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Nickel, Lead and Zinc Contamination in the Surface Sediments of Agh Gel Wetland, Iran

Soheil Sobhanardakani[a*], Lobat Taghavi[b]

[a]Department of the Environment, College of Basic Sciences, Hamedan Branch, Islamic Azad University, Hamedan, Iran.

[b]Department of the Environment, Faculty of Environment and Energy, Science and Research Branch, Islamic Azad University, Tehran, Iran.

***Correspondence** should be addressed to Dr. Soheil Sobhan-Ardakani, **Email:** s_sobhan@iauh.ac.ir

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A-B-S-T-R-A-C-T

Background & Aims of the Study: Due to the increased human activities around the Agh Gel wetland, this study aimed to measured accumulations of heavy metals (Ni, Pb and Zn) in the surface sediment samples taken from this wetland.

Materials & Methods: Samples were taken from 10 stations and exposed to bulk digestion and chemical partitioning. Finally, Ni, Pb and Zn concentrations were monitored with ICP-OES in the sediments. Also, geo-accumulation index, contamination factor and pollution load index were used to evaluate the magnitude of contaminants in the sediment profile.

Results: The results showed, the average of metal concentration in samples (mg kg^{-1} wet weight) were 34.20±3.58 for Ni, 25.37±2.52 for Pb and 127.20±15.21 for Zn, respectively. Therefore, the pattern of metal concentrations in sediment was determined as Zinc>Nickel >Lead. According to the mean I-geo values, sediments' qualities are classified as unpolluted category for Ni and Pb. Also, sediment's quality is classified as unpolluted to moderately polluted for Zn. The CF values for all elements are classified as moderate contamination. The PLI values indicated that metal pollution exists for all sampling stations.

Conclusions: The obtained results indicated that the Agh Gel wetland has a potential to threaten by chemical pollutants such as agricultural effluent. So, in order to preserve the environment of the Agh Gel wetland from deterioration, monitoring of water and sediment qualities is recommended periodically.

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Background

Because sediments provide a refuge and substrate for many organisms, they have known as essential components in the environment. Further, biotic and abiotic processes influencing the biogeochemical cycles of water bodies are conducted in sediments. Also, sediments serve as a deposit for a different kinds of contaminants. Nowadays, it is well known that sediments absorb toxic and persistent chemicals at higher levels than those present in the water column (1).

The availability of toxic metals in sediment is largely affected by hydrological conditions and sediment properties in aquatic ecosystems especially wetlands and the toxicity of metals; also, it depends on other factors such as concentration, speciation and bioavailability (2). The sediments of aquatic ecosystems are like a gold mine in terms of giving information about the past state of the ecosystem and surrounding area. In other words, sediments are an important source of examination and assessment of transformation of heavy and toxic metals such as Zn, Pb, Cu, Ni and Cd. In this regard, the assessment of metals in

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sediment has been used for long years in observing the environmental effects (3-5).

The main sources of toxic metals in aquatic ecosystems are human activities especially industrial activities, farming and mining as well as geological structure (6-8).

Due to some metals characteristics such as environmental persistence, toxicity and ability to spread through the food chain, they were regarded as serious pollutants of aquatic ecosystems (9,10). In other words, metals cannot be biodegradable like organic contaminants, thus they accumulate in the sediment by being absorbed in complex structures. Therefore, they may turn into factors threatening the aquatic ecosystem health and may constitute a risk factor for the environment (4).

When the environmental conditions of the water column over the sediments changed, pollutants in the sediments could be released into the water and cause deteriorating the quality of the water (11). It could poses many potential threats to human and ecosystems health, hence, the distribution and pollution levels of toxic metals in sediments of aquatic ecosystems such as rivers, wetlands, etc. had been extensively studied (1,12-23).

Bioavailability of metals in sediments has a direct impact on some aquatic animal species, many of which can accumulate high contents of metals that can cause chronic effects on their populations (24). Thus, heavy and toxic metals are among the most frequently monitored pollutants.

Agh Gel wetland is located between Hamedan and Markazi Provinces of Iran (49˚ 15' E; 34˚ 32' 34" N) with an area of 17.5 km2 and 0.5 m deep approximately (25).

Aims of the study:

Due to the knowledge of distribution and concentrations of heavy metals in the soils and sediments could help to detect the source of pollution in the terrestrial ecosystems (26), the objective of this study was to analysis of Ni, Pb and Zn content in the surface sediments collected from Agh Gel wetland which is located in Hamedan province, Iran.

Materials & Methods

Samples were taken from November 2012 to January 2013 at 10 stations (Figure 1), from Agh Gel wetland by Peterson grab sampler. To avoid the contamination, sediment was transferred into pre-cleaned polythene bags. Then the samples were dried at 25 °C, crushed to a powdered form and passed through a 63 µm screen. Approximately 1 g of samples which was digested with concentrated nitric acid (65%) and hydrochloric acid (37%) (3:1, v/v) was used to prepare the specimens for further analysis. All samples were diluted, using deionized water and filtered through a 0.45 µm nitrocellulose membrane filter (Sigma-Aldrich, Germany). Some blanks were prepared in the laboratory in a similar method to the field samples (2, 27).

All metals determined by ICP-OES (Varian 710-ES, Australia) as mg kg^{-1} wet weight with three replications. The absorption wavelength for Ni, Pb and Zn were 221.6, 220.4 and 213.9 in nm, respectively.

In this study I-geo, CF and PLI were used for assessing the metals content in the sediment profile. Geo-accumulation index was used to study the degree of metal contamination in soils and sediments which was calculated according to the equation 1 (28, 29):

$$I_{geo} = \frac{log_2(Cn)}{1.5(Bn)}$$

where

Cn= the concentration of metals measured in sediment samples;

Bn= the geochemical baseline concentration of the metal; Factor 1.5 is the background matrix correction factor due to the lithogenic effects (29).

The I-geo classified to seven grades. Class 0: I-geo≤0=unpolluted; Class 1: 0<I-geo<1 (unpolluted to moderately polluted); Class 2: 1<I-geo<2 (moderately polluted); Class 3: 2<I-

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geo<3 (moderately to strongly polluted); Class 4: 3<I-geo<4 (strongly polluted); Class 5: 4<I-geo<5 (strongly to very strongly polluted) and Class 6: 5<I-geo (very strongly polluted) (21).

The CF is a parameter which was obtained by dividing the concentration of each metal in the sediment by background value:

$$CF = \frac{C_{heavy\ metal}}{C_{background}}$$

CF values were suggested by Hakanson (30), where: CF<1= low contamination; 1<CF<3= moderate contamination; 3<CF<6= considerable contamination; and CF> 6= very high contamination (29).

The PLI index assessed the level of metal pollution and calculated according to the following equation:

$$PLI = \sqrt[n]{(CF_1 x CF_2 x CF_3 x \ldots x CF_n)}$$

PLI<1= unpolluted; 1<PLI<2= moderately polluted; 2<PLI<3= strongly polluted; and PLI≥ 3= extremely polluted (31,32).

Figure 1) Map of sampling stations

Results

The average of metals concentration dispersions for the stations and statistical differences between mean values of heavy metal contents among the different stations have been shown in Table 1. The results indicated that the total concentrations showed wide variations with Ni 29~41 mg kg^{-1}, Pb 16~34 mg kg^{-1}, and Zn 95~146 mg kg^{-1}. Also the mean values of metals concentration (mg kg^{-1}, means±S.D.) in specimens were: 34.20±3.58 for Ni, 25.37±2.52 for Pb and 127.20±15.21 for Zn, respectively. Therefore, Zn was mostly metal often found in the highest concentrations in sediments, followed by Ni, and Pb.

Table 1) Heavy metals concentration (mg kg^{-1}) in sediment samples of Agh Gel wetland

Sampling station	Metal		
	Ni	Pb	Zn
1	35^{d}	16^{a}	127^{d}
2	35^{d}	23^{d}	118^{c}
3	30^{ab}	27^{f}	95^{a}
4	36^{de}	20^{b}	113^{b}
5	33^{c}	22^{cd}	146^{g}
6	41^{f}	34^{h}	138^{e}
7	29^{a}	21^{bc}	142^{f}
8	37^{e}	25^{e}	135^{e}
9	35^{d}	30^{g}	130^{d}
10	31^{b}	28^{f}	128^{d}
Min	29	16	95
Max	41	34	146
Mean	34.20	25.37	127.20
SD	3.58	2.52	15.21
Background*	31	23	65

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*a, b, c – the letters represent the statistical differences between the mean values of heavy metal contents among different sampling stations according to Duncan Multiple Range Test (p= 0.05).

Pearson correlation coefficient between the elements and the I-geo, CF, and PLI values are presented in Tables 2 and 3, respectively. The results show no significant correlation between the heavy metals in sediment samples. Also, according to the mean I-geo values, the sediments' qualities are classified as unpolluted category for Ni and Pb. Also, the sediments' quality is classified as unpolluted to moderately polluted for Zn. The CF values for all elements are classified as moderate contamination. The PLI values indicated that metal pollution exists for all stations.

Table 2) Pearson correlation coefficient matrix for heavy metals.

Element	Ni	Pb	Zn
Ni	1	0.315	0.199
Pb		1	0.034
Zn			1

Table 3) Geo-accumulation index, Contamination factor and Pollution load index for sediments from Agh Gel wetland.

Sampling Station	Ni		Pb		Zn		PLI
	I_{geo}	CF	I_{geo}	CF	I_{geo}	CF	
1	-0.41	1.13	-1.12	0.69	0.38	1.95	1.15
2	-0.41	1.13	-0.58	1.0	0.27	1.81	1.27
3	-0.63	0.97	-0.36	1.17	-0.04	1.46	1.18
4	-0.37	1.16	-0.78	0.87	0.21	1.74	1.21
5	-0.49	1.06	-0.64	0.96	0.58	2.25	1.32
6	-0.18	1.32	-0.03	1.48	0.49	2.12	1.61
7	-0.68	0.93	-0.71	0.91	0.55	2.18	1.23
8	-0.33	1.19	-0.47	1.09	0.46	2.08	1.39
9	-0.41	1.13	-0.20	1.30	0.41	2.0	1.43
10	-0.58	1.0	-0.30	1.22	0.39	1.97	1.34
Mean	**-0.45**	**1.10**	**-0.49**	**1.07**	**0.37**	**1.96**	**1.31**

Discussion

The heavy metals concentration in sediments can be a secondary source of water pollution, once the environmental condition is changed. Therefore, monitoring of sediment quality is identified as a critical step for estimating the environmental risks caused with man-made pollution by metals in aquatic systems (21,34).

The results showed that mean value of the metals concentration (mg kg^{-1}, means±S.D.) in specimens were: 34.20±3.58 for Ni, 25.37±2.52 for Pb and 127.20±15.21 for Zn, respectively.

Pearson correlation coefficient between the elements indicated that there are no significant correlations between Ni/Pb, Ni/Zn and Pb/Zn. Thus, it can be concluded that these metals might have different anthropogenic as well as natural source.

Calculated I-geo index for heavy metal concentrations in Agh Gel sediment ranged from -0.03 to 0.58, suggesting unpolluted to moderately polluted in some sampling locations. Based on this scale, I-geo index for Ni and Pb were found to be unpolluted in classification. However, the sediments were unpolluted with Zn only at the station 3. The CF values for all elements are classified as moderate contamination. According to the rank partition of PLI, the pollution class of the whole area was 1, belonging to moderately polluted degree (1≤PLI<2).

Cluster analysis was performed in order to evaluate the heavy metal interactions between water and sediment. Accordingly, Zn is strongly contaminated metal which is originated from anthropogenic sources. Also, Ni and Pb with moderate contamination deriving from both human activities (anthropogenic origins) and natural sources.

With respect to Ni, Pb and Zn, the results showed an increase in the concentration along

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the Agh Gel wetland, from the north towards the south of study area; that the highest concentrations of Ni and Pb were observed in the station 6, reaching values of 41 and 34 mg kg^{-1}, respectively. Also, the highest concentration of Zn was observed in the station 5, reaching a value of 146 mg kg^{-1}.

Although the Ni has the essential function in hydrogenase and urease enzymes in most plants and some microorganisms, but this element is a carcinogenic metal and overexposure to it can cause skin irritation, heart and liver damages and decreased the body weight (35). Sediment samples from stations 6 and 8 recorded the highest values of Ni. This may be attributed to terrigenous input, rural wastewater and agricultural effluent discharge.

Zinc is one of the essential components for humans but could be toxic even at low level concentrations. In this context, ingesting extreme amounts of Zn can impair immune function and causes vomiting, nausea, headaches, dehydration, fatigue, possible kidney failure and prostate cancer (36).

Most Pb combinations are insoluble in water. Therefore, the mobility of this metal is limited to its adsorption capacity by organic matters, hydrated iron and/or manganese oxides (10,37). Thus, this element tends to accumulate near the emission source.

The comparison of average concentration of the metals with sediment quality guideline proposed by USEPA (Table 4) (8,10,38,39) indicated that, Pb is classified in non polluted category; Ni and Zn are classified in moderately polluted category. In this regard, the comparison of the results of this study with other studies indicated in Table 5.

Table 4) U.S.EPA sediment quality guidelines (mg kg^{-1})

Metal	Not Polluted	Moderately Polluted	Heavily Polluted	Present Study
Ni	<20	20-50	>50	34.20±-3.58
Pb	<40	40-60	>60	25.37±-2.52
Zn	<90	90-200	>200	127.20±15.21

Table 5) The **comparison of present average values in sediment samples (mg kg^{-1}) with other studies**

Study Area	Ni	Pb	Zn	references
Agh Gel wetland	34.20±-3.58	25.37±-2.52	127.20±15.21	this study
Kowsar Dam reservoir (Iran)	74	42.70	35	(38)
Anzali wetland (Iran)	103.52	24.65	120.98	(39)
Anzali wetland (Iran)	135.50±19.58	33.30±5.70	104.40±20.17	(40)
Mighan wetland (Iran)	31.54±7.55	19.18±3.28	136.63±49.12	(18, 21)
Shirin Su wetland (Iran)	-	27.90±32.48	5.02±0.97	(23)
Gorgan Bay (Iran)	32.0±4.50	-	85.2±9.2	(41)
Shefa-Rud (Iran)	50.75±3.10	20.25±0.46	59.0±3.0	(42)
Bushehr (Iran)	105.70±8.16	44.60±9.72	47.7±8.74	(43)
Bamdezh Wetland (Iran)	3.48±1.03	2.80±0.26	1.43±0.359	(44)

Conclusion

Our study demonstrated that the sediment samples of Agh Gel wetland were moderately polluted with heavy metals (Ni, Pb and Zn) due to the vehicle emissions, agricultural and industrial effluents, urban and rural wastewaters and atmospheric sources. Therefore, periodically monitoring of the water and sediment qualities is recommended.

Footnotes

Conflict of Interest:

The authors declared no conflict of interest.

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