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Heavy Metals Assessment of Surface Sediments in Mighan Wetland Using the Sediment Quality Index

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Background: Sediments are integral part of wetlands providing a valuable key to recognize heavy metal fluctuations in the past.

Materials and Methods: The surface sediment samples were taken from thirteen sites, then prepared and digested with percholoric acid and nitric acid at 1:4 ratio, followed by flame atomic absorption spectrophotometry analysis.

Results: The average of total metal concentration in 13 sites were found to be 9.182, 9.514, 45.351 and 43.456 µg g^{-1} for Pb, Zn, Cu and Ni, respectively. Also, comparison of sediment quality indices, including contamination factor (Cf), contamination degree (Cd), and modified contamination degree (mCd)) showed that Cu contamination was significantly different from the other heavy metals, while Ni contamination was average, and Pb and Zn contaminations were low.

Discussion and Conclusions: This research confirms that the Mighan wetland is polluted with heavy metals and their excessive accumulation in sediments.

Keywords: *Hakanson index, Mighan wetland, Sediment index*

1. Background

Among thousands of inorganic and organic matter entering to aquatic ecosystems, the heavy metals are of great importance due to their degree of toxicity, persistence, inseparability and bioaccumulation potential. The metals are not separated from water during the process of self-purification in many marine species, but accumulate in suspended particles, sediments, and aquatic organisms that eventually transmitted to human through the food chain (1). The main sources of heavy metals in the aquatic environment are sediment which plays an important role in the storage and transmission of these dangerous metals (2). This makes the evaluation of pollution in the relatively stable sediment much better than unstable water (3).

Among the enormous aquatic ecosystems, wetlands are of particular importance, providing significant economic, social and cultural benefits, including pastures, timber, fish, and support recreational and tourist activities. Wetlands at the same tome help diminishing impacts of storm damage and flooding, maintain good water quality in rivers, recharge groundwater, store carbon, stabilizing climatic conditions and finally control pests.

They also serve as a hot spot for biodiversity. Currently, pollution from various sources affects the sediment quality in wetlands. Various other factors, such as overexploitation of water and drainage of wetland, industrial and agricultural developments have caused serious damage in recent years (4).

Located in Markazi Province, Mighan is one of the most important wetlands of Iran. In recent years, about half of wetland has dried up and seriously damaged as well as endangering migrating birds (5). This wetland hosts many migratory birds, some of which are rare and protected species, hence boosting ecotourism and bird watching activities (6).

Given the aforementioned facts, several researches on ecological risks have been conducted all over the world (7, 8, 9, 10, 11, 12, 13), showing various concentrations of some heavy metals from different sources. In 2016, the risk assessment and environmental geochemistry of Pb, Cu and Fe in surface sediments were evaluated in Hashilan wetland in Iran, the results of which showed that the most common sources of Pb and Fe were natural while sources of Cu were anthropogenic (14).

2. Objective

Given the wetlands importance among aquatic ecosystems and the lack of study about Mighan wetland, we decided to study the heavy metals contamination in this wetland by using such sediment quality indices as contamination factor (Cf), contamination degree (Cd), and modified contamination degree (mCd).

3. Materials and Methods

3.1. Study Area

Covering an area of 50,000 ha and a watershed area of 12,000 ha in Markazi province, Mighan desert is located in the northeast of Arak city (49°40' 56" to 50° 04' 26" E, and 34° 06' 17" to 34° 19' 05" N) (Figure 1). All watercourses and groundwater of Arak region end up to this wetland. The Mighan is a seasonal wetland with a water depth reaching to 1.5 meters in some parts in wet seasons (spring and winter), but becomes a swamp in summer (15).

3.2. Sampling Method

Surface sediments (0–15 cm) were randomly collected with a plastic spoon in 3 replications from 13 sampling sites in autumn. Sites were selected by considering such points as vegetation cover, industrial centers around the wetland, ease and accessibility to sampling. The geographical position of all sampling sites was recorded by GPS device (Figure 1). The samples were placed in polyethylene bags and carried to the laboratory in an ice box and stored in a deep freezer for future analysis (16). They were dried in an air-circulating oven at 80°C., then crushed using a mortar and pestle and sieved through a 63 µm stainless steel sieve while shaken vigorously to produce homogeneity. About 0.5 to 1.0g dried sediments was digested in 10 ml mixture of HNO_3 (AnalaR grade, R & M 65%) and $HClO_4$ (AnalaR grade, R & M 70%) in the ratio of 4:1, starting at a temperature of 40$^{\circ C}$ for 1 h, then raised to 140$^{\circ C}$ for 3 h (17). The digested samples were diluted to 40 ml with double-distilled water (DDW) and filtered through Whatman No.1 filter paper into pre-cleaned 50 ml volumetric flasks. Then, trace metal concentrations (Cd, Zn, Ni, Cu, Pb, Fe) were measured using an air-acetylene flame atomic absorption spectrophotometer (SpectrAA Model VARIAN240), based on the method described by Naji and Ismail (18).

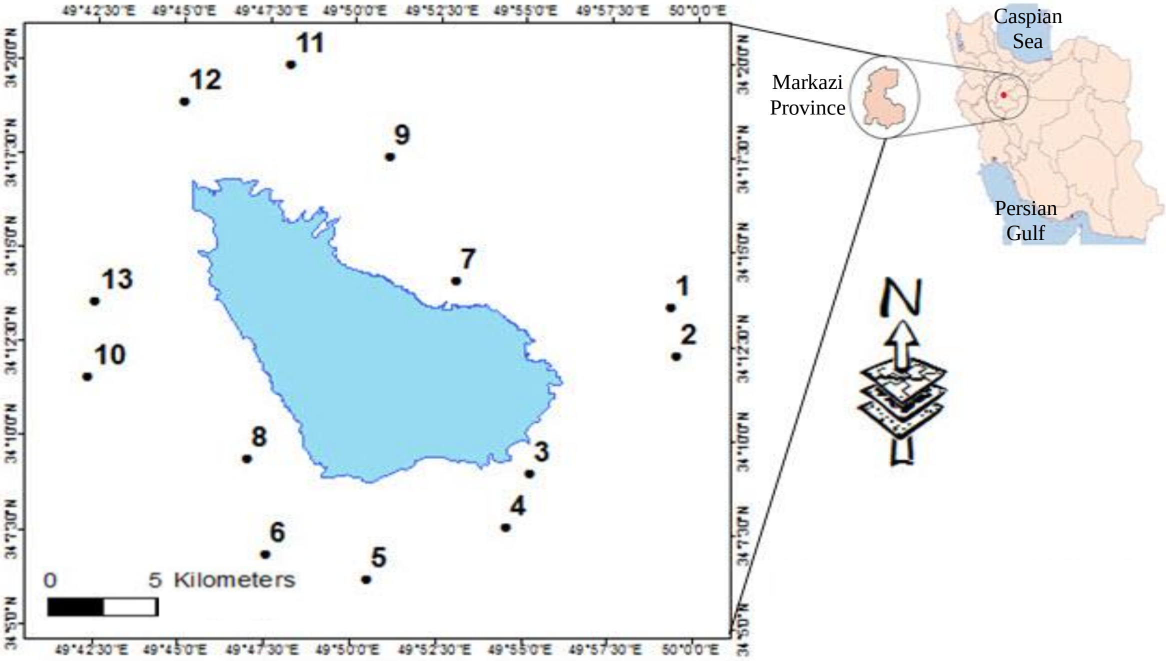

Figure 1 General location of the Mighan wetland and spatial pattern of sampling stations

Table 1 Elements in shale average concentration (µg g^{-1}) (19)

Heavy metals	Cu	Zn	Pb	Ni
Shale average (µg g^{-1})	45	95	20	50

3.3. Data Analysis

Statistical analysis was done using SPSS 21 software. The normality of data and heterogeneity of variance were investigated using the Kolmogorov-Smirnov and Leven test, respectively ($p > 0.05$). In order to examine the significant differences in metal concentrations in various sites, the one way ANOVA and Duncan test were applied. Also relationship between the existing concentrations was examined using Pearson test. Finally, pollution rate was determined using environmental sediment quality index. In order to determine the extent and the degree of sediment pollution with heavy metals, concentration of elements in the region were compared with some related index and standard, then the shale average provided by Wedephol Turkian (19) was used (Table 1).

Sediment Quality Index

The contamination factor (CF) and contamination degree (Cd), and modified contamination degree (mCd) were used to describe metal contamination of the sediments as following:

Contamination factor (CF):

Contamination factor (CF) was used to describe metal contamination (Table 2), based on Hakanson factor (20) obtained by Equation 1:

$$Cf = \frac{Mx}{Mb} \qquad (1)$$

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Where *Mx* is element concentration and Mb is the same metal concentration in shale average.

Contamination degree of (Cd):

Sum of the pollution coefficients implies overall sediment degree of contamination, so called Hakanson degree of contamination (Table 3). This factor is gained with Equation 2:

$$Cd = \sum_{i=1}^{8} C_f^i \qquad (2)$$

Where the Cf is factor of contamination and Cd is the total of Cf that is calculated with Equation 1.

Modified contamination degree (mCd):

Given the restrictions of Hakanson degree of contamination (20), Abrahim (22) presented the modified equation for degree of contamination (Table 4), as following Equation (3):

$$mCd = \frac{\sum_{i=1}^{8} C_f^i}{n} \qquad (3)$$

Where Cf is contamination factor and n is the number of analyzed parameters. The mCd allows studying a variety of heavy metals without any limitation.

Table 2 Hakanson rankings on the basis of sediment CF contamination factor (20, 21)

Contamination factor (CF)	Description
Cf ≤1	Low degree of contamination
1≤Cf≤ 3	Moderate degree of contamination
3≤Cf≤ 6	Considerable degree of contamination
Cf ≥ 6	Very high degree of contamination

Table 3 Hakanson rankings on the basis of contamination degree (20, 21)

Degree of contamination (Cd)	Description
Cd < 6	Low degree of contamination
6≤ Cd <12	Moderate degree of contamination
12≤ Cd<24	Considerable degree of contamination
Cd ≥ 24	Very high degree of contamination

Table 4 Classification of the sediments according to the mCd (21, 22)

(mCd) Modified degree of contamination	Description
mCd < 1.5	Zero to very low degree of contamination
1.5≤ mCd<2	Low degree of contamination
2≤ mCd <4	Moderate degree of contamination
4≤ mCd<8	High degree of contamination
8≤ mCd <16	16 Very high degree of contamination
16≤ mCd <32	Extremely high degree of contamination
mCd ≥ 32	Ultra high degree of contamination

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4. Results

The averages of the total concentration of metals in 13 sites (±standard deviation) were 9.182±3.314, 9.514±2.443, 45.351±2.634 and 43.456±2.618 μg g^{-1} for Pb, Zn, Cu, and Ni, respectively. The minimum and maximum concentrations of Pb were, respectively, 4.11 μg g^{-1} in site 12 and 13.03 μg g^{-1} in site 8; for Zn, 3.88 μg g^{-1} in site 11 and 20.34 μg g^{-1} in site 13; for Cu, 15.45 μg g^{-1} in site 12 and 152.19 μg g^{-1} in site 10; for Ni, 23.75 μg g^{-1} in site 2 and 64.33 μg g^{-1} in site 7, respectively (Figure 2). The lowest and highest average concentrations were attributed to Pb and Cu, respectively.

4.1. Statistical analysis

Significant differences ($p<0.05$) among heavy metal concentrations were observed at different sites (Table 5). The results of Duncan test showed significant differences in the heavy metal concentration between most of the northern and northwestern sites (9, 10, 11, 12 and 13) and the sites in south and southeast (1, 2, 3, 4, 5 and 6) of the wetland.

The correlation test indicated a significant positive correlation at 99% between concentration of Zn and Cu in the sediments a probability level of 99 (Table 6).

4.2. Contamination factor (CF):

The results of CF for the heavy metal in the wetland are presented in Table 7, according to which the CF for elements in various sites, as per Hakanson rankings, is as follows: the Pb and Zn elements in all sites have relatively lower CF. Contamination factor for Cu was significant in sites 3 and 10 and was average in sites 6 and 9, but low in the rest. Also, based on this ranking, CF for Ni was average in sites 1, 2 and 3 and lower in the rest.

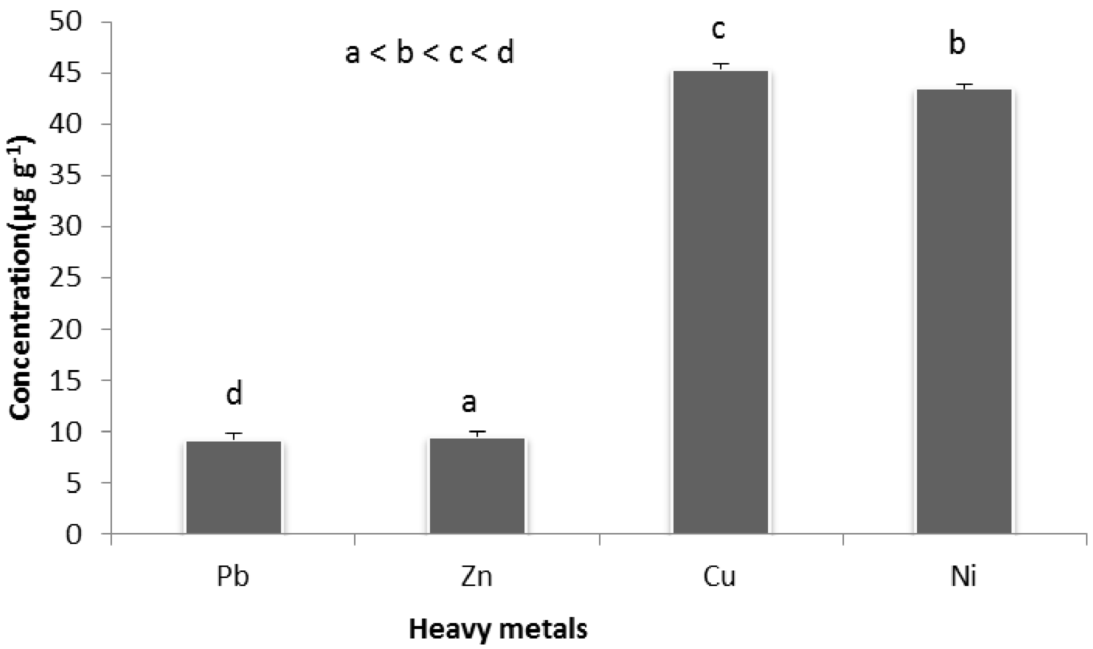

Figure 2 Total average of metal concentrations in Mighan wetland

Table 5 Normality and mean comparison data in Mighan wetland

Heavy metals	**significant level**		
	ANOVA	**Normality**	**Homogeneity**
Pb	0.00	∞	∞
Zn	0.00	∞	∞
Cu	0.00	∞	∞
Ni	0.00	∞	∞

Table 6 Correlation (Pearson) test among heavy metals of Mighan wetland ($p<0.01$)

Heavy metals	**Pb**	**Zn**	**Cu**	**Ni**
Pb	1	0.076	0.00	0.058
Zn		1	0.006**	0.00
Cu			1	0.00
Ni				1

Table 7 Contamination factor of metal pollution index in Mighan wetland sediment

Stations	**Cf**			
	Pb	**Zn**	**Cu**	**Ni**
1	0.45	0.10	0.37	1.25
2	0.25	0.10	0.67	1.28
3	0.64	0.08	3.07	1.10
4	0.52	0.30	0.39	0.83
5	0.38	0.08	0.53	0.87
6	0.62	0.08	1.12	0.95
7	0.37	0.08	0.49	0.47
8	0.64	0.09	0.46	0.59
9	0.59	0.06	1.10	0.52
10	0.28	0.21	3.38	0.87
11	0.52	0.04	0.39	0.77
12	0.20	0.06	0.34	0.93
13	0.45	0.21	0.74	0.90

4.3. Contamination degree (Cd):

To calculate the overall contamination, the degree of contamination was used, the result of which is presented in Table 8. The comparison of these values with Hakanson contamination factor show that the degree of pollution for Pb and Cu in the wetland sediment is low. Also, unlike the average grade of Ni pollution, the copper had a noticeable degree of pollution.

4.4. Modified contamination degree (mCd):

In addition to the earlier assessment methods, the mCd was also used to assess the heavy metal pollution of the area (Table 9) that showed a very low degree of pollution for all the metals.

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Table 8 Contamination degree for heavy metal pollution in Mighan wetland

Heavy metals	Pb	Zn	Cu	Ni
Cd	5.91	1.49	13.05	11.23

Table 9 Modified contamination degree (mCd) for heavy metal pollution in Mighan wetland

Heavy metals	Pb	Zn	Cu	Ni
MCd	0.45	0.11	1.00	0.86

5. Discussion

Analysis of sediments is important in terms of the evaluation of pollution of wetland's ecosystem. Sediments, especially the ones in wetland adjacent to the urban and industrial areas, like Mighan, have a potential ability to attract and deposit various pollutants, including heavy metals (23). Although pollutants will remain in sediments for a long time, they can enter the upper waters under the biological activities and change in chemical and physical conditions. Therefore, measuring the total concentrations of heavy element could provide the real picture of wetland environment pollution (24).

The impact of heavy metal pollution in soil and sediment varies upon their chemical participation. As a whole, sediment cleansing techniques against of pollutants is very limited compared with other solid waste. The study on dredging activities in different parts of the world showed that a very small part of the sediment will be cleared by some methods such as biological filtration treatment and thermal desorption. Also, implementation of these methods is not as easy as it seems. Hence measuring pollution situation, identification of pollution resources and use of managerial strategy based on the alleviation assessments is more important in comparison with cleaning methods. Hence, since the past decade many studies have been conducted on measuring pollution in different parts of the world (25).

The results of this study suggested a significant difference between the concentration of Pb, Zn, Cu, and Ni at several sampling sites in Mighan wetland. With regard to the position of mining activities, Arak refinery, airport and some unconventional applications, such as industrial aviculture, grazing cattle and agricultural activities in the south and southwest of the wetland, the difference is meaningful that stems from some polluting materials entering through mentioned activities. These results are in agreement with the earlier results from the Anzali wetland (26), where the heavy metal pollution in the area at vicinity of industrial and agricultural activities was significantly different.

The three factors, including contamination factor (CF), contamination degree (Cd), and modified contamination degree (mCd) gave a better understanding of the sediment quality. The results proved existence of contamination at three levels, viz. considerable, medium, and low, in the wetland ecosystem. The assessment of mentioned factors (CF and Cd) for each metal indicates the high pollution degree for Cu. Finally, the CF, Cd, and mCd showed lower level of pollution for Pb and Zn.

In general, region can be ranked in terms of total element concentrations and pollution degree of the studied metals (Pb, Zn, Cu, and Ni) as follows: Cu > Ni > Pb

The high concentration of heavy elements in the wetland can be attributed to anthropogenic and natural sources, such as excessive use of agricultural input (especially the micro- fertilizers and pesticides, the high ratio of surface to volume of fine sediment with

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less than 63 micron, high concentration of organic materials, increased sediment surface to volume ratio that attract more level of contaminants, putrefaction of plant and resistance to the dissolution that result in organic accumulation in sediment (27). These results are in line with earlier results from the Kour river (28), and also the Anzali wetland (29).

6. Conclusion

A general assessment of heavy metal pollution in Mighan wetland showed that Cu contamination was higher than other metals, the Ni concentration was in moderate and the Pb and Zn contamination were in low levels. The entrance of sewage from various industrial, urban and agricultural activities along with the natural conditions can be blamed for the accumulation of heavy metals in sediment.

Conflict of Interest

The Authors have no conflict of interest.

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Authors' Contributions

All authors contributed extensively to the work presented in this paper.

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برآورد فلزات سنگین در رسوبات سطحی تالاب میقان به کمک شاخص های کیفی رسوب

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مقدمه: رسوبات، بخش تفکیک ناپذیر بوم سازگان‌های تالابی می‌باشند که هم‌چون سندی تاریخی در ثبت روند تغییرات تجمع فلزات سنگین عمل می‌نمایند. پژوهش حاضر به بررسی آلودگی رسوبات اطراف حوزه آبگیر تالاب میقان می‌پردازد.

مواد و روش : نمونه‌برداری از رسوبات سطحی۱۳ ایستگاه در این تالاب انجام شد. آماده‌سازی و هضم نمونه‌ها با ترکیب ۴ به ۱ اسید نیتریک به اسید پرکلریک صورت گرفت و آنالیز نمونه‌ها با دستگاه اسپکتروفتومتر جذب اتمی شعله انجام شد.

نتایج: میانگین کل غلظت فلزات سرب، روی، مس و نیکل در رسوبات تالاب میقان به ترتیب شامل ۹/۱۸۲، ۹/۵۱۴، ۴۵/۳۵۱ و ۴۳/۴۵۶ میکروگرم بر گرم در ایستگاه‌های نمونه‌برداری می‌باشد. هم‌چنین مقایسه مقادیر حاصل از این مطالعه با شاخص‌های کیفیت رسوب ضریب آلودگی (CF)، درجه آلودگی (Cd) و درجه آلودگی اصلاح شده (mCd) نشان داد که این تالاب از نظر فلز مس در سطح قابل توجهی از آلودگی، از نظر عنصر نیکل در سطح متوسط و از نظر فلزات سنگین سرب و روی در سطح پایینی از آلودگی قرار دارد.

بحث و نتیجه‌گیری: با توجه به نتایج پژوهش حاضر و آلوده بودن تالاب میقان به فلزات سنگین مورد بررسی، در صورت ادامه روند آلودگی ناشی از ورود فاضلاب شهری، روستایی و صنعتی، زه آب اراضی کشاورزی، استقرار شرکت معدنی املاح ایران در مجاور تالاب، استقرار فرودگاه اراک در نزدیکی تالاب و نزدیکی تصفیه خانه شهر اراک به این اکوسیستم، احتمال می‌رود با افزایش میزان آلودگی و تجمع بیش از حد عناصر سنگین در رسوبات، تبعات غیر قابل جبران در این بوم سازگان تالابی حاصل گردد.

کلمات کلیدی: تالاب میقان، شاخص هاکینسون، شاخص‌های رسوب