ASSESSMENT OF SEDIMENTS POLLUTION WITH HEAVY ELEMENTS USING GEO-ACCUMULATION INDEX (I-GEO) IN AL- CHIBAYISH MARSH , SOUTHERN OF IRAQ.

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ABSTRACT

Sediments Samples from Al- Chibayish marsh were collected seasonally from four stations during August, 2017 to April,2018 , to determine the concentration of some heavy elements (Cadmium(Cd), Chromium(Cr), Nickel (Ni) and Lead(Pb)) in the exchangeable and residual phases of sediments .geo-accumulation Index (I-geo) was calculated as an indicator for sediments pollution with heavy elements , in addition to that the grain size and Total Organic Carbon (TOC) % were measured in the sediments samples. Results show that the concentrations of these elements in the exchangeable phase of sediments were (0.41 , 19.70 , 46.37, 25.20) µg/g-dry weight, respectively ,while in the residual phase were (0.27, 82.95 ,75.32, 14.41) µg/g-dry weight, respectively . According to Igeo values ,the sediments of Al- Chibayish marsh can be classified as unpolluted with Cd and Pb , while unpolluted to moderately polluted with Cr , and moderate to strongly polluted with Ni .In sediments grain size analysis show that the range of sand (1-24)% ,silt (59-86)% ,clay (7-25)% , while the range values of (TOC) were 9.93% to 13.49%.

Keyword: sediment ,heavy metals, pollution, AL-Chibayishmarshes,Iraq

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INTRODUCTION

The southern Iraqi marshes , freshwater wetland is unique ecosystem .Marshes are frequently or consistently overflowed wetlands characterized by emergent herbaceous vegetation adjusted to immersed soil condition, changing water streams, and mineral soil,they cover an area about 15000-20000 km^2 (Bedair*et al*.,2006 ;USEPA, 2008).

Iraqi southern marshes form large triangular region restricted by three major southern cities: Thi-Qar to the west, Maysan to the northeast and Basrah to the south. They are vast open zone that includes both permanent and seasonal marshes (Al-Ansari and Knutsson, 2011).

The central marshes are the heart of Iraq's southern marshes, are located at the top of the concourse of the Tigris and Euphrates rivers. The Central Marshes cover an area of 3,000 km2 and can expand to 4,000 km ^{2} during the flood season (UNEP, 2006).

In natural system, marshes sediment accumulate types of chemicals that enter the water through natural and anthropogenic activities (Mitsch and Gosselink, 2007;Lu *et al*., 2011). Marshes system can act as a sink of chemicals either through sedimentation or bio-concentration.The most important and harmful pollutants of the aquatic environment heavy elements that affect the water with its dissolved phase, particulate, organisms and sediments (Al-Saad*et al*, 2009).

Heavy elements which have specific gravity more than 5g/ cm^3 and have negative effects on the environment when over-utilizes and also influence the health of humans, animals and plants .These compounds are often called trace elements because of they are present in low concentrations in the earth's crust up to 0.1%(Minkoff and Baker, 2001).

In sediments, there are six different geochemical types of elements associated with sediments. In the first one, these elements are connected with the sediment in the most labile obtained mode; these are known as exchangeable elements. The second form extracts are joint mainly with carbonates and are highly sensitive to pH variations. In the third, the elements attached to Mn oxide and partly amorphous Fe oxide and in the fourth type, to amorphous and poorly crystalline Fe oxide. In the fifth, the elements associated with the organic matter and sulfides are released. Finally, the residual portion, a fraction of elementsare strongly united to the lithogenic minerals of the sediments (Hassan ,2007 ; Al-Haidarey, 2009; Al-Hejuje,2014).Sediments have a high level of accumulation and retention of elements and pollutants, however sediments may become a source of water contamination when their surfaces are saturated with heavy elements. This effect is most distinct at high temperatures, speed water flow and small sediment particles (Hassan *et al*., 2010)

Measuring the concentration of heavy elements in sediments gives a clear perception of the level of contaminations in the aquatic environment ,these elements bound to particulate materials, which finally settle down to the sediments (Laluraj and Nair, 2006).

The present study aimed to determined the pollutants levels including the accumulation of some heavy elements (Cadmium , Chromium , Nickel and Lead) in sediments of Al-Chibayish marsh as well as to estimate the organic matter and texture of sediments.

Material and Methods :

Study area :

Central marshes (Al- Chibayish) is bordered to the north by the Amara road, the Tigris River to the east, the Gharaf river to the west and the Chibayish road adjacent to the Euphrates River in the south. Hor al-Chibayish is one of the most famous of the central marshes. Hor al-Chibayishis located north of the Euphrates and in the middle of the central marshes, before the drying, it was supplied with water from the Tigris but after the rehabilitation in 2003, it became supplied from the Euphrates river (UNEP,2002; Hussain,2014).

Four stations were selected at Central marshes (Al- Chibayish), sampling points were geo-located using geographical positioning system (GPS) at the following coordinates: 31˚ 00- 34.7= N and 47˚ 01- 50.3= E (station 1); 31˚ 01- 57.5= N and 47˚ 02- 7.7= E (station 2); N 31˚ 02- 58.4= and 47˚ 00- 57= E (station 3); 31˚ 04- 32.4= N and 47˚ 00- 58.5= E (station 4) .

Sediments samples :

Sediments samples were taken seasonally from four station inAl-Chibayishmarsh using a van veen grab sampler, the water was allowed to drain off, using polyethylene bags for the samples preserved, then the samples were placed in an ice box until reaching the lab.

The sediments samples were dried in an oven at 50 °C for approximately 3 days , grind finely using an electrical mortar and sieved through a 63 μm mesh sieve ,and stored in polyethylene bags until analysis.

Total Organic Carbon (TOC %)

Amount of total organic Carbon in sediments were measured according to burning method (Ball,1964).taking 2 gm of dried and sieved sediments were placed in pre-weighted crucible and burned at 550°C for period 48hrs.then placed in desiccators and weighted more than one to reach constant weight, The difference in mass of crucible and sediments sample before and after burning was calculated as TOC.

Grain size analysis(%)

Mean grain size analysis was carried out using 20 g of dried sediments ,and using the pipette method for silt and clay grains and standard sieves (63μm pore size)for sand grains then the triangle texture had been applied to determine the percentage of particles in sediments, these techniques according to Folk (1974) .

Extraction the exchangeable elements from sediments:

From the fraction of the grinded and sieved sediments, put (1 g) in 50 ml polyethylene tube. The exchangeable heavy metals were extracted by added 30 ml HCl(0.5N) for over night in an orbital shaker with 300 rpm ,then the solution was centrifuged at 5000 rpm for 20 minute, thesupernatant was filtered using filter paper (Watman No. 1). The filtrate was stored in tightly stopper polyethylene vials to be ready for analysis using Atomic Absorption spectrophotometer (AAS). (Chester and Voutsinou, 1981).

Extraction the residual elements fromsediments :

The residue from the above mentioned steps was washed by 40 ml deionized water, then centrifuge for 20 minutes to remove the residual of the exchangeable phase. Then samples were digested with 5 ml concentrated HNO_3 acid in Polyethylene Tri Fluro Ethane(PTFE) beaker at 70° C on hot plate near dryness state. The digestion was further proceeded with 1:1 mixture of concentrated $HClO_4$and HF acids , digested near dryness state . The residue was dissolved in 30 ml of 0.5NHCl, put on hot plate at 70° C and then made up to 30 ml with deionized water ,filtered by filter paper (Watman No. 1). The samples were stored in tightly stopper polyethylene vials to be ready for analysis using AAS (Sturgen, *et al*. 1982).

Geoaccumulation Index (I - geo)

The geo accumulation index (Igeo) ,as introduced by Müller (1969) to assessment the pollution in sediments,as follows:

$I\text{-}geo = \log_2(Cn / 1.5\ Bn)$

Where:

Cn : the element concentration (n) which measured in the sediments.

Bn :is the background concentration to the element (n)

Table (1) : The classification of sediments pollution according to I-geo values

I-geo	Pollution Sediments Case
≤ 0	unpolluted
0 ≤Igeo≤ 1	unpolluted to moderately
1 ≤Igeo≤ 2	moderately polluted
2 ≤Igeo≤ 3	moderately polluted to polluted
3 ≤Igeo≤ 4	strongly polluted
4 ≤Igeo≤ 5	strongly to extremely polluted
Igeo≥ 5	extremely polluted

Statistical Analysis:

Analysis Of Variance (One –Way ANOVA) was applied by minitabver 16.1 software to identify the existence of spatial and temporal significant differences The relationship between the parameters and indices was tested using the Parsons correlation coefficients .

Results and Dissection :

Sediments consider as the final recipient of pollutants from natural and anthropogenic origin in aquatic environments (Hassan *et al*.,2010). Thus, theyare represent as a good bio-indicator for aquatic environment pollution. Also, the accumulation of elements in the

sediment that result of long term exposure ,while the concentration of element in the water as dissolved is mainly result of recent contamination (Brankovic*et al.* ,2011).
A major part of the heavy elements, which enter the aquatic environment eventually settle down in the sediment, therefore the sediment act as archives for many pollutants such as heavy elements (Al-Khafaji ,2010). The high concentrations in sediments than in water is due to the strong binding affinity of heavy elements to the sediments (Al-Hejuje ,2014).

Table (2)the concentrations of heavy elements in both the exchangeable and residual phases of sediments

Stations	Heavy elements	Exchangeablephase	Residual phase	Total
Station 1	Cd	0.464±0.137	0.257±0.149	0.721
	Cr	19.558±9.165	97.67±25.92	117.226
	Ni	61.96±17.30	85.97±18.79	147.927
	Pb	26.460±3.447	14.783± 3.556	41.243
Station 2	Cd	0.351±0.152	0.284±0.169	0.635
	Cr	11.554±5.755	67.76±19.65	79.312
	Ni	26.42±11.90	65.80±14.77	92.222
	Pb	24.008±4.364	13.539±4.068	37.547
Station 3	Cd	0.401±0.168	0.250±0.150	0.651
	Cr	30.400±11.231	91.06±25.77	121.458
	Ni	58.25±16.42	79.71±15.89	137.963
	Pb	24.674±3.745	15.267±4.052	34.941
Station 4	Cd	0.434±0.065	0.310±0.197	0.743
	Cr	17.283±9.847	75.32±25.16	92.608
	Ni	38.86±20.37	69.82±17.78	108.679
	Pb	25.678±1.450	14.053±4.501	39.735

The concentrations of cadmium in the exchangeable phase was ranged from (0.351μg/g dry weight) at station 2 to (0.464μg/g dry weight) at station 1. Non-significant differences ($P>0.05$) were found among stations. In the residual phase of sediments it's ranged from (0.250 μg/g d. w) at station 3 to (0.3106μg/g d. w) at station 4.Also,non-significant differences ($P>0.05$) were found among stations (Table2).
In sediments ,the concentrations of chromium in the exchangeable phase ranged from (11.554μg/g d. w) at station 2 to (30.400μg/g d. w) at station 3. Significant differences ($P<0.01$) were found among stations. The concentrations of chromium in the residual phase of sediments ranged from (67.76 μg/g d. w) at station 2 to (97.67 μg/g dry weight) at station 1, significant differences ($P<0.05$) were found among stations (Table 2) .
In sediments, the concentrations of nickel in the exchangeable phase ranged from (26.42μg/g d. w) at station 2 to (61.96μg/g d. w) at station 1. Significant differences ($P<0.01$) were found among stations. The concentrations of nickel in the residual phase of sediments was ranged from (65.80μg/g dry weight) at station 2 to (85.97μg/g dry weight) at station 1. Significant differences ($P<0.05$) were found among stations (Table 2) .
The concentrations of lead in the exchangeable phase of sediments ranged from (24.008μg/g dry weight) at station 2 to (26.460μg/g dry weight) at station 1. Non-significant differences ($P>0.05$) were found among stations. The concentrations of lead in the residual phase of sediments ranged from (13.539μg/g dry weight) at station 2 to (15.267μg/g dry weight) at station 3. Non-significant differences ($P>0.05$) were found among stations.

The results shown that the concentrations of Cd and Pb in the exchangeable phase of sediments were higher than those in the residual phase of sediments(Table2),this finding could be a good evidence that there is an anthropogenic origin of pollutants which incorporated into the sediment from water column by processes such as adsorption , organic complication and precipitation to sediments, this finding was in agreement with (Habeeb , 2015). Significant correlations between heavy elements in the sediments (Table 3) suggested that they had the same geochemical origin or behaviors (Song *et al*. , 2010 ; Manoj*et al*. , 2012).

Most heavy element in sediment positively correlated with clay particles and negatively correlation with the sand (Table 3) , this could be attributed to the sediment particles size which play an important role in the concentration and distribution of heavy element . Small particle size which have a large surface area ,such as clay and silt has an ability to accumulate higher concentration of heavy element because of these particles allowed to adsorption of element into their surface (Bentivegna*et al*. ,2004) .

Moreover, high concentrations of heavy elements in sediment may be due to the increasing plant abundant at these stations in marshes which played an important role to increasing the heavy elements in the sediments(Al-Atbee,2018 unpublished data). Plants work to reduce flow rate of water and this leads to deposit of suspended matter ,which containing high concentrations of heavy elements, to the sediments, this finding was in agreement with Mashkool (2012).

Table (3): The Perasons correlation coefficients between total heavy metals in sediments and the related environmental variable measured in Al-Chibayish marsh .

Variables	Cd	Cr	Ni	Pb
Cd	1			
Cr	0.66 **	1		
Ni	0.33 **	0.78 **	1	
Pb	0.88 **	0.70 **	0.37 NS	1
Sand %	-0.05 NS	-0.24 NS	-0.49 NS	-0.15 NS
Silt %	-0.09 NS	-0.05 NS	0.21 NS	-0.07 NS
Clay %	0.22 NS	0.40 NS	0.34 NS	0.32 NS
TOC %	0.09 NS	0.14 NS	0.16 NS	-0.04 NS

**** : Significant correlation at P<0.01 ; NS: Non- Significant correlation(P>0.05)**

The terms clay, silt , and sand represents the soil particles(Balasim, 2013).The grain size of Al-Chibayish marsh different in their percentage from station to another according to the geological origin and the effluent dischargesat each station . Generally, according to the texture compounds percentage (Fig 1), the sediments of Al-Chibayish marsh can be considered as silt-clay sediments .

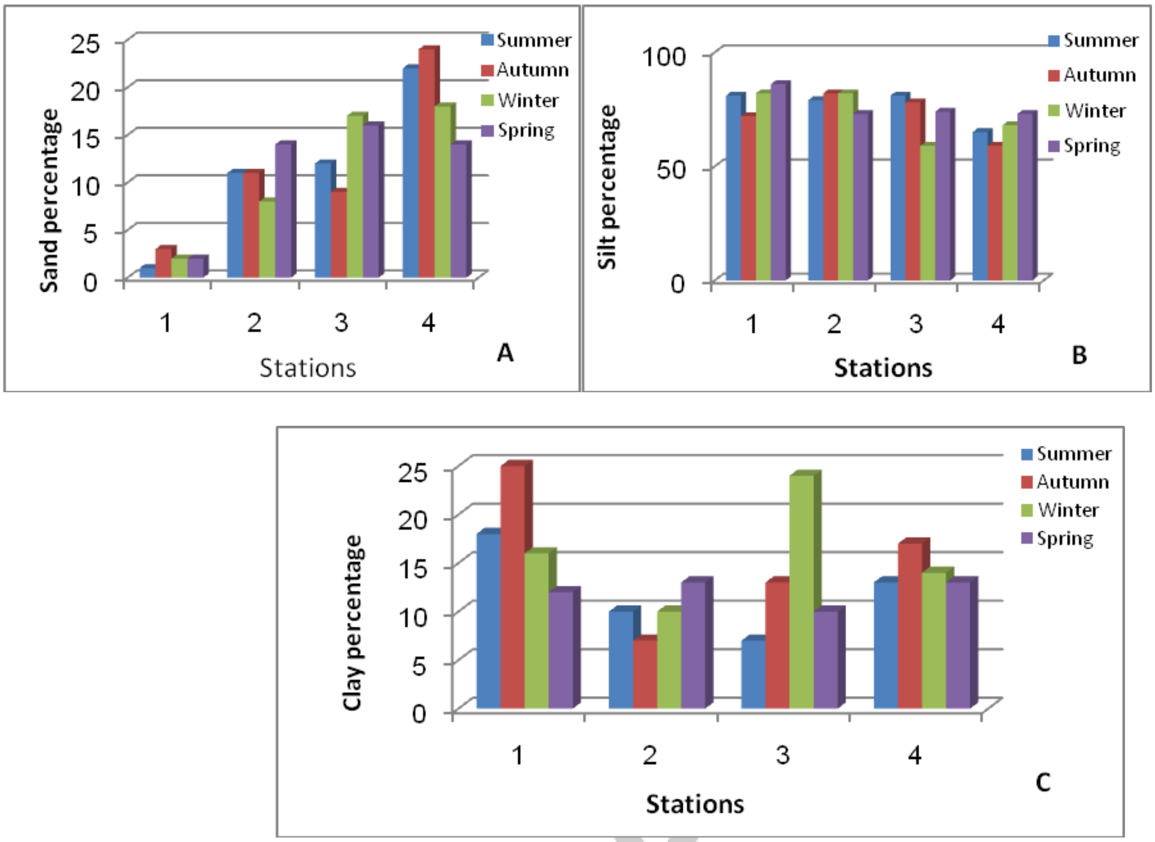

Fig (1) Grain size (%)in the sediments of the studied area

In sediments,the wastes of human and animal play an important role to increasing the content of organic carbon(Al-Hejuje,2014). The chemical and biological processes that take place in sediment greatly affect the proportion of organic carbon (Balasim , 2013). The highest values which recorded during winter (Table 4) related to high precipitation ratio of dead aquatic plants during winter, while the lowest values during summer at some stations may be due to the rise of temperature which stimulate microbial enzymes activities , therefore the biodegradation processes generally increases with the increasing temperature (Foghtet *al* ., 1996) . TOC values showed negative significant correlation with water temperatures (r=- 0.627,p<0.01) .Result of the present study were in agreement with (Al-Abadi ,2011;Maskhool,2012).

Table(4) Total Organic Carbon (TOC %) during the studied period in the studied area sediments

Stations	Season	TOC % (Mean ± SD)
Station 1	Summer	10.58 ±0.23
	Autumn	11.84 ±0.47
	Winter	12.68 ± 1.21
	Spring	12.26 ± 0.16
Station 2	Summer	9.93 ± 1.43
	Autumn	10.32 ± 0.20
	Winter	12.62 ± 0.12
	Spring	11.61 ± 0.17
Station 3	Summer	10.26 ± 0.64
	Autumn	10.06 ± 0.32
	Winter	11.14 ± 1.39
	Spring	11.43 ± 1.51
Station 4	Summer	11.49 ± 4.99
	Autumn	11.65 ± 0.22
	Winter	13.49 ± 0.16
	Spring	13.18 ±1.37

The Geo-accumulation Index (I geo) :

The I-geo values can be used effectively to determining the extent of heavy element accumulation in sediments .The I-geo grades for the surface sediments in the present study differ from element to element and from station to station . According the I-geo values the sediments at all the studied stations were considered as unpolluted with Cd and Pb ,but unpolluted to moderately polluted with Cr , and moderate to moderat-strongly polluted with Ni .This could be due to the high concentrations of these elements in surface sediments that exceeded the world surface rock average according to CBSQG(2003) values .The present result was in agreement with Al-Sabah and Aldhahi (2017)who found that the sediments of Auda marsh was unpolluted with Zn , Fe, Cu and Pb ,While disagreement with Al-Haidarey*et al*.,2010 found that the sediments of Al-Hawizeh Marshes were suffering from moderately to strongly contaminate with the As ,Cd, Cr, Co ,Cu and Pb according to I-geo values. The different in results may be due to the different in the studied areas characteristics and different the studies periods.

The values of I-geo in sediments for cadmium ranged from (-4.09, unpolluted) at station 3 in Spring to(-0.61 , unpolluted) at station 4 in Winter (Table5) . Non- significant differences

(P>0.05) were found among stations .While significant differences (P<0.01) were found among seasons, the lowest mean value (-2.87 unpolluted) was found in Spring , but the highest mean value (-0.90unpolluted) was found in Winter .

The values of I-geo in sediments for chromium ranged from (-0.44 , unpolluted) at station 2 in Spring to(1.29 , moderately polluted) at station 3 in Winter (Table5) . Significant differences (P<0.01) were found among seasons , thelowest mean value(0.02 unpolluted to moderately) was found in spring , but the highest mean value(1.07 moderately polluted) was found in Winter .Also significant differences (P<0.01) were found among stations, the lowest mean value(0.25 unpolluted to moderately) was found at station 2 , but the highest mean value(0.86 moderately polluted) was found at station 3.

The values of I-geo in sediments for nickel ranged from (1.00 , moderately polluted) at station 4 in autumn to(2.22 , moderate to strongly polluted) at station 1 in winter (Table5) . Significant differences (P<0.05) were found among seasons , the lowest mean value(1.55 t moderately polluted) was found in autumn, but the highest mean value(1.97 moderately polluted) was found in winter .Also significant differences (P<0.01) were found among stations, the lowest mean value(1.41 moderately polluted) was found at station 2 , but the highest mean value(2.1 moderate to strongly polluted) was found at station 1.

The values of I-geo in sediments for lead ranged from (-1.07 , unpolluted) at station 2 in spring to(-0.20 , unpolluted) at station 1 in autumn (Table5) . Significant differences (P<0.01) were found among seasons , the lowest mean value(-0.91 unpolluted) was found in spring, but the highest mean value(-0.29 unpolluted) was found in winter .Non-significant differences (P>0.05) were found among stations.

Table(5):The I-geo values and descriptions the status of sediments pollution at the studied stations during periods of the study.

Stations	Season	I-geo Cd value	Descriptions	I-geo Cr value	Descriptions	I-geo Ni value	Descriptions	I-geo Pb value	Descriptions
Station 1	Summer	-1.06	unpolluted	0.72	U-MPolluted	2.17	M –S polluted	-0.48	unpolluted
	Autumn	-0.77	unpolluted	0.85	U-MPolluted	2.00	M –S polluted	-0.20	unpolluted
	Winter	-0.89	unpolluted	1,27	Moderately	2.22	M –S polluted	-0.28	unpolluted
	Spring	-2.06	unpolluted	0.21	U-MPolluted	1.93	Moderately	-0.79	unpolluted
Station 2	Summer	-1.09	unpolluted	0.32	U-MPolluted	1.45	Moderately	-0.69	unpolluted
	Autumn	-0.92	unpolluted	0.17	U-MPolluted	1.31	Moderately	-0.32	unpolluted
	Winter	-1.08	unpolluted	0.72	U-MPolluted	1.62	Moderately	-0.30	unpolluted
	Spring	-3.28	unpolluted	-0.44	Unpolluted	1.18	Moderately	-1.07	unpolluted
Station 3	Summer	-0.86	unpolluted	1.00	Moderately	2.10	M –S polluted	-0.42	unpolluted
	Autumn	-0.99	unpolluted	0.81	U-MPolluted	1.89	Moderately	-0.22	unpolluted
	Winter	-1.02	unpolluted	1.29	Moderately	2.17	M –S polluted	-0.35	unpolluted

	Spring	-4.09	unpolluted	0.08	U-MPolluted	1.70	Moderately	-1.06	unpolluted
Station 4	Summer	-0.77	unpolluted	0.73	U-MPolluted	1.82	Moderately	-0.46	unpolluted
	Autumn	-1.21	unpolluted	-0.21	Unpolluted	1.00	Moderately	-0.46	unpolluted
	Winter	-0.61	unpolluted	0.98	U-MPolluted	1.87	Moderately	-0.25	unpolluted
	Spring	-2.09	unpolluted	0.21	U-MPolluted	1.82	Moderately	-0.71	unpolluted

U-M :unpolluted –moderately

M-S :moderate – strongly polluted

Conclusion :

Sediment pollution in the present study was assessed using geoaccumulation index (Igeo).According to Igeo values, the surface sedimentsof Al-Chibayish marsh can be classified as unpolluted with Cd and Pb , while unpolluted to moderately polluted with Cr , and moderate to moderate- strongly polluted with Ni .

The results shown that the concentrations of Cd and Pb in the exchangeable phase of sediments were higher than those in the residual phase of sediments .According to the texture compounds percentage , the sediments of Al-Chibayish marsh can be considered as silt-clay sediments .

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