

## Heavy metal concentration in the surface sediment of Bidkhun mangrove forest, Nayband bay, Iran

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**Abstract.** Bidkhun mangrove swamp, located in Nayband bay in Bushehr province in south of Iran is surrounded by huge establishments of refineries and natural gas industries of Pars South Gas Zone. Heavy metals, as a main pollution produced by oil and gas industries is considered in present study. Cadmium (Cd), nickel (Ni) lead (Pb), copper (Cu), zinc (Zn), vanadium (V) and arsenic (As) are measured in surface sediment using atomic absorption spectrophotometer. Total organic carbon and sediment grain size also were determined. Samples were collected from six stations distributed throughout the Bidkhun creek during two seasons of summer and winter. There was no correlation among sediment features and heavy metal concentration. Heavy metal concentrations were significantly different among various stations ( $p < 0.05$ ) but no significant difference between two seasons was observed ( $p > 0.05$ ). Results showed that heavy metals concentration exceed primary standards in most cases and reach to the secondary levels in stations affected by sewage canal.

**Key Words:** Persian Gulf, Bidkhun, mangrove, heavy metals, pollution.

**Introduction.** Heavy metals are one of the major pollutants in aquatic ecosystems (Ochieng et al 2007). Besides natural sources, industrial and agricultural activities as well as urbanization are named as artificial sources of heavy metals (Heba et al 2004). Although, most of them are required for normal growth of reproducers, but high level of them could be toxic for plants and other organisms (Nies 1999; Ke et al 2011) and have potential of bioaccumulation and biomagnification in live organisms (Usero et al 2005). Heavy metals enter the surface sediment of coastal area and show higher concentration in these areas and can threat human health (Dias et al 2009). Environmental persistence and toxicity of heavy metals including cadmium (Cd), nickel (Ni), lead (Pb), copper(Cu), zinc (Zn), vanadium (V) and arsenic (As) caused to be reported as serious pollutants of aquatic ecosystems which could affect food chains (Kishe & Machiwa 2003). Some of them (i.e. Ni and V) are toxic for mangrove trees too (Harbinson 1986).

The Persian Gulf with shallow water and narrow strait has been affected by several industrial activities including oil and natural gas exploration and extraction as well as intensive shipping and fishing. Bidkhun mangrove swamp as a part of northern coasts of the Persian Gulf also has been impacted with several anthropogenic effects and contaminants discharge (Parvinnia et al 2009). This habitat is located in northern coast of Nayband bay and is surrounded by industrial establishments of the biggest world natural gas field (South Pars, in Iran). These industries discharge contaminants including PAH's and heavy metals including Zn, Fe, Cu, Cd, V and Pb (Meyers 1997). Official and urban establishments also have affected this habitat. A concrete sewage canal enters the

northern part of this habitat and discharge sewages to this ecosystem that may contains toxic pollutants including heavy metals.

Some studies have showed high level of heavy metals in the northern part of the Persian Gulf (e.g. DOE Report 1996; Aminipouri et al 1999; ROPME report 1999; Zare-Maivan 2004) and some other studies reported high pollution of heavy metals in adjacent ecosystems to Bidkhun mangrove swamp (e.g. Zare-Maivan 2010; Amini et al 2013; Dehghani et al 2014), however there are few data about pollution in Bidkhun mangrove swamp. Davari et al (2012) reported high level of heavy metals in Nayband bay mangrove ecosystems in four years ago. Recently, this has been reported that discharge of sewage into the Bidkhun mangrove has made an eutrophication in regions around sewage canal opening, as a sequence of high nutrition levels of discharged sewage. These have led to excessive growth of reeds and algae and sequentially decrease of macrofauna communities and mangrove trees (Kamalifar et al 2016). Present study was performed to investigate the level of heavy metals and to study effect of sewage discharge and industries on heavy metal concentration of surface sediment in Bidkhun mangrove swamp.

## Material and Method

**Study area.** Bidkhun mangrove swamp is located in northern coasts of the Persian Gulf, in Nayband bay, Bushehr province, Iran ( $52^{\circ}66'04''$  E and  $27^{\circ}46'34''$  N). This habitat consists of mature mangrove trees (*Avicennia marina*) with the coverage of 171 hectares (Amiri et al 2011). The main canal located in the southern part; connect the Persian Gulf water to the creek. A sewage canal also discharges urban and official sewages to the northern part of the creek (Figure 1).

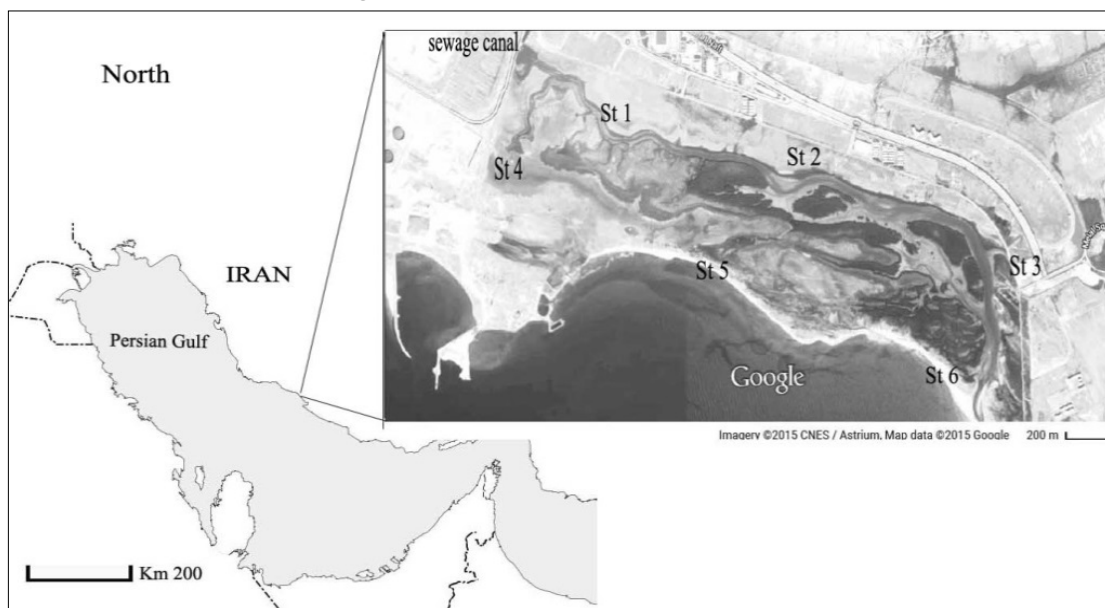


Figure 1. Sampling site, stations and location of sewage canal.

**Sampling design.** Sampling was performed in January and June 2014. Six stations were selected to cover the whole ecosystem. Three stations were close to land area and three stations in seaward sides of the creek. Station four and one were located near sewage canal entrance (Figure 1). Three sediment samples were taken with a hand-driven soil auger at each station from surface sediment to depth of 10 cm. Samples were stored and transported in a clean plastic container that had been rinsed off with warm deionized water in advance. Labeled containers were kept in cold temperature at  $4^{\circ}\text{C}$  or less until they were ready for chemical analysis.

**Sample preparation.** The sediment samples were dried in an oven for 24 hours at  $105^{\circ}\text{C}$ . Then sediments were sieved through  $25\ \mu\text{m}$  mesh size sieve. One gram of sieved sediment was poured into a round bottom flask and mixed with 10 mm of 65%  $\text{HNO}_3$  and 60%  $\text{HClO}_4$  at a ratio of 4:1. The samples were digested using a hot plate digester at

temperature of 40°C for one hour and 140°C for three hours, respectively. Digested and cooled samples were transferred into a 25 mL volumetric flask and brought to volume with deionized water. The samples were passed through Whatman 42 filters and kept in cold temperature until next stage. The heavy metal concentrations were determined using an atomic absorption spectrophotometer (Varian 240, USA) (APHA 2012).

**Sediment features.** To determine sediment grain size, sieve series of 4 mm to 63 µm was used (Eleftheriou & McIntyre 2005). Colorimetric method was used to determine Total Organic Carbon (TOC) (Gupta 2001).

**Statistical analysis.** The software, Microsoft Excel and Minitab 16 were used to perform statistical analysis. One way-ANOVA test was used to compare heavy metal concentrations among different stations and two seasons. Pearson correlation test was used to consider the correlation of sediment features (grain size and TOC) with heavy metal concentrations.

**Results and Discussion.** Concentration of Fe, Cd, Cu, Ni, Pb, V, Zn, As, total organic carbon (TOC) and mud content of sediment in Bidkhun creek is summarized in Table 1. Statistical analysis showed no significant difference in concentration of heavy metals during different seasons ( $p > 0.05$ ). There were significant differences in concentration of some heavy metals among different stations ( $p < 0.05$ ). Tukey analysis revealed that concentration of Fe, Ni and As are significantly higher in station one than those in other stations ( $p < 0.05$ ). Concentration of Cd and Cu were significantly higher in stations one and four than those in other stations ( $p < 0.05$ ). Other heavy metals showed no significant difference among various stations. Stations one and four have the least distance to the opening of sewage canal (Figure 1). It seems that constant discharge of human source sewages is the main reason for increase of some heavy metals in these stations.

Table 1  
Heavy metal concentration and sediment features of Bidkhun mangrove swamp

Station	Season	Fe (%)	Cd	Cu	Ni	Pb	V	Zn	As	TOC (%)	Mud (%)
St1	Summer	2.4	1.54	43	72	30	84	243	14	6.4±0.5	74.2±2.6
St2	Summer	2.1	0.88	14	54	33	72	134	7	6.5±0.2	82.98±2.2
St3	Summer	0.63	0.78	14	28	45	44	72	9	6.5±0.3	25.24±1.5
St4	Summer	2.6	1.85	34	46	28	58	187	9	6.4±0.2	65.5±6.3
St5	Summer	0.83	1.23	16	32	48	51	112	11	6.9±0.2	66±2.5
St6	Summer	0.73	0.75	15	27	38	43	82	8	6.6±0.1	82.6±2.2
St1	Winter	2.85	1.73	39	82	27	97	197	15	17.4±1.6	83.2±2.2
St2	Winter	2.24	0.93	17	44	26	53	83	9	16.2±1.5	74±3.9
St3	Winter	1.04	0.75	16	58	42	76	183	12	17.7±1.2	23.8±2.8
St4	Winter	2.23	1.81	32	60	25	57	87	10	18.2±1.6	74.9±3.1
St5	Winter	1.23	0.98	23	34	27	45	78	9	17.7±1.3	70.9±4
St6	Winter	0.98	0.87	17	44	40	67	132	10	18.4±1.3	82.4±3
Max.	-	2.85	1.85	43	84	48	97	243	15	18.4	83.2
Min.	-	0.63	0.75	14	28	25	44	72	7	6.4	23.8
Mean	-	1.82	1.29	27.4	56	32	65.4	146	10	12.1	67.14
S.D	-	0.79	0.41	11.8	19.8	8.2	16.8	58.3	2.5	5.79	20.86

Values in percent for Fe, TOC and Mud, and in ppm for others.

TOC was significantly different during various seasons ( $p < 0.05$ ), however no significant difference was observed among various stations ( $p > 0.05$ ). Sediment particle size did not change between two seasons ( $p > 0.05$ ) but was significantly different among different stations ( $p < 0.05$ ). Sediment characteristics including TOC and mud content had no significant correlation with heavy metal concentration ( $p > 0.05$ ). There are some studies that reported significant correlation between contaminants concentrations of sediment and sediment texture or TOC (i.e. De Mora & Sheikholeslami 2002; Dehghan et al 2008; Davari et al 2012). It seems that discharge of sewage and its effect on heavy metal concentration of northern stations have led to decrease of sediment features effects on metals concentration.

Concentration of heavy metals in present study is compared with some other places in the Persian Gulf, Middle East and some national standards of other countries in Table 2. Fe concentration in present study was lower than its concentration in Black Sea and Basatin mangrove swamp but more than Red Sea concentration. It was consistent with finding of previous study in the same place and Mele-Gonzeh by Davari et al (2012) that illustrated no change of Fe during recent four years. Mean concentration of Fe was also lower than existing standards (Guidelines for Metals in sediments, SEL and LEL).

Cd concentration was more than other regions far from the Persian Gulf (Caspian Sea, Black Sea, Red Sea and Singapore) and Khure-Musa bay in northern part of the Persian Gulf and equal to adjacent regions of Nayband and Mele-Gonzeh. Cd concentration of Bidkhun mangrove was more than its previous concentration in four years ago. Cadmium concentration was more than primary standard levels including: "Primary China National Standard", "Canadian sediment quality guidelines" (TEL), "Guidelines for Metals in sediments" (LEL) and "Swedish Environmental Protection Agency", but lower than secondary standards (Table 2).

Cu showed the same concentration to the other ecosystems, although it was less than its concentration in adjacent mangrove swamp of Basatin. Their level also has been reduced from former study performed in four years ago. It is more than some primary standards including: "Canadian sediment quality guidelines" (TEL), "Guidelines for Metals in sediments" (LEL) and "Swedish Environmental Protection Agency" (Table 2).

Ni concentration was less than concentrations attained in the other places of the Persian Gulf such as Nayband bay, Basatin, Khure-Musa and northern Persian Gulf. Its concentration has been reduced from four years ago. Other studies have shown less concentration of copper in Red Sea, Caspian Sea, Black Sea and Singapore (Table 2). According to the standards of "Guidelines for Metals in sediments" (LEL) and "Swedish Environmental Protection Agency" Ni concentration in Bidkhun mangrove swamp is higher than normal level. High level of Ni is reported harmful for mangrove trees (Harbinson 1986).

Pb concentration in Bidkhun mangrove swamp was higher than its concentration in other marine regions (Red sea, Caspian Sea, Black Sea and Singapore) but less than adjacent ecosystems (Nayband, Basatin, Mele-Gonzeh and northern Persian Gulf). It shows that lead concentration in the Persian Gulf is naturally higher than other marine regions and more than primary standards (Table 2).

V concentration of Bidkhun mangrove was lower than its levels in other adjacent ecosystems and also less than its concentration in four years ago. V concentration was also higher than natural level assessed by "Swedish Environmental Protection Agency" (Table 2). High level of this metal is reported as harmful element for mangrove healthy (Harbinson 1986).

Zn concentration similar to Ni and Pb was more than its concentration in marine ecosystems out of the Persian Gulf and less than most adjacent ecosystems. "Canadian sediment quality guidelines" (TEL), "Guidelines for Metals in sediments" (LEL) and "Swedish Environmental Protection Agency" standards indicated high level of this heavy metal in Bidkhun mangrove ecosystem (Table 2).

There was few data to compare As concentration of present study with other ecosystems, nevertheless, global standards indicated normal level of this heavy metal in Bidkhun creek (Table 2).

There are some difficulties to assess overall pollution status of estuaries and marine sediments (Rubio et al 2000) due to variations in analytical procedures between studies and the presence of an unknown natural background in the sediments (Nasr et al 2006). Nevertheless, regarding high concentration of heavy metals in some stations of Bidkhun mangrove, it could be concluded that this ecosystem is in polluted status for heavy metals, especially in stations one and four. Industries related to oil and natural gas extraction is reported as a main source of all mentioned heavy metals (Meyers 1997). Besides, sewage discharge enhanced their concentration in the northern part of the creek. These high levels of them could be toxic for mangrove trees and other organisms (Nies 1999; Ke et al 2011) and could threat human healthy too (Dias et al 2009).

Table 2

Heavy metal concentration in Bidkhun mangrove swamp and some other marine ecosystems as well as some environmental standards

<i>Location</i>	<i>Fe (%)</i>	<i>Cd</i>	<i>Cu</i>	<i>Ni</i>	<i>Pb</i>	<i>V</i>	<i>Zn</i>	<i>As</i>	<i>Reference</i>
Caspian Sea, Iran	-	0.01-0.24	-	29.4-67.8	11.3- 24.6	-	-	-	De Mora & Sheikholeslami (2002)
Black Sea, Turkey	0.5-5.4	0.02-0.93	4-95	13.5-65.2	0.05-31	-	34-267	-	Topcuoglu et al (2002)
Red Sea, Egypt	0-1.23	0.03-0.68	0.05-23.25	0.02-71.7	0.007-9.8	-	49.4	-	Mansour et al (2013)
Mangrove, Singapore	-	0.181	7.06	7.44	12.28	-	51.24	-	Cuong et al (2005)
Mangrove, Singapore	-	0.226	32	11.65	30.98	-	120.2	-	Cuong et al (2005)
Khure-Musa, Iran	-	0.27-1	15-35	65-171	7-29.7	-	65-379	-	Dehghan et al (2008)
Nayband bay, Iran	-	1.16-1.44	-	-	3.56-5.25	-	-	-	Dehghani et al (2014)
Nayband bay, Iran	-	-	-	102.7	-	126.3	-	-	Zare-Maivan (2010)
Persian Gulf, Iran	-	-	-	99.4	-	114.5	-	-	Zare-Maivan (2010)
Bidkhun mangrove, Iran	1.82	2	47.5	68.5	96.2	288	201	-	Davari et al (2012)
Basatin mangrove, Iran	3.61	1.9	64.3	82.1	138	360.2	254.5	-	Davari et al (2012)
Mele-Gonzeh mangrove, Iran	1.82	1.3	26.3	41.9	53.3	286	88.7	-	Davari et al (2012)
Primary China National Standard	-	0.5	35	-	60	-	150	20	CSBTS (2002)
Secondary China National Standard	-	1.5	100	-	130	-	350	65	CSBTS (2002)
Canadian sediment quality guidelines (TEL)	-	0.7	18.7	-	30.2	-	124	-	CCME (2002)
Canadian sediment quality guidelines (PEL)	-	4.2	108	-	112	-	271	-	CCME (2002)
Guidelines for Metals in sediments (LEL)	2	0.6	16	16	31	-	120	6	Persaud et al (1993)
Guidelines for Metals in sediments (SEL)	4	10	110	75	250	-	820	33	Persaud et al (1993)
Swedish Environmental Protection Agency (natural level)	-	0.3	15	10	5	20	100	8	SEPA (1998)
Present Study - Mean	1.81	1.29	27.4	56	32	65.4	146	10	-
Present Study - Max	2.85	1.85	43	84	48	97	243	15	-

TEL: threshold effect level; PEL: probable effect level; LEL: lowest effect level; SEL: sever effect level. Values in ppm dry weight unless otherwise noted.

**Conclusions.** Generally, concentration of heavy metals in the Persian Gulf ecosystems, especially in Bidkhun mangrove is more than several places around the world and exceed almost all primary pollution standards. With regard to high industrial activities related to oil and natural gas industries, it seems that these industries are the main reason for this increment. Bidkhun mangrove also receives high quantity of human source sewages from industrial establishments of the biggest world natural gas field (South Pars in Iran). These two factors have led to increase of average concentration of heavy metals and exceeding from primary standards. Effect of these factors increases in regions around sewage opening and causes of reaching concentration of some heavy metals to secondary standards. Decrease of sewage discharge or stop discharging is the best solution to save these valuable ecosystems. Establishment of treatment units also is necessary to decrease anthropogenic effects of sewage discharge. Totally, with regard to high average concentration of heavy metals in the Persian Gulf, it is necessary that a specific standard be introduced for this region.

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