

# Bioaccumulation of Heavy Metals in Fish and Prawn at Dammam Coast, SA, Arabian Gulf

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## ABSTRACT

Four species of fish and one species of shrimp have been collected from Dammam - Qatif Coast, Arabian Gulf, SA during winter and summer 2012. The highest concentrations of physical and chemical characteristics in water and sediment were obtained at sites 5, 6 and 7 as a result of waste water drainage. The average concentration of heavy metals (Cu, Zn, Pb, Cd and As) in sediment (0.33, 0.42, 0.25, 0.16 and 0.031ppm) were higher than that recorded in water (0.23, 0.35, 0.012, 0.09 and 0.017 ppm), respectively during summer. Sites 6 and 7 showed the highest values of heavy metals, while sites 1, 2 and 3 recorded the lowest concentrations. *Rhbdosargus haffara* and *Penaeus semisulcatus* recorded the highest concentrations of Cu, Pb, Cd and As (3.07, 0.92, 0.79 and 0.59), (2.66, 0.77, 0.65 and 1.67) ppm wet weight, respectively at site 7. Arsenic values in *Penaeus semisulcatus* increased at sites 5, 6 and 7. The bioaccumulation factor of heavy metals by fish and shrimp were duplicated 50-208 folds referring to water and sediment values.

**Keywords:** water, sediment, fish, prawn, heavy metals, Arabian Gulf.

## INTRODUCTION

The water and sediment quality is considered the main factor controlling the state of the aquatic environmental health. Pollution of the organic and inorganic chemicals play an important role in threatens to marine organisms including fish (Zyadah, 2010). Arabian Gulf is set as extremely arid region of a shallow semi-closed water basin, it receives a huge amount of waste water and other pollutants from global oil transportation, drilling oil, industrial and human activities, it leads to disturbance to the coastal environment (sadiq and Alam, 1989; Khan and Al-Homaid, 2008; Zyadah, 2011).

Therefore, the heavy metal contamination in water, sediment and marine organisms were monitored to determine the rate of accumulation in tissues of marine animals. The concentration of metals in the animal organs can be reasonable guide for public health standards and for the organisms condition also (Zyadah, 2011).

As a result high levels of heavy metals in aquatic ecosystems can be toxic and get incorporated into the food chain. Previous studies showed that heavy metals concentrations in marine organisms may exceed the allowable limits, where it may be lead to a risk to ecosystems and humans consumption also (El-Gendy, 2003; Zyadah and Al-Motairy, 2012).

There are few published articles on the background of heavy metals in marine organisms in Arabian Gulf, Saudi Arabia (Sadiq and Alam, 1989; Sadiq et al., 1992; Zyadah and Almoteiry, 2012). However, studies to detect the heavy metals values in fish in Saudi Arabia indicated the safety of fish for consumption (Al Saleh and Shinwari, 2002). Moreover, similar data from other studies in Arabian Gulf have been recorded (Al-Yousuf et al., 2000).

The aim of the present study is : to investigate the distribution of heavy metals and physico-chemical characteristics in water and sediment, to detect the heavy metals in commercial fish and shrimps at this Region Arabian Gulf, SA., and to compare the heavy metal bioaccumulation in organisms (related to water and sediment) with the local and international standards.

## MATERIALS AND METHODS

### Water and Sediment Analysis

Seven sampling sites were selected to represent the different activities in Dammam and Qatif coast from Arabian Gulf, SA during winter and summer 2012 (Figure 1). Lowering one liter glass bottle below the surface of the water

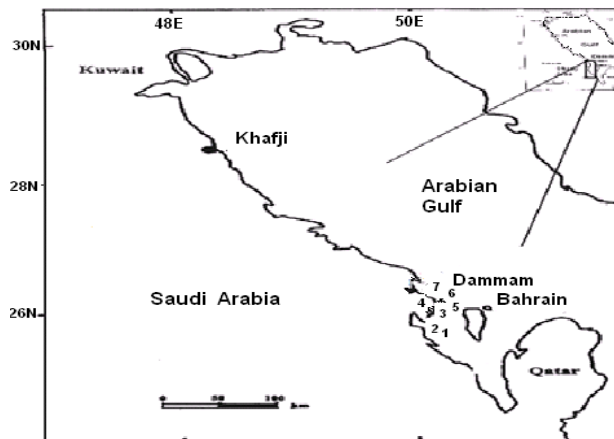


Figure 1. Map showing the sampling sites south of Dammam, SA.

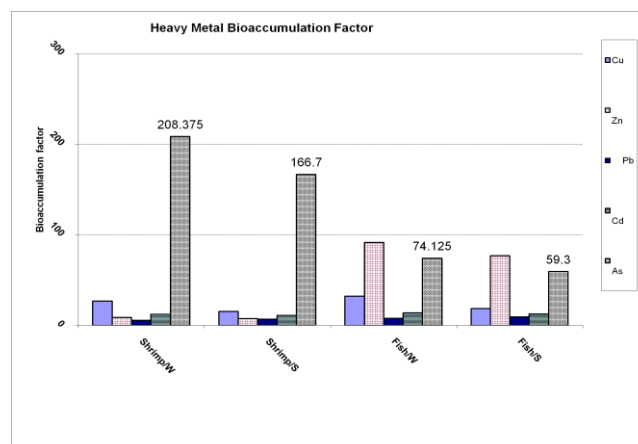


Figure 2.. The bioaccumulation factor of Heavy metal by fish and shrimp related to water or sediment (W, S).

(20-30 cm deep) to avoid any oil surface film carried out water samples. The bottles were put in an icebox then transport to laboratory for analysis. Physicochemical characteristics of water samples were measured according to the Standard methods (APHA, 2005). A dredge was used to collect sediment, washed using different mesh-size sieves, then, digested and analyzed to measure physical and chemical characteristics (Moore and Champan, 1986), heavy metal (Cu, Zn, Pb, Cd and As) in water and sediment were analyzed ( APHA, 2005) and were detected using ICP– Induced Couple Plasma.

### Fish Analysis

Three individuals of the common species of fish (*Liza alata*, *Siganus canaliculatus*, *Rhabdosargus haffara*, *Scomberomorus commerson*) and one shrimp only (*Peaneaus semisulcatus*) were sampled from each site. The organisms were transported from the field to the laboratory in an ice box, (Dalziel and Baker, 1983). Fish muscle was separated immediately, while if the sample is not analyzed soon, it was labelled and kept in the freezer. 5 ml of freshly prepared 1:1 V/V hydrogen peroxide / nitric acid was added to the samples (5 gm muscle). The glass tube was covered with a watch glass, it was placed aside for about an hour until the first reaction subsides, the glass tube was placed on a hot plate, the temperature was carefully allowed to rise to 160 C<sup>0</sup>, the boiling was continued gently for about 2 hr. (Dybern, 1983). The solution was reduced to about 2 ml, must not dry, then, cooled and diluted to 12.5 ml with DDW. The heavy metals were determined, using Induced Couple Plasma (ICP) and the values were expressed in µg/g wet weight. Statistical analysis was run using the Statistical Package for the Social Science (SPSS). One and two way ANOVA were employed to find the significant differences of heavy metals between water, sediment, and fish), also, means ± standard errors were derived for all data.

### RESULTS

The average concentration of physico-chemical characteristics in water showed higher concentrations at sites 6 and 7 than other sites. Hydrogen–ion concentration (pH) ranged between 8.0 and 8.35. Total dissolved solids (TDS) and sulphate increased at sites 1, 2 and 3 while its values decreased at sites 5 to 7. Dissolved oxygen concentration ranged between 6.3 and 8.1 mg/l at sites 7 and 2, while the lowest and highest concentrations of BOD (8.2 and 21.8 mg/l) were obtained at sites 2 and 7 respectively, there is negative correlation between DO and BOD concentrations. The concentrations of nitrate and total phosphorus increased at sites 6 and 7, while the lowest values were obtained at sites 1 and 2. The highest concentration of nitrate and total phosphorus are related to the rate of nutrients at these sites.

The average concentrations of heavy metal in water fluctuated within sites, the highest values of heavy metals

**Table 1.** Mean values of water quality parameters in Arabian Gulf, Dammam Coast

Sites	1	2	3	4	5	6	7	Average		St. Dev.	St. Error
								Summer	Winter		
Factor (ppm)											
pH	8	8.1	8.2	8	8.2	8.2	8.35	8.15	8.05	0.125	0.087
*TDS	46950	46850	46500	46000	44300	43500	42500	45085	44714	1751	1260
Sulfate	3860	3600	3650	3300	3175	3150	3175	3415	3307	284	215
*DO	7.9	8.1	7.3	7.3	7.2	7	6.3	7.3	6.6	0.592	0.35
*BOD	8.3	8.2	8.5	11.5	14.5	17.7	21.8	13.1	12.1	5.18	3.7
Nitrate	1.3	1.3	2.7	3.5	3.6	6.1	9	3.92	3.6	2.77	1.81
T. Phosphorus	0.9	0.9	1.3	2.9	5.1	5.9	6.9	3.41	2.8	2.53	1.91
Copper	0.04	0.04	0.06	0.08	0.11	0.16	0.2	0.095	0.078	0.059	0.041
Zinc	0.08	0.06	0.1	0.18	0.2	0.23	0.33	0.169	0.16	0.096	0.066
Lead	0.45	0.04	0.06	0.06	0.08	0.09	0.11	0.127	0.066	0.144	0.081
Cadmium	0.01	0.01	0.04	0.06	0.06	0.08	0.08	0.053	0.049	0.034	0.025
Arsenic	0.005	0.005	0.007	0.003	0.007	0.014	0.016	0.008	0.006	0.005	0.003

\* St.dev. Standard deviation, TDS: Total Dissolved Solids, DO: Dissolved Oxygen, BOD: Biological Oxygen Demand.

**Table 2.** Mean values of sediment quality parameters in Arabian Gulf, Dammam Coast

Sites	1	2	3	4	5	6	7	Average		St. dev.	St. Error
								Summer	Winter		
Factor (ppm)											
pH	8	8.1	7.9	7.9	8.1	8.3	8.3	8.1	8	0.168	0.131
TDS	43750	43850	44000	46350	45550	42650	41750	43985	42550	1575	1126
Sulfate	3550	3450	3450	3750	3300	3450	3200	3450	2970	175	114
NO <sub>3</sub>	1.3	1.3	2.3	2.5	2.5	2.8	3.2	2.271	2.1	0.723	0.555
T.Phosphorus	0.73	0.67	1.5	1.75	1.8	2.3	2.75	1.643	1.324	0.763	0.579
TOC (%)	7.9	7.6	10.2	10.1	13.2	15.9	15	11.4	10.1	3.323	2.816
Copper	0.055	0.065	0.07	0.11	0.24	0.3	0.31	0.164	0.12	0.145	0.102
Zinc	0.085	0.08	0.09	0.15	0.19	0.4	0.41	0.201	0.15	0.145	0.117
Lead	0.045	0.05	0.06	0.085	0.11	0.15	0.22	0.103	0.009	0.064	0.049
Cadmium	0.01	0.01	0.025	0.04	0.075	0.11	0.14	0.059	0.03	0.051	0.043
Arsenic	0.004	0.004	0.005	0.006	0.009	0.015	0.03	0.01	0.01	0.009	0.007

**Table 3.** Concentration of heavy metals ( $\mu\text{g/g}$  wet weight) in muscles of fishes and shrimps

Species	Metal	Season			Summer		
		Average	St. dev.	St. Eror	Average	St. dev.	St. Eror
<i>Liza alata</i>	Cu	1.97	0.345	0.269	2.39	0.534	0.42
	Zn	10.09	1.969	1.445	10.16	2.483	1.849
	Pb	0.67	0.111	0.089	0.78	0.252	0.2
	Cd	0.61	0.185	0.153	0.7	0.243	0.196
	As	0.59	0.148	0.122	0.66	0.184	0.145
<i>Siganus canaliculatus</i>	Cu	1.93	0.34	0.241	2.37	0.39	0.318
	Zn	9.19	1.981	1.469	10.19	2.424	2.012
	Pb	0.67	0.099	0.076	0.79	0.254	0.212
	Cd	0.54	0.151	0.122	0.61	0.195	0.159
	As	0.39	0.117	0.087	0.48	0.155	0.188
<i>Rhabdosargus haffara</i>	Cu	2.55	0.315	0.249	3.07	0.665	0.596
	Zn	12.03	0.702	0.576	15.46	2.038	1.78
	Pb	0.63	0.151	0.133	0.92	0.204	0.153
	Cd	0.63	0.214	0.176	0.99	0.281	0.241
	As	0.33	0.095	0.082	0.59	0.267	0.206
<i>Scomberomorus commerson</i>	Cu	1.81	0.604	0.474	2.36	3.23	2.08
	Zn	7.57	3.593	2.489	9.8	2.799	2.367
	Pb	0.53	0.138	0.118	0.69	0.111	0.089
	Cd	0.43	0.125	0.094	0.57	0.182	0.132
	As	0.43	0.138	0.098	0.51	0.135	0.102
<i>Penaeus Semisulcatus</i>	Cu	2.42	2.704	1.726	2.66	0.695	0.45
	Zn	7.14	3.461	2.197	10.48	0.974	0.825
	Pb	0.57	0.111	0.089	0.77	0.092	0.075
	Cd	0.44	0.141	0.102	0.65	0.237	0.167
	As	1.13	0.611	0.461	1.667	0.659	0.467

were recorded at sites 6 and 7 (Table 1). The average concentrations of copper, zinc, lead, cadmium and arsenic in water were (0.095, 0.169, 0.127, 0.053 and 0.008 and (0.078, 0.16, 0.066, 0.049 and 0.006) mg/l during summer and winter, respectively, the maximum values of heavy metals were found at site 7. Summer season recorded higher concentrations than winter values. The concentration of heavy metals in water at sites 6 and 7 (Tarout Island) were significantly higher than other sites ( $P < 0.05$ ).

The average values of chemical characteristics and heavy metals in sediment are given in Table (2). The pH values showed a little variation at the different sites. Total dissolved solids and sulfate values decreased at sites 6 and 7, respectively, while nitrate, total phosphorus, TOC and heavy metals increased at the same sites. The average concentrations of copper, zinc, lead, cadmium and arsenic in sediment are (0.164, 0.201, 0.103, 0.059 and 0.01) and (0.12, 0.15, 0.009, 0.03 and 0.01)  $\mu\text{g/g}$  dry weight during summer and winter, respectively, the maximum values of heavy metals were found at sites 6 and 7, respectively. The increase of chemical parameters in sediment was related to their concentrations in water. The concentration of heavy metals in sediment at sites 5, 6 and 7 were significantly higher than other sites ( $P < 0.05$ ).

The average concentrations of heavy metals in fish and shrimps are shown in Table (3). Copper, Zn, Pb, Cd and As values ranged between (1.81 and 3.07), (7.14 and 15.46), (0.53 and 0.92), (0.43 and 0.79) and (0.33 and 1.66)  $\mu\text{g/g}$  wet weight, respectively, the highest values appeared in summer. Sites 5, 6 and 7 showed the highest values while sites 1 and 2 recorded the lowest values. Generally, heavy metals in *Rhabdosargus haffara* recorded the highest concentration especially at sites 6 and 7, while *Scomberomorus commerson* showed the lowest concentration of heavy metals than other fish species. These values may be near to the maximum allowable limits at some sites, especially for Copper, Cadmium and Arsenic in *Rhabdosargus haffara*. However, most fishes are still within the allowable limits.

*Penaeus semisulcatus* recorded high values of Cu, Zn, Pb, Cd and As (2.66, 10.48, 0.77, 0.65 & 1.67  $\mu\text{g/g}$  wet weight), respectively during summer, this value may reach the maximum allowable limits especially for Arsenic, Cadmium and copper. Sites 6 and 7 recorded high concentration of heavy metals in fish and shrimp than other sites. Thus, the concentration of heavy metals in fish and shrimp was higher in summer than that found in winter.

Bioaccumulation factor of heavy metals by fish and shrimp regarding to water and sediment concentrations are shown in Figure (2). The factor of Arsenic concentration in shrimp and fish was duplicated from 166 to 208 folds and 50-74 times, respectively more than water and sediment concentration. The factor of Zinc concentration in fish was duplicated from 76 to 81 times more than water and sediment concentration.

Analysis of variance (ANOVA) for the biodiversity in water, sediment and heavy metals in fish (one-way and two-ways) showed a significant difference for both one-way (site) and two-ways (site  $\times$  heavy metals),  $P < 0.05$ . Therefore, the highest concentration in water, sediment, fish and shrimp may represent background study at this important area in Arabian Gulf. More practical and field studies of Arsenic bioaccumulation by shrimp are needed to explain the high concentration at Qatif and Tarout Island.

## DISCUSSION

The nitrate, total phosphorus and total organic carbon values in water were higher at sites 5, 6 and 7 than other sites which may be attributed to the wastewater discharged at these sites. The pH values showed a little variation at sites, similar results of pH concentrations were recorded in Arabian Gulf (Sadiq et al., 1992), in Mediterranean Sea, Greece Islands (Pangos, et al., 1992); Red Sea at Rabigh and Jeddah, Saudi Arabia (Zyadah, 2010) and Eastern Region Coast in Arabian Gulf, SA. (Zyadah and Almotairy, 2012).

The highest values of phosphorus and nitrate were recorded at sites 5, 6 and 7, it may be attributed to the high quantity of drainage water at this area; other reported data is in agreement with this result in Eastern Region Coast, SA (Zyadah and Almotairy, 2012). The high concentration of nutrient during summer may lead to eutrophication problem while the deficiency of phosphorus and nitrogen may be a limiting factor for biological growth (Mance, 1987; Abdel-Moati et al., 1992). Higher values of most physico-chemical parameters during summer than winter is related to high amount of sewage and other anthropogenic activities during summer. There is negative correlation between the concentration of DO and BOD during seasons at different sites, as oxygen is consumed in biological degradation of organic matter (Mance, 1987).

There is high concentration of phosphorus and nitrate at sites 5, 6 and 7 in sediment, these may be related to different sources of pollutants (sewage discharges and other effluents) in water at the same sites, It may lead to increase of nitrate, organic carbon and phosphorus (Zyadah and Almotairy, 2012) in Arabian Gulf. It is found that 5% of the phosphorus in Mediterranean Sea correlated with the organic detritus and 0.05% of phosphorus in Mediterranean Sea correlated with carbonate materials at Alexandria coast, Egypt (Ramzy, 1994).

Heavy metal concentration in water and sediment recorded high values at sites 6 and 7, this result may be related to the nutrients, sewage and agricultural discharges at this area, Which might be due to anthropogenic inputs from coastal area. This why these sites show higher concentrations of metals and other chemicals. It is found that there is a relationship between heavy metal concentration in water and sediment, where the concentration of heavy metals in sediment were higher than that recorded in water (Zyadah and Almotairy, 2012) in Arabian Gulf. Other articles recorded lower values of lead than the present study (Scoullou et al., 1992) in Greece coast (0.0001-0.0003 mg/l);

Abdel-Moneim *et al.*, (1994) in Alexandria, Egypt (0.003-0.004 mg/l), while other articles showed higher concentrations of lead than the present values (Pangos *et al.*, 1992) in Greece coastal water (0.018-0.91 mg/l).

Some heavy metals (Cu and As) concentrations in sediment are duplicated (10-100 times) than that recorded in water, while the bioaccumulation in fish and shrimp are duplicated hundreds folds than in water and sediment. The bioaccumulation factor of As by shrimp was 208 and 166 times more than that found in water and sediment. These values are considered a part of risk for fish and shrimp consumers and human health, especially for Arsenic and Cadmium. A monitoring plan of heavy metals in marine organisms is required, in addition to knowledge of biomagnifications or bioaccumulation factors to find a solution against pollution at this important area.

The concentration of heavy metals in fish and shrimps showed detectable levels in the present study, where these values were lower in other reported data in Qatar (Al-Jedah and Robinson, 2001), while this result was in agreement with other studies in Bahrain (Musaiger and D'Souza, 2008) and in Eastern Region coast of Arabian Gulf, SA (Zyadah and Almoteiry, 2012). The biomagnifications in sediment and organisms was clear and bioaccumulation by fish and shrimp was duplicated by hundred times than that concentration in water. The heavy metals in fish and shrimp were in the order of: Zn>Cu> Pb>As>Cd. ANOVA for fish species indicated that heavy metals concentrations showed significant differences within sites and fishes ( $P<0.05$ ). Therefore, monitoring programs should continue in order to maintain the quality of the aquatic environment in Eastern Region coast and to reduce the risk of pollution.

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