



The Ecologic Risk Evaluation of International Tiab and Kolahi Wetland through Heavy Metals Pollution Indexes in Sediments

Alireza Salarzadeh^{1*}, Sharbanoo Khosravani², Fatemeh Rezvani²

1) Department of Fishery, Bandar Abbas Branch, Islamic Azad University, Bandar Abbas, Iran

2) Young Researchers and Elite Club, Bandar Abbas Branch, Islamic Azad University, Bandar Abbas, Iran

*Corresponding author: reza1375bandar@yahoo.com

ABSTRACT

The heavy metals are among the pollutants that enter the water bodies through different human-made or natural sources and in direct or indirect manner. Therefore, the analysis of sediments as the primary absorbers of metal pollutants is highly significant. International Tiab and Kolahi Wetland is one of the significant ecosystems in south of Iran which is currently affected by different pollution sources due to development plans. To identify the environmental pollutions of heavy metals in bottom sediments of International Tiab and Kolahi Wetland, 22 surficial sediment samples are taken from 11 stations through GRP Sampler. To determine the index of toxicity and permissible elemental pollution limit in sediment, U.S Sediment Quality Standard developed by National Oceanic and Atmospheric Administration (NOAA) and Canadian Interim Sediment Quality Guidelines (ISQGs) are used. The results show that the concentrations of certain heavy metals such as cadmium, lead, nickel and copper are respectively 6.15, 23.22, 142.8 and 36.18 ppm. To determine the contamination limit of sediments, Muller geochemical accumulation index is used. Based on Muller classification scheme, the studied region is in moderate pollution level. In addition, the element saturation index shows that the pollution caused by lead and cadmium could be associated with oil and human-made pollutions in the wetland. Keywords: heavy metals, sediments, pollution index, International Tiab and Kolahi Wetland.

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INTRODUCTION

Industrialization has rapidly developed and led to increased environmental risks. One of the indices of negative effects is increase in the level of potentially toxic elements in soil and sediments [1]. Despite of their vastness, the seas and oceans have limited capacity for absorbing pollutants. The environmental problems of dry lands are often reflected in marine problems because any type of pollution over the dry lands with or without an identified source may finally influence the marine environment [2]. The pollution of the seas could originate from different factors such entry of industrial and civil waste, oil transportation and traffic of ships, oil discovery and exportation operations, waste disposal, and wastes of plants, emission of chemical materials, and unloading of balance water of ships that are followed by negative effects such as high death rate of organisms in the seas, pollution of beaches and wetlands [3]. The heavy metals enter water and soil as solutions, they result in pollution of surficial, underground and soil waters, and disrupt the ecologic balance of ecosystems [3,4].

The evaluation of ecologic risk is a criterion for environmental management as well as identification and reduction of factors that potentially damage the environment [5]. The application of pollution indices such as heavy metals determines the ecologic risk level of ecosystems [6]. In general, the heavy metals are the elements that are natural found at significantly low quantities in ecosystems. These elements are among the highly stable pollutants and they do not disintegrate during biological processes [7]. These metals usually enter marine environments through climatic activities, land erosion, and human activities such as industrial and domestic wastes and mining [8]. The accumulation of heavy metals in sediments is more than that of water [9].

The role of wetlands in marine products, maintenance of water level for agriculture, production of wood, saving water and reduced frequency of natural disasters especially flood has been verified. This is while this aqueous structures have high aesthetic value, significant potential for attraction of tourists and educational and research-oriented importance. In addition, they are highly critical habitats for different animal and herbal species such as fishes and birds [10]. However, one could certainly state that these

natural ecosystems could be categorized as the most vulnerable ones led to critical limits in the past due to direct and indirect human damages. The functions of wetlands that offer numerous products and services for human beings make these ecosystems non-substitutable [11]. The Mangrove forests are different from other forest ecosystems. These forests belong neither to the sea nor to the dry land but act as a common boundary between water and land [12]. The mangrove waterways are valuable habitats for aquatic species due to enrichment with organic-herbal particles and reception of leaked nutrients from dry lands. As a result, they play an outstanding role in sea food cycle. Mangrove as the first cycle of fishing economy is the largest function of these forests after ecotourism [10].

The measurement of pollution status of aqueous environments sediments, precise identification of pollution sources and application of managerial solutions considering the results of previous evaluations so as to reduce the addition of pollutants to aquatic environments are more significant than other cleaning methods. Since the past few decades, numerous studies have been done concerning the measurement of pollution status of aquatic environments' sediments in different parts of the world [13,14,15,16].

The International Tiab and Kolahi Wetland is highly significant due to presence of Mangrove forests and regional pollution sources. Therefore, measurement of heavy metals in water bodies of this ecosystem, especially sediments, could be influential upon determination and evaluation of ecologic risk of wetlands and its management, planning and protection.

MATERIALS AND METHODS

Sites descriptions

The International Tiab and Kolahi Wetland in the east of Bandar Abbas is at the same level with the sea with geographical coordinates of 27°, 5'N and 56°, 45'E. It is located at estuarine of salty and fresh water rivers. The area of Protected Tiab and Kolahi Region is estimated to be about 78099 hectares of which 45000 was registered as an international wetland in 1975 and during Ramsar Convention. The mangrove forests with an area of 1698.03 hectares are highly significant in this regard [17]. On the other hand, the development of urbanization and increase of population along with development of industrial, agricultural and economic activities in Tiab and Kolahi Wetland led to addition of metal and other pollutants to it followed by negative qualitative conditions of the wetland. The northern part of the wetland generally hosts shrimp culture ponds.

Sampling. In the present study, sampling of marine sediments was done on 11 sampling stations of study area during two steps in December (2014). The surficial sediment samples were taken by GRP Sampler (Ekman Model). Figure 1 represents the location of region and sampling stations

Preparation and measurement of heavy metals. Before sampling, the polyethylene containers of sediment carriage, GRP sampler, and sediment storage containers were completely washed by 5% nitric acid and doubly distilled water. The samples were transferred to clean and prepared polyethylene containers on which complete characteristics of sampling stations were registered [18]. Then, the sediment samples were stored in freezer of research ship, transferred to laboratory and grained. The sediments the size of which is less than 63micron were digested. To digest the sediments, the sediment method of soil and sediment samples with sand bath or heater was used. First, 0.5g dry sample was weighted in Teflon labeled bombs. Then, 2.5ml aqua regia (3:1 mixture of hydrochloric acid and nitric acid) and 15ml of thick hydrofluoric were added to samples. After 1 hour of placement in setting temperature, the door of bombs was closed, covered with aluminum insulator, and placed on heater for 2 hours and 30 minutes. In the next step, 6.75g boric acid was weighted and deionized water was added to a balloon containing 20ml water. After cooling, the samples were added to a container with boric acid until it attains the sufficient volume. After preparing the samples, the concentration measurement of heavy metals of cadmium, lead and copper was done through atomic absorption spectrometry. All steps of sampling and analysis of sediment samples in the present study were done in the present study through international standard methods developed by American Public Health Association [19].

Pollution Indexes

Determination of Muller's Geo-accumulation Index (I_{geo})

This index was first developed by Muller in 1979 for measurement and definition of pollution level of sediments through comparison of current concentrations of an element with its value in sediments before industrialization [20,21,22]. This index is determined through the following equation (1).

$$I_{geo} = \text{Log}2 \left(\frac{C_n}{1.5 B_n} \right) \quad (1)$$

Where I_{geo} is Muller's Geo-accumulation Index or Contaminated Sediment Severity Index, C_n is the concentration of pollutant in sediments with less than 63micron diameter, and B_n refers to pollutant concentration at the crust of the earth or initial concentration of elements when there is no pollution.

The 1.5 coefficient is used for correction of initial concentration of sediments under the influence of ground effects.

Muller referred to 7 different classes for classification of this index. In the highest class (i.e. Class 6), the values of elements is at least 100 times more than reference values. In table 1, the values of pollution degree are offered.

Determination of toxicity unit and comparison with international standards. One of the common methods in describing data of pollutants determination is to use the sediments quality guideline in which the obtained results are compared with reference values. The applied criteria are established based on biological response of organism to generated conditions by pollutants [23]. Different values of pollutants such as heavy metals could develop different effects in organism exposed to these pollutants. To do this, in some countries different standards have been offered the most common of which are U.S Sediment Quality Standard with three effect levels of ERL, ERM, and ERH developed by National Oceanic and Atmospheric Administration (NOAA) and Canadian Interim Sediment Quality Guidelines (ISQGs) with two common effect levels of LEL and SEL [24,25]. In the present study, the amounts of metals are calculated to be compared with existing standards. Then, the toxicity unit index is determined based on the following expression [26].

$$TUI = [M1] / [ERM1] + [M2] / [ERM2] + \dots + [Mi] / [ERMi] \quad (2)$$

Where $[Mi]$ is the observed concentration of metal i and $[ERMi]$ refers to the ERM values of metal i .

For each of the metals, if $[Mi]/[ERMi] > 1$, the probability of toxicity of that element in the sediment is high. Although the toxicity generated by metals should not linearly increase as the concentration enhances but due to the fact the increase in concentration of metals enhances the toxic effects, this index is suitable to be used as a pollution index of metals the concentration of which is more than the limit [26].

RESULTS

Concentration of Heavy Metals

The mean values of heavy metals concentration in samples of surficial sediments at the bottom of International Tiab and Kolahi Wetland are represented in table 2. In regard to copper, its minimum and maximum values are respectively 18.35 and 50.65ppm. In addition, the minimum and maximum quantity of lead are 13 and 62ppm respectively. The minimum values of nickel and cadmium are 109.81 and 2.61ppm respectively. The maximum quantities of these metals are 176.83 and 9.53ppm respectively. Based on table 2, one could observe that the mean absorption of certain metals such as lead, nickel and cadmium is higher than that of earth crust and mean international levels for sediments. Although the mean quantity of copper is less than earth crust but its maximum amount signifies that in some regions the concentration of this metal exceeds its value at earth crust. In general, one could state that considering the mean concentration of heavy metals the probability of pollution of sediments in International Tiab and Kolahi Wetland exists. Figure 2 shows the diagram of heavy metals concentration in International Tiab and Kolahi Wetland.

Muller's geo-accumulation index. The results of Muller's geo-accumulation index is calculated for each metal and represented in table 3.

Considering table 3 and Muller's classification of pollution of different metals, it is observed that in regard to pollution quality of intended metals the value of I_{geo} index of sediments is less than zero (i.e. 0.1 to 1.2) and its pollution degrees are 0, 1 and 2. This means that from viewpoint of pollution, the sediments are categorized into a class with zero pollution degree (i.e. non-polluted condition), class 1 (i.e. non-polluted to moderate pollution) and class 2 (i.e. moderate pollution). Cadmium is in the condition of moderate pollution, nickel and lead belongs to the range of non-polluted state to moderate pollution while copper is in non-polluted state. Based on this table, the quality of sediments in Tiab and Kolahi Wetland in regard to pollution by heavy metals has the following sequence:

$Cd > Ni > Pb > Cu$

As it could be observed, cadmium has the highest values in regional sediments.

Determination of toxicity unit index and its comparison with international standards. The ERM values for the intended metals in the present study based on the U.S Sediment Quality Standard developed by National Oceanic and Atmospheric Administration (NOAA) as shown in table 4 are: Lead (218 mg/kg), Cadmium (9.6 mg/kg), Copper (270 mg/kg) and Nickel (5.16 mg/kg) in Relation to Dry Sediments [24,27,28,29,30].

Based on the above values, the value of toxicity index for different stations is shown in table 5.

As the results show, the values of cadmium, copper, lead and nickel are less than ERM. Based on environmental standard of Canada, the values of cadmium and nickel are much higher than that of ISQGs. The values of copper and lead are much lower than that of ISQGs.

Table 1. Classification of Sediments Quality based on Muller's Geo-accumulation Index

Pollution Status (Muller's Range)	Degree of Pollution	I_{geo} Values
Non-polluted	0	≤ 0
Non-polluted to Moderate Pollution	1	0-1
Moderate Pollution	2	1-2
Moderate to High Pollution	3	2-3
High Pollution	4	3-4
High Pollution to Sever Pollution	5	4-5
Severely Polluted	6	>5

Table 2. Mean, Minimum and Maximum Values of Heavy Metals Measured in Studied Wetland (ppm)

Heavy Metals	Mean	Minimum	Maximum	The global average Sediments	Earth's crust
Cu	36/18	18/35	50/65	33	50
Pb	22/23	13/00	62/00	19	14
Ni	142/81	109/81	176/83	52	80
Cd	6/15	2/61	9/52	0/17	0/2

Table 3. Results of Muller's Geo-accumulation Index of Different Metals in Stations

I_{geo} Ni	I_{geo} Cu	I_{geo} Pb	I_{geo} Cd	Number of stations
0/13	-0/2	-0/21	1/30	station1
0/08	-0/3	0/46	1/28	station2
0/03	-0/34	-0/13	1/18	station3
0/03	-0/33	-0/09	0/93	station4
0/15	-0/17	0/14	1/19	station5
0/06	-0/26	-0/01	1/40	station6
0/16	-0/18	0/26	1/30	station7
0/16	-0/26	-0/19	1/36	station8
-0/03	-0/5	-0/02	1/34	station9
-0/02	-0/61	-0/31	1/37	station10
-0/04	-0/55	-0/21	1/49	station11
0/07	-0/31	0/04	1/31	mean

Table 4. Standard Values of Heavy Metals based on NOAA Sediment Quality Index in Canadian Environment (mg/kg)

The present study	Standard Environment Canada (CCME, 1999)		American Standard NOAA(Long, et al, 1995)		
	ISQGs ⁴	PEL ³	ERL ²	ERM ¹	
6/15	0/70	4/20	1/20	9/60	Cd
23/22	30/20	112	7/46	218	Pb
142/8	15/9	42/8	20/9	51/6	Ni
36/18	18/70	108	34	270	Cu

¹ Effect Range Medium

² Effect Range Low

³ Probable Effect Level

⁴ Interim Sediment Quality Guideline

Table 5. Values of Toxicity Unit Index based on Canadian Interim Sediment Quality Guidelines for Different Stations of Tiab and Kolahi Wetland

Ni	Cu	Pb	Cd	Number of stations
3/14	0/17	0/05	0/63	station1
2/88	0/13	0/28	0/6	station2
2/52	0/12	0/07	0/47	station3
2/52	0/12	0/07	0/27	station4
3/36	0/18	0/13	0/48	station5
2/7	0/15	0/09	0/8	station6
3/42	0/18	0/17	0/63	station7
3/38	0/15	0/06	0/72	station8
2/14	0/08	0/09	0/69	station9
2/22	0/06	0/05	0/73	station 10
2/12	0/08	0/05	0/98	station 11
30/4	1/42	1/11	7	TUI

Table 6-Comparison of Mean Concentration of Metals in Present Study and Other Part of Worlds

Ni ppm	Pb ppm	Cd ppm	Cu ppm	The study area
16/27	254/4	1/1	249/6	Jiries [31], Amman (Jordan)
41/1	48	1/6	466/9	Charlesworth, <i>et al.</i> , [32], Birmingham (England)
19	68	0/6	188	Rasmussen, <i>et al.</i> , [33], Ottawa (Canada)
67/9	386/9	0/2	172/4	Christoforidis and Stamatis [34], Kavala (Greece)
47/1	14/2	4/7	14/8	Hosseini Alhashemi, <i>et al.</i> , [35], Shadegan wetland (Iran)
75/94	24/48	0/28	62/3	Ghazban and Zare,[36], Anzali wetland (Iran)
35/99	53/19	0/76	31/4	Bai, <i>et al.</i> , [37], Lake Yylang(China)
80	14	0/2	50	Karbassi, <i>et al.</i> , [38], Bushehr(Iran)
142/8	23/22	6/15	36/18	This study

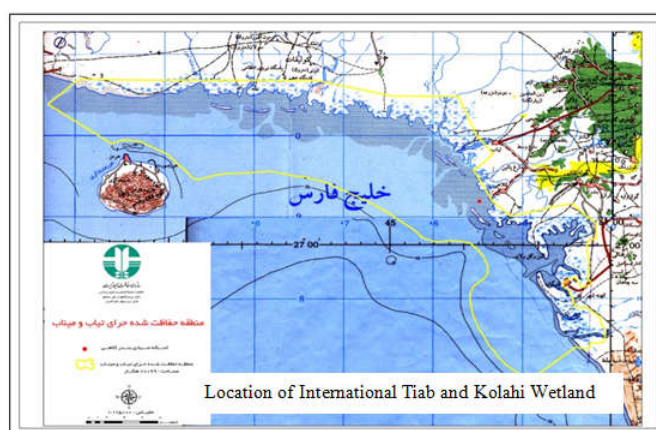
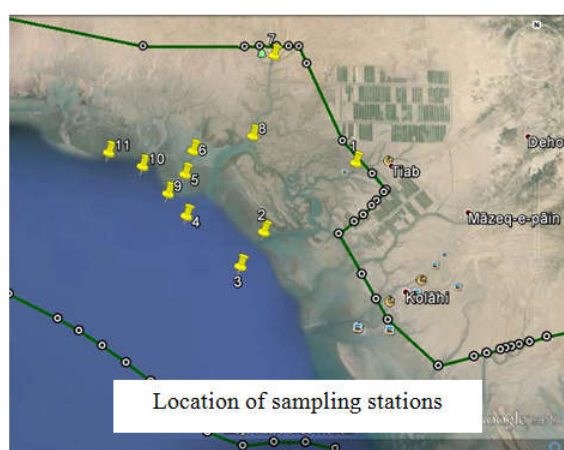


Figure 1. Location of sampling stations in International Tiab and Kolahi Wetland

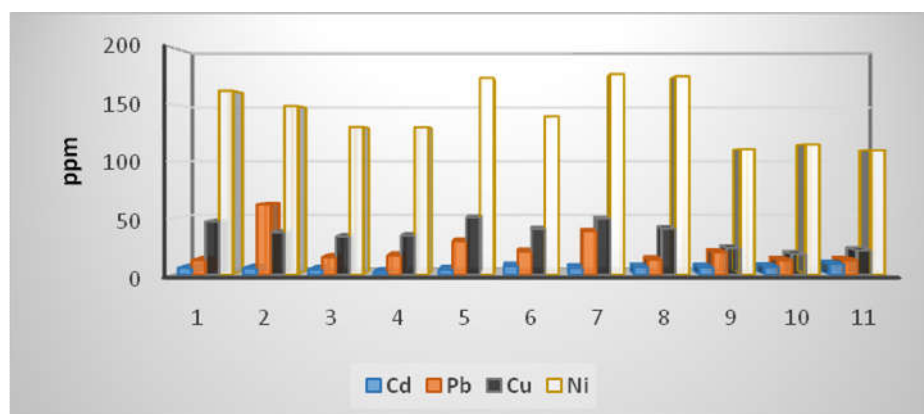


Figure 2. Concentration of heavy metals in sediments of 11 stations (ppm)

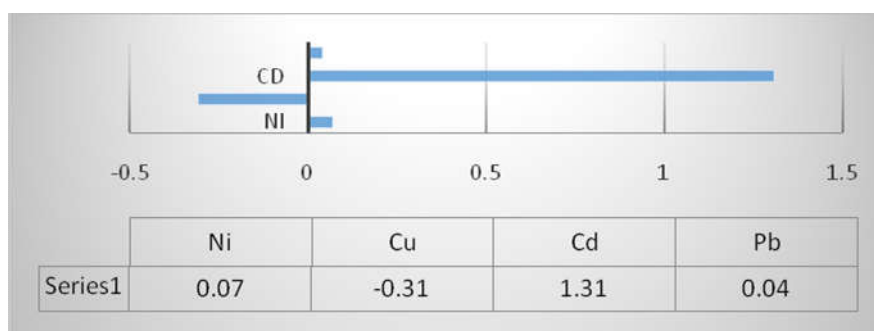


Figure 3. Diagram and values of heavy metals based on geo-chemical index

DISCUSSION

The results of present study offer valuable information regarding International Tiab and Kolahi Wetland. The minimum and maximum concentration of metals in ppm unit are as follows: Pb in Sediment (13-62), Ni in Sediment (109.81-176.83), Cd in Sediment (2.61-9.52), and Cu in Sediment (18.35-50.65). In table 6, the quantities of intended metals in sediments of International Tiab and Kolahi Wetland are represented along with results in regard to wetlands and aquatic ecosystems in other parts of the world [31,32,33,34,35,36,37,38]. Based on table 6, the mean concentrations of copper, cadmium, lead and nickel in sediments of International Tiab and Kolahi Wetland are higher than those of Shadegan Wetland in Iran. The quantities of copper, cadmium and nickel in the studied wetland are more than those of aquatic ecosystem in Jordan (Oman). In addition, the amount of cadmium and nickel in the present study is much more than other similar studies. The mean concentrations of intended metals in the present study are more than that in earth crust.

The mean quantity of copper in regional sediments was determined to be 36.18ppm. Azimi *et al* [39] measured the concentration of copper in northwestern sediments of Persian Gulf (Bandar Imam Khomeini) as 17.24ppm. The mean concentration of lead in the studied region was 23.33ppm while Maghzi *et al* [40] reported the mean concentration of lead in sediments of Babol Rood River as 29.98ppm. The mean concentration of nickel in the studied region was 142.81ppm while Rabani *et al* [41] reported the mean concentration of nickel in sediments of Asalouyeh Operational Region to be 27.2ppm.

The mean concentration of cadmium in regional sediments was 6.15 ppm that was less than that of Maghzi *et al* [40] in regard to sediments of Babol Rood River (i.e. 9.7ppm). The indexes of accumulation and geo-chemical accumulation showed that the current status of studies region for most of the metals with exception of cadmium is in the range of non-pollution to moderate pollution. This represents the match and congruency of obtained results by these two indexes. The Muller's geo-accumulation indices show that the pollution of sediments in sampling stations under the influence of cadmium is in the significantly high pollution range. In calculation of values of these indices, the mean concentration in earth crust was used instead of background concentration in the region. In addition, the results of geochemical accumulation index show that nickel and lead are with non-polluted to moderately polluted range while pollution by copper is in non-polluted state. The value of geo-chemical accumulation index as shown in figure 3 shows that these elements has non-critical accumulation of the heavy metals in surficial sediments compared with their background amounts in earth crust. Based on the accumulation index,

lead is in moderate accumulation level, nickel has low accumulation level and copper is in non-accumulation to low-accumulation range. The calculation of accumulation indices for the intended metals in this region shows the increase in accumulation index of cadmium in sediment due to human activity. This increase is due to accumulation of heavy metals in sediments in higher values than initial level and non-pollution case. The results of toxicity unit index compared with mean values of elements in sediments of earth crust show that the mean concentrations of lead, nickel and copper in wetland are less than their means in earth crust but concentration of cadmium in wetland is more than its earth crust concentration. Compared with U.S Sediment Quality Standard developed by National Oceanic and Atmospheric Administration (NOAA), the values of elements studied in the present study are less than ERM level. In addition, compared with Canadian Interim Sediment Quality Guidelines (ISQGs) the values of cadmium and nickel elements are much more than ISQGs level. In studies done on Anzali Wetland [42], based on the accumulation index the accumulation of cadmium, lead and chrome in sediments was evident. The results of a study by Maghzi *et al* [40] concerning the quality evaluation of sediments in Babol Rood River show that based on geochemical accumulation index, lead was in the range of non-pollution to moderate pollution while cadmium is in significantly high pollution range. In regard to accumulation index, cadmium is in significantly high range. In another study considering the coastal sediments of Shahid Rajaei Port [43], the comparison of results of present study with American and Canadian standards shows that the mean value of lead is less than ERL standard while the values of lead and nickel is a little more than limit but much less than ERM standard.

CONCLUSION

The sediments in adjacent wetlands of civil or industrial regions have the potential ability to absorb and deposit the metal pollutions originating from dry environments. In addition, due to the fact that high cadmium concentrations might be due to human activities one could conclude that there is a source for entry of pollutants into the wetland environment and as a result it has the potential to generate risk in the region.

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