

Distribution of Chemical Elements in Zooplanktons from Southern Iraqi Waters. Shaker G.Ajeel Dept.Marine Biology & Faris J. M. Al-Imarah and Maryam F. Hameed Dept. Marine Environ. Chem. Marine Science Centre/Basrah Univ. Basrah – Iraq. ABSTRACT

Chemical elements Silver (Ag), Aluminum (Al), Barium (Ba), Beryllium (Be), Bismuth (Bi), Bromium (Br), Boron (B), Calcium (Ca), Lithium (Li), Magnesium (Mg), Manganese (Mn), Phosphorous (P), Potassium (K) Silicon (Si), Sodium (Na), Thorium (Th), and Titanium (Ti) were estimated by adopting ICP/MS instrument, in Zooplanktons collected from different stations of southern Iragi waters at, 1) Shatt Al-Basrah channel, 2) Khor Al-Zubair, 3) Bouy 29, 4) Bouy 13, 5) Bouy 5 along Khor Abdullah, 6) Al-Masab (NW Arabian Gulf) as well as two stations along Shatt Al-Arab river estuary 7) Ras Al-Bisha, and 8) Al-Fao. Distribution of zooplanktons within these stations were different mostly Copepoda sp., Rotifers, and Cirripod larvae, being the most abundance are copepod sp. (30368 ind./m³ in st. 7 (Ras Al-Bisha) during July 2009, followed by Rotifers as polychaetes (15020 ind/m³ in St. 1 (Shatt Al-Basrah channel) during Feb. 2010, then Cirriped larvae (3614 ind./m³)in St,1. During Feb. 2010. The As a total zooplanktons, the most abundance was 24136 ind./m³ in St. 1 during Feb.2010, and the lowest was 152 ind./m³ in St.7 during March 2010. Levels of chemical elements reported (µg/g) in the zooplanktons from southern Iraqi waters were range (26580-135403 Ca), (791.62-16085.06 P), (4108.15- 12463.09 Mg), (1462.64-11749.05 Al), (406.15-6028.21 Na), (11.66-7086.87 Ba), (110.52-3597.44 Si), (43.38-1849.68 K), (53.55-554.83 Mn), , (81.81-1568.27 Br), (12.59-337.37 Cr), (1.88-29.74 B), (0.42-17.71 Li), (0.04-2.53 Ag), (0.21-1.07 Th), (0.08-1.07 Be), (0.01-1.07 Bi), (ND-0.07 Ti). Highly pollution in Sts. 1,2 and 3 is expected due to untreated domestic water thrown into Shatt Al-Basrah channel, while highly pollution in Sts, 4, 5, 6, 7, and 8 could be arises from water circulation in the northern part of the Arabian Gulf. Some elements are related to the radioactive series decay of ²³⁸U such as Th which exist in very low concentration.

Key Words: Zooplankton, Chemical elements. Pollution. Southern Iraq, Arabian Gulf INTRODUCTION:

Southern Iraqi water ways represented by Tigris river as fresh water and Shatt Al-Arab river Canal, Shatt Al-Basrah, Khor Al-Zubair Lagoon, Khor Abdullah, and regional waters at North West Arabian Gulf as saline waters are liable to be threatened by the discharge of untreated sewage wastes from residential cities as well as untreated industrial effluents. These wastes carry enormous level of toxicants particularly the trace elements which are capable to accumulate into the basic food chain and move up through the higher tropic level and results in negative impact on the marine and freshwater resources, thus causing economic loss (Robin et al. 2012).

Phytoplankton is the major food producers in marine and estuarine ecology, while zooplankton plays a fundamental role in food chains as a secondary producers. It considered 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 chemical elements 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 level 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 expanding to specific sources and there are particular concerns when such sources adjacent to estuarine and to marine systems supporting significant fisheries (Ninomiya, et al. 1995), such an example existed in Kuwait, south part of Iraq in Basrah governorate, and although no longer active, the legacy of its activities is still an important influence on the local contamination levels.

As in previous studies, the major point 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 closed to the Khour Al-Zubair (Al-Imarah, et al. 2010; Al-Imarah, et al. 2003; Karabedain, et al. 2009); and the salt and chlorine planet in Kuwait and petrochemical planet closed the north of Kuwait that has been affected on Northwest of Gulf under the influence of tide and sub tide of Gulf water (Al-Majed and Perston, 2000). The heavy metals in mixed zooplankton organisms generally found in higher concentration near the coast, due to the untreated discharged of many waste products of planets closed the coast or near the rivers (Rezai and Yusoff, 2011; Robin, et al. 2012).

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

The contamination of sea water, freshwater and estuarine water, due to direct exposure to atmospheric input, probably the major source of pollution in the all stations used in this study. There is significant industrial pollutant untreated waste has been discharged in River Shatt Al-Arab, Shatt Al- Basrah channel, Khour Al-Zubair, and the Gulf generated from discharging sewages; manufacturing industries such as of food, beverages palm, Oil refineries, petrochemical, manufacturing of fertilizers, textile pulp paper, tanneries and sugar (Chua, et al. 2000). The aim of this study is due to the lack of such studies concerned 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; has not been taken in considerable studies in this area such that carried in the closed countries, India, (Robin, et al. 2012) and Saudi Arabia (Al-Tison and Chandy, 1995).

The physiology and ecology of planktonic organisms are influenced by the concentration, chemical speciation and resulting bioavailability of some chemical elements. The determination of the elemental structure of plankton is important for interpretation of physiological and functional states of aquatic ecosystems. The present study is focused on



the structure and elemental composition of the zooplankton assemblages from the different aquatic zones along southern Iraqi water ways (Nekhoroshkov, 2014).

Study area:

This study covered the water ways of the Southern part of Basrah Governorate. Sampling stations for zooplanktons collection stretches from Shatt Al-Basrah channel Through Khor Al-Zubair, Khor Abdullah, towards the estuary of Shatt Al-Arab river. These stations are characterized by different nature and affected heavily by different factors.

Sampling

This study has been conducted during the period June 2009 – Feb. 2010. For collecting zooplanktons a plankton net of 120 micron mish-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). Samples were preserved in freezer after washed with same water of each sampling station. Dry weight of the zooplankton was estimated by filtering the sample through a filter paper using a vacuum pump. Then the filter paper was oven – dried at 60 $^{\circ}$ C for 24 hours.

Chemical analysis:

All samples collected were analyzed for chemical elements by ICP/MS in maxxam analytical INC. in Canada, followed the typical procedure for trace elements analysis. In Teflon beakers, zooplankton samples were digested with an aqua solution (2:1 concentrated nitric acid and hydrochloric acid) heated to 70 °C for 8–10 h. After digestion, samples were centrifuged. Trace elements in each sample were analyzed by inductively-coupled plasma mass spectrometry (ICPMS).(Chen et al.,2000)

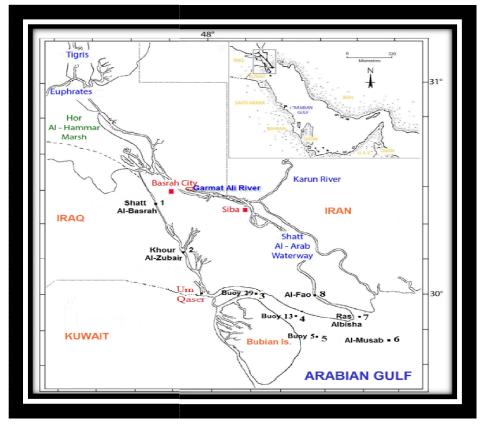


Figure 1. Location map of southern Iraq showing sampling stations.



Statistical Analysis

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

RESULTS

The density of zooplankton, categorized in groups according to their abundance as G1: Copepods, G2: Rotiffers, G3: Cirriped larvae, and G4: as minor species are shown in table I. The concentrations of 17 chemical elements : Li, Be, B, P, Na, Mg, Al, Si, K,Ca, ,Mn, , Br, Ag, Ba, Ti, Bi, and Th in the zooplankton communities of the aquatic ecosystems for all stations are shown in table II.

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

Stations&& periods	Zooplankton total	G1 Copepods	G2 Rotifers	G 3 Cirriped Iarvae	G 4
		sp.	t Al-Basrah	larvae	
June 2009	17500			170	
	17580	9895	7243	170	
Aug.2009	5811	4595	919	178	
Oct.2009	16533	12176	1284	1899 2080	
	Dec.2009 8453		3254 2939		
Feb.2010	24536	3017	15020	3614	
			ır Al-Zubair		Γ
June 2009	5632	4732 411		141	
Aug.2009	4967	3509	176	1122	
Oct.2009	20328	18148	503	391	391
Feb.2010	8919	2563	3769	443	
Oct.2010	14882	11786	2186	293	
			uoy 29	1	
Jul.2009	996	886	43	32	
			Buoy 13		
Jul.2009	5148	4896	72		
March 2010	2922	2691	77	55	
		St. 5	Buoy 5		
Jul. 2009	l. 2009 4484		412	303	
March 2010	6455	5804	Polychaet	Foraminifera	
			es 163	122	
		St. 6 A	l-Masab		
Jul. 2009	26601	17450	Bivalve	Cirripedslar.	Append. 556
			6765	588	
		St. 7 Ra	s Al-Bisha		
Jul.2009	32855	30368	Cirripedsl	Polychaetes	
			ar. 790	513	
March 2010	152	22	Megaloba		
			109		
		St. 8	Al-Fao		
Jul. 2009	16699	11826	Bivalve	CirripedLar.	
			3796	584	
March 2010	9800	9409			



The most abundant zooplankton species recorded within this study was copipoda which reported 30368 indiv. $/m^3$ in station 7 (Ras Al-Bishah) during July 2009 followed by Rotifera as polychaets to be 15020 indiv. $/m^3$ in station 1 (Shatt Al-Basrah) during Feb. 2010, then to a minor level Terriped larvae 3614 indiv. $/m^3$ in station 1 (Shatt Al-Basrah) during Feb. 2010. Most abundant zooplanktons as a total reported 32855 indiv/m³ in station 7 (Ras Al-Bishah) during July 2009, the highly individual zooplanktons were the copipoda sp. as 30368 indiv. $/m^3$, while the lowest were 152 indiv. $/m^3$ in the same site during March 2010 and again Copepoda was the lowest to be 22 indiv. $/m^3$.

	Shatt-Al-	Khor Al-	Buoy 29	Buoy 13	Buoy 5	Al-Musab	Ras Al-	Al-Fao
	Basrah	Zubair	(3)	(4)	(5)	(6)	Bisha	(8)
	(1)	(2)	(3)	()	(3)	(0)	(7)	(0)
Silver	0.180	0.914	0.330	0.330	0.305	1.020	0.180	0.750
Ag	±0.034	±0.277	±0.00	±0.057	±0.105	±0.000	±0.057	±0.369
- 0	(n=5)							
Aluminum	6192,02	3519.18	6225.95	3465.60	5572.80	1970.57	4832.30	8475.26
Al	± 1179.5	± 476.70	± 0.000	± 40.36	± 389.96	± 0.00	±1945.47	±1473.89
	(n = 5)	(n = 5)	(n = 4)					
Barium	1297.72	34.952	47.450	55. 555	357.320	19.070	61.445	21.510
Ва	± 781.009	± 3.942	± 0.000	± 16.336	±181.357	± 0.000	± 28.743	± 4.243
	(n = 5)	(n = 5)	(n = 4)					
Berelium	0.510	30.96	12.07	81.11	1510	11.58	156.5	30.52
Ве	± 76.	± 6.89	± 0.001	± 39.88	± 0.439	± 0.001	± 88.6	± 11.01
	(n = 5)	(n = 5)	(n = 4)	(n = 4)				
Bismoth	0.325	0.192	0.040	0.185	0.055	0.060	0.345	0.105
Bi	± 0.115	± 0.057	± 0.000	± 0.089	± 0.259	± 0.000	± 0.287	± 0.317
	(n = 5)	(n = 5)	(n = 4)	(n = 4)	(n = 4)	(n = 4)	(n = 4)	(n = 4)
Boron	18.673	11.290	16.160	9.710	21.485	10.000	4.955	7.640
В	± 2.620	±2.693	± 0.000	± 3.319	± 5.239	± 0.000	± 1.694	± 2.725
	(n = 5)	(n=5)	(n = 5)	(n = 4)				
Bromine	155.78	787.126	257.41	400.275	389.255	1391.280	1311.585	125.400
Br	± 23.299	±159.358	± 0.000	± 119.023	± 42.201	± 0.000	±596.007	± 18.571
	(n = 5)	(n = 5)	(n = 4)					
Calcium	86452.496	96054.35	74548.46	73914.805	78786.515	107728.28	72362.670	11625.960
Са	±11526.16	±7169.00	0 ± 0.000	±15304.59	±15304.59	0 ± 0.000	±26374.80	±11077.64
	9 (n = 5)	0 (n = 5)	(n = 4)	1 (n = 4)	1 (n=4)	(n = 4)	3 (n = 4)	8 (n = 4)
Magnesium	10291.980	7891.674	11601.30	7568.835 ±	11387.030	4188.460	9048.660 ±	14483.958
Mg	± 1690.842	± 992.368	0 ± 0.000	323.775	± 751.542	± 0.000	2646.146	± 43.685
Lithium	(n = 5)	(n = 5)	(n = 4)	(n = 4)	(n = 4)	(n = 4)	(n =± 4)	(n = 4)
Litnium Li	8.031 ± 1.947	5.398 ± 1.179	7.220 ± 0.000	6.030 ± 0.866	8.400 ± 0.404	2.350 ± 0.000	5.350 ± 1.708	9.410 ± 3.000
LI	± 1.947 (n = 5)	± 1.179 (n = 5)	± 0.000 (n = 4)	± 0.800 (n = 4)	± 0.404 (n = 4)	± 0.000 (n = 4)	± 1.708 (n = 4)	± 5.000 (n = 4)
Potassium	662.946	530.338	1148.82	442.345	1150.615	471.820	503.925	1183.500
K	±184.083	±116.092	±0.000	±230.342	±226.901	±0.000	±167.168	±265.754
Ň	(n=5)	(n=5)	(n=4)	(n=5)	(n=5)	(n=4)	(n=5)	(n=4)
Sodium	1298.523	3114.174	1198.310	2273.450	2856.025	3182.420	2133.200	1158.015
Na	±265.767	±523.736	±0.000	±264.362	±1114.889	±0.000	±323.223	±341.263
	(n=4)	(n=5)	(n=4)	(n=4)	(n=5)	(n=4)	(n=5)	(n=5)
	5463.670	5111.986	4035.340	1921.090	1368.115	2105.810	5415.205	1062.000
Phosphorou	±1491.380	±1010.49	±0.000	±325.827	±53.199	±0.000	±352.619	±156.103
s P	(n=5)	2 (n=5)	(n=4)	(n=5)	(n=5)	(n=4)	(n=5)	(n=5)
Silicon	1137.795	1219.042	340.570	1413.050	612.150	119.130	2338.165	544.255
Si	±318.001	±166.390	±0.000	±752.016	±129.222	±0.000	±726.886	±229.568
	(n=5)	(n=5)	(n=4)	(n=5)	(n=5)	(n=4)	(n=5)	(n=5)

Table II. Concentrations (in μ g/g) of chemical elements in zooplanktons from southern Iraqi waterways for the period June 2009 – Feb.



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Thorium	0.631	0.422	0.510	0.535	0.485	0.290	0.685	0.695
Th	±0,087	±0.048	±0.000	±0.106	±0.101	±0.000	±0.262	±0.020
	(n=5)	(n=5)	(n=4)	(n=4)	(n=4)	(n=4)	(n=5)	(n=4)
Titanium	o.030	0.026	0.060	0.030	0.090	0.010	0.000	0.030
Ti	±0.005	±0.000	±0.000	±0.005	±0.011	±0.000	±0.000	±0.011
	(n=4)	(n=4)	(n=4)	(n=5)	(n=5)	(n=4)	(n=4)	(n=5)

The highest levels of chemical elements measured in the zooplanktons were in the range of 26580.17 – 135403, 4108.15 – 12463.09, 791.62 – 16085.06, 1462.64 – 11749.05, 11.66 – 7086.87, 406.15 – 6028.21, 110.52 – 3597.44, μ g/g for Ca, Mg, P, Al, Ba, Na, and Si respectively. Ca and Mg are a part of the skeleton structure of the crustaceans, Na and K play a great role in regulating of the uptake and intake during the nutrition processes, Si has a great role in crustaceans. P is exists in each cell within the structure of the DNA. Al and Ba are exist within the earth crust. Moderate levels were in the range 43.38 – 1849.68, 81.81 – 1568.27, 53.55 – 554.83, 1.88 – 29.74 , μ g/g for K, Br, Mn, and B while lower values were recorded in the range 0.42 -17.71, 0.04 – 2.53, 0.08 – 1.07, 0.01 -1.07, 0.21 – 1.07, ND – 0.07 for Li, Ag, Be, Bi, Th, and Ti respectively.

The nutrients (P and N) are crucial for the regulating of the zooplankton composition. However, in the studied waters, a deficiency of phosphorus did not observed. The values of phosphorous concentrations were similar in all stations, so this factor did not affect zooplankton density and the structure (dominating groups). (Ciszewski et al.,2013).

Among zooplanktons, Copepoda was the most abundant group. It seemed that this group is the least sensitive to pollution by chemical elements within the study area (Jak et al. <u>1996</u>). It is possible that copepoda that live in saline water contaminated with chemical elements have been adapted to withstand the negative effects of those chemical elements. Other Groups such as rotofera and cladocera, which are more sensitive to chemical elements (Sarma et al. <u>2007b</u>), were less abundant. The high density and diversity of zooplankton in aquatic system is affected by chemical elements, proved that as with phytoplankton, plankton fauna adapt to long-lasting contamination.

Chemical elements with moderate and lower levels are either naturally existence such as K, Mn, B, Li, or as a pollutants like Be, Bi, and Ti as a result of sinking vessels erosion and Th as a result of radiation pollution as it is incorporated within the radiation decay of ²³⁸U pollutant reported in the study area (Al-Imarah and Ali,200). As well as the appearance of Uranium in the surrounding area (Fido and Al-saad, 2008).

Statistical significant differences (P < 0.01) were found obvious between zooplanktons and concentrations for all heavy elements. This result is mainly in agreement with the similar investigations of Abdullah et al., (2014) and Al-Saad et al., (2014)

Discussion

The results showed in table I indicate that differences in zooplanktons recorded in selected sites were following the differences in their water salinities (Toruan, 2012). It has become increasingly evident that biogenous processes in aquatic surface layers play an important role in removing chemical elements from water column and transporting them to the bottom sediments. Planktons are strongly implicated in these processes and



investigations of the chemistry of these organisms have demonstrated their ability to accumulate chemical elements to relatively high levels (Fowler, 1977).

Chemical elements which have the ability to form colloids in sea ,estuarine and brackish water will be able to adsorbed onto planktonic debris, resulted in higher concentration of these elements in zooplankton from aquatic waters (Robin, *et al.* 2012; Ritterhoff and Zauke, 1997; Safahieh, *et al.* 2011).

Pollution, associated with urbanization, agriculture, mining, or localized atmospheric deposition can lead to elevated and variable concentrations of chemical elements in aquatic organisms (<u>Suchanek et al., 2008</u>). Accumulation of toxic elements in aquatic food is an ongoing concern for human and wildlife health. At high levels, toxic elements can cause mortality or disease and suppress wildlife populations (<u>Hinck et al., 2009</u>). Even at low levels, effects of toxic elements together with other stressors can result in significant individual and population impacts on fish and other aquatic life (<u>Chen et al., 2004</u>; Folt et al., 1999)

Each chemical element had a consistent pattern of accumulation through the food web, and patterns differed widely across elements. These element-specific bioaccumulation patterns were consistent across the ecosystem, despite substantial differences in overall concentrations of most chemical elements across the ecosystem. **Conclusion**

It seems that all recorded zooplanktons from Southern Iraqi waters preferred waters that were higher in calcium and magnesium. The phase of chemical elements accumulation in zooplanktons within Iraqi aquatic system is either through uptake from the dissolved phase in water column or from phytoplanktos as an ingested food . For understanding the fate and effects of chemical elements in zooplankton, these two processes should be separated.

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