Applied heavy elements pollution index (HPI) as a water pollution indicator at Al- Chibayish marsh in Thi-Qar province, southern Iraq

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Abstract

Water samples were collected seasonally from four stations selected at Al- Chibayish marsh in Thi-Qar province, southern Iraq from the period August, 2017 to April, 2018 to determine the concentration of some heavy elements (Cadmium (Cd) ,Chromium(Cr),Nickel(Ni) and Lead(Pb)) and their distribution as dissolved and particulate phases (exchangeable and residual phase) in water . Heavy elements pollution index (HPI)was applied as an index for heavy elements pollution .Results showed that the mean concentrations of the studied elements(Cd, Cr, Ni and Pb) as dissolved phase were (0.06 , 2.03 ,0.56 , 2.97)µg/l, respectively , whereas in the exchangeable phase of particulate were(14.47 , 53.97 , 90.91 , 332.78)µg/g dry weight respectively , and in the residual phase of particulate were (12.21 , 225.60 , 243.66 , 242.25) µg/g dry weight respectively . The results indicated that mean HPI values were found to be below the critical pollution index value of 100 , HPI values were ranged from 4.39 to 12.51 referred to unpolluted water according to the permissible values of dissolved elements.

Key words : Al- Chibayish marsh , HPI , Heavy Elements pollution, Indices .

Introduction.

Heavy elements is one of the most important and dangerous types of pollution which threatens the aquatic environment with its living and non-living components, and therefore affects the living organisms (1).

These elements have specific gravity more than 5g/ cm^3 and harmful effects on the environment when over-utilizes and also influence the health of humans, animals and plants .These elements are often called trace elements because they are present in low concentrations in the earth's crust up to 0.1% (2).

Pollution of water with heavy elements is a serious concern in today's world (3). Consequently, pollution of heavy elements has become a main environmental problem because of its toxicity, non-degradable and constant nature .This leads to their accumulation in plants,   microorganisms, and various aquatic organisms, which, in turn are, transferred to humans through the food chain and therefore lead to multiple human health problems (4).

Heavy elements are present in the aquatic environment at very little concentrations when these water bodies are away from origin of pollution, but concentrations may increase as a result of fast growth of populations and different human activities (5). The elements concentrations may increase above natural levels due to the release of industrial, agricultural, household and other wastes (6).

There are various sources that supply the aquatic environment with heavy elements at different concentrations, and can be divided into two main sources: natural resources and anthropogenic resources (7).

Natural resources include the soil washing, weathering of natural mineral rocks, and natural events, which carried by rainwater, flood water to the aquatic environment. Also, heavy elements enter the aquatic environment because of organisms hydrolysis after death (8,9). While the other source of heavy elements is anthropogenic sources, they represent all sources of human activity like fertilizers, industrial waste, agricultural pesticides, textiles, traffic emissions, weathering of buildings, dyes, the utilization of oil refinery products and atmospheric deposition(10). The partitioning of metals between dissolved and suspended particulate matter determines their ultimate fate in the aquatic environment (11).

All heavy metals exist in surface waters in colloidal, particulate, and dissolved phases (12). The dissolved metals which consist the ions of elements and the organic or inorganic chemical compounds existent in the water column and which have a diameter lower than 0.45 μm(13).

The particulate heavy elements are the elements in the suspended matter that have a diameter higher than 0.45 μm. and have been divided into two kinds: biotic, which includes elements found in microorganisms (phytoplankton, zooplankton, bacteria, and fungi) and some vital activity products and abiotic which consists of the heavy elements that are present in the organic and inorganic chemical compounds like clay particles, silts, quartz, siliceous silica compounds and residues of dead organisms (14).

 In the Mesopotamian marshlands, heavy elements are introduced either in particulate phase or in soluble through different sources including urban runoff and agricultural discharge (15). Heavy elements can be double-edged sword; they possibly will have beneficial and dangerous effects on animal, plant and human life depending on their concentrations, toxicity, and ability to accumulate in aquatic environment (16, 17). Heavy elements can also reduction the growth rates of aquatic organisms and damage their reproduction. (18).

 The objectives of the present study is to determine the spatial and temporal variations of heavy elements at Al-Chibayish marshes, also to apply HPI (heavy metals pollution index) as an effective tool to assess the water pollution with heavy elements.

Material and Methods

 Water samples (5L), were collected from each of four stations at Al- Chibayish marsh, Southern of Iraq 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) . Water samples were collected from each stations at least 20 -30 cm under the water surface ,at the middle of the station by polyethylene containers and preserved cooling until reach the lab.Water temperature ,pH ,salinity , were measured at field using Multi meter type (Multi 350 I SET 5).While turbidity were measured using turbidity meter type (TURB 355 IR WTW).

 In the laboratory, water samples (5 L) were filtered as soon as possible through pre-washed (0.5N HCl) and pre-weighted millipore filters paper (0.45μm pore size). the retained matter on the surface of filters were considered as particulate phase while the filtrated water was considered as dissolved phase. Then , the filtrate was pre-concentrated according to (19) method, using chelating ion exchange resin (Purolite-C-100 resin in hydrogen form), about 5 L of filtrate was pass through 1.5 cm diameter ion exchange column which was filled with the resin to approximately depth 12 cm (20).

 The resin was packed freshly and reactive before use by passing 30 ml of (2N) HNO_3, then add 100 ml of deionized water, and 30 ml of (3N) NH4OH, and then 100 ml of deionized water. The filtrate water allowed to pass through the column with a flow rate of about 8 ml/min, the bounded heavy metals were eluted using 50 ml of 2N HNO_3. Then column was washed with 100 ml of deionized water, the elutes were collected in 100 ml clean teflon beaker, put on hot plate at $70°$ C until the sample volume became less than 25 ml, then the sample was completed to 25 ml with deionized water and placed in tightly stopper polyethylene vials to be ready for analysis of the metals using Flame Atomic Absorption Spectrophotometer (FAAS).

 The concentration of elements as dissolved (μg/L) was calculated according to the following equation:

$$\text{Concentration (μg/L)} = A*B*1000/V$$

Where:

A: Element concentration that calculated from standard curve (mg/L)

B: Final volume of extracted sample (mL)

V: Initial volume of sample (mL)

Particulate Phase:

Exchangeable elements :

  After filtration, the filters were dried in oven at 60C° until dry then cooled and weighted, to extracted the exchangeable heavy metals used 30 ml HCl (0.5N) for overnight in an orbital shaker with 300 rpm, then centrifuged at 5000 rpm for 20 minute, the supernatant was filtered using filter paper (Watman No. 1). The filtrate was stored in tightly stopper polyethylene vials to be ready for analysis the elements in the exchangeable phase (21).

Residual elements:

  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 residue were digested with 5 ml concentrated HNO_3 acid in teflon beaker at 70 C° on hot plate near dryness. The digestion was further proceeded with 5ml of 1:1 mixture concentrated $HClO_4$ and HF acids ,then digested near dryness state . The residue was dissolved in 30 ml of 0.5 HCl, 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 the elements in the residual phase (22).

  The concentration of elements as Particulate Phase (μg/g d.w.) was calculated according to the following equation:

$$\text{Concentration (μg/g d.w.)} = A*B/W$$

Where:

A: Element concentration that calculated from standard curve(mg/L)

B: Final volume of extracted sample (ml)

W: dry weight of sample (g).

Heavy Element Pollution Index (HPI):

  The heavy element pollution index (HPI) is a method of rating that shows the composite influence of all heavy element on the overall quality of water and contamination (6). HPI in water was developed by assigning weight or rating (Wi) for each selected element. The weighing factors was between zero and one, reflecting the relative importance of individual quality considerations.

$$Wi= K / Si$$

Where :

Wi: is the unit of weightage, k: is the constant of proportionality (k=1), and Si: is the recommended standard for ith parameter.

The sub index (Qi) of the ith parameter was calculated according to(6):

$$Qi = ([Mi-Ii]) / (Si-Ii) *100$$

where:

Mi: is the monitored value of heavy element of ith parameter in µg/l

Ii: is the ideal value

Si: refers to the standard value of the ith element.

The HPI model (23) was calculated as:

$$HPI= \sum_{i=1}^{n} Wi\,Qi \Big/ \sum_{i=1}^{n} Wi$$

The higher HPI value causes the greater damage to health. critical pollution index value is 100 (6).

Statistical Analysis

Analysis Of Variance (One –Way ANOVA) was applied by Minitab ver. 16.1 software to identify the existence of spatial and temporal significant differences The relationship between the parameters and indices was calculted using the Pearson, s Correlation Coefficients.

Results and Discussion

The physiochemical parameters of the study stations are showed in (Table 1). The values of water temperature ranged from 10.5 C ˚ at station 2 in winter to 33C˚ in summer at station 1. (ANOVA) test showed non-significant differences in water temperature among stations. In contrast, there were significant differences ($p \leq 0.05$,) were found among seasons. Hydrogen ion concentration (pH) were on alkaline side at all the studied stations were ranged from 7.24 at station 2 in spring to 8.15 in summer at station 4. Significant differences ($P \leq 0.05$) were found among stations, while non-significant differences were found among seasons. The highest levels of salinity was recorded in summer (3.4PSU) at station 4, while the lowest value (2.5 PSU) was recorded in winter at station 3. Non-Significant differences were found among seasons, while significant differences ($P \leq 0.05$) were found among stations . The highest value of turbidity was recorded in winter (50.55 NTU) at station 4, while the lowest value (1.3 NTU) was recorded in summer at station 2. Non-Significant differences were found among seasons, , significant differences ($P \leq 0.05$) were found among stations.

Table(1): Values of some environmental factors in the study stations during the study period.

Stations	Seasons	Water temp.C˚	pH	Salinity (PSU)	Turbidity
1	summer	33	7.8	2.7	8.22
	autumn	26.2	7.98	2.7	9
	winter	11.8	7.67	2.6	40.15
	spring	20.9	7.65	2.6	42.79
2	summer	29	7.59	2.8	1.3
	autumn	21.9	7.73	2.6	1.63
	winter	10.5	7.32	2.6	1.64
	spring	17.7	7.24	2.7	7.75
3	summer	32	7.83	3	10.17
	autumn	24.5	7.89	2.7	5.16
	winter	11.3	7.79	2.5	16.23
	spring	19.1	7.62	2.7	15.33
4	summer	32	8.15	3.4	48.82
	autumn	25.4	7.79	3.3	48.15
	winter	11.6	7.89	3.3	50.55
	spring	20	7.79	3.1	34.85

 Cadmium:The concentrations of cadmium in dissolved phase ranged from (0.003µg/l) at station 1 in summer to (0.116 µg/l) at station 1 in autumn (Fig.1). Non-significant differences were found among stations or among seasons.

In particulate phase, the highest concentrations of the exchangeable phase was (119.67µg/g dry weight) at station 2 in summer, while the lowest concentrations (ND) at station 3 in spring. Non-significant differences were found among stations or among seasons (Fig.2-A). In residual phase of particulate, the concentrations of cadmium ranged from (0.11µg/g dry weight) at station 1 in spring to (66.02 µg/g dry weight) at station 2 in summer. Non-significant differences were found among seasons, whereas significant differences ($P \leq 0.05$) were found among stations, the highest mean value (33.60µg/g dry weight)was recorded at station 2 and the lowest mean value (2.47µg/g dry weight) was recorded at station 4 (Fig.2-B).
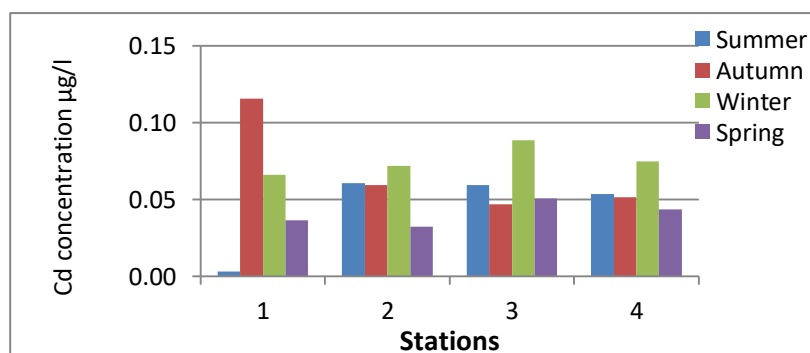

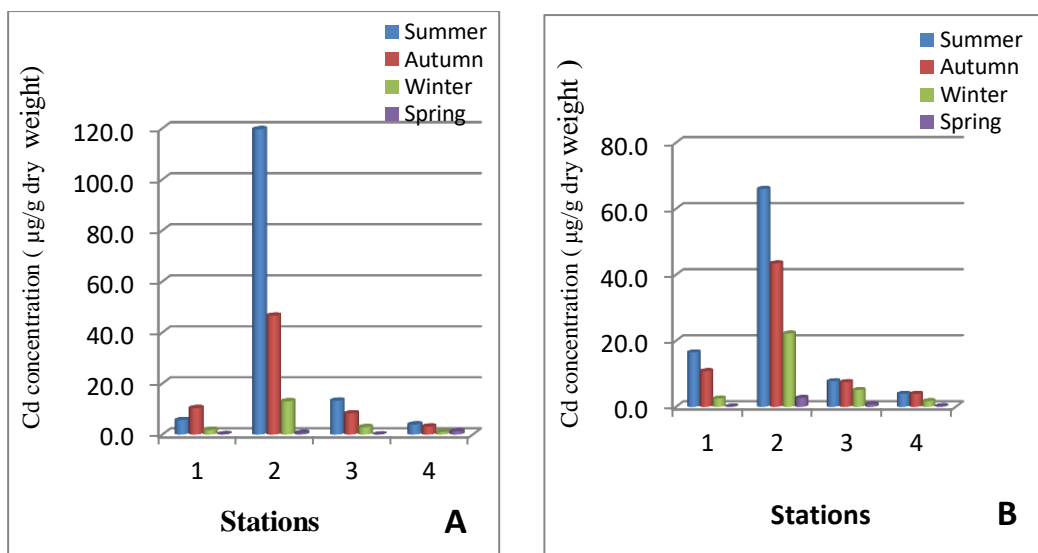Fig.(1) The concentrations of Cadmium in water as dissolved phase (µg/l).

Fig.(2) The concentrations of Cadmium in particulate phases : A (exchangeable) and B (residual).

Chromium : The concentrations of chromium in dissolved phase ranged from (0.344µg/l) at station2 in autumn to (4.465µg/l) at station 3 in winter (Fig.3). Non-significant differences were found among stations or seasons.

In particulate phase , the concentrations of the exchangeable phase ranged from (ND) at station 2 in spring to (129.28 µg/g dry weight) at station 2 in summer. Non-significant differences were found among stations. But significant differences ($P \leq 0.05$) were found among seasons, the highest mean value (94.22 µg/g dry weight) was recorded in summer and the lowest mean value (13.61 µg/g dry weight) was recorded in spring (Fig.4-A)

The chromium concentrations in the residual phase of particulate ranged from (2.53 µg/g dry weight) at station 4 in summer to (907.55 µg/g dry weight) at station 2 in winter. Non-significant differences were found among seasons, but significant differences ($P \leq 0.05$) were found among stations, the highest mean value (534µg/g dry weight) was recorded at station 2 and the lowest mean value (87.6µg/g dry weight) was recorded at station 4(Fig.4-B).
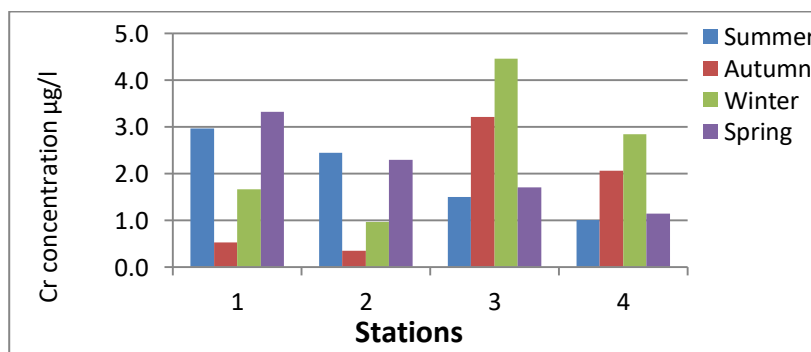

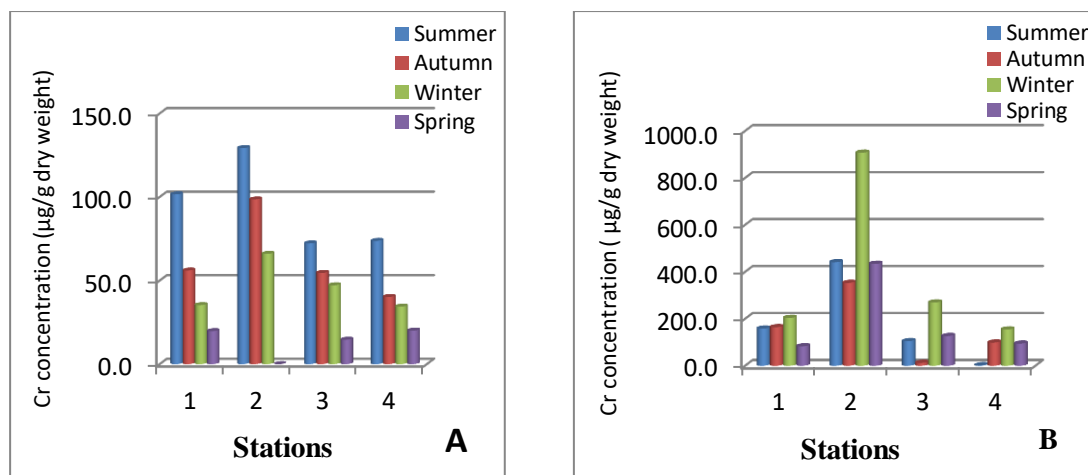Fig.(3) The concentrations of chromium in water as dissolved phase (µg/l).

Fig.(4) :The concentrations of chromium in particulate phases: A(exchangeable) and B (residual).

Nickel: The nickel concentrations as dissolved phase ranged from (0.20 µg/l) at station 4 in autumn to (1.05 µg/l) at station 3 in spring (Fig.5). Significant differences (P≤0.05) were found among seasons, the highest mean value (0.97 µg/l) during spring and the lowest mean value (0.32 µg/l) during summer. Whereas non-significant differences were found among stations.

In particulate phase , the concentrations in the exchangeable phase ranged from (26.16 µg/g dry weight) at station 2 in autumn to (191.60 µg/g dry weight) at station 2 in summer. Significant differences (P≤0.05) were found among seasons, the highest mean value (158.83 µg/g dry weight) was recorded in summer and the lowest mean value (59.45 µg/g dry weight) was recorded in winter, but non-significant differences were found among stations (Fig.6-A).The concentrations of nickel in the residual phase of particulate ranged from (13.33 µg/g dry weight) at station 3 in autumn season to (702.54 µg/g dry weight) at station 2 in summer . Non-significant differences were found among seasons, but significant differences (P≤0.05) were found among stations, the highest mean value (588.39 µg/g dry weight) was founded at station 2 and the lowest mean value (111.19 µg/g dry weight) was founded at station 4(Fig.6-B).
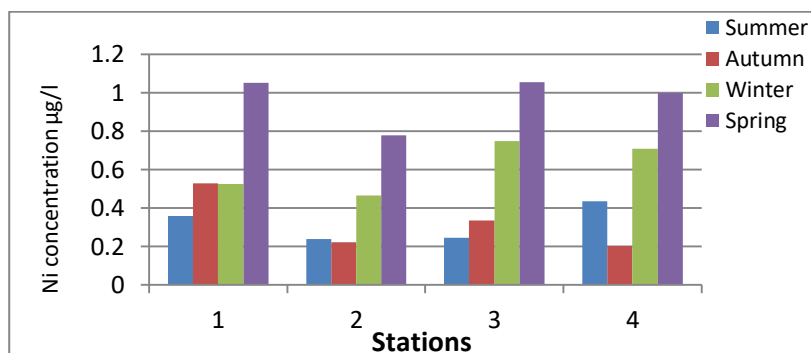

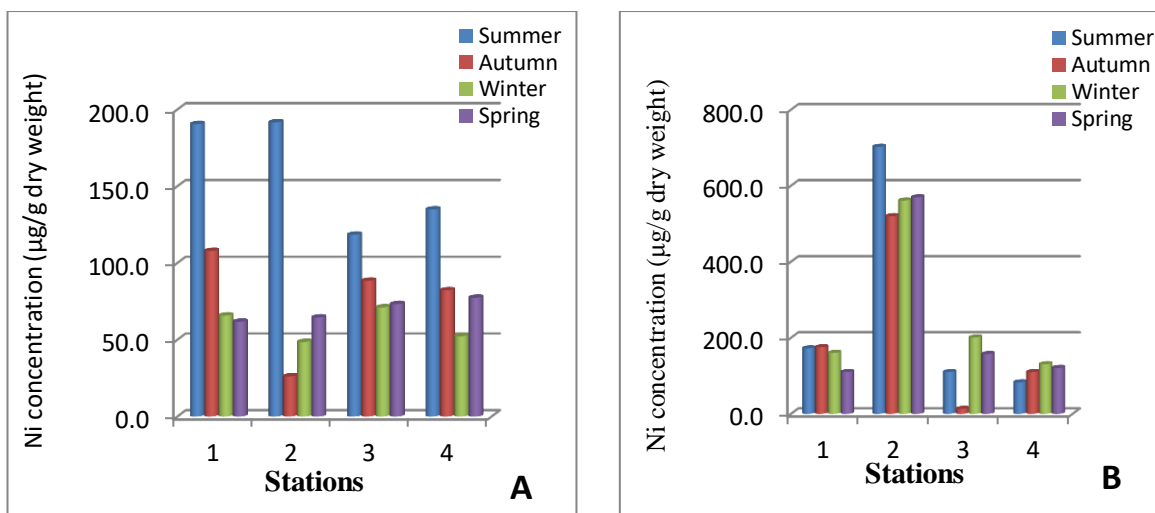Fig.(5) The concentrations of nickel in water as dissolved phase(µg/l)

Fig.(6) The concentrations of Nickel in particulate phases: A(exchangeable) and B(residual).

Lead: The lead concentrations in dissolved phase , was ranged from (1.59 µg/l) at station 2 in spring to (5.15 µg/l) at station 3 in summer (Fig.7) . Non-significant differences were found among stations. Whereas significant differences($P \le 0.05$) were found among seasons, the highest mean value (4.04 µg/l) during autumn and the lowest mean value (1.74 µg/l) during spring.

In particulate phase , the concentrations in the exchangeable phase ranged from (26.14 µg/g dry weight) at station 1 in spring to (1831.24 µg/g dry weight) at station 2 in summer. ANOVA test show non-significant differences were found among stations and seasons (Fig.8-A).The concentrations of lead in the residual phase of particulate ranged from (ND) at station 2 in spring season to (1357.27 µg/g dry weight) at station 2 in summer. Significant differences ($P \le 0.05$) were found among stations, the highest mean value (655.5 µg/g dry weight) was recorded at station 2 and the lowest mean value (50.5µg/g dry weight) was recorded at station 4. While non- significant differences were found among seasons (Fig.8-B).
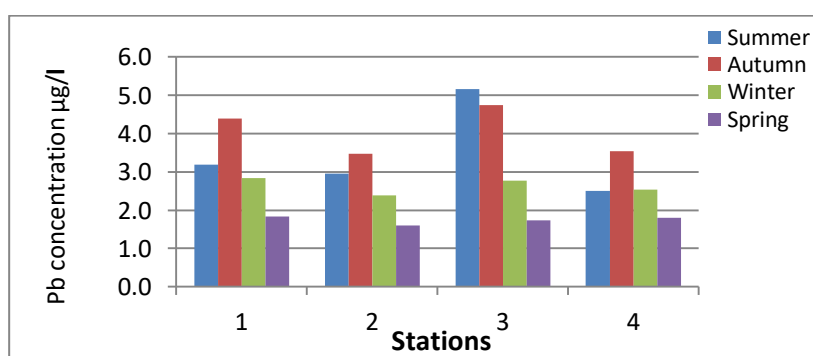

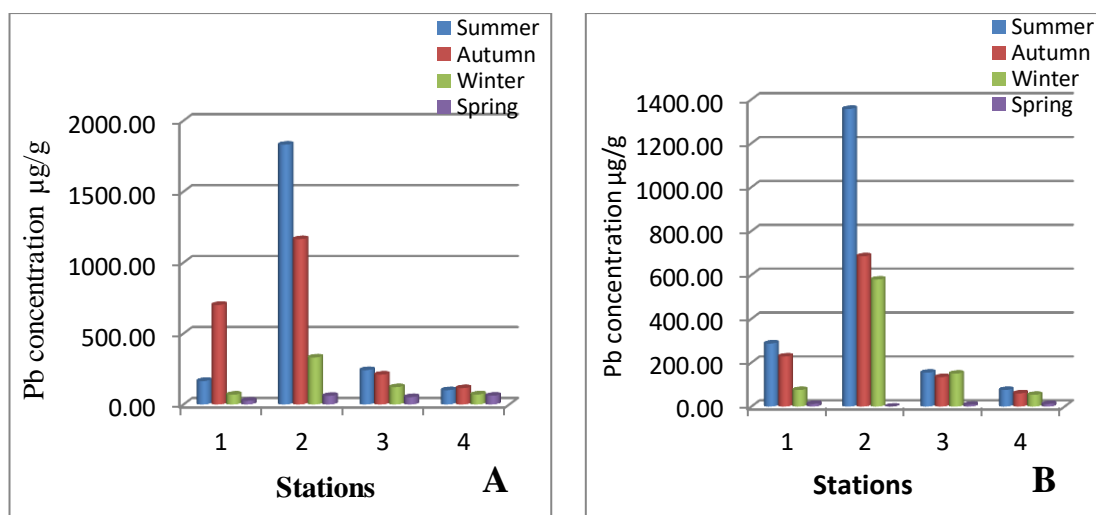Fig.(7) The concentrations of Lead in water as dissolved phase(µg/l).

Fig.(8):The concentrations of lead (µg/g dry weight)in particulate phases: A(exchangeable) and B(residual).

The partition between the elements in dissolved and suspended particulate matter determines their ultimate fate in the aquatic environment (24).

In the present study the concentrations of the studied heavy elements (Cd ,Cr ,Ni and Pb) as dissolved phase at most stations and seasons were below the permissible limits of drinking water according to (25), and this result was in agreement with most studies done at marshes , this decreasing of elements concentrations in the studied area may be due to many factors such us : the lowest level and flow rate of water in the marshes, quantities and qualitative of plankton and suspended material that load in the water, complexion with organic matter and precipitate to the sediment, accumulation of element in aquatic plant (26 , 27, 24).

Decreasing of heavy elements in dissolved phase in the present study may be due to the removal of these elements by their deposition on suspended materials, sedimentation and/or removal by the organisms, especially aquatic plants. This finding was in agreement with (28) who noted that the heavy elements in the water are eventually separated into suspended matter, sediments or living organisms.

Negative significant correlations between Ni and Pb (r=-0.73,P<0.01)suggested that they had different pollutants origin , or they have different characteristics (29, 30, 12)

Most of the studied elements, as dissolved form ,showed non-significant differences among stations . The fluctuation of concentrations could be attributed to the interactions between some factors such the aquatic plants and phytoplankton abundance which absorbed or adsorbed the ionic elements, the fuel burn emissions specially result from machines of fishing boats that released large amounts of lead and less amount of other compounds, that affect the concentrations of dissolved elements .

The mean concentrations of all the studied heavy elements in particulate phase were greater than their concentrations in dissolved phase ,this was attributed to the increased particulate matter in the water column, which include living and non - living components .The particulate, which contain organic matter ,colloids and element hydroxide , have large surface area therefore they can adsorb great concentrations of heavy elements from aquatic environments .So that ,the increased the suspended matter in water cause to the transfer of

elements from the dissolved to particulate phase (31, 32, 24) , this finding was in agreement with (33) and (34).

As well, there were high particulate concentrations of most elements Cd , Ni, and Pb in summer as compared to spring, this may be related to high growth rate of phytoplankton in summer which have the ability to accumulate heavy elements in their bodies   and   this cause to increased concentrations of heavy elements in particulate phase, and this finding was consistent with many previous studies(35, 36, 24).

In addition, high pH value leads to increased heavy elements in the particulate phase (37, 38). The high pH value tends to make the elements remain in the suspended materials and does not lead to the dissolution of the hydroxide ion of elements (37). This was confirmed by the results of the present study, where high concentrations of elements ,as particulate phase ,were founded in the summer while low concentrations in the spring , and this is consistent with many previous studies(35, 24).

Some heavy elements in particulate phase negatively significant correlated with their concentrations in dissolved phase, this could be due to the ability of suspended particulate to accumulated these   elements from the surrounding water, causing decreasing concentration in dissolved phase and increasing concentration in particulate phase (12).

The Heavy Element Pollution Index(HPI)

The highest value of HPI (12.512) was found at station 3 in summer , while the lowest value (4.385) was found at station 2 in spring (Fig.9). ANOVA test showed non-significant differences were found among stations ,but significant differences ($P \leq 0.05$) were found among seasons. The highest mean value(10.346) was recorded in autumn and the lowest mean value (4.736) was recorded in spring. Generally, the water was unpolluted with heavy metals along the studied period at all the studied stations at Al-Chibayish marsh.
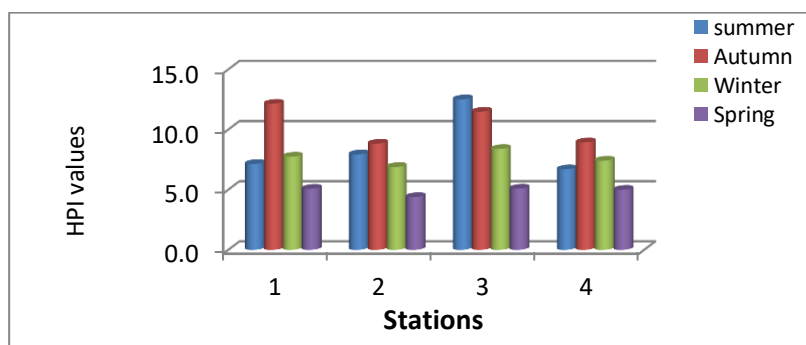

Fig.(9)The HPI values at the studied stations during the studied periods.

The HPI value is less than the maximum threshold value of 100 as proposed by (6) This result indicates that the influence of the four studied elements on the marshes water quality is not alarming because it's below the permissible limits of drinking water according to (25).

The concentrations of the four heavy elements in Al- Chibayish marsh water at all stations were found to be low and within guideline levels recommended. This finding were agreement with (39) who recorded the HPI value was (98.6) in Al- Gharraf river water slightly below the critical value100 for drinking water.

Conclusion

In the present study, the mean heavy metal pollution index (HPI) of Al-Chibayish marshes were found below the critical index value 100, according to permissible values of dissolved Cd ,Cr ,Ni and Pb, which indicates the water was unpolluted with heavy metals along the studied period at all the studied stations.

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