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Original Article

Environmental Fate Modelling of Lead Contamination in Water and Sediments of Hawizeh Marshes

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Abstract

Background: This study aimed to determine the maximum concentration of lead in the water and sediments of Hawizeh Swamp during 2020-2021.

Methods: The ECOFATE model was employed to calculate ecological risk parameters (RQ) along with total dissolved solids (TDS), total suspended solids (TSS), and total organic carbon (TOC) at four stations during summer and winter. Using the framework of environmental fate model of ECOFATE, comprehensive data on hydrological sections, input chemical quantities, chemical characteristics, and ecosystem attributes were measured.

Results: The findings indicated that lead concentrations were at the highest level in both sediment and water samples of the wetland across three-dimensional space during summer and winter. TSS, TOC and TDS values were estimated, of which the TDS was used to measure ecological risk due to its higher values.

Conclusion: The RQ values of lead indicated high and medium risk within the sedimentary and aquatic environments of the wetland ecosystem, respectively. Statistical calculations further revealed that this wetland was at risk of environmental pollution, posing potential hazards to humans through the food chain. The increase in the biological pollution of this wetland is due to the increase in the population and urban sewage. Therefore, it is imperative to raise public awareness regarding the significance of the wetland and advocate for its regular monitoring.

Keywords: Hawizeh marshes, Heavy metal, Environmental fate model, Sediment, ECOFATE

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Introduction

Heavy metals are the elements that naturally exist in ecosystems in trace amounts and have the potential to contaminate soil and water. Moreover, these metals tend to accumulate in plants and animals which become a part of the human diet.[1] Heavy elements enter into the soil from different routes such as precipitation, chemical and animal fertilizers, sewage sludge, pesticides, industrial effluents from manufacturing factories, metalworking, and mines. They are also removed from the system through absorption by plants and leaching from the root zone.[2] The outlet rate is lower than the inlet, leading to the gradual accumulation of elements in the soil. Since heavy metals accumulate in soil and sediments, they are very suitable tracers for showing the level of environmental pollution.[3] Wetlands hold strategic significance due to their habitat value, harboring a rich diversity of plant and animal communities. These ecosystems serve as critical habitats for vulnerable and endangered species.[4] The absence of soil moisture and vegetation loss in the Hawizeh Marshes has led to the direct exposure of soil to wind, resulting in a heightened potential for erosion.[5] Heavy metals constitute significant pollutants that enter into rivers through diverse pathways, including urban, agricultural, industrial, and sewage sources, causing irreversible harm to living organisms, including humans.[6,7] Heavy metals are of the most dangerous toxic pollutants in the environment, which cause poisoning, acute and chronic diseases in humans.[7] Lead is one of the four metals that has the most adverse effects on human health.[8] While some metals directly enter the water, others are initially released into the air and subsequently deposited on the ground, eventually entering surface water through sewage pathways.

The proportion of heavy metals in the water and body of living organisms is very small, and most metals accumulate in sediments, which sometimes includes more than 99% of all heavy metals. The uptake of heavy metals by fish in polluted aquatic ecosystems depends on ecological needs, metabolism, and other factors such as salinity and water pollution.[9,10] Previous researches evaluated heavy metals in the sediments of Hawizeh marshes by calculating the pollution indicators. The elements of cadmium, nickel and chromium were higher than the permissible limit, which was attributed to the pollutants from the factories, oil facilities, and chemical fertilizers. Some studies evaluated the ecological characteristics of Hawizeh marshes and found that changes in water quantity and quality may be associated to changes in the quality and quantity of vital fauna of the wetland.[11] The study investigated the transfer of heavy metals including lead, nickel, and vanadium in the food chain of Hawizeh marshes. It found a correlation between the concentration of heavy metals in the chain of sediment, water, plant, and fish. The sediment and reed plants were the main storage of heavy metals in the wetland.[11] Also, a study evaluated the heavy metals in the sediments of Hor-Al Azim lagoon by calculating the pollution indices. According to the calculated indices, the elements of cadmium, nickel and chromium were higher than the permissible limit, which can be attributed to factories, oil facilities and chemical fertilizers.[10] Another research assessed the heavy metals including nickel, cadmium and vanadium in the water and sediments of Hor-Al Azim wetland in Khuzestan province. It showed that the cadmium and nickel metal concentrations in the sediments of Hor-Al Azim wetland had low ecological risk levels. The calculated ecological risk potential index fell within the low range for both ecological and biological risk classes. The amount of cadmium and nickel in the water of Hor-Al Azim lagoon was higher than the national and international standards. Also, the amount of cadmium and vanadium in the sediments of Hor-Al Azim lagoon was lower than the national and international standards. However, the amount of nickel in the sediments was higher than the national and international standards.[12]

In aquatic environments, lead tends to accumulate predominantly in bed sediments, with its concentration being four times higher in sediments compared to the water. Solubility and surface absorption of lead is the most important primary mechanism controlling its concentration in water.[13] The amount of lead in aquatic environments depends on the pH, alkalinity, and hardness of the water, which is soluble in clean and acidic waters.[14] The entry of sewage from the surrounding cities into the wetland, the change in the quality of incoming water during the drought seasons due to the entry of agricultural drains, human sewage from villages and cities located on the banks of the Karkheh River and possibly the Tigris in Iraq, and eventually the intensification of this phenomenon in summer compared to winter has caused a transformation in the entire water of Hor-Al Azim ecosystem. Due to the higher importance of lead compared to other elements in the ecological model, we investigated this metal in our study. Therefore, the purpose of this study was to model the environmental fate of lead in the water and sediments of Hawizeh marshes during 2020-2021.

Materials and Methods

Area of Study

Hawizeh marshes are located nearby to the southeast of Iraq and southwest of Iran. They are also near to the provinces of Maysan (Al-Amara city) and Basra in Iraq and Khuzestan province and Hawizeh in Iran. The longitude and latitude of Hawizeh marshes are 47 25' to 47 50' and 31 00´ to 45 31´, respectively. They have an area of 3000 km^2 under normal conditions. During floods, it is more than 5000 km^2.[15] Two-thirds of this area is located in Iraq and one-third in Iran. Hawizeh marshes have been documented in various geographical locations across different sources, reflecting the dynamic changes in the wetland over different years and seasons. Hawizeh marshes encountered no issues with water supply until 1973. However, approximately 71% of its expanse experienced desiccation due to the diversion of water flow from the Tigris and Euphrates rivers, coupled with the construction of upstream reservoir dams. This alteration severely disrupted the natural environment of the wetland.[16] Furthermore, the commencement of activities by the oil company in the Azadegan oil field, the construction of roads to the wetland for oil drilling operations in Hawizeh Marshes and the Karkheh dam, coupled with the reduced water discharge, currently pose significant threats. These challenges not only jeopardize the livelihoods of residents in the villages surrounding the lagoon but also impact the local wildlife. Drainage from the upstream agricultural lands also brings many salts into the wetland, which probably turn it into a salt marsh in the future due to the intense evaporation of water from the wetland surface.[17] Hawizeh Marshes and their adjacent areas are located in a hot and arid region with low precipitation and very high evaporation (Figure 1).[10]

Sampling

A total of 48 samples were taken from a depth of 0-15 cm as the sediment samples, and water samples were taken from the surface to a depth of 2 m in a random and composite way. The exact location of the sampling points was determined using a global positioning system (GPS) (Table 1).

In this sampling, three samples were collected in close proximity to a single point and subsequently pooled together to enhance result accuracy. Consequently, the result of combined samples is representative of the samples from the analyzed point. The collected sediment samples were dried and passed through a 2 mm sieve. Subsequently, 2 g of the soil were digested using a 3:1 mixture of hydrochloric acid and nitric acid. The resulting digested samples were subjected to atomic absorption testing to quantify the total concentration of the heavy metal lead (Pb).[18]

Environmental Fate Model

The environmental fate model is a user-friendly virtual tool designed for windows, featuring distinct sections

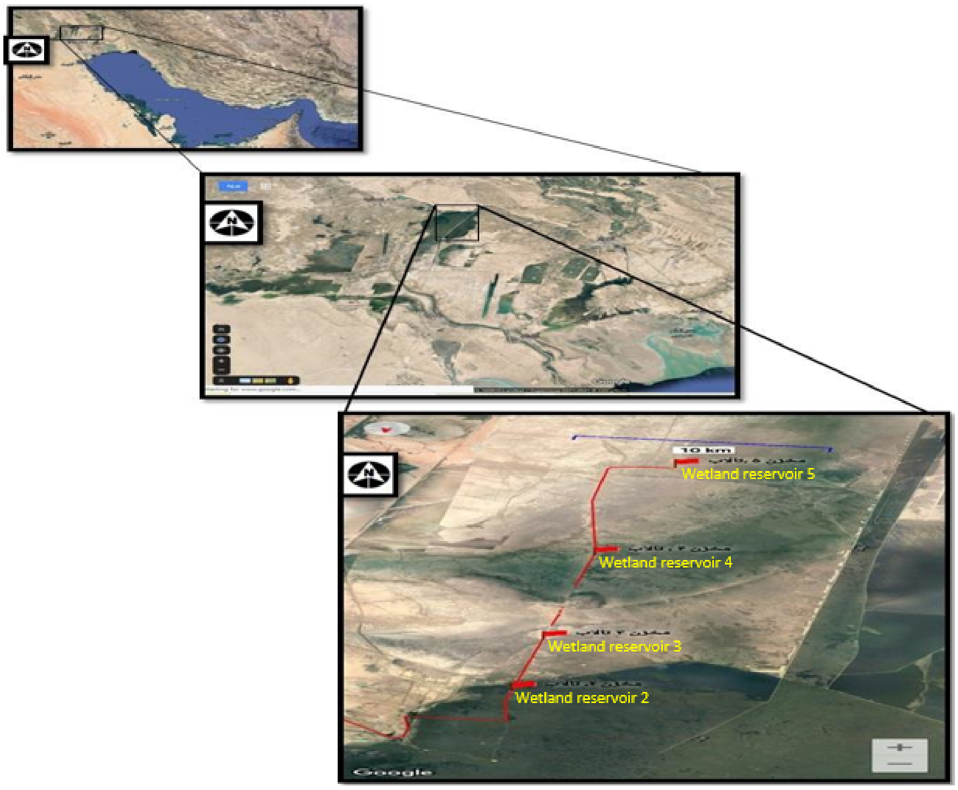

Figure 1. Geographical Location of the Sampling Area and the Studied Stations

Table 1. The Geographical Location of Selected 3D Spaces in Hawizeh Marshes During the Studied Period

Station No.	Station Name	UTM – (X/Y)
1	Reservoir 2	3477117Y 765322X
2	Reservoir 3	3470401Y 765355X
3	Reservoir 4	3459375 Y 765422 X
4	Reservoir 5	3447617Y 764449X

for physical, chemical, and biological inputs. This model predicts the concentrations of chemicals in water, sediments, and suspended substances within an ecosystem, taking into account the simultaneous release of multiple chemicals. Ecofate is a computer based model for evaluating the ecological and environmental risks caused by the release of chemicals into aquatic ecosystems which can be used for water systems such as sea areas, lakes, and rivers. The model assesses the cumulative impacts arising from the introduction of chemicals and pollutants into water, sediment, and biota. It interprets the concentration of these pollutants and evaluates their toxic effects on the ecosystem's biota, as well as the risks to fish consumers exposed to pollution. This model combines several environmental fate models, food web bioaccumulation, toxic substance hazards, and human health risk assessment model with a complete information organized by the user. The model complexity is high and realistic, which can be used in suitable geographical areas in a three-dimensional form so that the user can do the modeling in complex ecosystems.[3]

The data were analyzed using SPSS software version 17, and the average treatments were compared by one-way ANOVA.

Results and Discussion

Descriptive statistics of lead concentration and some physical and chemical properties are shown in Tables 2 and 3 in ppm.

As indicated in Tables 2 and 3, the highest average total dissolved solids (TDS) in the 3D space reached 8290 ppm during the summer and 14896 ppm during the winter, specifically in 3D space 4. Also, the highest average total suspended solids (TSS) for each 3D space was 0.41 ppm during the summer season and 0.16 ppm in the winter, which was specifically observed in 3D space 3. Furthermore, the highest average total organic carbon (TOC) levels for each 3D space were 4.13 ppm in the summer and 5.48 ppm in the winter, notably observed in 3D space 4.

Figures 2-5 represent the environmental fate of lead metal in the water and sediment of Hawizeh marshes in the form of risk maps.

Figure 2 illustrates the model output depicting the distribution of chemicals or the environmental fate of lead during the summer season in the sediment of Hawizeh marshes. The concentration of lead metal in the wetland sediment is highest in 3D space 4 and exhibits the lowest concentration in 3D space 1.

Figure 3 demonstrates the model output of chemical

Table 2. Lead Concentration and Physical and Chemical Parameters in the Summer

3D Space	Title	Pb (Sediment) (ppm)	Pb (Water) (ppm)	pH	TSS (ppm)	TDS (ppm)	TOC (ppm)	Temperature (°C)
1	Average	39	0.31	7.8	0.03	4480	2.26	34
2	Average	39.7	0.34	7.76	0.27	5620	2.07	33
3	Average	28.2	0.055	7.5	0.41	8230	3	37
4	Average	11	0.025	6.86	0.03	8290	4.13	36

Abbreviations: Pb, lead; TDS, total dissolved solids; TOC, total organic carbon; TSS, total suspended solids.

Table 3. Lead Concentration and Physical and Chemical Parameters in the Winter

3D Space	Title	Pb (Sediment) (ppm)	Pb (Water) (ppm)	pH	TSS (ppm)	TDS (ppm)	TOC (ppm)	Temperature (°C)
1	Average	25.1	0.127	7.01	0.033	2068	1.81	19.6
2	Average	35.2	0.171	7.18	0.14	3276	1.13	19.6
3	Average	36.4	0.45	7.3	0.16	12934	4.26	19.5
4	Average	54.2	0.55	7.5	0.06	14896	5.48	19.5

Abbreviations: Pb, lead; TDS, total dissolved solids; TOC, total organic carbon; TSS, total suspended solids.

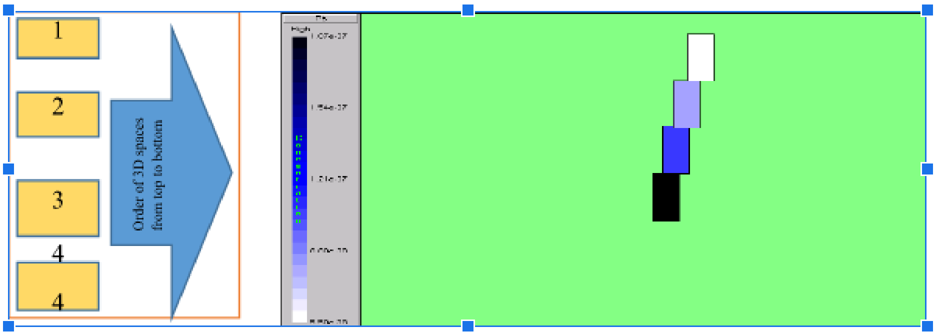

Figure 2. The output of Chemical Sub-model of Substance Inlet and Environmental Fate of Lead in the Sediment of Hawizeh Marshes From the Ecofate Model in the Summer (mg/L)

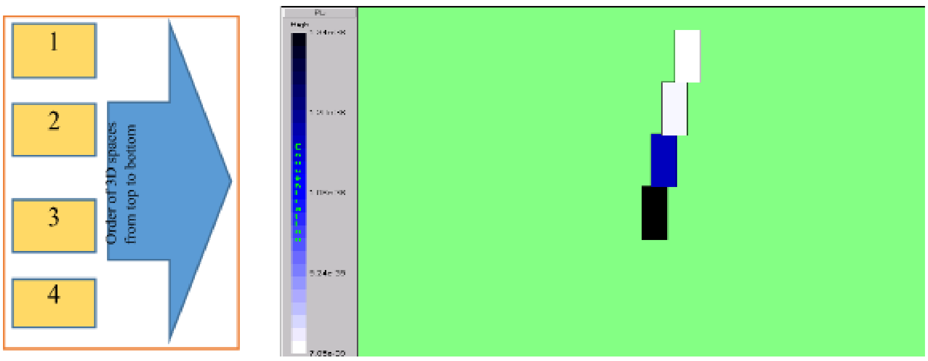

Figure 3. The output of Chemical Sub-model of Substance Inlet and Environmental Fate of Lead in the Sediment of Hawizeh Marshes From the Ecofate Model in the Winter (mg/L)

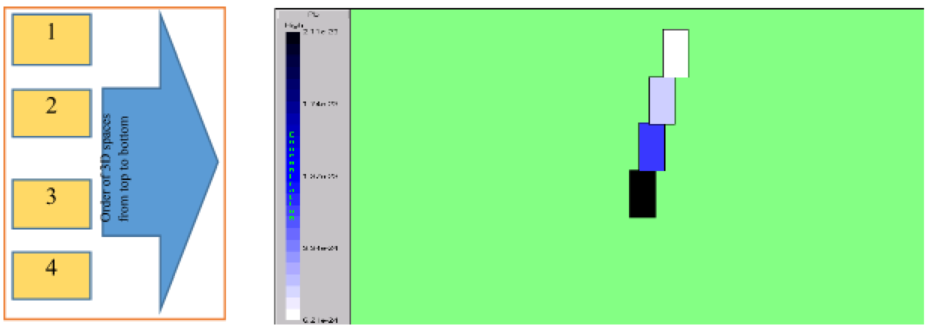

Figure 4. The Output of Chemical Sub-model of Substance Inlet and Environmental Fate of Lead in the Water of Hawizeh Marshes Derived by the Ecofate Model in the Summer (mg/L)

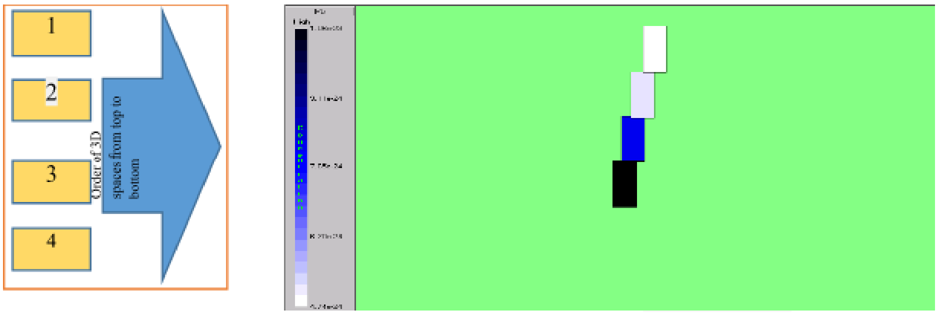

Figure 5. The Output of Chemical Sub-model of Substance Inlet and Environmental Fate of Lead in the Water of Hawizeh Marshes Derived by the Ecofate Model in the Winter (mg/L)

substances or the environmental fate of lead in Hawizeh Marshes in the winter. The concentration of lead metal in wetland sediment was elevated in 3D space 4, while the lowest concentrations were observed in 3D spaces 1 and 2.

Figure 4 illustrates the model output for chemical substances or the environmental fate of lead during the summer in Hawizeh Marshes. The concentration of lead metal in the wetland water was the highest in 3D space 4 and exhibits the lowest concentration in 3D space 1.

Figure 5 presents the model output for chemical substances or the environmental fate of lead during the winter in Hawizeh Marshes. As depicted, the concentration of lead metal in the wetland water was higher in 3D space 4, while 3D space 1 exhibited the lowest concentration.

Cross-correlation between lead concentration and sediment, water, and biological fate can help us to assess the environmental effects more accurately. The Pearson's correlation coefficient values are shown in Tables 4 and 5.

There was no significant correlation ($P = 0.298$) between the inlet lead and lead in the environmental fate. There was also no significant correlation between the inlet lead and lead in the sediment ($P = 0.286$).

There was no significant association between the inlet lead and lead in the water ($P = 0.590$).

Table 4. The Correlation Between the Lead, Environmental Fate and Sediment

		Inlet Lead	Lead in Environmental Fate	Lead in Sediment ppm
Inlet lead	Pearson's correlation	1	0.222	0.227
	P value		0.298	0.286
	N	48	48	48
Lead in environmental fate	Pearson's correlation	0.222	1	0.440
	P value	0.298		0.031
	N	48	48	48
Lead in sediment PPM	Pearson's correlation	0.227	0.440	1
	P value	0.286	0.031	
	N	48	48	48

*It is significant at the 0.05 level (2-tailed).

Table 5. The Correlation Between the Inlet Lead and the Lead in the Water

		Inlet Lead	Lead in Water
Inlet lead	Pearson's correlation	1	0.116
	Sig. (2-tailed)		0.590
	N	48	48
Lead in water	Pearson's correlation	0.116	1
	Sig. (2-tailed)	0.590	
	N	48	48

*It is significant at the 0.01 level (2-tailed).

Ecological Risk Assessment in Hawizeh Marshes

The ecological risk in Hawizeh Marshes was estimated using Equation 1[10]:

$$RQ = Exposure/Toxicity = MECi/TRVi = MECi/LC50 \quad or \quad EC50 \qquad (1)$$

MECi values were obtained from the total average of lead metal measured in the water and sediment of Hawizeh Marshes (Tables 6 and 7). The TRV values were extracted from literature[6,15] related to metals in water and sediment. The results showed that the risk index value for lead was 0.18 in water, and it was higher than 1 in sediments.

Due to the reduction of water discharge in summer, the amount of self-remediation decreases. As a result, the amount of organic matter increases. However, due to the suitable conditions of the primary producers and consumption of nutrients in autumn and winter, the increase in precipitation and self-remediation activity in the river, the amount of organic matter decreases which is less deposited in the bed sediments. Sampling station 4 (3D space 4) had a higher pollution load due to the activities related to oil exploration and related industries. The pH was higher in winter in 3D space 4 and summer in 3D space 1. The highest amount of TDS in both seasons was observed in 3D space 4. The concentration of metals in the sediments fluctuated due to the settling speed, particle size, sedimentation speed of suspended particles, and the amount of organic matter in sediments. The presence of organic substances in sediments affects the concentration of measured metals. However, the most important problem is the incompatibility of the obtained amounts of metals in sediments with the available amount of these stable pollutants for living organisms. Nevertheless, the measured values of TDS were higher than the standard set by Iran's Environmental Protection Organization. This

Table 6. Risk Fraction Values Related to the Metals in Hawizeh Marshes Water

RQ Risk Deduction (µg/L)	Total Toxicity Value of TRV (µg/L)	Measured Environmental Concentration of MCE (µg/L)	Metal Pollutant
0.18	1.32	0.25	Lead

Table 7. Risk Fraction Values Related to the Metals in Hawizeh Marshes Sediment

RQ Risk Deduction (µg/L)	Total Toxicity Value of TRV (µg/L)	Measured Environmental Concentration of MCE (µg/L)	Metal Pollutant
25.45	1.32	33.6	Lead

issue represents a serious threat and danger concerning the water status of the wetland due to the high amount of TDS in the water.

Results and Discussion

The presence of lead posed a threat to the ecological integrity of the wetland, placing 3D space 4 at a heightened risk of environmental crisis. The elevated concentration of lead in this particular 3D space can be linked to its proximity to the point where urban sewage enters the wetland. The presence of fishing areas in this space also increases its pollution load. Precipitation, winds, and water currents in winter lead to an increase in turbulence and water currents. The absorption of metals from water by suspended particles increases with the rising levels of turbulence and the load of suspended sediment materials. With the reduction of incoming runoff and water flows in summer, the organic and suspended content of metals settles in the bottom, and the concentration of heavy metals is accumulated in the suspended and the organic matter of the bed sediment reaches its maximum and increases significantly compared to the winter season. According to the results of the water and sediments of the wetland, the amount of lead in summer was higher than winter. Previous studies have indicated that hot and arid seasons effectively accumulate heavy metals in fish, water, and sediments. The number of heavy metals in the water and sediment of the Bahmanshir River located in Khuzestan, Iran, was higher in the hot and arid seasons than the cold seasons of the year, indicating the effect of dry seasons and water evaporation on increasing the concentration of heavy metals in the water, which is consistent with the results of this study. According to the calculated indicators, the cadmium, nickel, and chromium elements were higher than the permissible limit, which was attributed to the entry from the effluents of factories, oil facilities, and chemical fertilizers, which is consistent with our results. Abayat et al[10] confirmed that river water is contaminated with heavy metals in the rainy and hot seasons, and the concentration of these pollutants increases more in the summer than in the winter. A study examined the transfer of heavy metals (lead, nickel, and vanadium) in the food chain of Hawizeh Marshes and found a correlation between the concentration of heavy metals in the chain of sediment, water, reed plant and fish, and the sediment and reed plant were the main reservoir of heavy metals in the wetland.[11] The study also measured the level of risk in which the RQ ≤ 0.1 was considered as medium risk, and RQ ≤ 0.01 was considered as low risk. According to the calculations and RQ values determined for lead metal, it was found that the wetland ecosystem had a high risk level (RQ: 25.45 mg/L) in the sedimentary environment and a medium risk (RQ :0.18 mg/L) in the water environment.[11]

Conclusion

This study showed that the ECOFATE model for outgoing lead reached a specific answer regarding the environmental fate. The lead concentration in this wetland was higher than the national and international standards due to the increase in population, as well as industrial and urban wastewater, oil industries, traffic and the presence of boats in the region.

Recommendations

Based on our findings we suggest the following items:

- Identifying pollution sources and guiding the authorities to monitor the pollutants.
- Preventing the entry of pollutants into the main feeding source of the wetland
- Conducting similar research on other pollutants, especially heavy metals
- Cooperation of various environmental organizations, environmental health, fisheries research institute with universities and research centers of the country to create joint research projects
- Periodic monitoring of heavy metals regarding risk in the region
- Creating an ecological database regarding water fields as a reference for environmental studies
- Conducting research on the environmental fate of heavy metals in Hawizeh Marshes and its impact on the inhabitants of the area
- Conducting research on the food chain and the effect of heavy metals on them in Hawizeh Marshes
- Conducting research on the acute toxicity of heavy metals on the organisms of Hawizeh Marshes
- Conducting research on the effects of heavy metals on the human community living on the edge of the wetland

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Writing–original draft: Fatemeh Karimi Organi.
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Competing Interests

The authors declared no conflict of interest.

Ethical Approval

There were no ethical considerations to be considered in this research.

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