

## Accumulation of Heavy Metals in Zooplanktons from Iraqi National Waters

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**Abstract** Samples of zooplankton's were collected by special net from 8 sites within Iraqi national waters represented by stations: 1- Shatt Al-Basrah cannal, 2- Khour Al-Zubair, 3- Buoy 29, 4-Buoy 13, 5-Buoy 5, 6-Al-Musab, 7- Ras Al-Bisha, and 8-Al-Fao. Samplings were conducted during the period June 2009 and Feb. 2010. Zooplankton's were classified in groups: Copepods, Rotifera, Cirriped larvea, and some other minor species. Major abundant zooplankton's were Copepods, Rotifera, Cirriped larvea, Polychates, and Bivalves, while other zooplankton's which appear in minor abundance were Appendicularia, Castropod, Forminilifera, and Megalopa. Selected heavy metals Cd, Co, Cu, Fe, Hg, Ni, Pb, U, and Zn were determined in the collected samples by adopting a highly sophisticated ICP/MS at Maxxam Analytical Inc., Canada. Levels estimated of heavy metals in  $\mu\text{g/g}$  were high for most of studied metals due to two main reasons: 1- the marine vessels sank in the water ways, and 2- discharging of waste water from Basrah City and certain industrial estate around. Trend of descending concentrations of heavy metals accumulated in zooplankton's at southern Iraqi Waters were in the order:  $\text{Fe} > \text{Zn} > \text{U} > \text{Cu} > \text{Co} > \text{Pb} > \text{Cd} > \text{Hg}$ . Highest levels in  $\mu\text{g/g}$  for toxic heavy metals Co ( $1.91 \pm 6.62$ ), Hg ( $0.40 \pm 1.100$ ), Ni ( $15.52 \pm 40.15$ ), Pb ( $1.013 \pm 2.030$ ), and U ( $88.6 \pm 56.55$ ), were reported at site 7 the Ras Al-Bishah station at the top of the Northern West Arabian Gulf due to waste discharge from the Iranian industrial estate.

**Keywords** Heavy metals; Pollution; Zooplankton's; North West Arabian Gulf; Uranium

## Background

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 trophic 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). In aquatic system, the primary concentrator, the photosynthetic plants, take chemical elements from the surroundings, these plants are the phytoplankton's which has small size and offer large surface for adsorption. The accumulation of chemical elements by phytoplankton's will pass to marine animals through the food webs of the water ways (Chipman, 1959). 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 (Percy, 1993; Nilsson et al., 1995a; Nilsson et al., 1995b). 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 and 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). 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 wars. 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 (Rezai and Yusoff, 2011). A Certain levels of heavy metals Cd, Cu, Hg, Ni, and Zn were reported in zooplankton's of lake Kenon (Itigilova et al., 2016). 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 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 (Robin et al., 2012) and Saudi Arabia (Al-Tison and Chandy, 1995).

## 1 Materials and Methods

### 1.1 Sample collection

Eight sampling stations were selected in various localities along Basrah waters which include: 1) Shatt Al-Basrah Channel, 2) Khour Al-Zubair, 3) Buoy 29, 4) Buoy 13, 5) Buoy 5, 6) Al-Musab, 7) Ras Al-Bisha and 8) Al-Fao, as shown in Figure 1. The nature of these stations is quite different from one another. A net of Plankton characterized by 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, and the other was preserved in a freezer after washed with same water at each station. Dry weight of the zooplankton was estimated by filtering the 2 sample through a filter paper using a vacuum pump. The filter paper was then dried in oven at 60 °C for 24 hours.

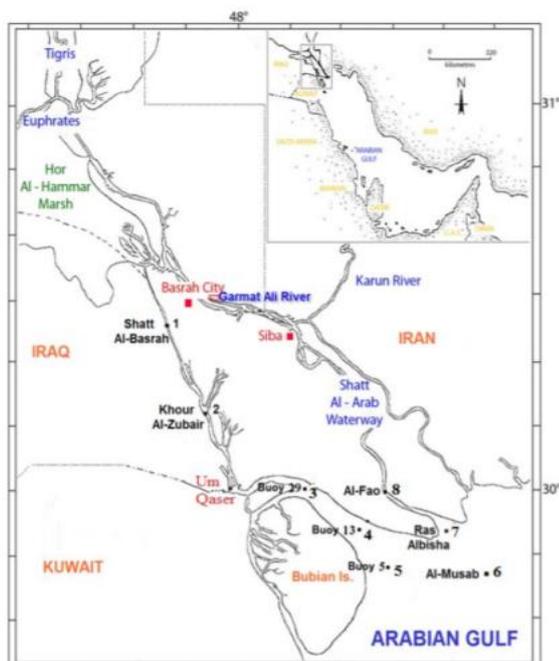


Figure 1 Map of southern part of Iraq showing the position of sampling stations 1-8

## 1.2 Chemical analysis

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

## 1.3 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.

## 2 Results

The density of zooplankton, their main diversity groups as classified earlier (Ajeel et al., 2015), is shown in Table 1 and Table 2. The heavy metals concentrations in zooplankton for all stations are shown in Table 3. The hierarchy concentrations of each individual metals from higher to lower concentration among the stations are summarized in Table 4.

## 3 Discussion

A literature review shows that both freshwater and planktons have trace elements and radionuclides concentrations in a factor of up to  $10^4$  (Marsh and Buddemeier, 1984).

The mercury concentration appears to be at the highest level at the Khuor Al-Zubair station and the lowest at Al-Fao station, as shown in Table 3. 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 moderate or high 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 which has been confirmed by local studies (Al-Imarah et al., 2010).

The Uranium 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 (UNEP, 2003; Al-Imarah et al., 2010) as well as in the surrounding countries such as Kuwait (Fido and Al-saad, 2008).

Sources of radioactive elements in the aquatic environment include naturally occurring radionuclide's (Al-Battat, 2016), fallout from atmosphere, due to emission from military waste as well as effluent runoff from that waste during raining and distributed between water column and sediments from which aquatic organisms receive radioactive elements (Al-Imarah and Ali, 2009).

The higher level of lead appeared in Ras Al-Bisha and the lowest level appeared in Buoy 29, as shown in Table 3. 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 5 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 plank tonic debris, which consequently might have resulted in a higher concentration of these elements in zooplankton from coastal water (Zauke, 1997; Safahieh et al., 2011; Robin et al., 2012).

Table 1 The density and diversity of zooplanktons (ind/m<sup>3</sup>) collected at study area, stations 1-2, during the period July 2009-March 2010

Zooplankton	Station / date									
	Station 1					Station 2				
	July 2009	Aug. 2009	Oct. 2009	Dec. 2009	Feb. 2010	July 2009	Aug. 2009	Oct. 2009	Feb. 2010	Oct. 2010
Copepoda	9895	4595	12176	3254	3017	4732	3509	18149	2563	11786
Appendicularia	-	-	56	-	-	116	-	223	-	-
Bivalve	34	-	56	45	-	26	32	168	-	133
Cirriped larvae	170	178	1899	2080	3614	141	176	391	1059	293
Fish eggs	102	59	168	90	1691	13	-	-	296	-
Fish larvae	1	1	-	-	-	13	-	-	-	27
Foraminifera	-	-	-	-	-	-	-	-	-	213
Mysidaceae larvae	-	-	-	1	-	-	-	1	-	-
Megaloba	1	1	-	-	199	411	32	279	567	-
Ostracoda	-	-	1	-	166	-	-	-	1	-
Polychaetes larvae	68	30	112	-	5471	64	1122	168	-	2186
Polychaetes adults	-	-	614	-	9549	-	-	-	197	27
Rotifers	7243	919	1284	2939	829	13	-	391	443	-
Gastropods	68	30	168	45	-	77	-	503	3769	-
Zoea of Crab	-	-	1	-	-	-	-	56	-	-
Mysis of shrimp	-	-	-	-	-	26	1	-	-	-
Cladocera	-	-	-	1	-	-	-	-	-	-
Sagitta	-	-	-	-	-	-	-	-	25	-
Tintinida	-	-	-	-	-	-	-	-	-	27
Total Zooplankton	17580	5811	16533	8453	24536	5632	4967	20328	8919	14882

Table 2 The density and diversity of zooplanktons (ind/m<sup>3</sup>) collected at study area, stations 3-8, during the period July 2009-March 2010

Zooplankton	Station / date											
	Station 3		Station 4		Station 5		Station 6		Station 7		Station 8	
	July 2009	July 2009	March 2010	July 2009	March 2010	July 2009	July 2009	March 2010	July 2009	March 2010		
Copepods	1094	4861	2658	3381	5774	8386	0368	51	1827	9413		
Cladocera	-	-	-	-	20	-	-	-	-	-		
Cirriped larvae	-	-	-	-	1	588	790	16	584	1		
Megaloba	43	18	1	36	20	65	79	109	1	-		
Mysis of shrimp	11	1	-	-	-	65	79	-	49	-		
Amphipods	-	18	-	12	-	1	-	-	-	-		
Zoea of Crab	-	-	-	73	-	-	-	-	-	1		
Foraminifera	-	-	-	-	122	-	-	-	-	-		
Bivalve	-	36	55	412	1	6765	-	-	3796	1		
Gastropoda	-	-	11	24	41	294	-	-	-	41		
Rotifers	-	36	-	303	20	163	158	1	-	276		
Polychaet larvae	32	18	-	24	122	261	474	1	97	-		
Polychaet adult	-	-	-	-	41	-	39	-	-	-		
Appendicularia	-	72	77	133	102	556	513	1	195	-		
Fish larvae	1	36	1	1	1	65	1	2	1	1		
Fish eggs	21	-	55	36	102	131	237	1	-	-		
Sagitta	21	18	11	63	41	163	118	-	-	-		
Ctenophore	-	-	11	-	-	-	-	-	-	-		
Platyhelmenths	-	-	1	-	10	-	-	-	-	-		
Total zooplankton	1223	5078	2881	4498	6391	7503	2856	182	6550	9734		

Table 3 Levels of heavy metals (in  $\mu\text{g/g}$ ) measured in zooplankton's at different stations within the Iraqi national waters (1-8)

Metals	Stations							
	1) Shatt Al-Basrah (n=5)	2) Khaur Al-Zubair (n=5)	3) Buoy 29 (n=4)	4) Buoy 13 (n=4)	5) Buoy 5 (n=4)	6) Al-Musab (n=4)	7) Ras Al-Bishah (n=4)	8) Al-Fao (n=4)
Cd	0.027 $\pm$ 0.185	0.264 $\pm$ 0.510	0.001 $\pm$ 0.090	0.129 $\pm$ 0.305	0.001 $\pm$ 0.110	0.001 $\pm$ 0.120	0.002 $\pm$ 0.105	0.017 $\pm$ 0.07
Co	1.32 $\pm$ 6.95	0.57 $\pm$ 4.58	1.25 $\pm$ 8.09	1.46 $\pm$ 16.83	1.21 $\pm$ 8.01	0.42 $\pm$ 2.29	1.91 $\pm$ 6.62	2.09 $\pm$ 10.41
Cu	6.09 $\pm$ 35.08	2.28 $\pm$ 46.98	0.01 $\pm$ 58.41	46.45 $\pm$ 108.53	24.48 $\pm$ 60.21	2.345 $\pm$ 47.77	5.76 $\pm$ 24.73	3.05 $\pm$ 19.85
Fe	1731 $\pm$ 9117	848 $\pm$ 6354	1118 $\pm$ 18113	3839 $\pm$ 13200	251 $\pm$ 11399	275 $\pm$ 5476	4265 $\pm$ 9730	1151 $\pm$ 15394
Hg	0.07 $\pm$ 0.402	0.19 $\pm$ 1.158	0.01 $\pm$ 1.24	0.53 $\pm$ 1.695	0.13 $\pm$ 1.105	0.01 $\pm$ 2.62	0.40 $\pm$ 1.10	0.03 $\pm$ 0.37
Ni	12.47 $\pm$ 53.6	4.86 $\pm$ 37.48	13.55 $\pm$ 64.93	0.72 $\pm$ 36.27	0.70 $\pm$ 60.55	1.23 $\pm$ 22.15	15.52 $\pm$ 40.15	6.87 $\pm$ 73.74
Pb	0.113 $\pm$ 0.85	0.451 $\pm$ 1.49	0.001 $\pm$ 1.02	0.140 $\pm$ 0.82	0.175 $\pm$ 0.700	0.001 $\pm$ 3.580	1.013 $\pm$ 2.000	0.040 $\pm$ 0.69
U <sup>235</sup>	76.81 $\pm$ 50.0	6.89 $\pm$ 30.96	0.01 $\pm$ 12.07	39.88 $\pm$ 81.11	0.43 $\pm$ 10.15	88.60 $\pm$ 156.55	88.60 $\pm$ 156.55	11.01 $\pm$ 30.52
Zn	1.81 $\pm$ 1040	534 $\pm$ 1861	20 $\pm$ 641	1072 $\pm$ 3331	24 $\pm$ 487	25 $\pm$ 577	168 $\pm$ 957	163 $\pm$ 696

Note: n =No. of samples

Table 4 The hierarchy for individual element from the higher to lower level of stations

Metals	Stations							
Cd	Al-Musab	Buoy13	Buoy29	Khor Al-Zubair	Buoy5	Ras Al-Bisha	Shatt Al-Basrah	Al-Fao
Co	Al-Fao	Buoy29	Buoy5	Shatt Al-Basrah	Buoy13	Ras Al-Bisha	Khour Al-Zubair	Al-Musab
Cu	Buoy13	Buoy29	Al-Musab	Khour Al-Zubair	Shatt Al-Basrah	Buoy5	Ras Al-Bisha	Al-Fao
Fe	Buoy29	Al-Fao	Buoy13	Buoy5	Ras Al-Bisha	Shatt Al-Basrah	Khour Al-Zubair	Al-Musab
Hg	Khour Al-Zubair	Buoy13	Shatt Al-Basrah	Al-Musab	Buoy5	Ras Al-Bisha	Buoy29	Al-Fao
Ni	Al-Fao	Buoy29	Buoy5	Shatt Al-Basrah	Ras Al-Bisha	Khour Al-Zubair	Buoy13	Al-Musab
Pb	Ras Al-Bisha	Shatt Al-Basrah	Buoy13	Khour Al-Zubair	Al-Fao	Buoy5	Al-Musab	Buoy29
U	Al-Musab	Ras Al-Bisha	Khour Al-Zubair	Buoy29	Shatt Al-Basrah	Buoy13	Buoy5	Al-Fao
Zn	Buoy13	Khour Al-Zubair	Shatt Al-Al-Basrah	Ras Al-Bisha	Al-Fao	Buoy29	A.-Musab	Buoy5

For Cadmium, the highest concentration appeared in Al-Musab station and the lowest level appeared in Al-Fao station (Table 3). 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 4). The Cd concentration in zooplankton reported within 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 compared to 0.402-2.620 ppm reported within this study. 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 higher concentration of Zn appeared in Buoy 13 and Khour Al-Zubair stations, as shown in Table 3. 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 showin in (Table 4). The Zinc concentration is very high in the zooplankton appears in the study comparing with other studies (Ritterhoff and Zauke, 1997; Rezai and Yusoff, 2011; Robin et al., 2012). The increases of high concentration of Zinc could be a result of industrialized plants being close to the stations of study (Figure 1).

Copper concentration, as listed in Table 3, showed a higher level at station 4 (Buoy 13) and the lowest concentration at station 8 (Al-Fao). The hierarchy from level of concentration was arranged from highest to lowest as follows Buoy 13, Buoya 29, Al-Musab, Khuor-AlZubair, Shatt-Al-Basrah, Buo 5, Ras Al-Bisha, Al-Fao (Table 4). The multi comparison between stations was significantly higher in Buoy13 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 (Ritterhoff and Zauke, 1997; Rezai and Yusoff, 2011; Safahieh et al., 2011; Robin et al., 2012).

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 3). The multiple comparison demonstrated high significant ( $P < 0.05$ ), when compared Buoy 29 with Shatt Al-Basrah, Khour Al-Zubair and Al-Musab only. On the 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 3).

Iron and Zinc are reported to be the highest accumulated chemical elements in zooplankton's (Masuzawa et al., 1988).

The level of cobalt was recorded in all stations, as shown in Table 3. 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 4). 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).

The Nickel concentration (Table 3) 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 tropic 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). 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 domestic sewages as well as sewages of the oil production industries and waste of sinking vessels for more than 30 years (Chua et al., 2000).

Finally, the zooplankton's removed nearly all the chemical elements available in the Iraqi National Waters, and help in decreasing pollution by these elements.

#### Authors' contributions

FJA carried out the analysis of results and writing the paper. TAK participated in the classification of Zooplanktons. SGA involved in the collection of the zooplankton samples. AYK carried out the processes before heavy elements determination, and RS carried out the ICP analysis for the heavy element in the samples.

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