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Effects of Heavy Metals from Petroleum Pollutions on Carbonate Surface Sediments of the Persian Gulf

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ABSTRACT: Persian Gulf is a tectonic intra-continental sediment basin in which 40% of global oil and gas trade carries out and is a rich oil and gas resource. Persian Gulf area is about 236000km2 that is one of the largest marine habitats including corals, sponges, crabs, fishes, clams, scaphpoodas, cephalopodas, foraminiferas, echinodermatas, ostracodas and bryozoas. some of them live in seabed sediments of Persian Gulf and their footprints of are still available and visible on the sediments. This study aimed to identify the effects of oil filters, drilling platforms and ship traffics on seabed sediments. we used 240 surface sediment, Sampled Sea cruise named (MG-2008-PG Cruise) within six fractions and sedimentary components were studied during morphoscopic and morphometric tests by Binocular Microscope as well as Electron Microscope in some cases. Chemical synthesis carried out with chemical analysis with ICP instrument and organic material proportion determination by Rock-Eval device. Results indicate that the effect of pollution in Persian Gulf has endangered fauna environments and absorption by shells has changed skin color to red, grey, and black. Some shells have deformed and lost their ornament. In addition, pollution has led to change the color of ooids. It identified that black color was due to existence of hydrous iron sulfide, organic materials, and oil pollutants. the source of elements could rather be from organic sources such as oil.

Key words: Persian Gulf, Petroleum, Pollutants, Sediment, Ooids

INTRODUCTION

Persian Gulf is a marginal sea that is on the continental shelf and its down slope is along Oman Sea (Aghanabati, 2004). Persian Gulf is asymmetric and its south coast slope is gentler than north coast. In other words, longitude axis of Persian Gulf divides it into two parts: one is southern stable single-slope that is Arabian foreland shield and it has very gentle slope and the other is northern unstable part that is a part of folded Zagros Mountains and its slope variation is 175 cm/km. Persian Gulf is at 26◦46" latitude north and 48◦-5637" east longitude to 2950" north latitude and 4848" east longitude of Greenwich meridian. Iran has the highest water joint border in Persian Gulf and it has a way through the Strait of Hormuz and Makran Sea (Oman) to Indian Ocean from the east and it leads to Arvand River in Iran's Khuzestan from the west which is composed of two Tigris and Euphrates Rivers in Iraq as well as Karun River attachment in Iran. Meteorologically, it has arid and semi-tropical climate with the average depth of 30m. Nowadays, Persian Gulf has surface area about 236000km2 (AGO, 2003). Persian Gulf sediments have three origins: clastic sediments carried by rivers and the wind, biochemical sediments including benthic fauna particles, and carbonate mud and ooids as chemical sediments (Lak *et al.*, 2011).

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Benthic organisms have effective role in the formation of carbonate components in sediments.
Main part of carbonate components in sediments of Persian Gulf has comprised calcareous foraminifera and mollusks. (Baltzer and purser, 1990; Al-ghadban *et al.*, 1998).

The textural characteristics and regional grain-size distribution of bottom sediments in the Persian Gulf have been discussed in detail by Al-Ghadban et al. (1996). Sedimentation rates of bottom sediments in the Persian Gulf show marked regional differences, depending on offshore morphology and/or type of sediment. The bathymetry of the Inner Sea basin has been subdivided into a series of bathymetric provinces (Purser & Seibold, 1973).

From the perspective of geology, Persian Gulf is low depth tectonic subsidence that was formed late tertiary in the southern margin of Zagros Mountains

(AGO, 2003). Iranian east coast islands in Persian Gulf from Lavan to Lark have considerably developed from special forms of coral reefs. Some of islands near the coast such as Lark and Hormuz are of most important salt domes that have a margin of coral reefs and marine terrace. They are small in size and circular in shape, formed by salt domes with a little marginal sediments and relatively smooth morphology (Ghazban, 2007).

Trace element pollution in aquatic environment sediments caused by industrialization has been reported by many researchers around the word (Al-Masri *et al.*, 2002 and Coker *et al.*, 1995).

Geochemical studies of sediment are helpful in the assessment of pollution (Farmer, 1991 and Holm, 1988). It is believed that metals in adsorbed carbonate, sulfide and organic bonds are more related to pollution and have higher risk of bio-availability and contamination of the environment (Lee and Cundy, 2001; Karbassi and Amirnezhad, 2004).

Between 19 and 30 January 1991, an estimated 10.8 million barrels (mbbls) of oil were spilled deliberately by Iraqi troops in Gulf waters, mainly from seven abandoned tankers and the Al-Ahmadi Sea Island terminal near the coast of Kuwait, in addition to smaller discharges from the Iraqi Mina Al-Bakr terminal and nearby sunken tankers, and the Saudi Ras Al-Zur refinery at Mina Sa'ud (Tawfiq & Olsen, 1993). It also is estimated that oil fallout from the smoke plumes of the over 600 oil-well blow-outs and fires, started in late February 1991 by departing Iraqi troops, doubled the size of the oil slick and made this event the largest of its kind in the history of marine pollution (Reynolds, 1993). Due to their hydrophobic character and bioresistant properties, these organic compounds also adsorbto the particulate matter and accumulate in bottom sediments below the aerobic surface layer, where they can remain unchanged and toxic for long periods, thereby having a long-term effect on the structure of the benthic community (Blumer, 1970).

Increasing development of industries without considering environmental concerns has caused serious and irreparable damages to the environment. The purpose of this study is to identify sediments of Persian Gulf's bed and to determine the effect of available pollutants on these components.

MATERIALS & METHODS

The study area includes bed sediments of the northern part of Persian Gulf at2646" north at latitude and 48-5637" east at longitude to2950" north at latitude and 4848" east at longitude of Greenwich meridian means to water border of Iran, as shown in Fig. 1.

Studied samples had been taken in MG-2008-PG Cruise of geology organization by the van veen grab with research vessel-owned Islamic Republic of Iran Navy. Sampling network was done on a grid with 15km distance and 240 samples of surface sediment were obtained for this study.

In order to identify sediment components , the samples were first dried and weighed and then they were soaked in distilled water. Sediment particles were separated with ultrasound device and sediment aggregate particles larger than 63µ were identified by wet sieving method. After drying each fraction, some samples in 2mm, 1mm, 500µ, 250µ, 125µ, 63µ fractions were studied by mineralogical, morphoscopy, and morphometric tests.

In this study, particles larger than 125µ were studied using SMZ 1500 Nikon Binocular microscope and particle shape, roundness and granularity was verified in each sediment class. After studying sediment particles by microscope, they were photographed by DS-Fi1 Nikon camera.

Electron microscope resolution is better than optimal microscope, means that smaller components can be seen with electron microscope such that the resolution depends on light wavelength shining on the sample. Electron microscope resolution is at least 100 times better than the best optical microscopes. The samples were investigated in Razi Research Institute by VEGA 2 TESCAN device with the ability of point analysis.

During the study, sediment components whose colors had been changed were separated using Binocular and then they were submerged in 0.1N hydrogen peroxide. After fully boiling and removing organic materials, they were analyzed (Carter & Gregorich, 2008). Meanwhile, the samples were analyzed for some other marine geology management purposes that their results are provided as follows.

Organic geochemical studies were conducted including Total Organic Carbon (TOC) determination by Rock-Eval II beside TOC Module available from Petroleum Industries Research Institute. During pyrolysis method, the kerogen oxygen content is proportional with released CO_2 and the kerogen hydrogen content is proportional with released hydrocarbon form kerogen thermal cracking, based on which oxygen index versus hydrogen index diagram is defined and plotted (Peters, 1986).

RESULTS & DISCUSSIONS

Generally, the most important chemical–biochemical sedimentary components in the sea sediment of Persian

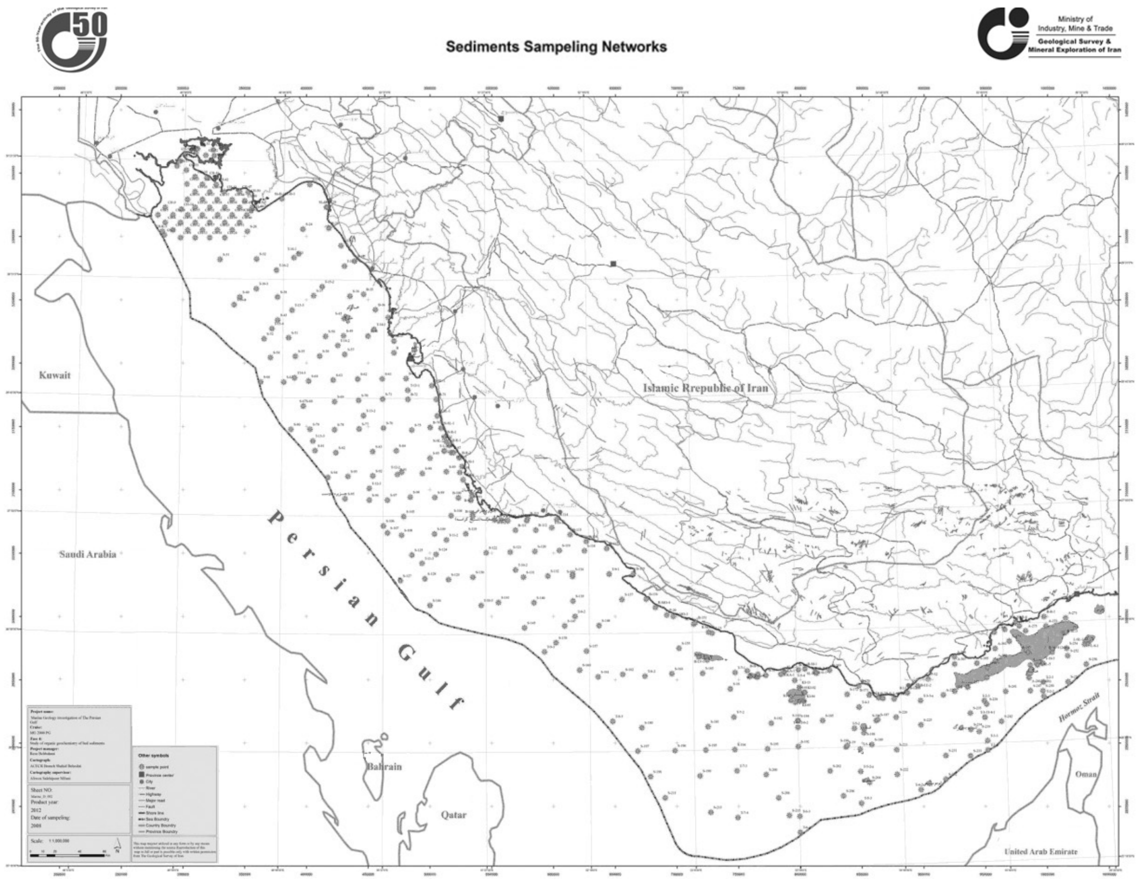

Fig. 1. Sediment sampling network of Persian Gulf (after lak *et al.*, 2010)

Gulf are of skeletal type. These parts and shell fragments include bivalves, milliolides, foraminifera (globorotalia, rotalia, textolaria and etc.), ostracod, gastropoda, echinoderm fragments, and broken pieces of crab, crinoid spine, coral, Bryozoa, scales and notochord of fish, pellets and ooids in the sediment of Persian Gulf (Perser, 1984).In larger fractions, percentages of shell fragments, rotalia, gastropoda, and sometimes notochord of fish, echinoderm fragments are more than other fragments. Shells are affected by the pollution and their colors are changed from white to red, brown and gray to black color.

There are some pieces of polluted colony of coral reef in the southern border of Qeshm Island which their colors have changed from cream, red, brown and gray to white color like shell skins.

Some deformed shells have lost their decorations and often became ooids cores such that their color has also changed (Figs 4-6). Ooids are formed in low-depth tropical areas when $CaCO_3$ratio has reached to over saturate level. Also, water turbulence, CO_2 emission and temperature rise, may be enough for depositing carbonate over the nucleus. Biochemical origin depends on organic cohesion that covered ooids and penetrate into them (Sheppard and Price, 1992). Due to gentle topography and favorable environment for carbonate-producer organisms, the sediments on the floor of Persian Gulf are rich of benthic organisms. These sediments which are mainly composed of foraminifera are observed in most beds (Berkowitz *et al.*, 2008). Clastic particles are less than %10of the sediments including quartz, feldspar, mica, opaque minerals, and rock fragments. Thus, Persian Gulf sediment environment is even carbonated in southern and south-eastern areas. Littoral sediments were determined in the study that biochemical components (shells) again have formed most of particles and pollution in the basin has led to shell color to be changed. Global changes in sea level and the topography of sedimentary basins, two important factors in the creation of oxygen-poor basins were considered suitable for the preservation of organic matter (Haq *et al.*, 1988).Global changes in sea level curve in the lower Eocene suggests that sea level rise has been greatest at this time (Haq *et al.*, 1988) The

Fig. 2. Samples from sediments of central Persian Gulf related to the area near coast of 500 microns fraction

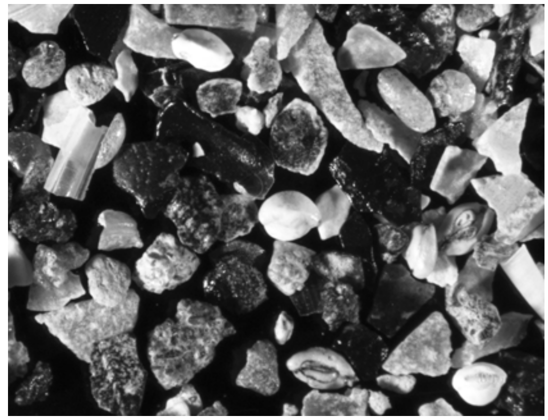

Fig. 3. taken sample from sediments of central Persian Gulf area related to 8 meters deep in littoral area of 125 microns fraction, milliolide has deformed and sediment color has changed to brown

Fig. 4. Samples from sediment of eastern Persian Gulf related to 80meters deep of 500 microns fraction

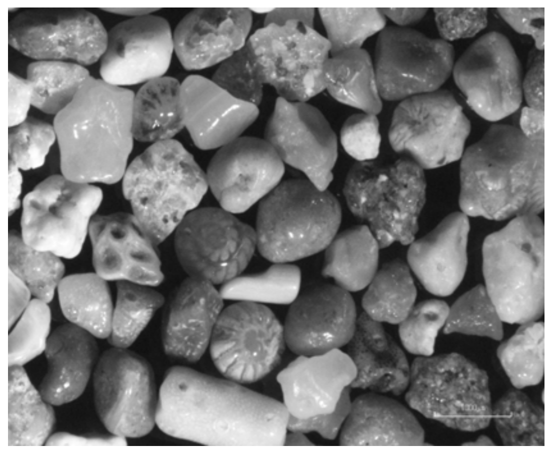

Fig. 5. taken sample from sediment of east Persian Gulf area related to 21 meters deep of 500 microns

best conditions for the preservation of organic matter in sedimentary basins (Emery and Mayers 1996).

Due to existence of high flows and intense waves, the shells had transported and displaced on the coast and the pollutions in the basin have led to shells color to be changed (Figs 2-6). Moreover, in more depths, the shells have remained more intact due to reduction of wave energy. Some shells due to exposing to oxidant environment, ferruginous minerals and clays have entered into their networks and they have been returned into the sea due to re-transportation thus they are observed in red to brown color. Sometimes, shell and/or littoral particles in red or brown color are carried by water to the depths. Unlike other elements, iron has environment cleanup property. Iron oxides and hydroxides have a high potential to absorb pollutant elements especially in alkaline pH (Faure, 1992). Of other methods of absorbing toxic elements and pollutants are clays. These minerals exist more at basin floor. An interesting characteristic of colloids is to release negative charges at alkaline pH and H positive charges in acidic pH in aquatic environment. All colloids are free of charge (between 6.5-8.5), (Moore, 2000), called zero point of charge (ZPC) (Hester and Harrison, 1997). Zero point of charge used for description of relative frequency of positive and negative electrical loads soil colloids.ZPC means positive and negative electrical loods of ZPC ph are equal In this level of pH, absence of negative or positive charge causes to approach colloid particles together and to coagulate. If environmental pH exceeds ZPC level of colloids, colloidal surfaces release more negative charges and vice versa. Therefore,

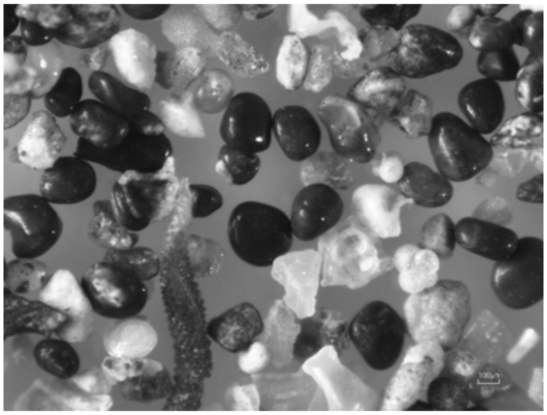

Fig. 6. taken sample from sediments of central Persian Gulf area related to littoral area that can be seen the effects of waves and pollutions on some shells

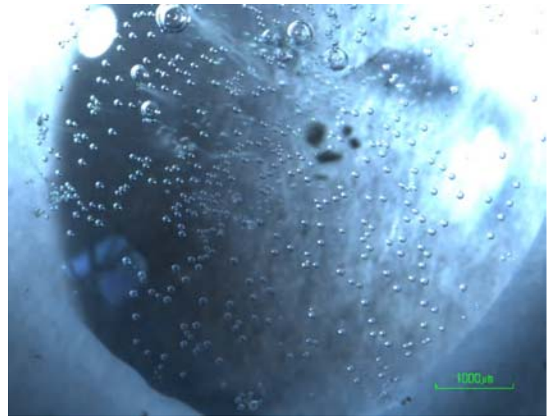

Fig. 7. Black color gastropode that are reacting with hydrogen peroxide

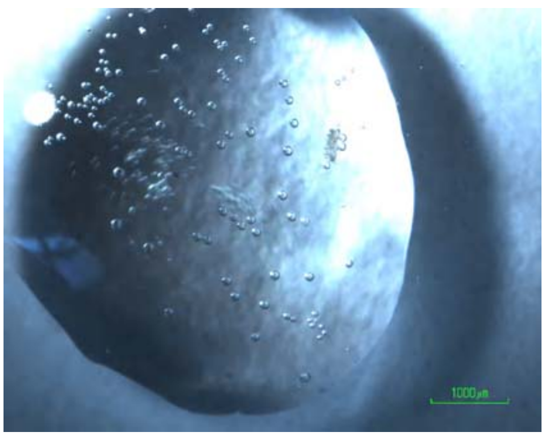

Fig. 8. Black color foraminifera that are reacting with hydrogen peroxide

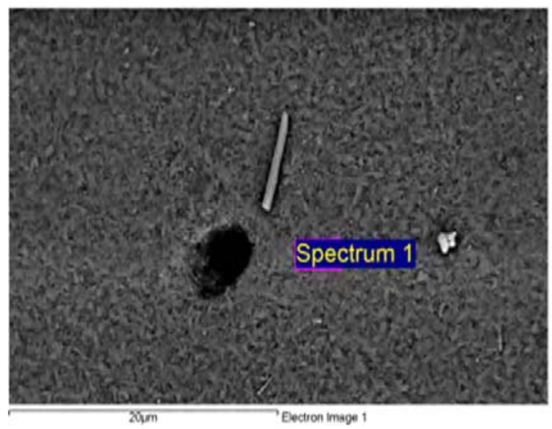

Fig. 9. black color ooid sample that we see in fig. 9. In this figure, it was drawn in study with electron microscope

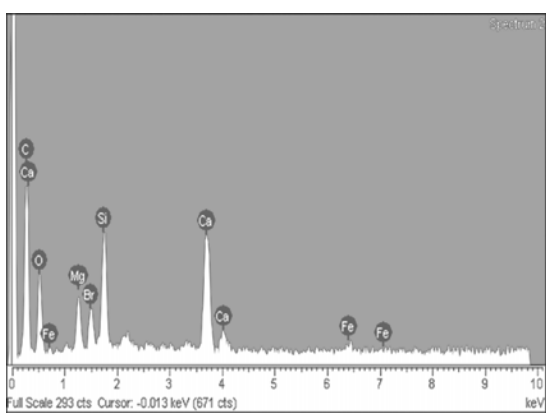

Fig. 10. black color ooid sample from western area sediment in study with electron microscope

carbonated particles in alkaline condition can absorb soluble metal cations. Also, organic material reacts against hydrogen peroxide (H_2O_2) and start to boil and vanish (Berkowitz *et al.*, 2008).

Black color gastropoda and foraminifera samples react with hydrogen peroxide are shown in Figs 7 and 8, respectively. Some shells and ooids were separated under Binocular microscope which are observed in black and then studied with electron microscope. A sample of ooids have affected by pollution can be seen in Fig. 9 and 10.

Chemical analysis with ICP results show frequency and confirmation of these elements with TOC. Therefore, we can infer that organics are the main source of metals. Here, the organic source is nothing but oil. In bed surface sediments, concentration of V reaches 100ppm, Ni 149ppm and Cr 219ppm but the average concentration of these elements in bed sediments of the Persian Gulf are 52ppm, 70ppm and 88ppm, respectively. Therefore, fauna shells have absorbed the contamination. TOC results are shown in Table 1.

Table 1. Results obtained from Rock-Eval pyrolysis for verification of organic material percentage (Behbahani, 2011)

	Sample	TOC	Cr	Ni	V		Sample	TOC	Cr	Ni	V
1	A-229	0.04	122	81	62	31	T-1-2	0.74	101	91	76
2	A-245	0.15	87	45	33	32	T-2-1	0.03	29	12	17
3	A-246	0.27	13	10	8	33	T-2-2	0.24	68	48	34
4	A-259	0.17	147	116	78	34	T-2-3	1.48	87	68	53
5	A-271	0.15	145	111	76	35	T-3-1	0.26	105	95	72
6	A-305	0.06	136	82	64	36	T-3-2	0.72	78	69	54
7	A-307	0.07	129	82	67	37	T-3-3	0.24	24	15	18
8	B-116	0.23	83	67	54	38	T-3-3-A	0.60	34	31	22
9	B-117	0.1	31	15	23	39	T-4-1	0.25	131	113	85
10	B-151	0.44	98	88	68	40	T-4-2	0.22	36	33	19
11	B-167	0.06	68	40	40	41	T-4-3	0.76	31	33	15
12	B-170	0.3	96	89	66	42	T-5-1	0.28	85	78	50
13	B-310	0.25	120	108	88	43	T-5-2	0.38	19	19	11
14	BLE-2	0.16	122	103	88	44	T-5-2A	0.88	78	68	49
15	BT-1	0.48	78	73	57	45	T-5-3	0.34	44	37	24
16	KH-D	0.05	198	127	91	46	T-5-4	1.17	51	38	26
17	KHJA-2	0.04	219	147	87	47	T-6-1	0.95	123	106	76
18	KH-T	0.09	216	149	99	48	T-6-2	0.49	76	60	45
19	LS-1	0.06	66	16	18	49	T-6-3	0.89	70	65	40
20	P-23	0.52	104	97	74	50	T-6-4	0.51	31	30	19
21	S-18	0.09	80	63	67	51	T-7-1	0.25	54	41	34
22	S-19	0.11	107	90	79	52	T-7-2	0.68	104	86	60
23	S-20	0.11	110	105	85	53	T-7-3	1.13	73	62	42
24	S-21	0.24	112	94	84	54	T-7-4	1.24	50	36	25
25	S-24	0.27	103	94	91	55	T-8-1	1.04	88	91	58
26	S-26	0.22	107	91	90	56	T-8-2	0.86	73	69	46
27	SL-B-1	0.22	95	78	17	57	T-8-3	0.25	42	29	24
28	SL-D-1	0.04	24	18	19	58	T-9-1	0.91	96	79	59
29	SL-H-1	0.21	5	4	4	59	T-9-2	1.31	92	81	59
30	T-1-1	0.30	154	122	100	60	T-9-3	0.94	103	103	64

*mg/kg

As seen, average TOC is 0.36 %. The greatest TOC value is 1.48% (Behbahani, 2011). It can be concluded that contamination existed in sea water which is really heavy metals soluble in sea water has been absorbed by skin organisms and entered to deposit phase.

CONCLUSIONS

Components of surface sediments in the northern part of the Persian Gulf comprises bivalve, milliolide, foraminifera (globorotalia, rotalia, textolaria and etc.), ostracoda, gastropoda, the pieces of ecinodermata, broken pieces of crabs, the crinoid spine, the coral, bryozoa, scales and notochord of fish, pellets and ooids. Bivalve, gastropoda, ecinodermata and crabs shell is mostly observed in littoral zone Sea sediments are mostly included inter-basin foraminifera, gastropoda, ostracoda. Clastic particles are seen in smaller fractions. Shells have been carried due to flow intensity in the coast. In some littoral samples, decorations on the shells are eliminated due to more transportation and abrasion of shells. From the coast to the more depths, the amount of more intact shells is increased, and the amount of clastic sediments is decreased. Obtained results of chemical analysis of discolored samples that contain environmental pollutants show that the maximum concentration of V ~100ppm, Ni ~149ppm and Cr ~219ppm in black color samples while the average value of these elements in bed sediments of the Persian Gulf is 52ppm, 70ppm and 88ppm, respectively. The average TOC is 0.36 %and highest TOC is 1.48%.

Every 4 to 5 years the water of Persian Gulf is exchanged with those of Oman Sea and this provides ample time for oil pollution to adversely affect the shells of organisms.

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REFERENCES

Aghanabati, A. (2004). Geology of Iran, Geological Survey of Iran. P.578-582.

Al-Ghadban, A. N., Massoud, M. S. & Al Abdali, F. (1996). Bottom sediments of the Arabian Gulf; I. Sedimentological characteristics. J. Univ. Kuwait (Sci), **23,** 71-88.

Al-Masri, M.S., Aba, A., Khalol, H. and Al-Hares, Z. (2002). Sedimentation rates and pollution history of a dried Lake: Al-Oteibeh Lake. Science of the Total Env.**293 (1-3),** 177-189.

Army Geography Organization. (2003). Geography of Iran Islands (Gheshm, Larak, Hormoz and Hrngam); p. 627.
Army Geography Organization.(2003). Geography of Iran Islands (Lavan), p. 267.

Baltzer, F. and Purser, B. H. (1990). Modern alluvial fan and deltaic sedimentation in a foreland tectonic Setting: the lower Mesopotamian Plain and the Arabian Gulf. Sedimentary Geology. 16:pp. 175-197.

Behbahani, R. (2011). Organic Geochemistry study of bed sediments Persian Gulf. Geological Survey of Iran, 95p. (In Persian).

Berkowitz, B., Dror, I. and Yaron, B. (2008). Contaminant Geochemistry: Interactions and Transport in the Subsurface Environment, Springer-Verlag Berlin Heidelberg, pp. 412.

Blumer,M. (1970). Oil contamination and the living resources of the sea. Food and Agriculture Organization Tech. Conf. Rome, FIR: MP/'IO/R-1, p. 11.

Coker, W.B., Kettles, I.M. and Shilts, W.W. (1995). Comparison of mercury concentrations in modern lake sediments and glacial drift in the Canadian Shield in the region of Ottawa/Kingston to Georgian Bay, Ontario, Canada: Water, Air and Soil Poll. 80, 1025-1029.

Dehghan Chenari, A., and Lak, R. (2011). Morphometery and mineralogy of the Persian Gulf sediments,Geological Survey of Iran, p.498.

Ghazban, F. (2007). Petroleum Geology of the Persian Gulf, Tehran University. 2007; p.658-660.

Gruijter, J.D., Brus, D., Bierkens, M., Knotters, M., (2005). Sampling for Natural Resource Monitoring. Springer pub. 332p.

Farmer, J.G. (1991). The perturbation of historical pollution records in aquatic system : Environmental Geocchemistry and Health. **13(2),** 76-83.

Faure, G. (1992). Principles and application of inorganic geochemistry, John Willey, pp. 526.

Folk, R. L. (1974). Petrology of Sedimentary Rocks. Hamphill,p. 182.

Hester, R. E. and Herrison, R.M. (1997). "Contaminated Land and Reclamation", issues in environmental science technology, The Royal society of chemistry, p.145.

Hester, R. E. and Herrison, R.M., (1997). "Contaminated Land and Reclamation", issues in environmental science technology, The Royal society of chemistry:145 pp.

Karbassi, A. R. & Amirnezhad, R. (2004). Geochemistry of heavy metals and sedimentation rate in a bay adjacent to the Caspian Sea. Intl. J. Env. Sci. Tech., v.1., No.3, pp. 199-206.

Lak, R., Behbahani, R., Chanani, N. (2001). Marine geology of the Persian Gulf (Faz 1 sedimentology), Geological Survey of Iran, p. 220.

Lak, R. (2007). Paleoceanography (paleogeography, paleoclimatology and sea level change) of the Persian Gulf, Geological Survey of Iran report, Marine geology department. 2007.

Lee, S.V. and Cundy, A.B. (2001). Heavy metal contamination and mixing processes in sediments from the Humber Estuary, Eastern England. Estuarine Coastal and Shelf Sci. **53 (5),** 619-636.

Moore, YA. (2000). Chemical speciation modeling as an aid to the cost-effective evaluation of hazards from mine Waste, British Geological Survey Technical Report WC/99/39.

Peters, K. E. (2010). "Guiedlines for evaluating petroleum source rock using programmed pyrolysis", AAPG Bulletin, 2010: V. 70, pp.318-329.

Purser, B.H. (Ed.) (1973a). The Persian Gulf: Holocene Carbonate Sedimentation and Digenesis in a Shallow Epicontinental Sea. Springer Verlag, Berlin, 471 pp.

Purser, B. H. & Seibold, E. (1973). The principal environmental factors influencing Holocene sedimentation and diagenesis in the Persian Gulf. In The Persian Gulf ed. B.H. Purser. Springer, New York, USA, pp. 1-9.

Reynolds, R. M. (1993). Physical oceanography of the Gulf, Strait of Hormuz, and the Gulf of Oman: results from the Mt Mitchell Expedition. Mar. Pollut. Bull., **27,** 35-59.

Sheppard, C. and Price A. (1992). Marine Ecology of the Arabian Region: Patterns and Processes in extreme tropical environments London, Academic Press.

Tawfiq, N. & Olsen, D. A. (1993). Saudi Arabia's response to the 1991 Gulf oil spill. Mar. Pollut. Bull., **27,** 333-345.

Carter, M. R. & Gregorich, E.G. (2008). Soil Sampling and Methods of Analysis. Canadian Society of Soil Science, 1224 pp.