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Toxicity and bio-accumulation of chromium, cadmium, and arsenic in some common fish species captured from fish ponds of Kandhkot Sindh, Pakistan

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Abstract

The purpose of this study was to evaluate the risk assessment of toxic elements in fish species, sediment, and its respective water samples from different fish ponds. The concentration of toxic elements including arsenic, chromium, and cadmium was determined in gills, liver, and muscle of two different fish species *Labeo rohita* and *Cirrhinus mrigala* and medium. Microwave-assisted digestion method was applied and analysis was performed by using (ICP-OES). It has been observed that (EDI) value in case of chromium was found (0.002) for cadmium was noted (0.0075) and Arsenic was calculated (0.0038). The PLI factor for total toxic elements was found in five sampling stations (2.24) due to enrichment of metals through water and sediments. The (THQ) of Chromium was found (0.01), for Cadmium (0.4) and for Arsenic (0.004) respectively. The (CF) value in case of Chromium (1.3) while for Cadmium (7.0) and for Arsenic (1.2). While BAF for accumulation of elements to fish organs through sediment and pond water was and found that BAF factor in case of Chromium was (0.11), while in case of Cadmium it was found (0.13) and for Arsenic (0.05) in factor was noted. Targeted hazard quotient and estimated daily intake values of toxic elements were found in the decreasing order such as As < Cd < Cr and As < Cr < Cd respectively. It was further noted that the targeted hazard quotient and estimated daily intake in both varieties of fish samples were <1. It indicates magnitude toxicity toward sediment and pond.

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Introduction

The world utilization of fish has been significantly increased with the increasing requirement of their dietary and therapeutic benefits during recent years. Beside this fish is major source of protein, it typically have rich contents of essential minerals, un-saturated fatty acids and vitamins. Fish play a major role of is humans nutrition, therefore we have to be more careful and make sure that unnecessary level of hazardous metals are not being shifted to the health of human through consumption of fish. Eating of fish minimally twice a week is strongly recommended by the American Association of Heart and diseases to complete requirement of daily intake of omega-3 fatty acids. Intake of toxic metals to fish in contaminated aquatic environment is depended on various types as on metabolism, ecological requirements, level of pollution, sediment food and many other factors such as salinity (Odoemelan *et al.*, 2017).

The contamination of aquatic environment with toxic elements has been worldwide crisis during last two decades because they are indestructible and most of them have hazardous effect on the living organisms (Mutasim E El *et al.*, 2018). Residues of metal in the flesh of fish are, though a very serious matter because of the high concentration of toxic metals recorded within the sediments and water of the ponds (Wong *et al.*, 2014). Beside this fish sample are often considered as most important indicators in water system for assessment of metals contamination level. Due to harmful effect and bio-accumulation of toxic elements into aquatic system among all environmental pollutants they have divert the specific concern of researchers across the world. The heavy elements has tend to accumulate into water and then move up through the food web thus it is necessary to calculate the level of these toxic elements in the aquatic environment and also determine the poisonous effect on the health of human being (Haram Hassan (Abass Bakhie *et al.*, 2015). Greater concentration of heavy elements may be a big threat to the health of human and also to the aquatic organisms which are present due to the

contamination of the aquatic environment (A. S. Hamed, *et al.*, 2015). They may come into the aquatic system from various human activities and natural sources, like shipping, domestic or industrial wastewater, leaching from landfills, atmospheric deposits, usage of pesticides and inorganic fertilizers, harbor activities and geological weathering of the world crust (Elagba Haj Ali Mohamed, *et al.*, 2014; Haram H A Bakhiet, *et al.*, 2015).

The present study was conducted to evaluate the exposure of toxic elements in fish samples by monitoring the toxicity and bioaccumulation of elements via sediment and water. In this regards the minimum and maximum level of target hazard quotient (THQ), contamination factor (CF), bio-accumulation factor (BAF), and pollution load index (PLI) were investigated in two famous fish species *Labeo rohita* and *Cirrhinus mrigala* from two biggest fish ponds i.e Muhammadani and Suhriyani of taluka Kandhkot district Kashmore, Sindh Pakistan.

Materials and methods

Study Area description

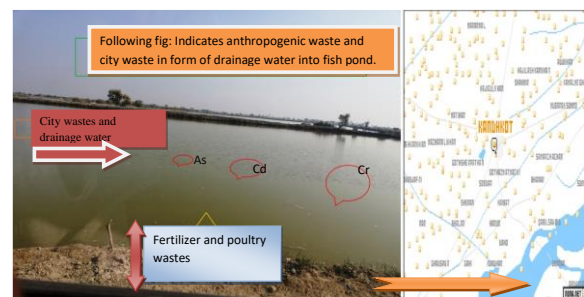


Fig. 1. Map of district Kashmore @ Kandh kot.

Kandhkot is a big city and having tehsil Kashmore in the Sindh, Pakistan. The latitude of Kandhkot is 28°14' 38.26" N and the longitude is 69°10' 56.46" E (NRB: Local Government Elections, 2012). As for as fish production is concerned by local farmers though open lacks and man-made fish ponds as well. More than 500 fish ponds are available in the Kandhkot city and its surroundings. Hence fish culture contributes vital role in socio-economic life of local consumers and it also plays an important role to enhance the GDP of our country by exporting the fish and fish products to abroad.

Collection of Fish Samples

Twenty five samples of each fish species like wise, Morakhi (*Cirrhinus mrigala*) and Rohu (*Labeo rohita*) were collected from two different fish ponds of mentioned study area with the help of professional fishermen. The collected samples of fish were kept in an icebox up to 04°C till transported to the laboratory of Institute of chemistry Shah Abdul Latif University Khairpur, where these samples were weighed with electronic balance. After this dissection of different required specimens i.e. muscle, gills, and liver were carried out through the sterilize instruments and cutters.

Preparation of Samples

Experimental reagents and Standards

All chemicals used were of analytical reagent grade. The stock solutions of 1000mg/L Cd, Cr and As were prepared from their metals which were dissolved in nitric acid and diluted with de-ionized water. All standard solutions contained the same volume percentage of acid as the digested samples. The Muhammadani and Suhryani fish ponds reference to sediments and water from the both fish ponds were obtained. All filtrations of solutions were carried out with Whatman No. # 42 filter paper. The samples were processed through Inductively Coupled Plasma–Optical Emission Spectrophotometer (ICP-OES). Background correction was accomplished with a deuterium lamp except no background correction was used for the measurement of Cd, Cr and As. Sediment digestions were performed with a hotplate, a 1000 W domestic microwave oven (Samsung, Japan) with 32L capacity and an ultrasonic bath (Branson, USA) with 1.9L capacity. All glassware, digestion tubes, teflon vessels and polyethylene bottles were soaked in 10% nitric acid for at least 24 hours and then rinsed several times with Milli-Q water prior to use.

Heavy Metals in Sediment Samples

Procedures Influence of acids on metal recoveries by hotplate digestion

The influence of 5 acid mixtures on the recovery of metals from reference materials was investigated by varying the acids used in the digestions. The composition of acid mixtures were as follows: HNO₃-

H₂O (1:1), HNO₃-H₂SO₄, (1:1), HNO₃-HCl (1:3) Aqua regia, HNO₃-HCl (3:1) reverse aqua regia, and HNO₃-H₂O₂ (1:1). Each sediment sample was digested in triplicate by each of these acid mixtures. Sample pre-treatment: 10mL of acid mixture was added to 4 grams of sediments. All digestions were carried out for 3 hours at 120°C on a hotplate. The digested samples were then filtered and made up to 25mL. These solutions were analyzed with the help of Inductively Coupled Plasma–Optical Emission Spectrophotometer (ICP-OES)-AAS.

The recovery of the metals by microwave digestion was carried out through three most effective acid mixtures used in hotplate digestion were then tested in microwave digestion to see if the metal recoveries improved. The power supplied to the microwave oven and the digestion times used were varied for each of the different acid mixtures. The standard sediment samples were digested in triplicate with each acid mixture in closed teflon vessels with pressure relief valves. Water samples n=100 were collected from required sampling stations to measure the pH, temperature, and electrical conductivity. For analysis of elemental contains triplicate water samples were taken in polypropylene bottles free from trace elemental contamination previously soaked with 10% HNO₃ solution. All collected samples were added 2 to 3 drops of concentrated HNO₃ for preservation.

The recovery of the metals by ultrasonic digestion plus (Blrther hotplate treatment), Ultrasonic digestion was performed with the use of the most effective acid mixtures obtained using microwave digestion to see if the metal recoveries.

Toxic elements from fishes and its estimated daily intake (EDI)

Estimated daily exposure of metals depends on the mean concentration of elements in fish's ingestion along with body weight. The following formula by which estimated daily intake of metals can be calculated by using formula (MdSaiful Islam and Hoque, M. F. 2014).

$$\text{Estimated Daily Intakes of metals} = \frac{\text{Daily Intake of elements/ Metals}}{\text{Body Weight}}$$

Here; daily intake of metals = consumption of fishes in daily basis × mean concentration of metals in fishes (Bangladesh Bureau of Statistics; 2010).

Bio-accumulation factor (BAF)

Bio-concentration factor is the transfer of toxic elements from sediment to of fishes. It is calculated as the concentration of toxic elements ratio in the vegetables to the corresponding sediment from which fish samples on dry weight were collected.

$$\text{The bioconcentration factor} = \frac{[M]_{\text{fish}}}{[M]_{\text{sediment}}}$$

Pollution Load Index (PLI)

The Pollution Load Index (PLI) is obtained as concentration Factors (CF). This CF is the quotient obtained by dividing the concentration of each metal. The PLI of the place are calculated by obtaining the n-root from the n-CFs that was obtained for all the metals. With the PLI obtained from each place. Generally pollution load index (PLI) as developed by (Adel Mashaan Rabee *et al.*, 2011), which is as follows:

$$CF = C \text{ metal} / C \text{ background value}$$

$$PLI = n\sqrt{CF_1 \times CF_2 \times CF_3 \dots \times CF_n}$$

The PLI value of > 1 is polluted, whereas <1 indicates no pollution.

Toxic Risk Assessment (THQ)

Targeted Health Quotients (THQs) is a human health risk assessment concerned with the accumulation of vegetables used by the local residents. Targeted Health Quotients (THQs) of toxic elements has been

computed using Equation $THQ = EF \times ED \times FI \times MCRfd \times BW \times AT \times 10^{-3}$. (Hang Zhou *et al.*, 2016).

Result and discussion

In an aquatic organism the pollution of toxic elements has a great attention for the scientific community. The pollution in the waste of chemical industries, mining, and agronomic was highly severe. Table 1 shows the mean values of physicochemical parameters like pH, EC, TDS, Chloride and Alkalinity of both ponds. Muhammadani pond shows results for pH (8.2), (8.9) EC (2726 μs/cm), (2828 μs/cm), TDS (1688mg/l), (1987mg/l), chloride (295mg/l), (321mg/l), alkalinity (653mg/l), (725mg/l). Whereas the Suhriyani pond shows the results for pH (7.9), (8.3), EC (2689 μs/cm), (2735 μs/cm), TDS (1968mg/l), (1972mg/l), chloride (315mg/l), (320mg/l) and alkalinity (712mg/l), (729mg/l) respectively. It was noted that the physicochemical parameters values of Muhammadani fish pond was higher than Suhriyani samples. It was observed that the water of both ponds shows highest levels of pH, EC, TDS, and Chloride than recommended by the WHO values but alkalinity was observed within the range of WHO values.

Table 1. Physicochemical parameters water in Muhammadani fish pond and Suhriyani fish pond.

Parameters	WHO limits	Muhammadani Pond	Suhriyani Pond
pH	6.5-8.5	8.2-8.9	7.9-8.3
E.C μs/cm	2500	2726- 2828	2689-2735
TDSmg/l	1000	1688- 1987	1968-1972
Chloridesmg/l	250	295- 321	315-320
Alkalinitymg/l	1000	653-725	712-729

Table 2. Average values of different metals in fish samples obtained from both Muhammadani and Suhriyani fish Ponds.

Metals	Muhammadani Pond						Suhriyani Pond					
	C.marigala			L.rohita			C.marigala			L.rohita		
	Muscle (mg/kg)	Gills (mg/kg)	Liver (mg/kg)	Muscle (mg/kg)	Gills (mg/kg)	Lliver (mg/kg)	Muscle (mg/kg)	Gills (mg/kg)	Liver (mg/kg)	Muscle (mg/kg)	Gills (mg/kg)	Liver (mg/kg)
Cd	0.54	0.57	0.55	0.16	0.15	0.18	0.35	0.48	0.46	0.21	0.17	0.22
Cr	0.47	0.56	0.66	0.56	0.66	0.77	0.42	0.54	0.76	0.20	0.17	0.21
As	0.001	0.002	0.003	0.002	0.002	0.003	0.001	0.002	0.003	0.002	0.002	0.003

Table: No.02. Indicates the level of Cr, Cd, and As in both species of Muhammadani and Suhriyani fish ponds. The obtained results were showed that the

levels of chromium, cadmium, and arsenic were higher in the liver of both fish species *C. mrigala* and *L.rohita* captured from both fish ponds.

Results of chromium, cadmium and arsenic in *C.mrigala* were found in range of (0.47-0.66mg/kg), (0.54-0.57mg/kg) and (0.001-0.003mg/kg) for Muhammadani pond while in Suhriyani pond (0.42-0.76mg/kg), (0.34-0.47mg/kg) and (0.0012-0.0034mg/kg). The concentration of cadmium, chromium, and arsenic in *L. rohita* were found in range of the (0.03-0.16mg/kg), (0.5-0.77mg/kg), and (0.0015-0.032mg/kg) for Muhammadani pond and (0.017-0.18mg/kg), (0.016-0.2mg/kg) and 0.0016-0.0034 respectively. The concentrations of toxic elements in all fish samples were found in the decreasing order, such as As < Cd < Cr. The level of chromium and cadmium were found slightly higher in *C. mrigala* fish species of Muhammadani and Suhriyani pond than in the

FAO/WHO. The possible sources of element exposure in fish samples of the study area may be due to environmental pollutants, industrial or domestic sewage, drainage, and feed. The average concentration of cadmium in all fish samples were nearly within same values as (0.56mg/kg) reported by (Sadam Hussain *et al.*, 2019), concentration of chromium in fish slightly higher as compared (0.48mg/kg) to the work of (Indrajit Sen *et al.*, 2011), and average concentration of arsenic was found lower as reported by (O.J. Aderinola *et al.*, 2010). Overall, the average concentration of cadmium and Chromium were detected higher in almost all fish samples than permissible limit given by WHO and FAO, (2011).

Table 3. Averages of different statically/mathematical factors in water and sediments of both fish ponds.

Metals	Muhammadani Pond							Suhriyani Pond						
	sediment	water	BAF	CF	PLI	EDI	THQ	sediment	Water	BAF	CF	PLI	EDI	THQ
Cd	0.40	0.32	0.13	6.01	3.61	0.002	0.41	0.38	0.32	0.09	3.01	2.81	0.007	0.14
Cr	0.51	0.45	0.11	1.31	2.62	0.003	0.50	0.62	0.37	0.35	1.51	2.32	0.008	0.07
As	0.04	0.03	0.05	1.23	1.44	0.004	0.05	0.03	0.03	0.05	1.43	1.80	0.006	0.05

Table 3 indicates the results of water, sediment, BAF, CF, PLI, EDI, and THQ of chromium, cadmium, and arsenic in samples of both fish ponds. Results of Cr, Cd, and As for water were found in the range of (0.4mg/l), (0.8mg/l), and (0.035mg/l) in Muhammadani pond while in Suhriyani pond the result shows in the range of (0.45mg/l), (0.7mg/l), and (0.026mg/l) respectively. In case of sediment, the chromium (0.62mg/kg) and cadmium (0.7mg/kg) shows higher accumulation in various specimens in both fish ponds. The average concentration of arsenic was noted maximum up to (0.044)mg/kg in sediment samples of both fish ponds that were in safe limits proposed by WHO. It was shown in the above table that the level of both chromium and cadmium were higher than the guided limits proposed by FAO/WHO.

The bio-accumulation factor (BAF) was <1.0 in all the samples collected from both fish ponds. It was assessed that the concentration of toxic elements

were found high in sediment as compared to the fish species collected from both fish ponds. There were minimum uptakes of toxic metals to the fishes. The results for CF, PLI, EDI, and THQ shows higher concentration in cadmium and chromium of Muhammadani pond as compare to the Suhriyani pond, while the level of chromium and cadmium of all these factors show high than the allowable limit. And the values of PLI pollution load index were also higher than 1 in all stations of both ponds. This results that the ponds of taluka Kandhkot facing many problems like environmental pollution and industrial waste with these toxic elements which is very dangerous.

The values for EDI and THQ of chromium, cadmium, and arsenic were (0.003), (0.002), (0.002) for Muhammadani pond and in case of Suhriyani pond values were (0.008), (0.007), and (0.002) respectively. It was observed that the THQ of each metal via consumption of fish decreased in order of the cadmium < chromium < arsenic.

Table 4. Correlation coefficients of Cadmium in various specimens of both fish species collected from Muhammadani and Suhriyani fish ponds.

		Muhammadani Pond	Suhriyani Pond
Muhammadani Pond	Pearson Correlation	1	-1.000**
	Sig. (2-tailed)		.
Suhriyani Pond	Pearson Correlation	-1.000**	1

** . Correlation is significant at the 0.01 level (2-tailed).

Table 5. Correlation coefficients of Chromium in various specimens of both fish species collected from Muhammadani and Suhriyani fish ponds.

		Muhammadani Pond	Suhriyani Pond
Muhammadani Pond	Pearson Correlation	1	-1.000**
	Sig. (2-tailed)		.
Suhriyani Pond	Pearson Correlation	-1.000**	1

** . Correlation is significant at the 0.01 level (2-tailed).

Table 6. Correlation coefficients of Arsenic in various specimens of both fish species collected from Muhammadani and Suhriyani fish ponds.

		Muhammadani Pond	Suhriyani Pond
Muhammadani Pond	Pearson Correlation	1	1.000**
	Sig. (2-tailed)		.
Suhriyani Pond	Pearson Correlation	1.000**	1

** . Correlation is significant at the 0.01 level (2-tailed).

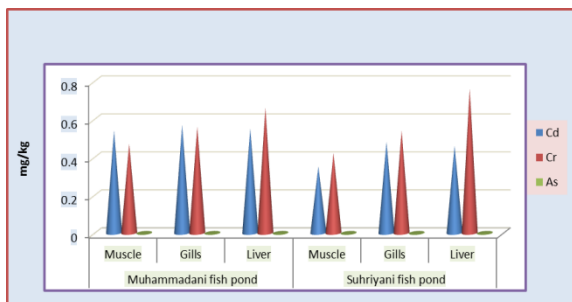


Fig. 2. Comparative graph of different heavy metals in various specimens of *C.mrigala* collected from both fish ponds.

Fig. 2 shows comparative values of *C.mrigala* collected from both fish ponds of different organs having various heavy metals including Cadmium, Chromium and Arsenic. The Muhammadani fish pond showed highest values of Cadmium in liver

among same samples compared to gills and muscle in same fish pond. Similarly lowest values were observed in muscle as compared to other specimens of same fish pond. Arsenic was found lowest in every organ of same species captured from both fish ponds as compared to Cadmium and Chromium. Whereas sample collected from Suhriyani fish pond had maximum values of Chromium in liver and minimum values were observed in muscle of same samples. As mentioned in Fig:01 Cadmium was found highest in gills of fish samples collected from Muhammadani fish pond as compared to Suhriyani fish pond. Although the concentration of Cr was found high in liver of fish sample collected from Suhriyani fish pond as compared to Muhammadani fish pond. The concentration of heavy metals were observed as Cr > Cd > As and order of their values were found in various specimens as Liver>Gills>Muscle of both fish pond.

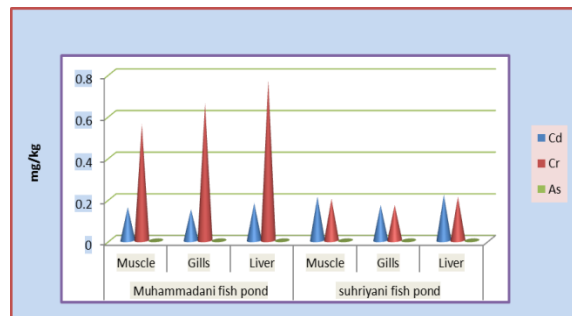


Fig. 3. Comparative graph of different heavy metals in various specimens of *L.rohita* collected from both fish ponds.

Fig. 3 describes comparative values of *L.rohita* collected from both fish ponds of different organs having various heavy metals including Cd, Cr and As. The Muhammadani fish pond show highest values of Cd in liver among same samples compared to gills and muscle in same fish pond. Similarly lowest values of chromium were observed in muscle as compared to other specimens of same fish pond.

Arsenic was found lowest in every organ of same species captured from both fish ponds as compared to Cadmium and Chromium. Whereas sample collected from Suhriyani fish pond had maximum values of

Chromium in liver and minimum values were observed in gills of same samples. As mentioned in Fig:01 Cd was found highest in liver of fish samples collected from Muhammadani fish pond as compared to Suhryani fish pond. Although the concentration of Chromium was found high in liver of fish sample collected from Muhammadani fish pond as compared to Suhriyani fish pond. The concentration of heavy metals were observed as Cr > Cd > As and order of their values were found in various specimens as Liver > Gills > Muscle of Muhammadani fish pond where as in case of Suhriyani fish pond the order of specimen as Liver > Muscle > Gills.

Conclusion

It was concluded that the concentration of Chromium and Cadmium were found higher than the FAO/WHO limits, whereas, Arsenic concentration was found within the recommended values of FAO/WHO. The observed concentration of toxic metals in *C.mrigala* fish species order was noted as Cr > Cd > As in both fish ponds. In *L.rohita* level order was noted as Cr > Cd > As in both fish ponds. Results of associated water samples indicate the higher level of cadmium and chromium in its samples while the concentration of arsenic was examined within permissible limits. Further, that estimated daily exposure of toxic elements indicates the value of chromium, cadmium, and arsenic were below < 1 and estimated daily intake (EDI) of elements via consumption of both fish species in the study area were in the order of Cr > Cd > As. In the case of bioaccumulation factors (BAF) of elements were observed below < 1.0 and decreasing order of (THQ) targeted health hazard quotient ingested via fish's were as Cr > Cd > As.

Recommendations

It is recommended to governmental agencies to set some standards for the quality of feedings, water, and sediments of fishponds with continuous monitoring. Similarly, the finding of the current study strongly supports the idea of routine bio monitoring for metal contents of edible fish from ecosystems subjected to sport fishing. Simple analyses of environmental heavy metals are not enough to detect risks for consumers.

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Conflicts

The authors declare that they have no conflict of interest.

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