		SC III	S-06	Core	47.5	50	Mud	Clay
		SC XII	S-07	Surface	20.5	-	Sandy Mud	Clay
		SC IV	S-08	Core	56	0	Mud	Clay
		SC IV	S-09	Core	56	50	Sandy Mud	Clay
		SC	S-10	Surface	2.5	-	Mud	Clay
		SC	S-11	Surface	11.7	-	Mud	Clay
		SC V	S-12	Core	50	0	Mud	Clay
		SC V	S-13	Core	50	50	Mud	Clay
East Mazandaran	Amirkola lagoon	SC VI	S-14	Core	2.5	0	Mud	Clay
		SC VI	S-15	Core	2.5	34	Mud	Clay
	Marine	SC VII	S-16	Core	40	0	Mud	Bulk
		SC VII	S-17	Core	40	0	Mud	Clay
		SC VII	S-18	Core	40	28	Mud	Bulk
		SC VII	S-19	Core	40	28	Mud	Clay
		SC XV	S-20	Surface	10	-	Muddy Sand	Clay
		SC	S-21	Surface	10	-	Muddy Sand	Bulk
		SC	S-22	Core	40	0	Mud	Clay
		SC	S-23	Core	40	28	Mud	Clay
		SC	S-24	Core	40	28	Mud	Bulk
	Holocene outcrops	SC IX	S-25	Outcrop	-	0	Sand	Bulk
		SC X	S-26	Outcrop	-	160	Sand	Bulk
		SC XI	S-27	Outcrop	-	90	Mud	Bulk
		SC XI	S-28	Outcrop	-	520	Mud	Bulk
		SC XI	S-29	Outcrop	-	520	Mud	Bulk

RESULTS

Sedimentary pattern

The bottom morphology of the sea in the study area is characterized by a relatively steep slope. The South Caspian shelf is relatively narrow and the bottom depth of 50 m lies about 10 km off the CG shores, while about 12 km off the EM coast (Voropaev *et al.* 1998). The shores in CG and EM are covered by sandy sediments with more than 80% sandy fraction. Fine-grained portion (silt and clay) appears from depth of 5 m off the EM and east CG, whereas the bottom sediments of the west CG, toward Anzali lagoon, are mainly composed of sands. Mineralogically, main heavy minerals found in the sediments are ilmenite, magnetite, titanomagnetie, pyroxene, apatite, zircon and garnet which are transported by rivers from hinterland into the sea (Lahijani & Tavakoli 2012). Toward the EM, the proportion of the heavy minerals gradually decreases (Zenkovich 1957; Lahijani 1997).

Generally, core sediments were composed of silt and clay (Fig. 2, Table 1). Mean carbonate content of the samples were around 17% (range = 2.3% - 56.55%). The carbonate content in the EM samples averaged about 19% (range = 10.2 - 32.5%) with a slight increase toward the east (Table 2). The mean amount of organic matter is around 3.5% in CG and 1.8% in EM (Table 2).

According to the studies on the Late Holocene outcrops (Lahijani *et al.* 2009), the past sedimentary environment was a coastal lagoon, being deposited by sediments of the early historic period due to sea level fall.

The grain size and mineralogical composition of the sediments affect distribution pattern of heavy metals (Buccolieri *et al.* 2006; de Mora *et al.* 2006). Fine-grained materials have potential to adsorb soluble pollutants, while coarse grains may contain heavy metals in their mineralogical composition (Sageman & Lyons 2004). However, some heavy minerals naturally fall in the small - size fraction.

Kholodov & Lisitsina (1989) studied the association of heavy metals concentration and particle size in sediments of the Caspian Sea and found that certain heavy metals are associated with specific sediment groups.

Sedimentation rate

According to Lebedev *et al.* (1973), accumulation rate in the Novo-Caspian sediments varies from 0.6 mm.y^{-1} in the south east shelf to 0.06 mm.y^{-1} in deep basin of South Caspian Sea, while its maximum rate, 6 mm.y^{-1} was found in the west shelf of the Sea in front of Kura Delta. They concluded that the sedimentation rate in the near shore zone must be higher than that in the shelf and deep basin. The latest dating in Kura Delta (Hoogendoorn *et al*. 2005) indicated that the sedimentation rate is around 12mm.y^{-1}. Sefidrud and Kura, as the greatest rivers of the South Caspian Sea, provide annually around 30 and 20 million tons of sediments into the basin, respectively (Mikhailov, 1997; Krasnozhon *et al.* 1999). Sefidrud River provides huge volume of sediment to develop the delta on a relatively narrow shelf of the South Caspian sub-basin. Long-shore currents transport the sediments eastward and consequently bend the delta lobes in the same direction (Naderi Beni *et al.* 2013). Based on ^{210}Pb and ^{137}Cs dating, the sedimentation rate in Sefidrud Delta is around 8 mm.y^{-1} for the west side and 14 mm/y for the east side (Vahabi Moggadam *et al.* 2008) which is comparable with Kura Delta.

In spite of different coastal settings, the EM and west CG coasts show similar characteristics in many aspects. The CG and EM are depositional coasts even during the sea level rise (Voropaev *et al.* 1998). Streams with similar rate of water discharge and load supply flow into the coasts. Moreover, the coastal morphology, shelf slope, the eastward long-shore and sea currents (Vorapaev *et al.* 1998; Terziyev 1992) are other main common features. As a result, a sedimentation rate of 8 mm.y^{-1} could be proposed for the regions. It means that the base of a core with 40 cm long could be attributed to 1960s with less influence of industrial activities. The estimated rate of sedimentation in Anzali lagoon is around 5 mm.y^{-1} (Vahabi-Moghadam *et al*. 2006).

According to Lahijani *et al.* (2009) the Late Holocene outcrops are attributed to 2400 years BP and are not influenced by anthropogenic activities.

Table 2. The concentration of heavy metals, main oxides, calcium carbonate, organic matter and grain size.

Sample No	Cr	Cu	Zn	Ni	Pb	Co	Ga	V	Sr	Ba	MnO	MgO	Al_2O_3	Fe_2O_3	$CaCO_3$	OM	Sand	Silt	Clay
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
S-01	110	37	110	65	55	18	18.2	139	356	372	0.29	2.78	13.8	6.92	4.50	7.50	0	75.2	24.8
S-02	120	61	106	73	21	20.2	20.2	178	375	401	0.21	3.16	15.9	7.57	2.30	6.50	0	82.7	17.3
S-03	110	32	85	65	20	16.8	15.2	138	575	594	0.11	3.11	13.15	5.65	26.13	3.08	0	68.7	31.3
S-04	100	31	81	66	13	17	15.2	138	587	357	0.13	3.11	12.95	5.45	17.75	2.88	0	59.8	40.2
S-05	110	37	89	68	23	18	15.2	140	577	434	0.12	3.07	12.7	5.46	23.23	3.74	0	61.5	38.5
S-06	100	30	83	65	12	16.9	15.2	136	657	428	0.13	3.3	13.1	5.64	22.00	3.30	0	57.6	42.4
S-07	90	38	85	53	17	16.9	15.8	150	465	462	0.11	3.16	13.85	6.22	12.23	2.28	21.2	14.7	64.1
S-08	100	37	84	61	63	17	15.4	138	552	451	0.1	3.22	13.25	5.73	14.28	3.82	0.0	56.2	43.7
S-09	100	34	78	62	14	17.4	14.8	138	534	432	0.1	3.03	13.35	5.63	9.70	2.94	2.4	63.3	34.3
S-10	90	47	98	61	22	19.8	17.8	146	296	425	0.11	3.5	14.65	6.23	18.20	3.28	1.2	52	46.8
S-11	90	48	86	53	17	17.8	15.6	136	361	446	0.11	3.27	13.65	5.83	13.66	3.62	0	56.1	43.9
S-12	100	41	85	60	20	17.1	15.4	138	539	403	0.11	3.33	13.35	5.92	12.10	3.10	0	64.2	35.8
S-13	100	43	84	59	15	17.6	15.3	140	478	439	0.12	3.21	13.6	5.9	9.80	1.20	0	61.25	38.75
S-14	50	19	49	29	9	8.8	8.5	62	923	371	0.18	2.29	7.27	3.32	56.55	6.96	0	67.6	32.4
S-15	110	39	82	41	18	17.3	15	156	477	537	0.12	3.04	13.25	6.23	14.29	1.37	0	65.6	34.4
S-16	100	26	94	52	18	17	14	106	554	341	0.07	3.09	11.3	5.2	10.20	1.57	0.1	74	25.9
S-17	100	29	81	50	18	17.8	15	116	596	350	0.08	3.32	11.9	5.45	10.20	1.57	0.1	74	25.9
S-18	90	37	118	56	22	18.8	16	122	636	350	0.08	3.38	11.35	5.43	17.10	0.74	0.1	76.3	23.6
S-19	90	30	84	50	18	17.2	15	113	568	343	0.08	3.54	11.55	5.52	17.10	0.74	0.1	76.3	23.6
S-20	100	14	80	39	17	14.9	11	97	492	379	0.09	3.32	8.11	5.2	24.00	0.25	89.87	6.45	3.68
S-21	90	19	79	44	17	15.3	14	98	401	358	0.09	2.87	10.55	5.09	18.00	2.97	65.05	21.2	13.75
S-22	90	30	81	49	29	16.5	14	109	644	369	0.08	3.47	11.65	5.5	14.20	1.92	0	72.3	27.7
S-23	90	29	80	50	16	16.6	15	116	607	344	0.08	3.56	11.85	5.45	16.20	1.32	0	75.8	24.2
S-24	90	27	87	49	17	16.8	15	112	541	359	0.08	3.46	11.9	5.46	16.20	1.32	0	75.8	24.2
S-25	40	10	74	28	12	9.7	11	56	664	416	0.06	2.08	8.09	3.47	32.50	2.00	96	4	0
S-26	100	26	93	47	12	14.7	16	121	697	297	0.08	2.44	11.7	5.59	25.00	1.50	88	10	2
S-27	100	23	88	49	10	14.8	16	122	417	277	0.06	2.54	12.3	5.25	26.00	5.50	92	6	2
S-28	60	12	61	31	11	11.1	9	63	511	295	0.08	2.73	7.34	3.88	31.00	2.50	0	52	48
S-29	130	16	98	49	11	13.8	21	148	232	438	0.04	2.28	15.8	5.99	0.00	0.00	0	52	48
Mean	95	31	86	53	20	16.3	15	123	528	395.45	0.11	3.057	12.18	5.52	17.74	2.74	15.73	54.57	29.7
STD	18	11	13	12	12	2.63	2.67	28	137	68.44	0.05	0.40	2.21	0.86	10.81	1.91	33.28	24.54	15.54
Min	40	10	49	28	9	8.8	8.5	56	232	277	0.04	2.08	7.27	3.32	0	0	0	4	0
Max	130	61	118	73	63	20.2	21	178	923	594	0.29	3.56	15.9	7.57	56.55	7.5	96	82.7	64.1

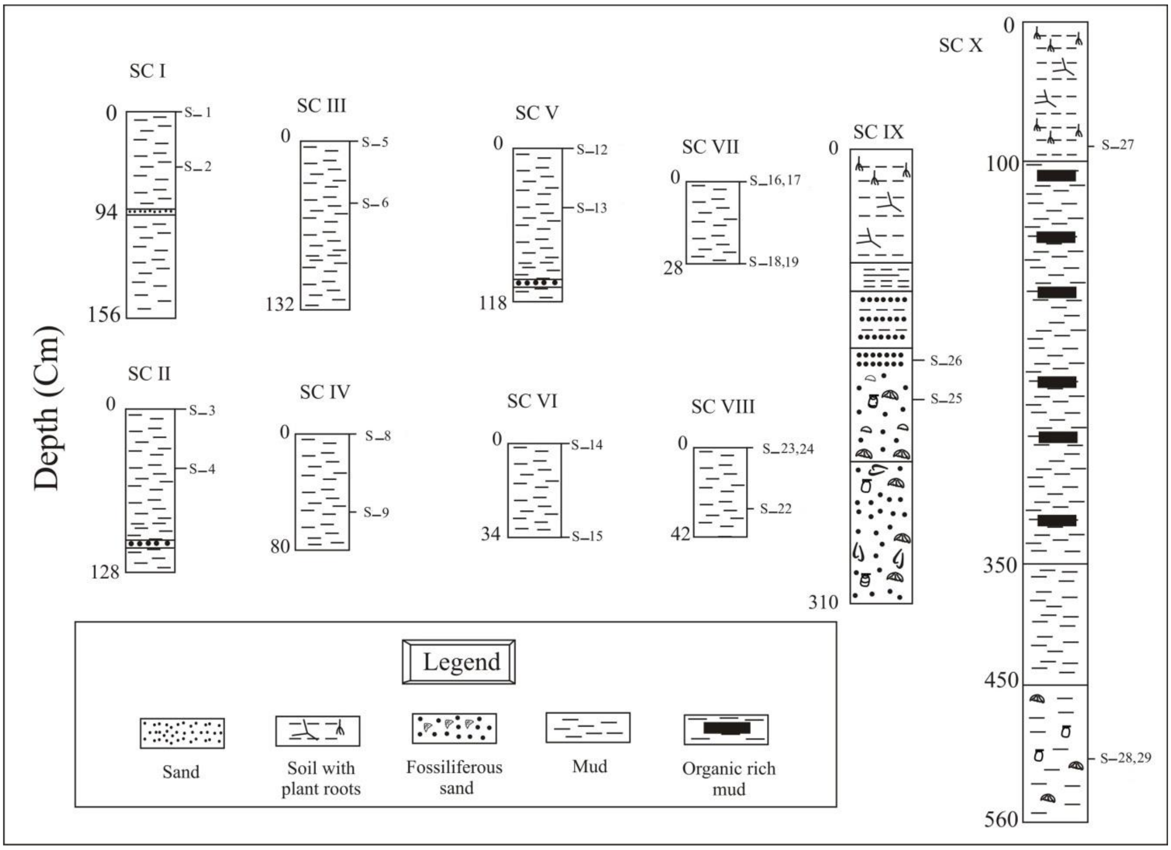

Fig. 2. Lithological column of the cores and outcrops and subsampling horizons.

Heavy metal distribution

According to Table 2, Cr, Zn, V, Ba and Sr exhibited a mean concentration of 94, 85, 122, 395 and 528 ppm, respectively. The samples were averagely characterized by 12% Al_2O_3, 5% Fe_2O_3, 0.1% MnO and 3% MgO content. Concentration of Cr, Ni, Co, Ga and V showed elevated values for samples from Anzali Lagoon, EM cores and the outcrops. A sharp decrease of the above-mentioned metals occurred for the EM outcrops and Amirkola Lagoon in the east CG.

Little variations were observed for these elements in the samples (St. 10 and St. 20). The last mentioned elements had relatively similar variations compared to Al_2O_3 and Fe_2O_3. Cu had a mean value of 31 ppm that shows higher concentration in the CG. The mean value for Sr and Ba were 528 ppm and 395 ppm, respectively. Sr had higher values in EM where Ba had elevated values in CG. MgO demonstrated a little variation in sediments with average of 3%. MnO varied from 0.29% in CG to below 0.04% in EM.

Pb had higher concentration on top of the Anzali Lagoon core (S-01) as well as the CG marine core (S-08). The value of Zn displayed similar trend with Pb in CG except for Anzali lagoon. The concentration of Zn in the EM samples was comparable with Cr, Co, Ni and V. Generally the heavy metal concentrations had slightly higher values for the CG samples in comparison with those for the EM. The observation was more obvious for V, Ni and Pb.

DISCUSSION

Relation of metal concentration and sediment type

Fine-grained sediments contain organic matter that has potential to adsorb heavy metals during settlement. The higher concentration of the metal in these sediments occurs due to ionic attraction and higher surface area relative to volume (Mc Cane 1984; de Mora *et al.* 2004). Investigation of the heavy metal distribution in the Caspian Sea sediments revealed that fine-grained sediments display a higher value for the metal concentration (de Mora *et al.* 2004). Kholodov & Lisitsina (1989) in their comprehensive investigation of the Caspian surface sediments suggested that the heavy metals could be classified in three groups: the first group (Cr, Zr) is tended to be accompanied with silty sediments, which are mainly associated with Piconite and Zircon. The second group (Cu, Co, Ni, Ga, Mo, Mn, Fe) and in some regions Pb, exhibit association with clay sediments. They exist in wide variety of minerals and in soluble phase which absorbed by clay sediments during settlements. The third group (Ti, V, Ge) show mutual association either with fine-grained and coarser - grained sediments.

In the studied area, the distribution of some metal concentration (Cr, Cu, Pb, Ni, Co) in the sedimentary samples are closely related to the silty fraction. Ba and V have more correlation with clay fraction. The main oxides have positive correlation with silty sediments except for Al_2O_3 which is more associated with clay (Table 3). There is not any correlation between organic matter content and heavy metal concentration except for Pb and Ni that are moderately correlated. There is a relationship between MgO concentration and organic matter content in sediment samples. The heavy metal concentration is strongly correlated with Al_2O_3 and Fe_2O_3, while it is less obvious for Ba and is negative for Sr. Calcium carbonate show negative correlation with the metals where sharply associated with Sr. Whereas Al_2O_3 and Fe_2O_3 are the main products of weathering, the association of the metals with them indicate the terrigenous source of the metals. Pb and Ba could have human - induced sources. Higher value of Ba could be due to the sea-based human activities for oil exploration (de Mora et al., 2004). The association of Pb with organic matter is thought to be due to the presence of Pb in seawater and enrichment of the metal in organic matter. The land-based industrial activities in CG are thought to be the cause of elevated concentration of Pb (Sajjadi *et al.* 2007). The correlation and enrichment of Sr in sediments with high carbonate content may be related to biological processes. Sr is one of the constituting elements of aragonite secreted by organisms and can be found in shells (Gillikin *et al.* 2005). The Caspian coastal environment is rich in bivalves from Cardiidae and Dreissenidae families (Logvinenko *et al*. 1968). The shell structure of these families composed of aragonite (Pathy & Mackie 1992). Biogenic sediments could be attributed as the source of Sr and its association with calcium carbonate.

Origin of heavy metals

The ratio of surface area of the Caspian catchments basin to the sea surface is around 9:1 (Voropaev 1998). According to the land-locked nature of the Caspian Sea, human activities as well as the natural background of the watershed area could be reflected in the sediments of the depositional environment. The geological setting, topography and climate determine the rivers discharge into the Caspian Sea. Riverine input, wind - driven sediments and biogenic sediments are responsible for sediment distribution pattern in the Caspian Sea (Klige & Selivanov 1995). The Caspian Sea with three sub-basins including north, middle and south basins has different geological settings. Riverine input (Klenova *et al.* 1962; Kuprin *et al.* 1974), mud volcanoes (Glazovskii *et al.* 1976), submarine groundwater seepage (Brusilovskii & Turchkina 1974) and wind - driven sands (Lebedev *et al.* 1973) are the main natural sources for heavy metals. There is strong relationship between the heavy metal concentrations with the sediment distribution pattern (Kholodov & Lisitsina 1989). Since the beginning of industrial activity in the Caspian littoral states in the past century, anthropogenic source of heavy metals in the sediments can be considered as a new important factor (Komorov 1998). However, development and intensity of the human activities have not been identical to the littoral states of the Caspian Sea (Tarasov 1994; Komorov 1998; Lahijani 2001). The industrial activities had begun at the end of 19th century at the north and west Caspian coasts while the activities in the South Caspian coasts began later in 1960's.

Land-based and sea - based anthropogenic sources of the heavy metals are reflected in the geochemistry of the surface sediments as anomalies. The higher values of Ba are partially attributed to the human-induced origin (de Mora *et al.* 2004). Agriculture, urban development, tourism and fishery are the main human activities in the Iranian catchments basin (Lahijani 2001). Assuming 8 $mm.y^{-1}$ as the average rate of sedimentation for the South Caspian coast, the basal core subsamples provide indicator of marine environment with negligible human impact. Moreover, heavy metal concentration in the Late Holocene outcrops offers opportunity compared to approximately unaffected environment. Quantitative assessment of aquatic sediments based on comparison with background values originally introduced by Müller (1979). This method is widely applied for the evaluation of marine sediments (Rubio *et al.* 2000; Zhang *et al*. 2007). Selection of the background level for quantitative analysis is a matter of debate (Rubio *et al.* 2000). Background values should be derived from uncontaminated sediments with the same environmental setting. Using average worldwide shale or soil metal contents for the background could cause misinterpretation for a specific region (Gibbs 1993). The natural metal sources have different distributions which cause regional and local impacts on the sediment quality. Heavy metal geochemistry of the Caspian Sea has been introduced by Kholodov & Lisitsina (1989) and de Mora *et al.* (2004). Both of the investigations have focused on the surface sediments that could include anthropogenic and natural effects on the sediment quality. It is difficult to make an assessment of the degree of metal contamination in marine sediments especially when the amount of natural background in the sediments is not available (Rubio *et al.* 2000). Therefore, choosing a background value for the sediments of the Iranian coast of the Caspian Sea is essential to assess the pollutant level. Müller (1979) proposed an index of geo - accumulation (Igeo) as a useful tool to compare the modern sediments relative to the pre-industrial ones.

The Igeo depends on the used background data. Here in this research the Igeo has been calculated using the average of the heavy metal concentration in the base of the marine core samples. Based on the Müller's classification (1981), the values around zero represent the unpolluted environment. Positive increasing of Igeo values shows a very strong polluted environment for the values higher than 5 (Table 4).

In addition to gaining more precise results and better comparison, we used the average values of the heavy metal concentration from the previous results (Kholodov & Lisitsina 1989; de Mora *et al.* 2004) summarized in Table 5.

Table 4. Müller's classification for the geo-accumulation index (Müller, 1981).

Igeo Value	Class	Quality of Sediment
≤ 0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly to extremely polluted
> 5	6	extremely polluted

The calculated Igeo shows mainly negative values except for Pb, Ni, Cu, Sr and Ba in the sediment samples of CG. The Ni values have a maximum of 0.4 that fall in the unpolluted - to moderately-polluted classes. The samples from Anzali Lagoon and the core samples of the marine environment adjacent to Anzali Port show elevated amounts of Igeo for Pb which exhibit second class with unpolluted-to moderately-polluted sediments.

Table 3. Correlation matrix of elements, main oxides, calcium carbonate, organic matter and grain size.

	Cr	**Cu**	**Zn**	**Ni**	**Pb**	**Co**	**Ga**	**V**	**Sr**	**Ba**	**MnO**	**MgO**	**Al_2O_3**	**Fe_2O_3**	**$CaCO_3$**	**OM**	**Sand**	**Silt**	**Clay**
Cr	1	0.46	0.63	0.70	0.24	0.69	0.79	0.84	-0.54	0.28	0.15	0.29	0.79	0.83	-0.73	-0.05	-0.25	0.25	0.13
Cu		1	0.51	0.74	0.33	0.81	0.60	0.80	-0.31	0.37	0.47	0.53	0.74	0.78	-0.50	0.31	-0.50	0.47	0.34
Zn			1	0.60	0.36	0.70	0.81	0.63	-0.50	0.03	0.18	0.24	0.64	0.73	-0.67	-0.02	-0.10	0.19	-0.09
Ni				1	0.38	0.82	0.70	0.82	-0.31	0.30	0.40	0.47	0.79	0.76	-0.57	0.27	-0.45	0.43	0.30
Pb					1	0.36	0.26	0.27	-0.17	0.16	0.44	0.23	0.26	0.39	-0.33	0.33	-0.25	0.26	0.12
Co						1	0.69	0.81	-0.43	0.24	0.23	0.75	0.75	0.85	-0.72	-0.02	-0.44	0.45	0.22
Ga							1	0.85	-0.64	0.21	0.18	0.18	0.93	0.86	-0.78	0.06	-0.24	0.23	0.16
V								1	-0.53	0.47	0.30	0.38	0.95	0.92	-0.70	0.11	-0.39	0.29	0.37
Sr										-0.17	-0.06	-0.09	-0.60	-0.61	0.68	0.00	0.04	0.08	-0.21
Ba										1	0.16	0.11	0.42	0.31	-0.15	-0.02	-0.31	0.15	0.44
MnO											1	-0.01	0.23	0.41	-0.06	0.76	-0.30	0.34	0.11
MgO												1	0.29	0.45	-0.40	-0.26	-0.48	0.49	0.26
Al_2O_3													1	0.88	-0.76	0.11	-0.42	0.31	0.40
Fe_2O_3														1	-0.81	0.12	-0.32	0.30	0.21
$CaCO_3$															1	0.21	0.32	-0.30	-0.21
OM																1	-0.08	0.11	0.00
Sand																	1	-0.90	-0.72
Silt																		1	0.35
Clay																			1.0

The Anzali Lagoon receives pollutants from the west CG cities (Ghodrati & Zahedi 2001) including Rasht, the capital of the Guilan Province with over 500,000 population and light industries. Anzali lagoon, the host of 11 rivers (Afshin 1994) with untreated - and poorly-treated sewage inflow of relatively low - energy environment and fine - grained material (Kazanci *et al.* 2004), provides a potential environment for settling the pollutants. Some parts of the pollutants through Anzali inlet enter to the Caspian Sea which moves eastward by littoral currents. The currents in offshore have the same direction as the near-shore (Shipilova 2000) that facilitate the eastward distribution of the pollutants. The elevated values for Pb in the CG marine core could be attributed to the Anzali lagoon source.

Table 5. Heavy metal concentration in the Caspian sediments from Kholodov & Lisitsina (1989), de Mora *et al.* (2004) and the present study.

	Cr (ppm)	Cu (ppm)	Zn (ppm)	Ni (ppm)	Pb (ppm)	Co (ppm)	Ga (ppm)	V (ppm)	Al_2O_3 (%)	Fe_2O_3 (%)
Mean values of core samples	97.50	34.58	83.83	55.50	16.25	17.32	15.48	131.08	12.70	5.78
Mean values of surface samples	91	29.8	83.2	52.7	26.7	15.67	14.19	114.2	11.646	5.262
Mean values of outcrop samples	50	11	67.5	29.5	11.5	10.4	10	59.5	7.715	3.675
Mean value of South Caspian Sea (de Mora *et al.* 2004)	85.2	34.7	85.3	51.6	18	15.9	15.9	116	6.05	3.55
Mean value of South Caspian Sea (Kholodov & Lisitsina 1989)	98	55	-	53	-	18	-	129	-	-

Principal component analysis (PCA) was applied to the data sets achieving a new insight to the results. The PCA method have widely used for reduction and elaboration of environmental data (Danielsson *et al.* 1999; Rubio *et al.* 2000; Buccolieri *et al.* 2006). Three primary PCs (principal components) make up 67% of total variance for data variables and 72% for stations (Fig. 3). The plot of three loading components is presented in Fig. 4. In which, variables are defined as data values (A) and stations (B). In the plot of PCs, based on data values, two main groups have been identified. The first group contains main heavy metals and organic matter. The metals which are closer to the organic matter, partially reflect their anthropogenic input. The others are mainly related to the terrigenous origin of the metals. The second group including calcium carbonate and Sr indicate their biogenic sources.

The terrigenous source of the CG and EM samples can not be distinguished based on the PCA plot of stations. Only three stations are scattered from the main groups that reflect partially polluted areas in CG (St. 1, 2 and 14). The South Caspian coastal sediments are rich in heavy minerals which bearing different heavy metals originated from its vast catchment basin through riverine inflow (Lahijani & Tavakoli 2011). Their signatures are reflected in the sediment geochemistry as elevated concentration of some heavy metals, however they are attributed as natural sources (de Mora *et al.* 2004; Sohrabi *et al.* 2010; Ghanbarpour *et al.* 2014). The densely-populated area of the South Caspian coast mostly engaged in agriculture, fishery and service sectors, while light industry is concentrated in the Central Guilan & Central Mazandaran (Lahijani 2001; Pak & Farajzadeh 2007). Several ports and coastal industries are located in the Anzali, Nowshahr and Amirabad areas. In spite of limiting urban and industrial land-use to around 1%, they introduce high-pollutant load to wetlands (Ghafouri *et al.* 2010). Heavy metals bounded in mineralogical lattice are not bioavailable, moreover enrichment factors and compared to the background levels indicate their natural sources for most studied areas and elements. The slightly-elevated concentration of Cd and Pb as moderately pollution are attributed to the anthropogenic activities (Sohrabi *et al.* 2010; Zaman-Ahmadmahmoodi *et al.* 2013).

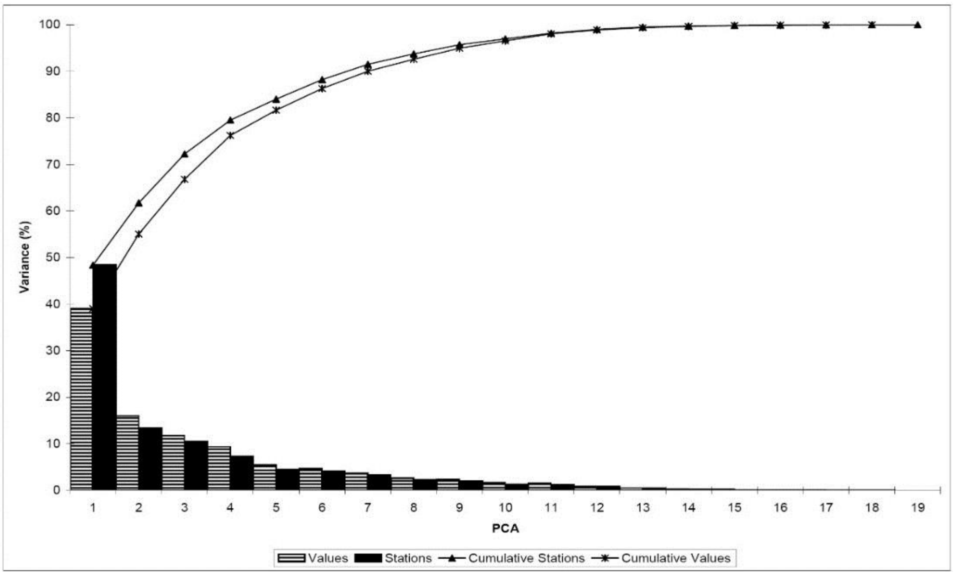

Fig. 3. Factor loading of the first three principal components and their cumulative frequencies.

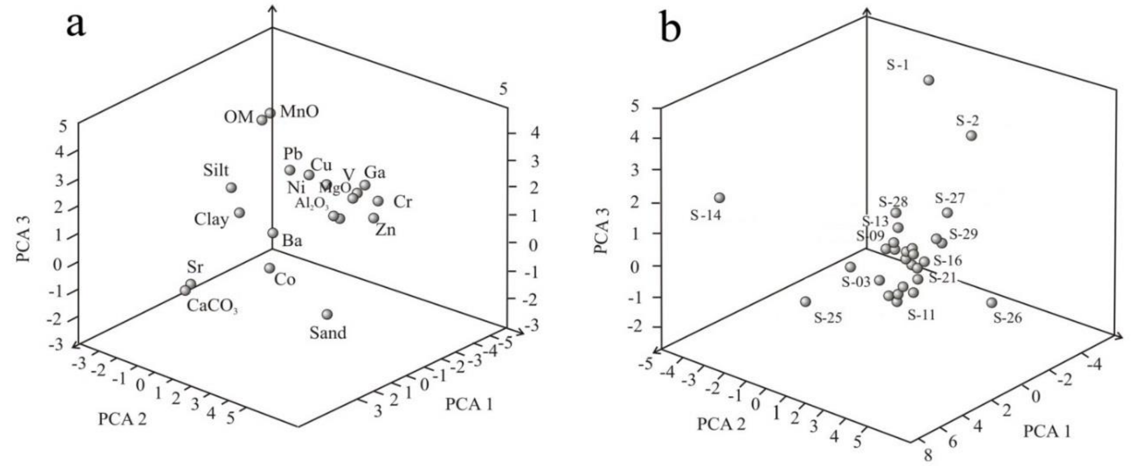

Fig. 4. PCA plot of loading factor 1, 2 and 3. **a)** variables are data values; **b)** variables are stations.

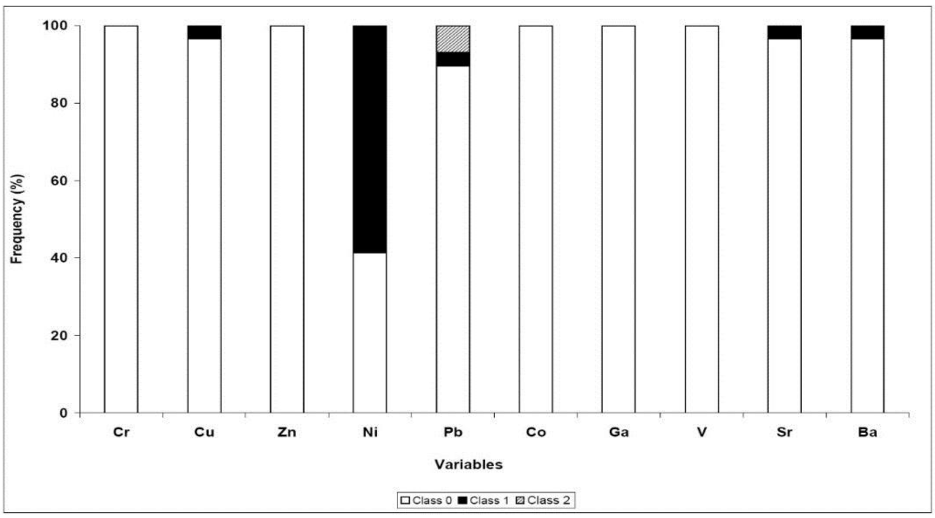

Fig. 5. Frequency of samples for Cr, Cu, Zn, Ni, Co, Ga, V, Sr and Ba in Müller's classification (1981).

CONCLUSION

In the present research the South Caspian coastal sediments have been analyzed for the heavy metal concentration which provided background information for the region.

Geo-accumulation index was calculated on the base of the average values of heavy metals in the basal samples of the marine cores as a background level. They exhibit unpolluted sediments for the most metals while Pb and Ni show elevated values for the CG samples. Based on the Müller classification (1979) they fall in the moderately - polluted class. The pollutant could be supplied from the CG to Anzali Lagoon and then through eastward currents to the coastal sediments.

Statistical elaboration revealed that the heavy metals have good association with Al and Fe as the indicators of source rock origin. They partially differentiate the terrigenous, biogenic and anthropogenic source of the heavy metals. In general, concentration of the selected heavy metals in the surface sediments in comparison with those in the basal cores and the Late Holocene outcrops display the influence of the natural sediment supply on the metal geochemistry. Higher concentration of the heavy metals in the CG samples reflects both natural and anthropogenic sources for Pb and Ni.

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فلزات سنگین در رسوبات خزر جنوبی: منشاء طبیعی یا انسانی؟

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چکیده

تمرکز پژوهش حاضر بر روی الگوهای توزیع فلزات سنگین در رسوبات بخش مرکزی گیلان و شرق مازندران در سواحل دریای خزر در ایران است. آزمایش‌ها بر روی نمونه‌های رسوب سطحی از بخش دریایی ساحل، نمونه‌های گرفته شده از مغزه‌های رسوبی دریایی و تالابی و همچنین نمونه‌های رخنمون‌های رسوبی هولوسن پایانی انجام شد. برای تعیین مقادیر فلزات سنگین، روش‌های ICP-MS و ICP-AES مورد استفاده قرار گرفت. تغییرات غلظت فلزات سنگین در نمونه‌های رسوبی نشان می‌دهد که این تغییرات تا حدی مربوط به اندازه دانه و محتوای ماده آلی است. از شاخص غنی شدگی و روش‌های آماری برای تجزیه و تحلیل مقادیر مطلق فلز استفاده شد. نتایج شاخص غنی شدگی نشان داد که توزیع فلزات، متاثر از زمینه ژئوشیمیایی منطقه حوضه آبریز است. برخی از عناصر شامل سرب، نیکل، کروم، استرانسیم و باریم نشان‌دهنده غلظت بالاتر در بخش مرکزی گیلان هستند که می‌تواند به توسعه فعالیت‌های صنعتی مرتبط باشد. مقایسه غلظت فلزات در رسوبات دریایی و رخنمون‌های رسوبی هولوسن نشان داد که سطح غلظت فلزات در دریا به طور کلی با زمینه ژئوشیمیایی منطقه مرتبط است. حوضه آبریز دریای خزر در ایران با لیتولوژی متنوع، منبع اصلی رسوباتی است که از طریق رودخانه‌ها به خزر جنوبی وارد می شود.

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