

Estimation of heavy metals in zooplankton organisms, of NW Arabian Gulf

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:Abstract

This study was chosen to be executed at different stations which expect high density of zooplankton. As well as areas of hatchery, biological biodiversity of marine and estuarine water. Samples were collected and analyzed for heavy metal using a highly sophisticated instrument ICP/MS at Maxxam analytical INC. in Canada, the level calculated is in ppm . The concentration of heavy metals in stations as hierarchy for higher levels recorded are Hg , U, Cd, Pb, Cu, Zn, Fe , Co and Ni. The stations for which the metals samples were collected were, Khour Al-Zubair, Al-Musab, Ras Al-Bisha, Buoy13, Buoy 29, and Al-Fao, respectively. The high concentration metals which appear in this study may be caused by the industrialized untreated discharged waste products, the discharging untreated sewage in the river and areas of accumulation of elements due to the daily tide and sub-tide currents. The results of stations 5-8, might be resulted from the water circulation in the Arabian Gulf which is arising to the north along the Iranian cost and directed from the NW Arabian Gulf .along the Arabian coast

. *Key words: Pollution, heavy metals, zooplankton, Uranium, NW Arabian Gulf*

:Introduction

The Marine and fresh water ecosystems are being threatened by the discharges of untreated sewage wastes and industrial effluents. This ultimately affects the sustainability of living resources and public health. The wastes carry an enormous level of toxicants, especially the heavy metals that have the tendency to accumulate into the basic food chain and move up through the higher tropic level. Also, the wastes have negative impacts on the marine and freshwater resources which cause economic loss by affecting the migration of many aquatic Creatures. As well as, anyone exposed to the waters which will cause the government to spend large amount .(of money to treat the polluted area (Robin *et al.* 2012

Phytoplankton is the major food producer in marine and estuarine ecology. In addition, zooplankton plays a fundamental role in food chains as secondary producers. It is considered to be major food sources for the marine mammals, birds and fishes (Nilsson *et al.*1995a; Nilsson, *et al.* 1995b; Percy, 1993). Thus, zooplankton organisms may contribute to the transfer of metals to the higher trophic levels and have been chosen among other as recommended organisms in baseline .(studies for marine environment (AMAP, 1995

There is a variety of significant human health and environmental associated issues with the geographically widespread prevalence of elevated levels of both organic, inorganic compounds in freshwater and marine biota. A linkage is evident between the bioaccumulation of heavy metals and aquatic system and the atmospheric mobilization and deposition of heavy metals, which has local regional and global

components (Manson, *et al.* 1994). Many pollutant problems can be linked to the expansion of specific sources which include oil refineries, untreated sewage wastes, and paper factories. There are particular concerns when such sources are adjacent to estuarine and to marine systems supporting significant fisheries (Ninomiya, *et al.* 1995). Areas that faced similar types of pollutions were Kuwait, the southern part of Iraq in Basrah. Although, the pollution increases, no laws or actions were done to prevent or treat the contaminated areas

As in previous studies, the major sources of pollution by heavy metals in southern Iraq are the heavy casualty using of projectiles used in the first and second Gulf war. The discharging of untreated sewages in rivers, the waste product discharges from oil refineries and petrochemicals are present near the Khour Al-Zubair (Al-Imarah, *et al.* 2010; Al-Imarah, *et al.* 2003; Karabedain, *et al.* 2009). The salt and chlorine plant in Kuwait and petrochemical plant near the north of Kuwait has affected Northwest of the Gulf under the influence of tide and sub tide in the water (Al-Majed and Perston, 2000). The heavy metals in mixed zooplankton organisms can generally be found in higher concentration near the coast, due to the untreated discharged of many waste products of plants close to the coast or near the rivers (Rezai and Yusoff, 2011; Robin, *et al.* 2012

Marin zooplankton constitute is a major component of total biomass of marine environment, and there by plays a vital role in the biogeochemical cycling of heavy metals in the sea (Shulz-Blades, 1992). Plankton is capable of concentrating traces of metals from seawater. The average heavy metals content in zooplankton from north of Mediterranean was reported by many studies (Rezia and Yusoff, 2011

The contamination of sea water, freshwater and estuarine water, due to direct exposure to atmospheric input, is probably the major source of pollution in all of the stations used in this study. There is a significant amount of industrial pollutant untreated waste which has been discharged in River Shatt Al-Arab, Shatt Al-Basrah channel, Khour Al-Zubair, and the Gulf. It has been generated from discharging sewages and manufacturing industries such as of food, beverages palm, oil refineries, petrochemical, manufacturing of fertilizers, textile pulp paper, tanneries and sugar factories/plants (Chua, *et al.* 2000). The aim of the study is to bring awareness to the lack of studies concerned with the evaluation of heavy metals especially in the zooplankton and phytoplankton in this area. The phytoplankton and zooplankton are the primary and secondary producers in the food chain. This fact has not been taken into consideration in this area and other areas including countries such as India, Saudi Arabia (Al-Tison and Chandy, 1995

Materials and Methods

:Sample collection

Eight sampling stations were selected in various localities in Basrah waters which include Shatt Al-Basrah Channel, Khour Al-Zubair, Khour Abdulla of NW Arabian gulf } Buoy 29, 13, and 5 {, Al-Musab, Ras Al-Bisha and Al-Fao (Fig. 1). The nature of these stations is quite different from one another. A net of Plankton which was 120 micron mesh-size and 40 cm in diameter of mouth aperture, was towed behind a boat for 15 min. A flow-meter was mounted at the mouth of the net to determine the volume of water filtered by net (DeBernardi, 1984

Two identical samples of zooplankton were collected at the same time for the same period one for counting, another was preserved in a freezer after washed with same water of station. Dry weight of the zooplankton was estimated by filtering the

sample through a filter paper using a vacuum pump. The filter paper was then oven-dried at 60 °C for 24 hours

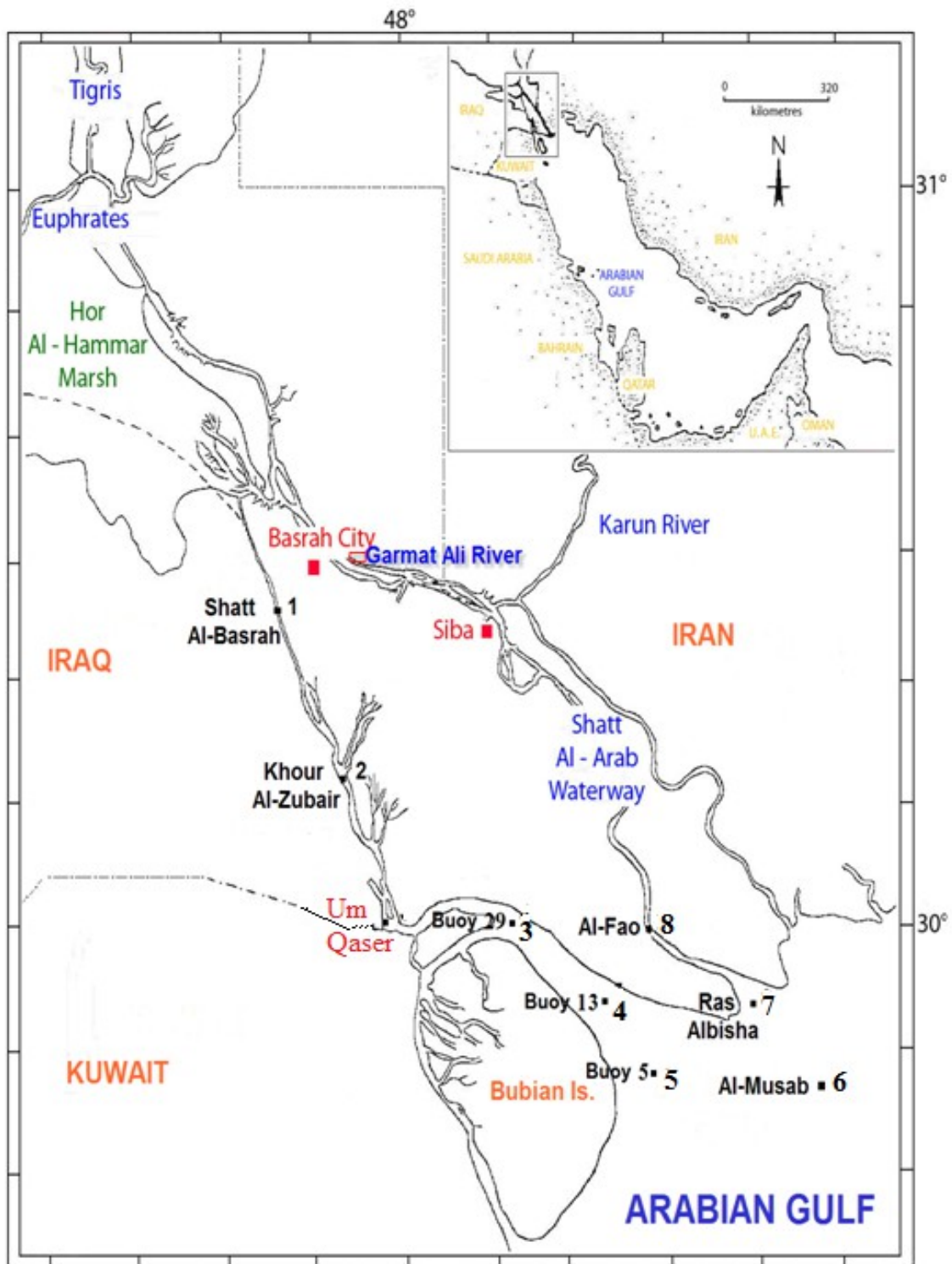


Fig. 1. Location map of the studying area

:Chemical analysis

All samples of zooplankton collected were analyzed for heavy metals by ICP/MS in .maxxam analytical INC. in Canada, which followed the procedure used by the company

:Statistical analysis

Statistical analysis was performed using analysis of variance (ANOVA) without replication. This was carried out to observe the special variation of metals variables. .Significant level was considered at 95% confidence limit

Results and Discussion

The density of zooplankton, their main diversity groups, is shown in table 1. The heavy metals concentrations in zooplankton for all stations are shown in table 2. The hierarchy concentrations of each individual metals from higher to lower concentration .among the stations are summarized in table 3

Table 1. Shows the density and the diversity of zooplankton collected (ind/ m³) from all selected stations in the studying area. (G1= group 1, G 2= group 2, etc.as .(dominant groups

G 4	G 3 Cirriped larvae	G2 Rotifers	G1 .Copepods sp	Zooplankton (total (ind/ m ³	Stations & periods
					St.1 Shatt Al-Basrah
	170	7243	9895	17580	June 2009
	178	919	4595	5811	Aug.2009
	1899	1284	12176	16533	Oct.2009
	2080	2939	3254	8453	Dec.2009
	3614	Polychaetes 15020	3017	24536	Feb.2010
					St.2 Khour Al-Zubair
	141	Megaloba 411	4732	5632	June 2009
	Polychaetes 1122	176	3509	4967	Aug.2009
Rotifer. 391	391	Gastropod.503	18148	20328	Oct.2009
	Rotifers 443	Gastropod.3769	2563	8919	Feb.2010
	293	Polychaetes 2186	11786	14882	Oct.2010
			No. 3		St. 3 Buoy 29
	Polychaetes 32	Megaloba 43	886	996	Jul.2009
					St. 4 Buoy 13
		Appendicularia 72	4896	5148	Jul.2009
	Bivalve 55	Appendicularia 77	2691	2922	March 2010
					St. 5 Buoy 5
	Rotifers303	Bivalve 412	3368	4484	Jul. 2009
	Foraminifera 122	Polychaetes 163	5804	6455	March 2010
					St. 6 Al-Musab
Append. 556	Cirripeds lar. 588	Bivalve 6765	17450	26601	Jul. 2009
					St. 7 Ras Al-Bisha
	Polychaetes 513	Cirripeds lar. 790	30368	32855	Jul.2009
		Megaloba 109	22	152	March 2010
					St. 8 Al-Fao
	Cirriped Lar. 584	Bivalve 3796	11826	16699	Jul. 2009
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The mercury concentration appears to be at the highest level at the Khour Al-Zubair station and the lowest at Al-Fao station, which can be seen in table 2. The multiple comparisons between the stations for the mercury did not show significant difference. In general, the concentration level of mercury in all stations was either with moderate concentration or high concentration compared with that of other studies (Chvojka, *et al.*

1990; Al-Majed and Prestona, 2000). This revealed that territories in Basrah are highly contaminated with mercury. This has been confirmed by other studies (Al-Imarah, *et al.* (2010

The Uranium (U^{238}) concentration which appeared in analyzed samples showed high levels of concentrations at Al-Musab station, which was significantly high ($P < 0.01$) when compared with all other stations of study except Ras Al-Bisha which did not have a significant difference in concentrations level. Also, the hierarchy was arranged highest to lowest as follows Al-Musab, Ras Al-Bisha, Khour Al-Zubair, Buoy 29, Shatt Al-Basrah (channel, Buoy 13, Buoy 5, and Al-Fao (Table 3

The appearance of Uranium was confirmed in the samples analysis and by other studies carried out in this area (Al-Imarah *et al.* 2010; UNEP, 2003). In addition, the Uranium (metals appeared in the surrounding countries such as Kuwait (Fido and Al-saad, 2008

Table2. Shows the level of Mercury, Uranium, Lead, Cadmium, Zinc, Copper, Iron, Cobalt, and Nickel measured in different stations in zooplankton (ppm), the number of samples shows in parenthesis

Hg	U^{235}	Pb	Cd	Stations
Mean \pm Se (n = 5) 0.07 \pm 0.402	Mean \pm Se (n = 5) \pm 76.81 150.00	Mean \pm se (n = 5) 0.113 \pm 0.850	Mean \pm Se (n=5) 0.027 \pm 0.185	Shatt-Al-Basrah
(n= 5) 0.19 \pm 1.158	(n= 5) 6.89 \pm 30.96	(n= 5) 0.451 \pm 1.490	(n=5) 0.264 \pm 0.510	Khour Al-Zubair
(n= 4) 0.01 \pm 1.24	(n= 4) 0.01 \pm 12.07	(n= 4) 0.001 \pm 1.020	(n= 4) 0.001 \pm 0.090	Buoy 29
(n= 4) 0.53 \pm 1.695	(n= 4) 39.88 \pm 81.11	n= 4) 0.140 \pm 0.820	n= 4) 0.129 \pm 0.305	Buoy 13
(n= 4) 0.13 \pm 1.105	(n= 4) 0.43 \pm 10.15	(n= 4) 0.175 \pm 0.700	(n=4) 0.001 \pm 0.110	Buoy 5
(n= 4) 0.01 \pm 2.620	(n= 4) 88.60 \pm 156.55	(n= 4) 0.001 \pm 3.580	(n= 4) 0.001 \pm 0.120	Al-Musab
n= 4) 0.40 \pm 1.100	(n= 4) 88.60 \pm 156.55	(n= 4) 1.013 \pm 2.030	(n= 4) 0.002 \pm 0.105	Ras Al-Bisha
(n= 4) 0.03 \pm 0.37	(n= 4) 11.01 \pm 30.52	(n= 4) 0.040 \pm 0.690	(n= 4) 0.017 \pm 0.07	Al-Fao
CO	Fe	Cu	Zn	
(n = 5) 1.32 \pm 6.95	(n = 5) 1731 9117 \pm	(n = 5) 6.09 \pm 35.08	(n = 5) 181 \pm 1040	Shatt-Al-Basrah
(n = 5) 0.57 \pm 4.58	(n = 5) 848 6354 \pm	n = 5) 2.28 \pm 46.98	(n = 5) 534 \pm 1861	Khour Al-Zubair
(n = 4) 1.25 \pm 8.09	(n = 4) 1118 18113 \pm	(n = 4) 0.01 \pm 58.41	(n = 4) 20 \pm 641	Buoy 29
(n = 4) 1.46 \pm 16.83	(n = 4) 3893 13200 \pm	(n = 4) 46.45 \pm 108.53	(n = 4) 1072 3331 \pm	Buoy 13
(n = 4) 1.21 \pm 8.01	(n = 4) 251 11399 \pm	(n = 4) 24 487 \pm	(n = 4) 24 487 \pm	Buoy 5
(n = 4) 0.42 \pm 2.29	(n = 4) 275 5476 \pm	(n = 4) 2.345 \pm 47.77	(n = 4) 25 577 \pm	Al-Musab
(n = 4) 1.91 \pm 6.62	(n = 4) 4265 9730 \pm	(n = 4) 5.76 \pm 24.73	(n = 4) 168 957 \pm	Ras Al-Bisha
(n = 4) 2.09 \pm 10.41	(n = 4) 1151 15394 \pm	n = 4) 3.05 \pm 19.85	(n = 4) 163 696 \pm	Al-Fao

Ni

Mean \pm Se	Stations
n =) 12.47 \pm 53.60 (5	Shatt Al- Basrah
(n = 5 b) 4.86 \pm 37.48	Khour Al-Zubair
n =) 13.55 \pm 64.93 (4	Buoy 29
n =) 0.72 \pm 36.27 (4	Buoy13
n =) 0.70 \pm 60.55 (4	Buoy 5
n =) 1.23 \pm 22.15 (4	Al-Musab
n =) 15.52 \pm 40.15 (4	Ras Al-Bisha
n =) 6.87 \pm 73.74 (4	Al-Fao

The mean concentration of lead in all stations is shown in table 2. The higher level of lead appeared in Ras Al-Bisha and the lowest level appeared in Buoy 29. The multiple comparisons between the stations did not show any significant differences. The results could be related to the high variable in the readings. The high concentration of Pb which appeared in this study could be a result of the stations

which are located near industrial sources. These sources distribute discharges into rivers which increases the bio-availabilities thereby uptake of metal by zooplankton. Metal accumulation by zooplankton is mainly of two pathways which are direct uptake from water and the assimilation from injected food and detritus (Davis, 1978). Also, the observed high level of Pb in zooplankton could be attributed to the high influxes of these regions, primarily from automotive exhausts. These exhausts load and unload large quantities of general and bulk cargo at these localities. Pb is known to form colloids in sea, estuarine and brackish water. These colloids can be absorbed onto planktonic debris, which consequently might have resulted in a higher concentration of these elements in zooplankton from coastal water (Robin, *et al.* 2012; Ritterhoff and Zauke, 1997; Safahieh, *et al.* 2011).

The Cadmium concentration in the collected samples from different stations is shown in table 2. The highest concentration appeared in Al-Musab station and the lowest level appeared in Al-Fao station (Table 2). Though, the hierarchy of Cd concentration in all stations is ranked from highest to lowest as follows Al-Musab, Buoy 13, Buoy 29, Khour Al-Zubair, Buoy 5, Ras Al-Bisha, Shatt-Al-Basrah channel, Al-Fao (Table 3). The Cd concentration in zooplankton in this study was higher than that in other study carried in Arabian sea (Rezai and Yusoff, 2011) which was ranged between 0.32 – 0.49 ppm, whereas in this study was 0.402- 2.620 ppm. This indicates that this particular area is highly polluted; which might be very close to the industrialized area than that of other studies. (Safahieh *et al.* 2011).

The concentration of Zinc and Copper which appeared in all of these stations, can be found in table 2. The higher concentration of Zn appeared in Buoy 13 and Khour Al-Zubair stations. The multi comparison between buoy 13 and the other stations showed higher differences $P < 0.01$, except that of Ras Al-Bisha which had no significant difference in concentrations. The hierarchy of Zinc concentration ranked from most to least concentrated as follows Bouy 13, Khour Al-Zubair, Shatt Al-Basrah, Ras Al-Bisha, Al-Fao, Buoy 29, Al-Musab, and Buoy 5 as shown in (Table 3). The Zinc concentration is very high in the zooplankton appears in the study comparing with other studies (Robin, *et al.* 2012; Rezai and Yusoff, 2011, Ritterhoff and Zauke, 1997). The increases of high concentration of Zinc could be a result of industrialized plants being close to the stations of study (Fig 1).

Copper concentration in table 2. Showed a higher concentration at station Buoy 13 and the lowest concentration at Al-Fao. The hierarchy from level of concentration was arranged from highest to lowest as follows Buoy 13, Buoy 29, Al-Musab, Khour-Al-Zubair, Shatt- Al-Basrah, Buoy 5, Ras Al-Bisha, Al-Fao (Table 3). The multi comparison between stations was significantly higher in Buoy 13 by $P < 0.001$ than other stations except for Buoy 29 which had no significant change in levels comparing to Buoy 13. The levels of concentrations in the conducted study was higher comparing to other studies in the surrounding areas. (Robin *et al.* 2012; Razai and Yusoff, 2011; Ritterhoff and Zauke, 1997; Safahieh, *et al.* 2011).

The iron concentrations in most stations appeared at high levels. The highest concentration was recorded at Buoy 29 and the lowest reading was at Al-Musab (Table 2). The multiple comparison demonstrated only significant $P < 0.05$ high, when compared with Buoy 29 with Shatt Al-Basrah, Khour Al-Zubair and Al-Musab only. On other hand, when comparing Khour Al-Zubair to the other stations, a significant difference was observed between Khour Al-Zubair and Buoy 29, Buoy 13 and Al-Fao ($P < 0.01$, (Table 2

The level of cobalt appeared in all stations shown in (Table 2).The hierarchy concentration ranked from highest to lowest was as follow Buoy13,Fao,Buoy 29, Buoy 5, Shatt Al-Basrah, Rass Al-Bisha, Khour Al-Zubair, and Al-Musab (table 3). The cobalt concentration which in this study appeared higher than that of other studies (at the Iranian side of the Gulf (Rezai and Yusoff 2011

Table 3: Showed the hierarchy for individual element from the higher to lower level of station

Zn	Cd	Hg	Pb	U²³⁸
Buoy 13	Al-Musab	Khour Al-Zubair	Ras Al-Bisha	Al-Musab
Khour Al-Zubair	Buoy 13	Buoy 13	Shatt Al-Basrah	Ras Al-Bisha
Shatt Al-Basrah	Buoy 29	Shatt Al-Basrah	Buoy 13	Khour Al-Zubair
Ras Al-Bisha	Khour Al-Zubair	Al-Musab	Khour Al-Zubair	Buoy 29
Al-Fao	Buoy 5	Buoy 5	Al-Fao	Shatt Al-Basrah
Buoy 29	Ra Al-Bisha	Ras Al-Bisha	Buoy 5	Buoy 13
Al-Musab	Shatt Al-Basrah	Buoy 29	Al-Musab	Buoy 5
Buoy 5	Al-Fao	Al-Fao	Buoy 29	Al-Fao

Ni	Fe	Co	Cu
Al-Fao	Buoy 29	Al-Fao	Buoy 13
Buoy 29	Al-Fao	Buoy 29	Buoy 29
Buoy 5	Buoy13	Buoy 5	Al-Musab
Shatt Al-Basrah	Buoy 5	Shat Al-basrah	Khour Al-Zubair
Ras Al-Bisha	Ras Al-Bisha	Buoy 13	Shatt Al-Basrah
Khour Al- Zubair	Shatt Al-Basrah	Ras Al-Bisha	Buoy 5
Buoy 13	Khour Al-Zubair	Khour AL-Zubair	Ras Al-Bisha
Al-Musab	Al-Musab	Al-Musab	Al-Fao

The Nickel concentration (Table2) shows the highest level at Al-Fao station and the lowest was at Ras Al-Bisha. A reason for the result could be due to the priority of the oil loading terminals

In conclusion, the increase in concentration of Zn, Pb, Cu, Cd, and Hg in zooplankton of coastal samples is relatively higher than that off shore samples in other studies. The high levels of Iron, Cobalt, Nickel and the appearance of Uranium in this study could be attributed to their industrial sources carried through rivers discharges which increases the Bio availabilities thereby uptake of metals by zooplankton. Zooplankton is very important in the cycling processes of elements in the coastal water since it is a secondary producer in the food chain. Moreover, being a major

source of food for larger animals, their role in transporting the metals to the higher trophic level (Gajbhiye *et al.* 1985). Metals accumulation by zooplankton is mainly by two pathways such as direct uptake from water, the assimilation from injected food (and detritus (Davis, 1978

The observed high levels of metal, including Pb in zooplankton in the area of study, could be attributed to the high influxes at this region, primarily from automotive exhausts. Pb is known to form colloid salt and brackish water. The colloids would have adsorbed onto planktonic debris, which consequently might have resulted in higher concentration of this element in zooplankton from coastal water ((Robin, et al. 2012

:Acknowledgment

Our great full thanks due to the Dr. Adil Yousif Al-Dubaikel for his great efforts in the statistical analysis of the data

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Note: We replaced the table 8 by table 3, where it was difficult to do it as histogram Due to the wide range of varieties in the values of concentration of different metals, .so they will be more than 3 Figs. If convert them to histogram

