

Distribution Of Some Heavy Metals In Water, Sediment & Fish *Cyprinus carpio* in Euphrates River Near Al-Nassiriya City Center South Iraq .

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Abstract:

The heavy metals Cd, Cu, Fe, pb, and Zn were determined in dissolved and particulate phases of the water, in addition to exchangeable and residual phases of the sediment and in the selected organs of the fish *Cyprinus carpio* collected from the Euphrates River near Al-Nassiriya city center south of Iraq during the summer period / 2009 .Also sediment texture and total organic carbon(TOC) were measured. Analysis employing a flame Atomic Absorption Spectrophotometers . The mean regional concentrations of the heavy metals in dissolved ($\mu\text{g/l}$) and particulate phases ($\mu\text{g/gm}$) dry weight were Cd (0.15,16.13) ,Cu (0.59,24.48) ,Fe (726,909.4) ,Pb (0.20, 49.95) and Zn (2.5,35.62) respectively, and those for exchangeable and residual phases of the Sediment were Cd (0.2,0.1) ,Cu (13.75,16.65) ,Fe (683 , 1351) ,Pb (10.1,1.07) and Zn (7.3,16.75) $\mu\text{g/gm}$ dry weight respectively. The heavy metals concentrations in *C. carpio* organs followed the trend gill > liver > kidney > muscles . The mean concentration in the muscles were Cd (ND) , Cu (0.07) , Fe (4.7) , pb (0.06) and Zn (6.4) ($\mu\text{g/gm}$) dry weight . The statistical analysis proved a significant correlation between metal concentration in the sediment and total organic carbon, also a positive correlation was proved between its concentrations in the liver organ and the water (particulate phase) . In conclusion the trace metals concentration in particulate phase were higher than its concentration in the dissolved phase . The fish organs showed variations in the metals concentration and the muscle organs showed less concentration than the other organs .

Key words: Heavy metals , Water , Sediment , Fish , Euphrates River

Introduction:

There are numerous types of pollutants found in the aquatic environment such as organic materials, major and trace metals which contribute to both natural and anthropogenic sources [1]. The investigation of the distribution and concentration of heavy metals in water, sediment and biota is fundamental to the study of the aquatic environmental pollution by these types of pollutants[2] .Heavy metals were regarded as serious pollutants of aquatic environment because of their persistence , toxicity in low

concentration and their ability to be incorporated into food chains and concentrated by aquatic organisms such as fish[3].As a result of direct discharge of waste-water from municipal effluents, seepage from agricultural lands and disposal from industrial , the level of heavy metals increased in water column [4] .Heavy metals appear in fresh water naturally and in trace concentrations and varied according to kind of sediment[5].These metals have strong affinities for sediment, so sediment can serve as an indication of time history and

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extension of pollutant discharge in a specific area[6]. Fishes are part of aquatic ecosystem and any thing which damages this environment is potentially harmful to fishes, so they can be used as bioindicators of pollution[7]. Intensive studies were concerned with heavy metals concentration in fish species [8 ; 6 ; 9 ; 2 ; 10]. The present study aimed to determine monthly variations in the distribution and concentration of some heavy metals in water, sediment and four organs in the body of commercial fish species *Cyprinus carpio* collected from Euphrates River near Al-Nassiriya city south of Iraq. These data may be used by other researchers who require a baseline for comparison of heavy metals distributions.

Materials and Methods:

Water, sediment and fish *Cyprinus carpio* were collected from the Euphrates river (Fig-1) during summer/ 2009. The present study encompassed two stations in the Euphrates river as follows: station(1) near electric power station (EPS) of Al-Nassiriya province, while station(2) was near the waste-water treatment unit. 20L of water samples were taken by using acid-washed polyethylene bottles, these samples have been suction filtered through prewashed preweighed 0.45 µm Millipore membrane filters. Materials passing through the filters were considered as dissolved, while those retained as particulate. The analysis of dissolved heavy metals were achieved according to procedure of [11]. Bed sediment were obtained by means of van Veen grab sampler from representative sites, the surface sediment about 5 cm upper layer was used for the present study. Heavy metals analysis were performed

<63µm fraction of the sediment which had been separated by sieving after oven-drying and grinding. The determination of the heavy metals in particulate and sediment samples were done following the procedure described by [12]. Sediment texture was analyzed and the percentage of three size fractions (sand, silt and clay) were calculated according to [13]. Total Organic Carbon (TOC) in the sediment were determined according to [14] by using exothermic heating and oxidation of 0.5gm ground dry sample with chromic acid. Fish samples were captured from the study area by using gill nets 25*25 mm mesh size. The captured fish were then placed in polyethylene bags and frozen immediately. In the laboratory, the fish were thawed, rinsed with deionized water, standardized 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 and kidney were separated, whereas muscle was taken from the left posterior side of each fish, tissues were then dried under 105°C for 24 hr. by using dried oven, then ground and sieved by 0.5 mm mesh nylon sieve. Tissues were digested by acid mixture (Nitric and Perchloric), following the procedure of [15]. Heavy metals were extracted in triplicate from water, sediment and fish samples. Cd, Cu, Fe, Pb and Zn were determined in air/acetylene flame Atomic absorption spectrophotometry AAS-Model Sp9 pye – Unicam. Blank values negligible for all studied metals. Acids used were ultrapure and water was deionized. ANOVA test were done to know the significant difference between parameters by using Minitab program.

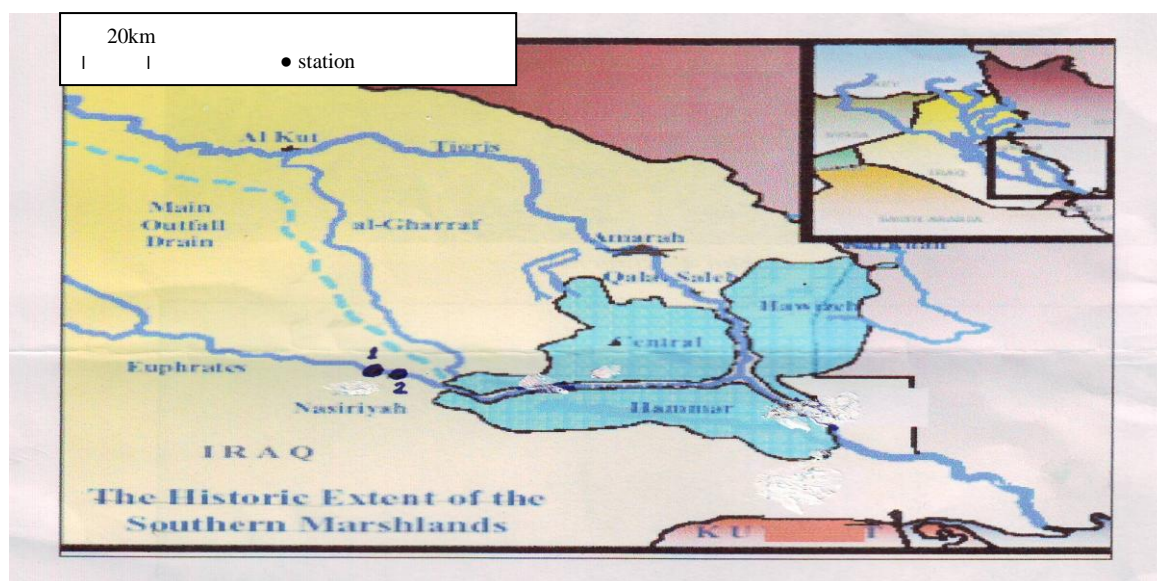


Fig. 1: Map of the study stations.

Results and Discussion:

Heavy Metals in Water Samples :-

The analysis of heavy metals in the dissolved and particulate phases of water in the study area were presented in Table 1. The partitioning of metals between dissolved and suspended particulate matter determines their ultimate fate in the aquatic environments. Concentration of Cd and pb in dissolved and particulate phases in the station 2 were higher than their concentrations in station 1, this may be due to the high metals content discharged from the waste-water treatment unit which was located near station 2. The effluents of municipal and industrial waste contain considerable amount of heavy metals [16]. Therefore, the concentrations of

heavy metals in suspended particulate matter are higher than their concentrations in dissolved phase for both stations (Table 1). This may be due to the high amount of particulate matter in the study area during the study period. It has been reported that the particulate matter consist of biotic and a biotic components the former include zoo and phytoplankton, bacteria and Fungi, whereas the latter includes sand, silt, clay, feldspar and quartz [17]. The concentration of dissolved heavy metals is similar to those reported elsewhere, also its concentrations in the present study are in an acceptable range compared with the world wide (Tables 1 and 2) respectively

Table -1- Heavy metals concentration range and mean \pm SD in water (dissolved $\mu\text{g/L}$ and particulate $\mu\text{g/gm}$ dry weight) and mean conc. In the region.

Metal	Station 1		Station 2		Mean con. In the region	
	Diss.	Part.	Diss.	Part.	Diss.	Part.
Cd	(0.09-0.15) a 0.13 \pm 0.01	(11.5-17.3) a 15.36 \pm 0.6	(0.1-0.2) b 0.17 \pm 0.03	(13-18.2) a 16.9 \pm 0.8	0.15	16.13
	(0.40-0.75) a 0.62 \pm 0.03 (450-780)	(13.2-17.5) a 16.85 \pm 3.7 (760-961)	(0.33-0.7) a 0.55 \pm 0.05 (683-802)	(28-35) b 32.1 \pm 0.2 (830-980)	0.59	24.48
Fe	(0.11-0.17) a 0.14 \pm 0.05 (0.92-3.2)	(28-39) a 35.9 \pm 0.40 (25-29.3)	(0.18-0.28) b 0.25 \pm 0.02 (1.3-3.2)	(58-71) b 64 \pm 6.3 (38-45)	726	909.40
	(0.11-0.17) a 0.14 \pm 0.05 (0.92-3.2)	(28-39) a 35.9 \pm 0.40 (25-29.3)	(0.18-0.28) b 0.25 \pm 0.02 (1.3-3.2)	(58-71) b 64 \pm 6.3 (38-45)	0.20	49.95
Zn	(0.11-0.17) a 0.14 \pm 0.05 (0.92-3.2)	(28-39) a 35.9 \pm 0.40 (25-29.3)	(0.18-0.28) b 0.25 \pm 0.02 (1.3-3.2)	(58-71) b 64 \pm 6.3 (38-45)	2.5	35.62
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Mean with different letter are significantly different (n=15, p<0.05)

Diss. = Dissolved

Part. = Particulate

Con. = Concentration

Table -2- Comparison of mean values of dissolved heavy metals ($\mu\text{g/l}$) of Euphrates river with the same in other regions .

Location	Cd	Cu	Fe	Pb	Zn	References
Euphrates river near Al-Nassiriya	0.15	0.59	726	0.20	2.5	Present study
Shatt Al-arab estuary	0.19	0.47	389.2	0.18	0.93	Al-Khafaji , 1996
Al-Hilla river	1.11	1.81	6.74	4.21	8.73	Al-taee , 1999
Qarmatt – Ali river – Iraq	0.13	0.55	690.5	0.31	2.0	Al-Khafaji , 2001
Al-Garat river Nassiriya	26.70	10.72	-	-	17.51	Fahad , 2006
Iraqi wetland	7.86	23.02	7621.14	67.62	118.51	Al-Imarah et al. 2007
World wide	0.22	7.0	-	3.0	20	Burton , 1976

Heavy Metals in Sediment Samples:-

Sediment acts as archive for many pollutants one of them is heavy metals. Knowledge of the concentration and distribution of heavy metals in the sediment can therefore play a key role in detecting sources of pollution in aquatic ecosystem [18]. The range and mean of the heavy metals concentration in both phases (exchangeable and residual) of the surficial sediment from the study area are summarized in(Table 2) . The relatively higher concentration of metals in the sediment than their concentrations 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 heavy metals . Heavy metals occur naturally in the sediment and thus have both a natural and anthropogenic signal, [19;18] have indicated that heavy metals concentration are $10^3 - 10^5$ time higher in sediment than in overlying water . Heavy metals concentration in exchangeable phase were less than in residual phase . The exception was in Cd and pb , this could be due to the

anthropogenic sources [6]. The elevated level of studied metals in the sediment especially in station 2, could be due to the higher content of TOC and fine grain size of silt clay texture in the mentioned station (Fig.2 & 3) respectively . The high content of TOC in both stations was due to the high organic matter content in these stations. [20] have reported TOC in the sediment act as indicator of organic pollution . Heavy metals in the sediment affected by many factors such as textural characteristics of the sediment and TOC content [6], so the amount of adsorbed metals are related to the organic content and/or grain size of the sediment[21]. [22] has indicated that the particles size in the sediment is an extremely important parameter related to sediment metals concentration found in nature, and also found that the highest metal concentration are usually in the finest grain size. The relatively higher concentration of metals in the sediment found in the station2. than that in station1.(Fig.2), this could be due to the high discharge of wast-water from the WTU near the former station, also the highly content of fine grain size of the sediment texture in the mentioned station ,while metal concentration in the sediment of station 1 could be due to the discharge of EPS , which contain metals resulted from the corrosion process of the colder water pipes which are used in this station .The high pb concentration in the sediment of the study area Table(3)reflect atmospheric input and the heavy traffic in the center of the city . while the high concentration of the mentioned metal in station 1 may be due to the burning of the fuel (heavy oil) which was used for EPS operation.Metals concentration in the sediment in the present study are in acceptable range compared with the seam studies elsewhere Table (4) .

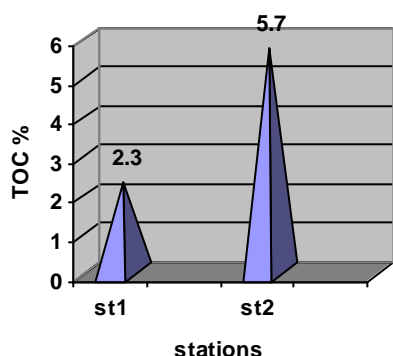


Fig:2 Mean total organic carbon content (TOC %) in the sediment from the study area .Means with different letters are significantly different (n=15, p<0 .05)

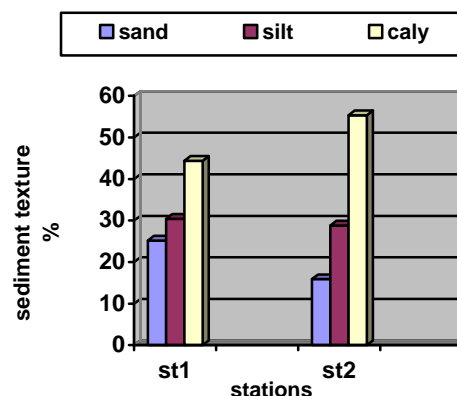


Fig:3 Sediment texture % of the study area

Table -3- Heavy Metals concentration range and Mean ± SD (ug/gm. of dry weight) in the sediments (Exchangeable and Residual phases)from the study area

Station	phase	Cd	Cu	Fe	pb	Zn
1	Exch.	(0.11-0.15) a	(0.8-12.2) a	(450-660) a	(7.3-11.5) a	(5.4-8.3) a
		0.12±0.02	10.3±0.06	553±30.1	9.2±1.3	7.2±0.6
	Resid.	(0.01-0.025) b	(14.5-17.5) a	(980-1230) b	(0.2-0.5) b	12.5-18.6 a
		0.078±0.01	15.5±0.3	1122±24.5	0.33±0.02	15.2±1.2
2	Exch.	(0.22-0.30) b	(15.7-19.2) b	(630-920) a	(8.7-12.6) a	(6.2-9.3) b
		0.28±0.05	17.2±0.5	813±22.5	11.0±0.6	7.4±0.5
	Resid.	(0.15-0.2) a	(11.5-21.3) a	(1250-2460) b	(0.8-4.2) a	(15.3-21.7) a
		0.18±0.03	17.8±1.1	958±61.5	1.8±0.02	18.3±0.6
Mean	Exch.	0.2	13.75	683	10.1	7.3
	Resid.	0.1	16.65	1351	1.07	16.75

Exch.=Exchangeable

Resid.=Residual

Table -4- Comparson of mean values of heavy metals (µg/gm) dry wt in the sediment of Euphrates river with other studies .

Location	Cd	Cu	Fe	pb	Zn	References
Euphrates river	0.30	30.40	2034	11.17	24.05	Present study
Khar Al-Zubier	0.26	28.0	72.0	29.0	72.0	Al-Edanee et al (1991)
Shatt Al-Arab	0.05	30.0	31800	25.5	135.0	Al-Muddafar et al (1992)
Shatt Al-Hilla	3.92	34.54	73.41	58.20	73.41	Al-Khafaji , (1996)
Al-Garaf river Nassiriya	26.70	10.72	-	-	17.51	Fahad , 2006
Iraqi wetland	7.86	23.02	7621.14	67.62	118.51	Al-Imarah et al. 2007
World wide	0.22	7.0	-	3.0	20	Burton , 1976

Heavy Metals in Fish Samples:-

As a part of the an aquatic ecosystem, fish accumulate certain heavy metals from the ambient environment and may be used as bioindicators of pollution by these type of pollutants [23;24]. The present study showed that the different tissues of *C. carpio* were varied from one to another in their accumulation of heavy metals (Table5). Fish organs indicated alternative values for metals concentration , so kidney accumulate most Cd, while this metal disappears in other organs, many authors found that kidney in different fish species were site having the highest Cd level ,[1 ;2] .[26] has reported that Cd doesn't accumulate in fish tissues because it is actively excreted through the kidney .The results indicated that the kidney concentrated all the studied metals, this may be due to the laet that the kidney tissues accumulate all heavy metals appear in the blood circulation probably in dependently on their rate of in take [6]. Fe and Cu revealed high concentration in a liver , this may be due to the food type and feeding habitat of the studied fish , [26] has indicated that *C. carpio* is omnivorous and bottom feder , whereas [27] have indicated that the plankton has concentration of heavy metals . Fish have the ability to accumulate heavy metals from water and sediment [28;29]. Lead observed high concentration in the gills more than the other metals, this attributed with the presence of chloride calls in the gill which facilitate accumulation of heavy metals[25]. Lower concentration of the

metals were obtained in the muscle, this may be due to the ability of this species of fish to regulate the uptake and intake of the studied metals in the mentioned organ .The higher concentration of Fe and Zn in the muscles are due to the elevated concentration of these metals in the particulates and sediment (Table 1 and 3) respectively .The results revealed absence of more toxic metals (Cd and pb) in the muscles tissues which account for most of the body and are outstanding important as food . Heavy metals concentration in the muscle of *C. carpio* more less than the world wide values (Table 6) . This may be due to the ability of this species of fish to control the uptake and elimination of these metals from the ambient environment .The over all order of enrichment for heavy metals in different tissues were :

Gill : $Fe > Cu > pb > Zn > Cd$.

Liver : $Fe > Cu > Zn > Cd > pb$

Kidney : $Fe > Zn > Cu > Cd > pb$.

Muscles : $Zn > Fe > Cu > pb > Cd$.

In conclusion , the Euphrates river ecosystem in the present study area has considerable amount of heavy metals came from anthropogenic sources . Metals in this study concentrated in the particulate phase more than the dissolved phase of the water , while their concentrations in the sediment were higher than their concentration in water . Different patterns of metals concentration were observed in the different tissues , and muscle tissues contain less concentration of these metals .

Table-5- Heavy metals concentration rang and Mean \pm SD(mg /L) dry weight in different organs of *C. carpio* standard length ranged (20-28) cm with XL=25 \pm 1 cm.

Metal \ organ	Gill	Liver	Kidney	Muscles	NO-of Specimen
Cd	ND	ND	(0.1-0.12) 0.08 \pm 0.01	ND	50
Cu	(0.2-6.7) a 5.1 \pm 0.03	(1.2-7.5) a 6.3 \pm 0.01	(0.2-1.8) b 1.2 \pm 0.02	(0.01-0.09) b 0.07 \pm 0.01	50
Fe	(6-15) b 12.1 \pm 0.3	(11.0-22) a 17.5 \pm 0.05	(2.0-9.1) c 7.5 \pm 0.03	(3.3-5.1)	50
Pb	(0.03-0.22) a 0.18 \pm 0.01	ND	ND	(0.03-0.08) 0.06 \pm 0.01	50
Zn	(0.8-2.5) c 1.7 \pm 0.02	(1.2-4.1) c 2.02 \pm 0.1	(2.1-4.2) b 3.3 \pm 0.02	(2.5-8.1) 6.4 \pm 0.02	50

Mean with different letter are significantly different (n=50 p<0.05)

ND.=Not detected

XL.=Mean of standard length.

Table -6- Comparson the Concentration (μ g/gm dry wt.) of heavy metals in the muscles of *Cyprinus carpio* with other species .

Species	Cd	Cu	Fe	Pb	Zn	References
<i>Cyprinus carpio</i>	ND	0.07	4.7	0.06	6.4	Present study
<i>Nematolosa nasus</i>	0.03	2.49	-	1.6	7.34	Al-khafaji,(1996)
<i>Tenulosa ilisha</i>	ND	0.71	-	0.07	3.40	Al-khafaji,(1997)
<i>Barbus sharpeyi</i>	1.95	1.03	-	-	20.58	Al-Tae,(1999)
<i>Cyprinus carpio</i>	2.23	1.91	-	-	40.5	
<i>Aconthopargus latus</i>	ND	1.3	-	1.1	2.5	Al-khafaji,2005
<i>Liza abu</i>	1.68	14.75	-	-	84.26	Fahad,2006
<i>Liza carinata</i>	ND	10.0	-	25	40	
<i>Chalcal burnus</i>	0.2	7.5	-	ND	325	Al-Doghachi,2008
World wide	0.2	3.0	50	3.0	80	Bryan,(1976)

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توزيع بعض المعادن الثقيلة في الماء، الرواسب وسمكة الكارب الاعتيادي *Cyprinus carpio* في نهر الفرات قرب مركز مدينة الناصرية جنوب العراق

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**كلية العلوم-جامعة كركوك

الخلاصة:

قيست المعادن الثقيلة الكاديوم والنحاس والحديد والرصاص والخاصين في الماء بجزيئية الذائب والعالق والرواسب بجزيئها المتبادل والمتبقي وفي بعض اعضاء سمكة الكارب الاعتيادي *Cyprinus carpio* جمعت من نهر الفرات قرب مركز مدينة الناصرية جنوب العراق خلال موسم الصيف / 2009 . تم تحليل نسجة الرواسب، يضاف الى ذلك قيس محتوى الكربون العضوي الكلي في الرواسب. اتبعت الطرق القياسية في الاستخلاص واستخدم جهاز مطياف الامتصاص الذري اللهب في تقدير تراكيز المعادن . بلغت معدلات تركيز المعادن الثقيلة في الماء بجزيئية الذائب (مايكروغرام \ لتر) والجزء العالق (مايكروغرام \ غرام) وزن جاف كالاتي : كاديوم (0.15 , 16.13) , نحاس (0.59 , 24.48) , حديد (726 , 909.4) , رصاص (0.20 , 49.95) والخاصين (2.5 , 35.62) على التوالي . اما تركيزها في الرواسب بجزيئها المتبادل والمتبقي (مايكروغرام \ غرام) وزن جاف فقد بلغت كالاتي : الكاديوم (0.1 , 0.2) , النحاس (13.75 , 16.65) , الحديد (683 , 1351) , الرصاص (10.1 , 1.07) والخاصين (7.3 , 16.75) على التوالي . اما تركيز المعادن الثقيلة في اعضاء سمكة الكارب فكان ترتيبها كالاتي الغلاصم < الكبد < الكلية < العضلات في حين بلغ معدل تركيزها في العضلات، الكاديوم (ND) والنحاس (0.07) والحديد (4.7) والرصاص (0.06) والخاصين (6.4) مايكروغرام/غم وزن جاف . اثبت التحليل الاحصائي وجود علاقة معنوية بين تركيز المعادن الثقيلة ومحتوى الكربون العضوي في الرواسب، كذلك ظهرت علاقة موجبة بين تراكيزها في الكبد والجزء العالق للماء . استنتج من هذه الدراسة ان تراكيز المعادن المدروسة في الجزء العالق للماء اعلى مما هو عليه في جزئه الذائب ، وان اعضاء سمكة الكارب تتباين في تركيزها وتوزيعها للمعادن في تلك الاعضاء في حين اظهرت العضلات تراكيز اقل للمعادن مقارنة بالاعضاء الاخرى