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Heavy metal concentrations in water, sediments, Cladophora and two fish species from Al-Masab Alamm River, Al- Nassiriya, Iraq

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ABSTRACT

Heavy metal pollution is a serious threat for human health relating to their toxicity and bioaccumulation in the food chain which made this problem as global public health issue. The current study aimed to determine the heavy metal concentrations and their toxicity in water, sediment, Cladophora and the gill, liver and muscle of *Liza abu* and *Barbus barbus* in Al-Masab Alamm River, Al Nassiriya, Iraq. The samples were included thirty fishes and there were three selected sample stations covered the area on the river. The heavy metal levels were determined using an atomic absorption spectrophotometer (AAS). The results showed that the heavy metal concentrations in water, sediment, algae and the sampled fishes exceeded the acceptable levels for World Health Organization and Food and Agriculture Organization of the United Nations. Heavy metal levels were estimated in different tissues of fish. The results revealed that most of the heavy metal concentrations were high in gills, liver and muscles respectively. Lead and copper accumulated higher in liver than in the other tissues.

Keyword: Heavy metals, Water, Sediment, Fish, Cladophora.
Article type: Research Article.

INTRODUCTION

One of the most serious problems facing aquatic environments is heavy metal pollution, where the aquatic environment is considered a natural sink for minerals, however, their levels have increased due to industrial waste, agricultural activities and mining. Some of the heavy metals such as Cd, As, Pb, Cu, Zn, and Ni are common pollutants that come from multiple natural and human sources (Al Naggar *et al.* 2018). Water pollution by heavy metals is one of the main types of contamination that may stress bio-living community in aquatic ecosystems. Heavy elements are of particular interest in environmental toxicology, including essential and nonessential metals, since they are extremely persistent and all have the prospect to be toxic to living organisms (Zulkifli *et al.* 2010). The heavy metal concentrations in an aquatic ecosystem is measured in three conditions including water, sediment and organisms. Commonly, heavy metals are found in the lowest concentration in water and reach significant concentrations in sediments, followed by the level of bioaccumulation in living organisms (Ebrahimpour & Mushrifah 2008). Sediments are a mixture of metal various, and are an important pelvis for many contaminants in aquatic systems, including trace metals, and play a useful role in assessing heavy metal pollutions (Alkarkhi *et al.* 2009). Contaminated sediments in coastal areas, lakes and rivers have the ability to transport environmental sediments, and the rivers are the main carriers of heavy elements in the aquatic environment. Heavy metals are released from sediments to water bodies, then to living organisms (Li *et al.* 2000). Most of the heavy metals are deposited after entering the rivers in their sediments and are concentrated in them higher than in other parts (Garai *et al.* 2021). On the other hand, the physical and chemical conditions may change, thus the heavy metals in the sediments are re-absorbed or re-suspended, causing a new pollution to the water surface (Kouidri *et al.* 2016). High levels of heavy elements in living organisms can have negative effects on the environmental health of aquatic

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animals and may contribute to a decline in their populations (Malik & Maurya 2014; Luo *et al.* 2014). Pollution of aquatic and terrestrial ecosystems by heavy elements is an environmental problem of public health concern. Since trace metals are persistent pollutants, hence accumulate in the environment, and pollute food chains (Ali *et al.* 2019). Ecological systems contain various food chains, therefore, they can accumulate heavy metals also in food in addition to water and sediments. Fish is the main component in the aquatic ecosystem food chain, which is used by most the humans (Obasohan *et al.* 2010). Heavy metals in an aquatic ecosystem are transmitted to humans through the consumption hierarchy in the food chain of aquatic living organisms. Thus, humans are in danger of health effects from heavy element contamination (Mansour & Sidky 2002). The bioaccumulation and bio-magnification of trace elements in living organisms describes the processes and pathways of these contaminants from any trophic level to another (Baby *et al.* 2010). There are two groups of heavy elements. The group I contain minerals essential for the growth and function of living organisms, including zinc (Zn), copper (Cu) and Iron (F). Another group contains non-essential metals that cause high toxicity to living organisms, even in trace concentrations, including lead (Pb), mercury (Hg) and cadmium (Cd) (Koki *et al.* 2015). The bioaccumulation of minerals in animals depends on many factors: biotic factors such as age, sex, diet and metabolism while abiotic factors represented by mineral distribution, temperature, salinity, pH, the habitat and interactions of minerals with each other. However, diet has the greatest effect on the accumulation of minerals in animal tissues (Jakimska *et al.* 2011). Heavy metals fundamentally enter the fish body through the gills, surface of the body, and the gastrointestinal tract while ingesting accumulated mineral nutrients. Cadmium, lead and others are the most common heavy element contaminants that cause severe toxicity in fish (Shyleshchandran *et al.* 2018) (Sattari *et al.* 2019a,b,c,d; Sattari *et al.* 2020a,b,c,d; Forouhar Vajargah *et al.* 2020, 2021). Fish act as biomarkers of environmental pollution as public health studies are conducted on a large scale in order to assess the physiological variation of aquatic ecosystems (Shah 2017). The accumulation of metals such as lead (Pb), cadmium (Cd) and other metals in plants and aquatic organisms above the permissible limits according to the instructions and guidelines of the World Health Organization (WHO) and the Federal Environmental Protection Agency (FEPA) causes harmful effects on the aquatic ecosystem, therefore should be reduced (Jaiswal *et al.* 2018) Heavy metal contamination is widespread in the different Iraqi aquatic systems, where Al-Massab Alamin River is considered as one of the essential rivers in Iraq, which subjected to different anthropogenic activities. The present study aimed to evaluate the level of heavy metals in water, sediments, *cladophora* and two fish species in this river and estimate the potential hazard of metals.

MATERIALS AND METHODS

Sample collection and preparation

Al-Masab Alamm is a river used to discharge the sewages of agriculture wastes. The river length is about 565 km between Tigris and Euphrates and extended from Saklawiya towards Shatt Al-Basrah canal and to the Khor Al-Zubair. It passes across Euphrates River close to Nassiriya City by siphon to continue its track to Basrah (Mohammed 1993). Three stations were selected in the southern sector of the river.

Station 1: It is located 10 km before Holandy bridge.
Station 2: It is located close to Holandy bridge beside the sewage pipe of Nassiriya City.
Station 3: It is located close to Al-Fadhliya bridge south of the pump station of Main out full drain.

Water and sediments samples were collected from the studied stations. Triplicate samples were taken from water that was collected from the middle of the river by polyethylene bottles. A Van Veen Grab Sampler was used for collecting sediment samples. Then, they were placed in plastic containers with ice till reaching the laboratory. Work procedures were followed the Standard Methods of the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF) for examination of water and wastewater (APHA WWA 2005). For analyses of fishes, *Liza abu* and *Barbus barbus* 2.5 g muscle, the entire liver, and gills of each samples were separated, weighed, and dried at 70 ºC for 24-48 h. 0.5 g samples were placed in beakers and 5-mL HNO_3 (65%) was added to each sample at room temperature for 24 h, then heated at 120 ºC 2 h. After cooling we added 1 mL H_2SO_4 (30%) and diluted to 25 ml with deionized water. The determination of heavy metals was done by using an atomic absorption spectrophotometer (AAS) which is FSAA240 from Agilent Technologies, made in the USA. The concentrations of metals in fish tissues were reported as µg/g per wet weight. Data statistics were performed using as mean and standard deviation (SD) using one-way analysis of variance (ANOVA) followed by Duncan's new Multiple Range Test (MRT).

RESULTS AND DISCUSSION

Heavy metals in water (mg L^{-1}) and sediment (mg g^{-1})

Trace element levels in the water and sediment samples from in Al-Masab Alamm River, Al Nassiriya, Iraq are shown in Tables 1 as mean and standard deviation (± SD). The results showed that the highest values of Cd concentration in water and sediment were 0.006 and 3.220 in St. 2; Pb level in water was 9.630 in St. 3, while in sediment was 3.940 in St. 2. Cu levels in water and sediment were 19.500 and 22.120 in St. 2 while Mn levels were 0.014 and 29.130 in St. 3 respectively. The heavy metal concentrations in water were distributed according to the following pattern: Cu > Pb > Cd > Mn, while for sediment were Mn > Cu> Pb > Cd. The average of dissolved Cd, Pb, Cu, Mn concentrations during this study were higher than the acceptable levels (Table 1). The mean concentrations of the studied metals were high which may be due to the upraised temperature during summer and also the level of evaporation (Liang & Worng 2003; Muhsin 2011). St. 2 exhibited the higher heavy metal levels than the other stations, since it located beside the high density of population and car washing shops which discharge waste to Al-Masab Alamm without any treatment.

In the case of sediment, the mean metal concentration was higher than water, since suspended substance deposed in bottom, and adsorb in clay. Many factors affect the heavy metal levels in sediment from the organisms that accumulated the metals in their bodies (Nakanishi *et al.* 2004). The present study showed that the mean metal concentrations in sediments are very high compared to their levels in water, since metals tend to be accumulated by suspended matter and also exhibit strong affinity for particles (Dauvalter 1998). Hence these elements were high in the bottom of river, due to sinking to the bottom with dead plants and animals (Dauvalter 1998).

Heavy metals in *Clodophora* (mg g^{-1})

The results showed the presence of heavy metal pollutions in the studied areas. The mean concentrations of Cd was 2.533 in St. 2; Pb was 2.656 in St. 3, Cu was 623.050 in St. 1 and Mn was 312.106 in St. 1. The *clodophora* exhibited the ability to accumulate Cd and Pb especially in St. 2 and St. 3 due to vicinity to the large population and the increased human waste from sewage as well as the elevated number of cars and various means of transportation (Yingjun *et al.* 2012). *Clodopora* could play essential role in adsorbing many kinds of metal since the green algae species are characterized by its thick cellulose layers in its cell wall, branchy, filamentous, long and setaceous green fronds (Aleem 1978; Sargin *et al.* 2016). Although adsorption on the cell surface is the dominant mechanism, however, both surface adsorption and internal diffusion are involved in the uptake of metals by algae (Congeevaram). Bio-sorption occurs by both metabolically and non-metabolically mediated processes.

Heavy metal in fishes (μg g^{-1})

Fish are considered one of the main protein sources for humans and a useful bio-indicator for water pollution especially, the assessment of heavy metal level in aquatic ecosystems (Lamas *et al.* 2007). The mean concentration of heavy metals in gills, muscles, liver of *Liza abu* and *Barbus barbus* were depicted in Table 2. In the case of fish gill, the highest values of Cd, Pb and Cu were 1.230, 1.670, 1.760 in St. 2, while Mn value was 2.230 in St. 3. In the case of fish muscle, the highest means of Cd, Pb and Cu were 1.350, 1.770, 1.550 in St. 2 and that of Mn was 2.180 in St. 3 respectively. In the case of liver, the highest mean concentrations were 1.213, 2.130 2.570 and 1.960 in St. 2 respectively. The heavy metal levels in gills, muscles and liver were distributed according to the following pattern: Mn > Pb > Cu > Cd; Mn > Pb > Cu > Cd; and Mn > Cu > Pb > Cd respectively. Generally, fish living in polluted waters tend to accumulate heavy metals in their tissues since heavy metal levels in the fish and benthic invertebrate tissues were strongly correlated which mean transfer through nutrition pathway (Twardowska *et al.* 2006). According to the present results, the heavy metals were accumulated in gills and liver in *Liza abu* which it similar to result of (Karadede *et al.* 2004). The St. 2 exhibited the highest mean concentration of metals, due to discharging untreated waste and vicinity to high population density. Interestingly, gills displayed the highest concentration of metals, since the metals stick to the gills lamellae and mucus (Ikem & Egiebor 2005). Furthermore, muscle could accumulate low metal concentrations due to being inactive tissue for accumulating metals. Generally, the mean concentrations of Cu were very high in liver, since liver is the responsible organ in detoxification of heavy metals (Al Saad & Al Nagare 2010). The results were in agreement with (Ali 2007). The mean concentrations of Pb were high in liver than in the other organ, since liver exhibits different mechanism and storage time depending on their biological function. Pb result was in line with (Abdel Baki *et al.* 2011). In the case of *Barbus barbus*, the highest mean of Cd were 1.940, 1.850 and 0.990 in St. 2 for gill, liver and muscles respectively. The mean concentration of Pb were 1.940 and 1.920 in St. 2 and 1.233 in St. 3 for gill, liver and muscles respectively. Cu mean concentrations were 3.406 and 1.420 in St. 3 and 0.906 in St. 2 for liver, gills and muscles respectively. Mn concentrations were 2.730^{a} 2.730 in St. 3 and 2.730 in St. 2 for gill, liver and muscles respectively. The heavy metal concentrations in gill, muscles and liver were distributed according to the following pattern: Mn > Pb > Cd> Cu; Mn > Pb > Cd > Cu and Cu> Mn> Cd > Pb respectively. According to the resent results, the second sampling station (St. 2) exhibited the highest heavy metal concentrations, since this area receive more industrial pollutants and effluents from garage and is located adjacent to a lot of populations. Most of metal accumulationswere found in gills then liver, except for Cu which was high in liver then in gills. Our result was agreed with (Olsson *et al.* 2013). The mean heavy metal concentrations obtained in this study were higher than the World Health Organization (WHO) maximum permissible levels in freshwater fishes (World Health Organization 2011). The accumulations of Cd, Pb and Mn in gills were occurred due to the fact that gills were the main entry point for any dissolved heavy metals (Olsson *et al.* 2013). Liver could concentrate the heavy metals, since these metals react with special groups in the metallothionein protein (Al Yousuf *et al.* 2000). Previous studies reported that the heavy metals are accumulated in gills and liver, higher than in muscles (Karadede Akin & Ünlü 2007; Mohammadi *et al.* 2011; Mustafa *et al.* 2020).

Table 1. Mean concentrations of heavy metals in water and sediments.

Station	**Water (μg L^{-1})**							
	Cd		**Pb**		**Cu**		**Mn**	
	Mean	**± SD**	**Mean**	**± SD**	**Mean**	**± SD**	**Mean**	**± SD**
St. 1	0.004^{c}	0.001	7.990^{c}	0.040	17.240^{c}	0.140	0.009^{c}	0.000
St. 2	0.006^{a}	0.000	8.860^{b}	0.050	19.500^{a}	0.010	0.011^{b}	0.000
St. 3	0.005^{ab}	0.000	9.630^{a}	0.100	18.970^{b}	0.020	0.014^{a}	0.002
Total	0.005	0.001	8.826	0.713	18.570	1.026	0.011	0.002
LSD	0.002		0.27		0.32		0.004	
Station	Sediment (μg g^{-1})							
St. 1	2.110^{c}	0.040	2.700^{c}	0.030	11.810^{c}	0.100	10.160^{c}	0.020
St. 2	3.220^{a}	0.000	3.940^{a}	0.043	22.120^{a}	0.060	22.430^{b}	0.010
St. 3	2.900^{b}	0.020	3.870^{b}	0.010	19.540^{b}	0.040	29.130^{a}	0.020
Total	2.743	0.495	3.503	0.603	17.823	4.646	20.573	8.331
LSD	0.10		0.12		0.28		0.06	

Table 2. Mean concentrations of heavy metals (μg g^{-1}) in Cladophora.

Station	**Cd**		**Pb**		**Cu**		**Mn**	
	Mean	**± SD**	**Mean**	**± SD**	**Mean**	**± SD**	**Mean**	**± SD**
St. 1	1.650^{c}	0.000	1.730^{c}	0.010	623.050^{a}	0.050	312.106^{a}	0.005
St. 2	2.533^{a}	0.011	2.450^{b}	0.000	422.310^{b}	0.000	287.910^{b}	0.010
St. 3	2.356^{b}	0.005	2.656^{a}	0.005	385.420^{c}	0.020	219.070^{c}	0.010
Total	2.180	0.404	2.278	0.421	476.926	110.750	273.028	41.803
LSD	0.02		0.02		0.12		0.03	

Table 3. Mean concentrations of heavy metals (μg g^{-1}) in *Liza abu*.

Station	**Gill**							
	Cd		**Pb**		**Cu**		**Mn**	
	Mean	**± SD**	**Mean**	**± SD**	**Mean**	**± SD**	**Mean**	**± SD**
St. 1	0.950^{c}	0.010	1.333^{c}	0.005	1.450^{c}	0.010	1.873^{c}	0.030
St. 2	1.230^{a}	0.010	1.670^{a}	0.010	1.760^{a}	0.050	2.156^{b}	0.045
St. 3	1.050^{b}	0.000	1.610^{b}	0.010	1.530^{b}	0.030	2.230^{a}	0.000
Total	1.076	0.123	1.537	0.155	1.580	0.142	2.086	0.165
LSD	0.03		0.03		0.13		0.12	
Station	Muscle							
St. 1	0.906^{c}	0.011	1.650^{c}	0.000	1.160^{b}	0.010	1.890^{c}	0.030
St. 2	1.350^{a}	0.010	1.770^{a}	0.010	1.550^{a}	0.030	2.080^{b}	0.017
St. 3	1.183^{b}	0.005	1.740^{b}	0.000	1.520^{a}	0.010	2.180^{a}	0.000
Total	1.146	0.194	1.720	0.054	1.410	0.188	2.050	0.128
LSD	0.03		0.02		0.07		0.07	
Station	Liver							
St. 1	0.660^{c}	0.000	1.830^{b}	0.030	2.060^{c}	0.030	1.700^{c}	0.020
St. 2	1.213^{a}	0.011	2.130^{a}	0.030	2.570^{a}	0.020	1.960^{a}	0.000
St. 3	0.990^{b}	0.000	2.110^{a}	0.010	2.410^{b}	0.010	1.800^{b}	0.000
Total	0.954	0.241	2.023	0.146	2.346	0.226	1.820	0.114
LSD	0.02		0.10		0.08		0.04	

Table 4. Mean concentrations of heavy metals (µg g^{-1}) in *Barbus barbus*.

Station	Gill							
	Cd		Pb		Cu		Mn	
	Mean	± SD	Mean	± SD	Mean	± SD	Mean	± SD
St. 1	1.300[c]	0.010	1.906[c]	0.015	1.150[b]	0.050	2.210[c]	0.010
St. 2	1.940[a]	0.040	1.940[a]	0.010	1.350[a]	0.030	2.730[a]	0.050
St. 3	1.860[b]	0.020	1.926[ab]	0.015	1.420[a]	0.020	2.640[b]	0.040
Total	1.700	0.302	1.924	0.018	1.306	0.125	2.526	0.242
LSD	0.10		0.04		0.14		0.14	
Station	**Muscle**							
St. 1	0.866[c]	0.005	1.150[b]	0.040	0.860[c]	0.010	2.086[b]	0.075
St. 2	0.990[a]	0.000	1.163[b]	0.011	0.906[a]	0.005	2.216[a]	0.015
St. 3	0.936[b]	0.005	1.233[a]	0.015	0.890[b]	0.000	2.300[a]	0.030
Total	0.931	0.053	1.182	0.044	0.885	0.021	2.201	0.101
LSD	0.01		0.10		0.02		0.18	
Station	**Liver**							
St. 1	1.400[c]	0.000	1.630[c]	0.030	3.156[c]	0.005	1.900[c]	0.020
St. 2	1.850[a]	0.010	1.920[a]	0.010	3.200[b]	0.000	2.300[a]	0.020
St. 3	1.826[b]	0.005	1.820[b]	0.040	3.406[a]	0.035	2.110[b]	0.010
Total	1.692	0.219	1.790	0.130	3.254	0.117	2.103	0.173
LSD	0.02		0.11		0.08		0.06	

CONCLUSION

The current study showed that the levels of heavy metals in water, sediment, *Cladophora* and also in the gill, liver and muscle of *Liza abu* and *Barbus barbus* in Al-Masab Alamm River, Al Nassiriya, Iraq were higher than the acceptable limit by FAO and WHO. The accumulations of heavy metals were very high in different tissues of fish which reflect the pollution of the river due to the increased discharge of waste materials and pollutant. Interestingly, algae and fish could use as a good bio-indicator for pollution. The dispersal of heavy metals and their increased levels made the need from government to monitor water of river and fish more effectively and create public awareness of the heavy metal accumulation in food.

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