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DISTRIBUTION OF SOME TRACE METALS IN AL-CHIBAYISH MARSH OF PART ECOSYSTEM IN THI-QAR PROVINCE IN SOUTHERN IRAQ

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ABSTRACT

The trace metals Cd, Cu, Mn, Pb and Zn were determined in dissolved and particulate phase of the water, in addition in sediment and in the selected organs of the fish *Acanthopargus latus* and *Cyprinus carpio* collected from Chibayish Marshes, during summer / 2014. Also sediment texture and total organic carbon (TOC%) were measured. Analysis employing a Flam Atomic Absorption Spectrophotometers . The mean cocentrations of the trace metals in dissolved (ug /L) and particulate phase (ug /gm dry weight) were Cd (0.12, 13.5) , Cu (1.4, 14.25), Mn (0.36, 47), Pb (0.24, 20) and Zn (0.3, 610) respectively and those for sediment were Cd (3.5), Cu (2.75), Mn (7.5), Pb (6.75) and Zn (127) (ug /gm dry weight) respectively. The present study showed a difference in concentration of studied metal in different Organs of fish. These concentration varies from one to another and the Organs of same species showed difference in concentration of studied metals. This due to the nature and the function of the Organs and ability fish or regulating the level of the metals in their bodies during uptake and elimination processes. And the result showed that trace element concentration in muscles of two the species were in the international acceptable limits ,so it can be safety having related to this type of pollutants now days. Considered good indicator of accumulation for trace element in the water.

KEYWORD: Al-Chibyish marsh, fish, trace metals, water, sediment.

INTRODUCTION

Water is one of the main natural sources of human life and is important for economic and social reasons (Al-Helaly, 2010). Water has a variety of purposes, including for drinking, agriculture, industrial and energy production (Chapman *et al*. 1996; Gleick 1996; Shiklomanov 1998).

Trace metals are natural constituents for all environments. They are very dangerous materials because of their persistence, toxicity at low concentration and their ability to be incorporated into the food chains and concentrated by aquatic organisms (Al-Khafaji, 1996; Windom *et al.*,1999).

Upon entering aquatic system, metals move through the water column towards the sediment during which time they can be accumulated by organisms (fish, zooplankton and phytoplankton). The accumulation and distribution of trace metals in fish organ depend on many factors, concentration of metals, exposure time, temperature and salinity, food habits, physiological condition, growth, age, sex of fish and pollutants interactions (Al-Khafaji, 1996).

Pollution generally affects on the fishes either directly or indirectly. The directly acting pollutants create a lethal effect either through their action on the epithelial surfaces of gills or by absorption in the body which affects in the internal structure and metabolism of the fish. Indirect effects are created by the destruction of the food supply, covering the river with intert or oxidisable matter or by the destruction of spawning nich (Chale, 2002). Fish are part of aquatic ecosystem and any thing which damages this environment is potentially harmful to fishes , so they can be use as a bioindicators of pollution (Mersch *et al.*, 1993). Intensive studies were concerned with Trace metals concentration in fish species (Al-Khafaji, 1996 ; Al-Khafaji, 2005 ; Al-Doghachi,2008, Al-Awady, 2012; Lazim ,2013).

The present study aimed to determine variations in the distribution and concentration of some trace metals in three organs in the body of two fish species *Acanthopargus latus* and *Cyprinus carpio* collected from Al-Chibayish Marsh south of Iraq. And from which they can determine the levels of these elements in the study area.

MATERIALS and METHODS

Water, Sediment and Fish *Acanthopargus latus* and *Cyprinus carpio* collected from Al-Chibayish Marsh (Fig -1) during summer / 2014. The present study encompassed two stations in Al-Chibayish Marsh as follow station (1) is exposed to pollution , because many people living nearby, the people huge different livelihoods, while station (2) is not exposed to pollution and is far about 5 km from the first.

Water samples were collected using plastic bottles (polyethylene) with capacity of 5 liters per sample, these samples have been suction filtered through prewashed preweighed 0.45um millipore membrane filters. Materials passing through the filters were considered as dissolved, while those retained as particulate.

The analysis of dissolved Trace metals were achieved according to procedure of (Riely and Taylor, 1968). Bed sediment were obtained by mean of van grab sampler from representative sites, the surface sediment about 5 cm upper layer was used for the present study. Trace metals analysis were performed <63um fraction of the sediment which had been separated by sieving after oven –dring and grinding.

The determination of the Trace metals in particulate and sediment samples where done following the procedure described by (sturgeon ,*et al*,1982). Sediment texture was analyzed and the percentage of three size fractions (sand, silt and clay) were calculated according to (Shepard and Folk, 1974). Total Organic Carbon (TOC) in the sediment were determine according to (El-Wakeel and Riely,1957) by using exothermic heating and oxidation of 0.5gm grind dry sample with chromic acid.

Fish samples were captured from the study area by using gill nets 25*25 mm mesh size. The capture fish were then placed in polyethylene bags and frozen directly .In the laboratory, the fish were thawed, rinsed with deionized water ,standard length and weight were measured to the nearest mm, and mg respectively . then the abdominal cavity of each specimen was opened and the organs ,gill, liver were separated , when as and muscle was taken from the left posterior side of each fish, (50 fish per station for each species in length ranged 18 - 26 cm, ie, the total Fish 200) tissues were then dried under 105˚c for 24 hr , by using dried oven, then grinded and sieved by 0.5 mm mesh nylone sieve.

Tissues were digested by acid mixture (Nitric and Perechloric) , following the procedure of ROPME (1982).

Trace metals were extracted in triplicate from Water, sediment and fish samples. Cd , Cu, Mn, Pb and Zn were determined in air /acetylene flam Atomic absorption spectrophotometer AAS –Model Shimadzu 6300 . Blank values negligible for all studied metals –Acid used were ultrapure and water was deionized .

ANOVA test were done to know the significant differency between organs and metals using Minitab program.

RESULT &DISCUSSION

1- Trace metals in water samples

Five of Trace metals (Cd, Cu , Mn , Pb and Zn) has been discussed in the present study. The measured of these pollutants in the studied water sample shown in Table (1).

The particulate of metals between dissolved and suspended particulate matter determine their ultimate fate in the aquatic environment.

Concentrations of the studied trace metals was higher in particulate phase than its concentration in dissolved phase all study stations.

The mean concentration of the mentioned in dissolved phase at the study station (1 and 2) was as follow; Cd (0.15, 0.09), Cu (1.6, 1.2) ; Mn (0.42, 0.3) ; Pb (0.3, 0.18) and Zn (0.38, 0.22) ug /L respectively , where as their concentration in the particulate phase was ; Cd (15, 12), Cu (16, 12.5) ;Mn (50, 44) ; Pb (25, 15) and Zn (700, 520) ug / gm dry weight respectively.

Metals concentration in station (1) were higher than their concentration in station 2, this may be due to the exposure of station (1) to the various types of pollutants such as sewage, oil spill from boats, animal, wastes and chemical used in fishing, because this station was located close to the residential area (Al-Khafaji *et.al;* 2012). As well as we know , the particulate the former mostly Zoo and phytoplankton, while the latter, were mostly , silt and clay, so the high concentration of trace metals in particulate phase was due to these components.

Bowen, (1966) has indicated that planktonic organisms tend to concentrated trace metals as higher as 10^6 times than their levels in the surrounding water also the concentration of trace metals in aquatic environment depends on many factors such as water discharge of the river, seasonal variations in quantitive and qualitative of plank ton and suspended material load of river (Nolting , 1986). The results of this study agree with many previous studies (Qzar, 2009; Al-Abadi,2011; Al-Awady ,2012 , Mashkhool ,2012).

2- Trace metals in sediments

The concentration of trace metals in sediments is affected by several factors, including human activities and some environmental factors such as temperature, salinity, the proportion of organic matter in sediments, and sediment grain size (Bentiveyna *et .al* ; 2004), as well as plant density. In the present study there were higher concentration of trace metals at station 1 compared to station 2 (Table 2).

This was due to the location of station 1 near to residential area , which discharge their waste directly into the Marshes. These wastes increased the organic matter in the sediments, which absorbed the trace metals.

The relatively higher concentration of metals in the sediments than their concentration in water could be due to the high precipitation of materials in water column ,and the sediment represent the final sink for many matters which exist in the water column among them trace metals. trace metals occur naturally in the sediment and thus have both a natural and anthropogenic signal, (Forstner and wittwan, 1979, Agemain and Chau, 1979) have indicated that trace metals concentration are $10^3 – 10^5$ time higher in sediment than in over ling water many factors such as TOC content and sediment texture were affected upon the metal concentration in the sediment, so the mean Toc% in the sediment from the study station were (2.1 – 1.95)% respectively (Fig 2). Toc% showed significant correlation $p<0.05$ with all studied metals in the sediment. This is also was proved thorny the result of this study where the mean concentrations of Zn (127.5) ug /gm dry weight were higher then Mn (7.5) ug /gm, Pb (6.75) ug /gm, Cd (3.5) ug/ gm and Cu (2.75) ug /gm in sediment were more than the mean concentration in the dissolved phase of water.

In addition, increasing plant density in the marshes played an important role in increasing the trace metals in the sediments. Plant work to reduce the velocity of water flow and this leads to the deposition of suspended matter containing trace metals in sediments. This was confirmed by the result of the current study which found high concentrations of trace metals in sediment compared with concentrations it in the dissolved phase (Table 2).

Sediment grain size also played an important role in the distribution and accumulation of trace metals in the sediments. Small particle size such as silt and clay, tended to have higher concentrations of trace metals of the availability of a large surface area that allowed adsorption of metals on the particles surface (Bentivegna *et .at* ; 2004). This was confirmed by results of the present study which found that the concentration of trace metals in sediment at station 1 was higher than their concentration at station 2. This due to the station contained a high level of clay (40%) and silt (38%) compared with station 2, which contained a high a mount of sand (39%) (Fig .3). this result was consistent with other studies finding (Al-Sadi ; 2009, Al-Khafaji ,2010, Lazim, 2013).

3-Trace metals in fish samples

As a part of the an aquatic ecosystem , Fish accumulate certain trace metals from the ambient environment and many be used as bio indicators of pollution by these type of pollutants (Al-Khafaji, 2005; Al-Nagar ,2009 and Al-Awady 2012). The present study showed that the different tissues of the two species were varied from one to another in their accumulation of trace metals (Table 3).

Fish accumulated trace metals from their environment, they are excellent organism for the study of some long – term changes of trace metals in the environment (Radeef *et. at*; 2013). The mean concentration of the mentioned metal in Gill, Liver and Muscle in *Acanthopargus latus* were Cd (0.06, 0.24 and 0.05), Cu (0.65, 6.8 and 0.40), Mn (2.9, 2.5 and 1.9) , Pb (0.53, 0.6 and 0.43), and Zn (6.55, 8.85 and 5.65) (ug / gm) dry weight respectively , while in *Cyprinus carpio* were Cd (0.05, 0.12 and 0.035), Cu (0.3, 2.42 and 0.21), Mn (2.3, 2.1 and 1.6) , Pb (0.45, 0.54 and 0.34), Zn (5.2 , 7.0 and 4.25) (ug /gm) dry weight respectively.

The concentration of the mentioned metals varied among the organs of the studied species , this may be due to the species –specific mechanisms (Cross *et . al ;*1973) indicated that the differences in accumulation metals patterns in the organs of the fish species interdependency of uptake and elimination rates of metals.

Gill and liver concentrated all the studied metals, this my be due to the fact that the gill is the first organ to which is exposed to the metals through the respiration process, while the liver is an important organ which convert the food after transmission the latter from the gut . The present study showed that the concentration of the studied metals in *A .latus and C. carpio* are as follows or the over all order of enrichment for trace metals in different tissues for both species were in *A . latus* :

Gill Zn > Mn > Cu > Pb > Cd .

Liver Zn >Cu > Mn > Pb > Cd .

Muscle Zn > Mn > Pb > Cu > Cd .

In *C. carpio* :

Gill Zn > Mn > Pb > Cu > C d .

Liver Zn > Cu > Mn > Pb > Cd .

Muscle Zn > Mn > Cu > Pb > Cd .

This indicate that the difference in the accumulation pattern of Pb and Cd in fish tissues depend on uptake elimination rates of metals (Abdel-Bak *et. al* ;2011). The results of the present study agree with (Cross *et .al* ; 1973, Al-Khafaji *et .al* ; 2012), low concentrations of trace metals were recorded in the muscles of both species . The present result agree with those reported by (Raphael *et .al* ; 2011).

The concentration of most metals in most tissues of *A. latus* were higher than in *C. carpio* , which promote the have mentored phenomenon (Windom *et .al* ;1973) indicated that difference in metals accumulation in fish bodies may be due to the difference in their diet during the growth of the species.

The present values of metals concentration in the muscle of the studied species in comparison with other species from the same environment (Table 4)., which shows that the concentration of the studied metals in the muscle is in the acceptable range in comparison with world wide studies (Brayn, 1976) knowledge of metals concentration in fish muscle is important both with respect to nature management and human consumption of fish and to determine the most useful bio monitor species for human health .The observed differences can be explained by the fact that , the concentration of trace metals depend to a great extent on species, sex, biological cycle and on the part of the fish analyzed (Tuzen, 2003) .moreover, ecological factors such as season ,location, environment of development, nutrient availability, temperature and salinity of water, may contribute to variation in the metals concentrations in fishes (Romeoa *et .at* ; 1999).

Western Australian food and Drink Regulations recommended a level of 40 ug /gm Zn for human consumption (Mark *et .al* ;1980). According, the concentrations of Zn in the muscle of the studied fish are still below the permissible level .The concentration of Cu in the muscles of the studied fish are still below the permissible level for Cu (30ug /gm) recommended by the National Health and Medical Research Council (Mark *et .al* ;1980).

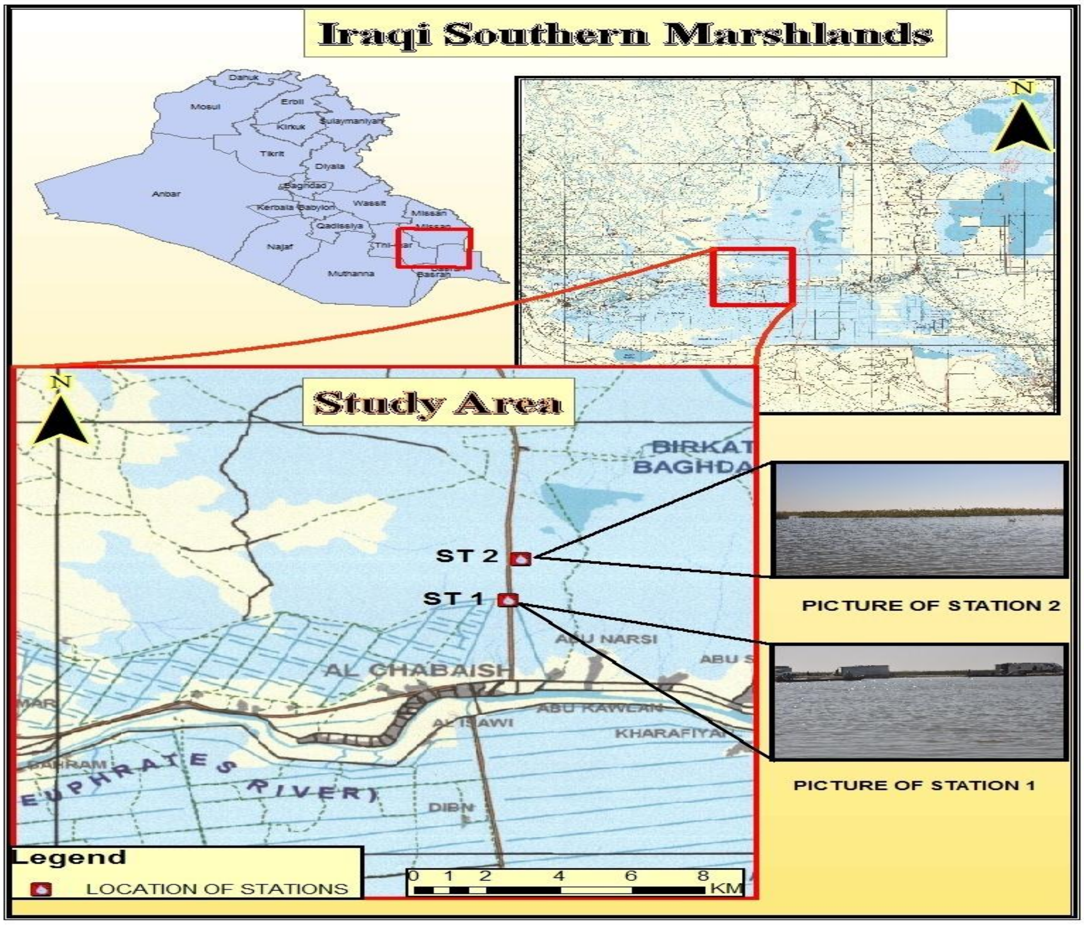

Figure (1): Study area within the Iraqi marshlands

Table -1- Trace metals concentration rang and Mean ± SD in water Dissolve (ug/L and particulate (ug / gm dry weight) and mean conc .In the region.

Metal	Station 1		Station 2		Mean con. In the region of study	
	Diss.	Part.	Diss.	Part.	Diss.	Part.
Cd	(0.1-0.18) ±0.07 0.15	(13-18) ± 0.3 15	(0.05-0.1) ±0.02 0.09	(10-15) ± 1.00 12	0.12 ± 0.045	13.5 ±0.65
Cu	(1.5 - 2) ± 0.8 1.6	(13 -19.5) ± 2.00 16	(1- 1.6) ± 0.6 1.2	(11-14.5) ± 1.02 12.5	1.4 ± 0.7	14.25 ± 1.51
	(0.35-0.46)	(43 - 56)	(0.31-0.4)	(41-48)		

Mn	± 0.1 0.42	± 3.10 50	± 0.01 0.3	± 2.96 44	0.36 ±0.055	47 ± 3.03
Pb	(0.25-0.38) ± 0.02 0.3	(23.4-30) ±4.01 25	(0.12 - 0.22) ± 0.7 0.18	(13 - 20) ± 1.20 15	0.24 ±0.36	20 ± 2.61
Zn	(0.3-0.41) ± 0.09 3.8	(650-800) ±6.70 700	(0.18-0.24) ± 0.05 2.2	(480-550) ± 5.06 520	3 ± 0.07	610 ± 5.88

Table 3- Trace metals concentration rang and Mean ± SD (ug / gm dry weight) in different organs of *A. latus* and *C. carpio*

Organ / Metal	**Gill**	**Liver**	**Muscle**	**Species**
Cd	(0.04 -0.1) ± 0.03 0.06	(0.15 – 0.40) ± 0.05 0.24	(0.035-- -0.9) ±0.01 0.05	*Acanthopargus latus*
	(0.03 -0.07) ±0.01 0.05	(0.9 – 0.15) ± 0.02 0.12	(0.03 -0.05) ± 0.01 0.035	*Cyprinus carpio*
Cu	(0.55 – 0.75) ± 0.09 0.65	(5.2 – 7.5) ± 2.01 6.8	(0.3 – 0.6) ± 0.08 0.40	*A. latus*
	(0.25 – 0.35) ± 0.02 0.3	(1.8 -3.7) ± 0.96 2.42	(0.15 -0.3) ±0.03 0.21	*C. carpio*
Mn	(2..4 -3.5) ± 0.8 2.9	(2.2 -3.4) ± **0.6** 2.5	(1.5 -2.4) ± 0.99 1.9	*A. latus*
	(1.7- 3.2) ± 0.7 2.3	(1.8 -2.2) ±0.5 2.1	(1.4 – 1.9) ± 0.06 1.6	*C. carpio*
Pb	(0.45 -0.7) ± 0.08 0.53	(0.55 – 0.8) ± 0.07 0.6	(0.3 -0.55) ±0.09 0.43	*A. latus*
	(0.34 -0.54) ± 0.06 0.45	(0.45 – 0.74) ± 0.05 0.54	(0.28 -0.44) ± 0.04 0.34	*C. carpio*
Zn	(5.9 – 8.8) ± 2.01 6.55	(6.8 -9.6) ± 3.00 8.85	(4.9 – 7.6) ± 1.01 5.65	*A. latus*
	(5.5 – 7.0) ± 1.52 5.2	(6.2 -80) ± 2.00 7.0	(3.8 – 5.5) ±1.00 4.25	*C. carpio*

Table -2- Trace metals concentration rang and Mean ± SD (ug / gm dry weight) in the Sediment and mean conc .In the region.

Metal	Station 1	Station 2	Mean con. In the region of study
Cd	(4-6) ± 1.00 5	(1.5-3) ± 0.96 2	3.5 ± 0.98
Cu	(3-5) ± 0.9 4	(1-2.3) ± 1.00 1.5	2.75 ± 0.95
Mn	(6-10) ± 2.03 8.5	(5-5.9) ± 1.20 6.5	7.5 ±1.62
Pb	(6.5-8.5) ± 1.90 7	(6-7.5) ±1.80 6.5	6.75 ± 1.85
Zn	(140-150) ± 7.00 145	(105-115) ± 5.01 110	127.5 ± 6.01

Table -4 – Comparison of mean values of trace metals (ug/gm dry weight) in the muscles of *A.latus* and *C .carpio* with other species

Species	Cd	Cu	Mn	Pb	Zn	References
Acanthopargus latus *Cyprinus carpio*	0.005 0.035	0.4 0.21	1.9 1.2	0.43 0.34	5.65 4.25	**Present study**
Nematolosa nasus *Liza subviridi*	0.03 0.03	2.49 1.57	1.33 1.70	0.03 0.06	7.34 8.58	**Al-Khafaji ,1996**
Asbius vorax *Barbus sharpeyi* *Cyprinus carpio*	2.01 1.95 2.23	1.13 1.03 1.91	1.86 1.93 1.32	15.15 12.81 11.26	19.99 20.58 40.5	**Al- Taee, 1999**
Acanthopargus latus	ND	1.3	-	1.1	2.5	**Al-Khafaji , 2005**
Liza aba	1.68	14.75	-	-	84.26	**Fahad,2006**
Chalcal burnus	0.2	7.5	-	ND	325	**Al-Doghachi ,2008**
Cyprinus carpio	ND	0.07	-	0.06	6.4	**Al-Khafaji ,2010**
Barbus latus *Cyprinus carpio*	0.05 0.04	12.86 16.65	13.50 34.79	42.83 35.03	2.16 35.03	**Al-Awady , 2012**
Barbus latus *Cyprinus carpio*	0.14 0.07	0.59 0.30	- -	0.59 0.61	2.32 2.48	**Lazim , 2013**
World wide	0.2	3.0	10	3.0	80	**Bryan , 1976**

ND= Not detected

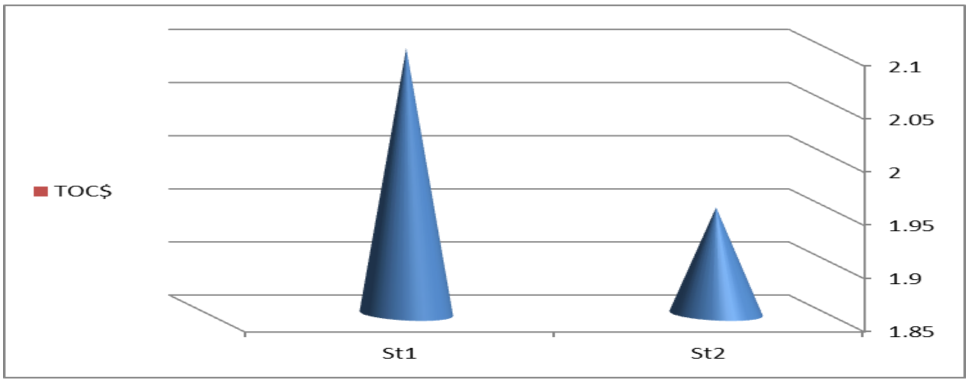

Fig: 2 Mean total organic carbon content (TOC%) in sediment from the study are.

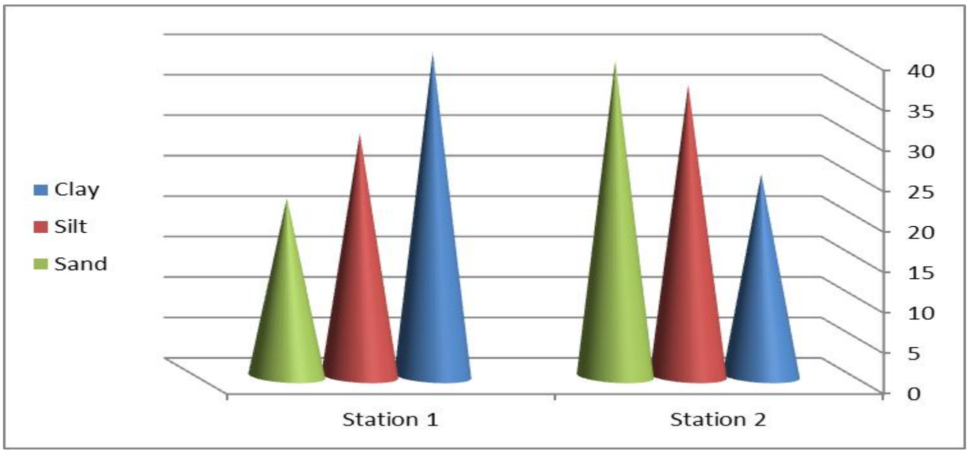

Fig: 3: Sediment texture % of study area.

CONCLUSIONS

1- Clear difference in the concentration for the studied metals in station 1 was compared with station 2.
2- The former was affected by human activities within the marsh such as sewage discharge , use of chemicals in fishing as well as oil spill from fishing boats.
3- The trend of metals concentrations was arranged as follows:
   Particulate > sediment > fish > dissolved phase.
4- The level of trace metals in both water and sediment were in acceptable range according to WHO.
5- The distribution of trace metals within tissue of study species showed that gill and liver the main strange liver for Cu, gill for Cd and Pb .
6- Different patterns of metals concentration were observed in the different tissues and muscle tissues contain less concentration of these metals , this mean that the trace metals in the edible parts of *A. latus* and *C.carpio* were within the safety permission level for Human use

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