

Bioaccumulation of heavy metals in marine and freshwater fishes of Sikka, Jamnagar coast of GoK, Gujarat

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Abstract: Sea food is taken by most of the people in the world, and it serves as an important factor in the economy of a country in exports. Bioaccumulation of heavy metals in sea foods is a major threat to the world. Considering the present scenario and Kachchh becoming a fastest growing industrial hub with different category of industrial units, the present study was attempted to determine the heavy metal accumulation of ten different species of marine and freshwater fishes (Silver pomfret, Malai pich, Sherri, Tilapia, Surmai, Orange pomfret, Boye, Lady fish, Golden fish and Cat fish) collected from local market of Sikka- Jamnagar, Gujarat. The tissues of the fish samples were processed for estimation of Chromium, Cadmium, Mercury, Zinc, Nickel, Cobalt, Copper, Lead and Arsenic using Atomic Absorption Spectroscopy. The concentrations were compared with WHO/FDA's permissible limits of heavy metals in fishes. Among the metals tested, Fe was found to be recorded with a maximum concentration of 2.6 ± 0.03 /g wet.wt. followed by Cu, Zn, Pb and As respectively. Toxic metal mercury was recorded in the range of 0.11 ± 0.01 – 0.13 ± 0.01 μ g/g. Cobalt and manganese were not found in any of the fishes studied. The overall heavy metal accumulation in fish species were in the order Cat fish >Golden fish >Sherri>Malai pich>Boye > Orange Pomfret >Sherrirrespectively. Other fishes have recorded almost near similar concentrations of metals.

Keywords: Bioaccumulation; Biomagnification; Toxicity; Pollution; Sea foods.

1. INTRODUCTION

Fishes are deliberated as vital source of protein for human health. Marine pollution has increased the toxic metal concentration in the aquatic environment and adversely affects fish health. Marine pollution could be caused by several sources such as agricultural drainage, industrial effluent discharge, sewage discharge, accidental chemical waste spills, and gasoline from fishing boats (Handy, 1994; Mishra et al., 2007; Satheshkumar and Kumar, 2011; Velusamy et al., 2014). The bioaccumulation of heavy metals in marine organisms leads to biomagnification process, which is a serious threat to the aquatic ecosystems and risk to the consumers. Though, many fish species are predominantly used as bio-indicators of heavy metal pollution and the metal concentration in aquatic organisms could clearly indicate the status of the environment in which the fish species live (Farkas et al., 2000). The metal accumulation in fishes are determined by the location, distribution, habitat preferences, trophic level of fishes, feeding habits, size of fish, duration of exposure and homeostatic regulation activity (Sankar et al., 2006).

Heavy metal pollutants are of high ecological implication which cannot be removed from marine environment by self-purification. Moreover, they can accumulate in suspended particles in the water column and sediment, and then enter into the food web through lower trophic level to higher consumers (Cevik et al., 2009). However, heavy metals might enter into aquatic ecosystems through natural as well as anthropogenic sources, such as industrial wastewater discharges, sewage, fossil fuel combustion, and atmospheric deposition (Sekabira et al., 2010). The most important heavy metals such as Cu, Zn, Pb, Cd, Cr, Ni, and Hg are predominantly polluted in water column. Metals transfer from the water to sediment under certain conditions by different processes, such as ion exchange, metal substitution, adsorption, and dissolution. Fish, crabs and shrimps are an important link in transferring the metals from lower trophic level to humans.

Gulf of Kachchh is one of the fast industrial development regions in Indian subcontinent has contributed to rapid increase of heavy metal pollution in this region. Due to their diligence and bio-accumulative nature, the expulsion of heavy metals into the marine environment can condense the biodiversity of marine ecosystem (Rahman et al., 2010). The consumption of such polluted sea foods such as fishes, shrimps and crabs by humans might be affected with various health risks such as liver damage and hepatic dysfunction. Several studies have been made to examine the heavy metal contamination in fishes along Indian coast but very limited study has been reported in this study region. In this present study, concentration of heavy metals in commercially available fish's from Sikka, Jamnagar, Gujarat.

2. MATERIALS AND METHODS

Sample preparation

Ten commercially available fish species (Silver pomfret, Malai pich, Sherri, Tilapia, Surmai, Orange pomfret, Boye, Lady fish, Golden fish and Cat fish) were collected from Sikka, Jamnagar. The collected specimens were transported to laboratory in an ice-box and stored at -20°C until analysis. The specimen was thawed to room temperature for morphometric measurement such as length and weight was examined for all the collected specimens. All the specimens were measured to the nearest mm, whereas weights were recorded with the use of electronic balance to the nearest 0.01 g. The fishes were washed with distilled water and scales were removed. Five gram of boneless tissue was taken from each species of fish in a clean 50ml beaker.

Table 1: Freshwater and marine fish species samples for heavy metal analysis

S. No	Local Name	Common Name	Scientific Name	Average Weight (g)
1	Thalapia	Tilapia	<i>Oreochromis niloticus</i>	250
2	Silver pomfret	Silver pomfret	<i>Pampus argenteus</i>	250
3	Sherri	Emperor/Mula	<i>Lenthrinidae</i> spp.	100
4	Surmai	King fish	<i>Scomberomorus guttatus</i>	200
5	Orange pomfret	Chinese pomfret	<i>Pampus chinensis</i>	250
6	Singhara	Cat fish	<i>Sperata seenghala</i>	350
7	Lady fish	Lady fish	<i>Elops Spp.</i>	100g
8	Malaipich	Big eye tuna	<i>Thunnus obesus</i>	300
9	Golden fish	Yellow fin tuna	<i>Thunnus albacares</i>	250
10	Boye	Mirgal	<i>Cirrhinus mrigala</i>	250

Acid digestion and analysis of Heavy metals

In the present experiment all digestive reagents, acids and chemicals used were analytical grade. For acid digestion, boneless tissues were dissected using stainless knife and scissors. Five gram (wet weight) of each sample were kept in a 100 ml glass beaker with 10 ml of mixed reagent (Con. H₂SO₄ and HNO₃, 1:3 ratio) and heated on a hot plate at 120 °C until the tissue gets complete digestion, after that it was allowed to cool at room temperature (Duraliet al., 2010). Finally, digested suspension was filtered and made up to 50 ml with double distilled water and stored in acid cleaned fresh polypropylene containers at room temperature until analysis. Blanks were also prepared using above procedure without adding fish samples. The samples were analysed for As, Cd, Cr, Co, Cu, F, Pb, Hg, Ni, Mn and Zn by Atomic Absorption Spectrophotometer (Perkin Elmer A Analyst 400) using air-acetylene flame with digital read out system, deuterium lamp background corrector, and automatic zero to compensate the blank. Settings were followed as recommended by the manufacturer. Calibrations using standard solutions were made by stepwise dilution of the stock solution. The absorption wavelength and detection limits were 228.8 nm for Cd, 324.7 nm for Cu, 217.0 nm for Pb, 193.7 nm for As, 240.7 nm for Co, 357.9 nm for Cr, 248.3 nm for Fe, 253.7 nm for Hg, 279.5 nm for Ni, 279.5 nm for Mn and 213.9 nm for Zn. Quality assurance and Quality control testing was relied on the control of blanks and yield for chemical procedure. For precious quantification triplicates of the samples, blanks and standard references were used throughout the analysis.

Statistical analysis

One-way analysis of variance (ANOVA) was used to compare metals between species (significant value $p \geq 0.05$). All data were checked, beforehand, for the homogeneity of variance and normality. ANOVA was followed by Duncan's multiple range tests to determine the position of the variance. Tukey's test was used to single step comparison within the metal accumulation. All statistical calculation was carried out with SPSS 16.0.

3. RESULTS

The concentration of heavy metals (Zn, Ni, Co, Cd, Cr, Cu, Fe, Pb, As, Mn and Hg) accumulation in muscles of fishes collected from fish market at Sikka Jamnagar are given in Table. 1. Accumulation pattern of the heavy metals were significantly different ($p < 0.001$) between different species and metals.

In the present study metal accumulation in all species of fish contained the lowest concentration of metals in muscles, while almost all fish species showed highest concentration of Cu and Fe in their muscles. The metal cobalt and manganese were reported below detectable level in all species as shown in Table 2.

Table 2: Heavy metal concentration in the fish species in Sikka, Jamnagar coast

S. No	Heavy Metals Fishes	Chromium ($\mu\text{g/g}$)	Cadmium ($\mu\text{g/g}$)	Mercury ($\mu\text{g/g}$)	Zinc ($\mu\text{g/g}$)	Nickel ($\mu\text{g/g}$)	Copper ($\mu\text{g/g}$)	Lead ($\mu\text{g/g}$)	Arsenic ($\mu\text{g/g}$)	Iron (Fe)
1	Tilapia	0.22±0.02	0.07±0.02	0.13±0.012	0.43±0.04	0.22±0.01	1.47±0.03	0.40±0.006	0.29±0.23	1.6±0.07
2	Silver pomfret	0.02±0.0	0.06±0.006	0.12±0.006	0.84±0.02	0.14±0.03	1.31±0.03	0.34±0.008	0.01±0.01	1.4±0.06
3	Malai pich	0.18±0.03	0.05±0.02	0.12±0.003	1.38±0.06	0.17±0.07	1.67±0.04	0.35±0.009	0.02±0.01	2.0±0.07
4	Shein	BDL	0.07±0.02	0.12±0.001	0.86±0.04	0.27±0.05	1.64±0.03	0.37±0.007	BDL	2.4±0.08
5	Surmai	0.01±0.01	0.07±0.001	0.11±0.01	0.44±0.02	0.15±0.02	1.28±0.02	0.44±0.015	0.09±0.1	1.5±0.03
6	Orange pomfret	0.08±0.01	0.07±0.001	0.13±0.01	0.64±0.04	0.16±0.03	1.73±0.04	0.49±0.008	0.08±0.06	2.1±0.06
7	Boye	BDL	0.7±0.01	0.12±0.04	0.80±0.01	0.21±0.10	1.60±0.05	0.53±0.008	0.08±0.04	1.8±0.06
8	Lady fish	BDL	0.06±0.01	0.12±0.003	0.49±0.02	0.16±0.05	1.45±0.05	0.59±0.009	0.08±0.03	1.5±0.1
9	Golden fish	BDL	0.10±0.01	0.12±0.002	0.96±0.03	0.22±0.02	1.96±0.02	0.67±0.005	0.03±0.01	2.5±0.05
10	Cat fish	0.13±0.01	0.05±0.02	0.13±0.01	0.36±0.01	0.24±0.01	1.28±0.03	0.70±0.007	BDL	2.6±0.03

***NOTE: Cobalt and Manganese were reported in below detection limit (BDL)**

3.1. Zinc (Zn)

The fish species Malai pich, *Thunnus obesus* exhibited a trend to accumulate high concentration ($1.38 \pm 0.06 \mu\text{g/g}$) of Zn in the muscles followed by Golden fish, *Thunnus albacares* ($0.96 \pm 0.03 \mu\text{g/g}$ wet wt.). One way ANOVA analysis expressed the metal accumulation among the fishes showed highly significant at 0.05% level ($p < 0.05$) ($r^2 = 0.9915$). Statistically proved that the silver pomfret fish expressed high significant with other fish species.

3.2. Nickel (Ni)

Concentration of Ni in muscles of fish species ranged from $0.14 \pm 0.03 \mu\text{g/g}$ (Silver pomfret, *Pampus argentous*) to $0.24 \pm 0.1 \mu\text{g/g}$ (Cat fish, *Sperataseenghala*). The highest concentration heavy metal accumulation was recorded in Sherri, *Lenthrinidae* Spp. ($0.27 \pm 0.05 \mu\text{g/g}$) followed by cat fish, *Sperataseenghala* ($0.24 \pm 0.1 \mu\text{g/g}$). One way ANOVA analysis expressed Ni accumulation in among the fishes significantly low ($p < 0.05$) Whereas, Tukey's multiple comparison showed no significant relationship found among the fish species.

3.3. Cobalt (Co) and Manganese (Mn)

Cobalt and manganese concentration in all fish species were below detection limits at $\mu\text{g/g}$ level (BDL).

3.4. Copper (Cu)

Accumulation copper in fish muscles varied from $1.371 \pm 0.03 \mu\text{g/g}$ (Silver pomfret, *P. argentous*) to $1.289 \pm 0.03 \mu\text{g/g}$ (Cat fish, *S. seenghala*), while, highest concentration of metal accumulation was recorded in golden fish ($1.967 \pm 0.02 \mu\text{g/g}$) and lowest concentration was recorded in Surmai fish ($1.277 \pm 0.02 \mu\text{g/g}$) (Table 1). Cu accumulation was highly significant among the fish species ($p < 0.005$) ($r^2 = 0.9761$). Among them, silver pomfret showed highly significant (p value < 0.001) relationship with Malai pich, Sherri, Orange pomfret and Boye.

3.5. Lead (Pb)

Cat fish showed highest accumulation of Pb content in their body tissues ($0.701 \pm 0.007 \mu\text{g/g}$) showed significantly higher than other species of fishes ($p < 0.001$). Golden fish also showed higher accumulation of Pb content in their body mussels ($0.67 \pm 0.005 \mu\text{g/g}$). The lowest concentration of Pb was recorded in *Silver pomfret*. One way ANOVA analysis showed no significant difference found among the species.

3.6. Cadmium (Cd)

A wide range of Cd concentrations were recorded among the studied fishes, with the lowest concentration ($0.51 \pm 0.02 \mu\text{g/g}$ wt. weight) was recorded in Malai fish and an extremely higher concentration ($0.96 \pm 0.01 \mu\text{g/g}$ wt. weight) was

recorded in Golden fish. One-way ANOVA analysis of heavy metal accumulation in fish muscles showed significant difference among the fish species. Post-Hoc analysis of Cd accumulation in Malai pich and golden fish showed relatively significant ($< 0.05\%$).

3.7. Chromium (Cr)

Tilapia fish *Oreochromis niloticus* showed the highest concentration of Cr concentration ($0.26 \pm 0.3 \mu\text{g/g}$ wt. weight) followed by Malaipich *Thunnus obesus* ($0.18 \pm 0.02 \mu\text{g/g}$ wt. wt.). Below detectable level of chromium was reported in Sherri fish, Surmai fish, Orange pomfret, Boye fish, Lady Fish and Golden fish. One way ANOVA analysis expressed Cr accumulation among fishes showed significantly higher than others ($p < 0.001$).

3.8. Iron (Fe)

Highest iron concentration was reported $2.63 \pm 0.3 \mu\text{g/g}$ wt. weight) in cat fish followed by Golden fish ($2.54 \pm 0.3 \mu\text{g/g}$ wt. weight). Lowest iron concentration was recorded in Silver pomfret ($1.38 \pm 0.06 \mu\text{g/g}$ wt. weight). Accumulation of Fe was significantly higher among the fish species ($p < 0.05$).

3.9. Arsenic (As)

Arsenic accumulation among the fishes showed lowest concentration in all fishes when compared to the metal concentration recorded in other metals. The Sherri and Cat fish showed the below datable level of arsenic concentration fish tissues.

3.10. Mercury (Hg)

Hg accumulation ranged from $0.11 \pm 0.005 \mu\text{g/g}$ wt. weight in to $0.13 \pm 0.007 \mu\text{g/g}$ wt. weight. The highest concentration of Hg was reported in Tilapia, Orange pomfret and cat fish. One way ANOVA analysis showed no significant between the fishes ($p > 0.05$).

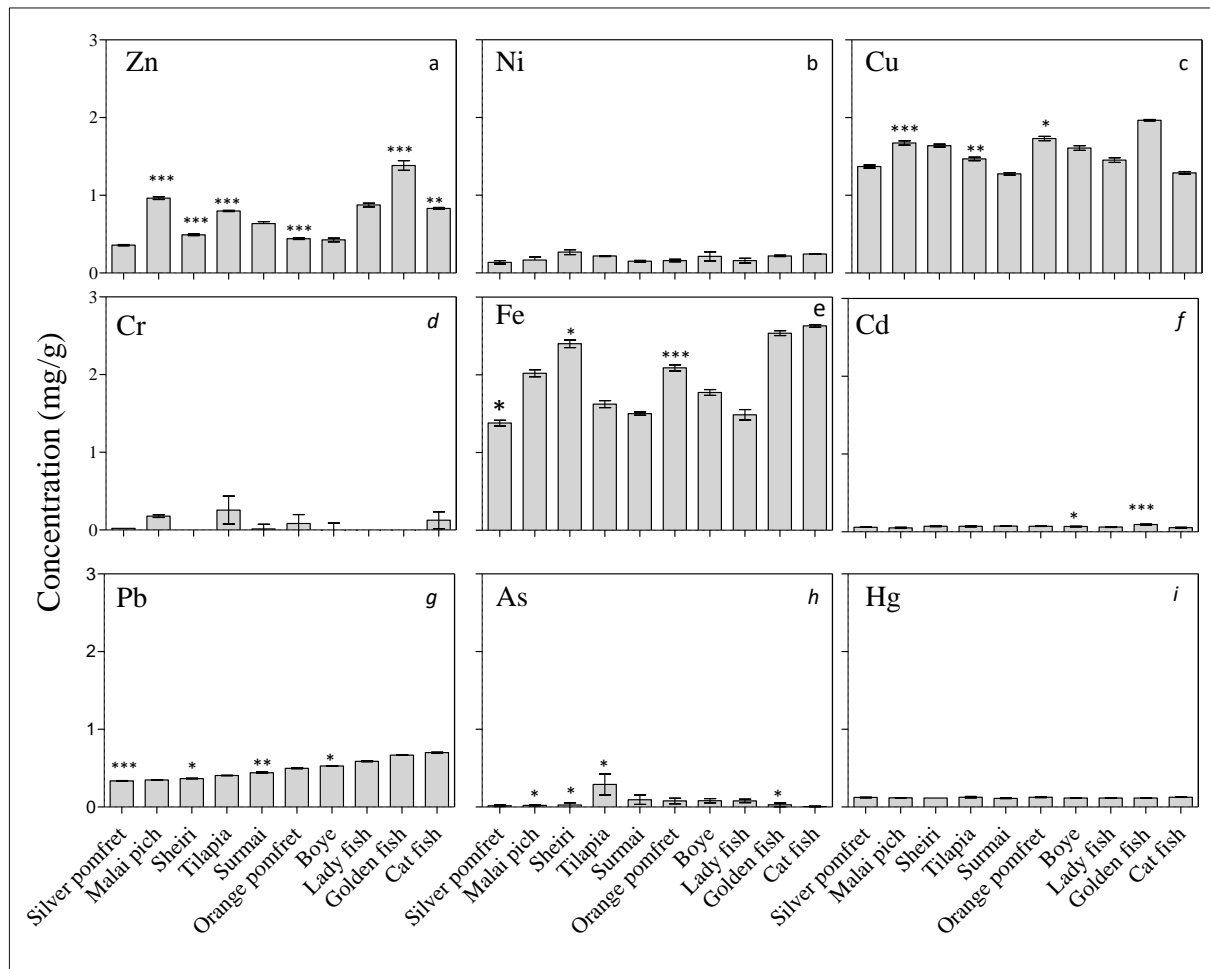


Figure 1: Heavy metal concentration in the fish species in Jamnagar coast

4. DISCUSSION

Increase of heavy metals accumulation in fish tissues from the marine environment is a good indicator of pollution status of the environment. In the present study deals with the heavy metal contamination (Ar, Cd, Cr, Cu, Pb, Co, Fe, Mn, Hg, Ni and Zn) of ten fishes from Jamnagar coast and assessment the pollution status of the environment. Results of the present study demonstrated that all heavy metal accumulation in fish species have been detected to some extent, except Co and Mn concentration which was in below detection level (BDL) in all fishes. The present data indicated that the mean concentration of heavy metal concentration of muscles of ten fish species differed significantly ($p > 0.05$). In the present data, it is demonstrated that the concentration of toxic metals such as Hg, Pb and Cd was low which compared to other Fe, and Cu. The similar results were reported by (Shukla et al., 2007; Visnjic-Jeftic et al., 2010).

The highest mean Zn concentration in ten species was $0.72 \mu\text{g/g}$ wt. weight, while highest concentration was reported Malai pich $1.38 \pm 0.06 \mu\text{g/g}$ wt. weight. Previous study showed the Zn accumulation marine fishes in Gulf of Khambhat 25.7 mg/kg dry wt. (Jebakumar et al., 2015). Our present result which has been compared with the previous study (Jebakumar et al., 2015) was significantly low. The Zn accumulation in ten fishes showed ($P < 0.05$). A significant correlation of Zn accumulation in the marine fishes implies the role of diffused anthropogenic and industrial activity present in Jamnagar coastal waters.

Fe plays a vital role to formation of haemoglobin and the iron deficiency results in anemia. This is in agreement with the findings of Goutam et al. (2015). The mean value of essential metal Fe is $1.94 \pm 0.06 \mu\text{g/g}$ wt. weight. Highest concentration of Fe metal was found in Cat fish, *Sperata seenghal* followed by Golden fish, Sherri and Orange pomfret. Statistically, iron accumulation among the fishes significantly differ among the fish species ($p < 0.005$). Tukey's multiple comparison test analysis expressed silver pomfret fish expressed relatively higher significant when compared to other nine fish species. Results of the present study showed low iron accumulation which compared to previous study was done by Velusamy et al. (2014) and Senthil et al. (2012).

Cu has a major role in functioning for metabolic growth of many organs. Cu is an essential micro-nutrient required for the haematologic and neurologic systems (Tan et al., 2006). Cu is incorporated into a many proteins and metal coenzymes performing significant metabolic functions, it is necessary for growth and development of bones, for the maintenance of health, brain, heart, connective tissues and other organs present in human body. The concentration of Cu accumulation in ten fish's exhibited in Table 1. The highest concentration of Cu was reported in golden fish ($1.96 \pm 0.02 \mu\text{g/g}$ wt. weight.). The similar results of Cu concentration have reported previous study from Gulf of Kambat by Jebakumar et al. (2015). Yasmeen et al. (2016) reported the Cu concentration in fish species in the muscles, skin and heart from Arabian Sea. The results of the present study showed similar concentration reported by Yasmeen et al. (2016). Moreover, the concentration of Cu in ten study fishes expressed significantly ($P < 0.005$) higher between the fish species.

The toxic metals such as Cd, Hg, Co and Pb were low in the present study. Similar report of Cd values in fishes from west Bengal coastal area (De et al., 2010). However, lower than south west coast of India (Rejomon et al., 2010), Red sea (Ahmed and Naim, 2008), but comparatively higher than the fishes from Turkey (Dural and Bickici, 2010), southeast coast of India (Raja et al., 2009) and fishes from Indonesia (Agoes and Hamami, 2007). Hg concentration fish muscles are low in the present study. Similar Hg concentration was reported in previous study on Gulf of Cambay (Reddy et al., 2007), and higher than Saudi Arabia (Nawal, 2008; Waqar, 2004). Arsenic and cobalt were reported in below detected levels. Lower arsenic concentration was reported on Gulf of Combay (Reddy et al., 2007). Among the fishes studied, Tilapia fish has reported to have the highest accumulation of three heavy metals out of ten metals, which includes Cr ($0.22 \pm 0.02 \mu\text{g/g}$), Hg ($0.13 \pm 0.012 \mu\text{g/g}$) and As $0.29 \pm 0.23 \mu\text{g/g}$.

Health risk assessment for fish consumption

It is well known that muscles are not an active site for metal biotransformation and accumulation (Elnabris et al., 2013). Whereas, in polluted aquatic environment the concentration of heavy metals in fish muscles might be exceed the permissible limits for human consumption and indicate severe health threats. Rapid growth of Industrial development of the world has intensely increased the metal toxin into the environment globally. At present metals are abundant in our drinking water, air and soil due to the increased use of metal compounds in drastically. Though, it is very difficult to avoid exposure to many harmful metals that are so prevalent in our environment. Heavy metal toxins contribute to a variety of adverse health effects such as behavioural, physiological, and cognitive changes in exposed humans.

To conclude, metal accumulation in ten fishes, statistically difference in the metal concentration were observed based on the mean concentration values obtained from different fish species. In this present study, the concentration of toxic metals such as Cd, Hg, Co and Pb were recorded in lower concentration in all the ten fish species. The essential metals such as Fe, Zn and Cu were reported in all ten fish species significantly higher which was compared to other metals. Various Industrial and Anthropogenic activity along the Jamnagar coast was plays avital role in the heavy metal accumulation in marine fish species.

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