



DETERMINATION OF TOXIC ELEMENTS IN FISHES COLLECTED FROM WESTERN COAST OF INDIA

Ms. Siddhi Kuperkar

M.Sc. Student, Department Of Forensic Chemistry & Toxicology, Institute Of Forensic Science, Mumbai

Mr. Santosh Lohakare

Assistant Professor, Department Of Forensic Chemistry & Toxicology, Institute Of Forensic Science, Mumbai

Ms. Deeksha Moolya*

M.Sc. Student, Department Of Forensic Chemistry & Toxicology, Institute Of Forensic Science, Mumbai *Corresponding Author

ABSTRACT

This study assessed heavy metal concentration in 149 commercial fish samples of four species - *Fenneropenaeus indicus*, *Harpadon nehereus*, *Pampus argenteus*, and *Rastrelliger kanagurta* - collected from fish markets along the Western Coast of India. The levels of Chromium (Cr), Zinc (Zn), Copper (Cu), and lead (Pb) were determined using Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometry after wet digestion. Results showed significant variation among species: *F. Indicus* had the highest Cr and Zn levels, while *H. nehereus* showed the highest Cu and Pb concentrations. Arsenic, cadmium, mercury, and tin were detected in less than 50% of samples and excluded from detailed analysis. The concentrations were in the permissible limits set by FAO/WHO, EU, FSSAI, and Codex Standards. However, Pb levels exceeded safety limits in all fish species. The study emphasizes the need for regular monitoring to ensure seafood safety.

KEYWORDS : fish, heavy metals, food safety, pollution, seafood

1. INTRODUCTION

Fishes are considered as a vital source of protein, carbohydrates, fatty acids, vitamins, and mineral nutrients (copper, zinc, and iron) for millions of people worldwide.^[1] According to FAO statistics fish accounted for about 16% of the global population's intake of animal protein and 6% of all protein consumed.

Environmental pollution is one of the major challenges in today's world. Environmental contamination and pollution by heavy and toxic metals is a threat to human society, plants, and animals.^[1] Rapid industrialization and urbanization have caused contamination of the environment by heavy metals, and their rates of mobilization and transport in the environment have greatly accelerated since the 1940s.^[1]

Aquatic ecosystems are polluted by heavy metals from different sources. These include mining operation, industrial effluent, domestic sewage, and agricultural run-off. The release of industrial waste without treatment into the water bodies is a significant source of water pollution. Since heavy metals are perpetual in the environment, they collocate in living organisms and are transferred from one trophic level to another in the food chain.

Heavy metals are introduced to the body of an organism directly from an abiotic environment i.e. water, sediment and soil or may enter the organism body from its food/prey. The retention of the heavy metal in the body of an organism depends on many factors such as speciation of metal concerned and the physiological mechanisms developed by the organism for the regulation, homeostasis, and detoxification of the heavy metal. Methylated forms of heavy metal such as Hg are accumulated in biota to a greater extent and therefore biomagnified in food chains due to their lipophilicity.

The bioaccumulation of heavy metal in fish depends on various factors, both fish characteristics and external environment factors. Heavy metal accumulation is higher in the tissues of gill, liver and kidney compared to other tissues such as skin and muscles. Bioaccumulation of trace metals in muscles of fish is mostly species specific. Most studies on bioaccumulation of toxic metals in fish have investigated metal concentrations in fish muscles as this tissue is edible

and thus is the most relevant regarding human health.^[1,2]

The organisms at higher trophic levels in the food chains are at greater risk. To preserve human health from the catastrophic effects of toxic heavy metals, the human food chain should be regularly monitored for bioaccumulation and biomagnification of heavy metals.

2. MATERIALS AND METHODS

2.1 Study Site

The sample collection was done from western coast of Indian sub-continent. The western coast of India is located at 16°53.78'71"N latitude and 72°34.84'82"E longitude on the map. It is located between Kerala and Gujarat and extends from the Arabian Sea to the Western Ghats. Its total length is 1400 km, width ranges from 10 km to 80 km, and the elevation ranges from 150 m to 300 m above sea level.

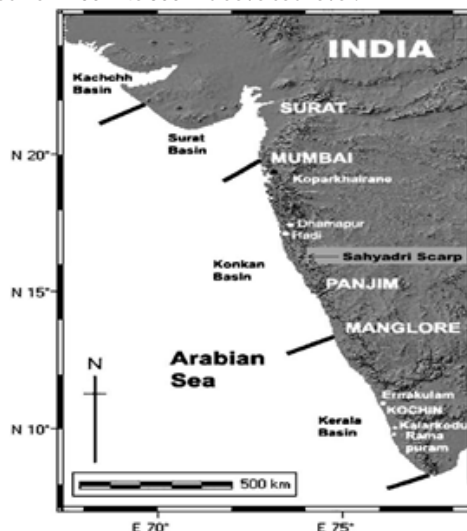


Figure 1. Western Coast of India (Kumaran et al., 2005)

2.2 Sample Collection

Fish samples from the specified region were purchased from the local fishermen in December. The fishes were washed with deionized water, labelled according to species, sealed in polyethylene bags, kept in freezer at -20°C. It was brought to the Regional Forensic Science Laboratory, Surat in January.

2.3 Sample Preparation

2.3.1 Digestion Mixture

The digestion mixture contains 50% concentrated Nitric acid (Rankem, 70%, 15.8M) and 50% concentrated Hydrochloric acid (Rankem, 36%, 11.65M). The sample weighing 1-15 gm was taken, the digestion mixture used was 10mL-20mL for the sample weight ranging 15-30gm, 30mL mixture was used for sample weight of 30-50gm and for the sample weight above 50gm, the acid mixture used was 50mL approximately.

2.3.2 Sample Preparation Of Fish

The fishes were thawed before analysis, The muscular tissues from dorsal, abdominal, and tail regions of each fish were chopped using a pair of scissors. The total body weight of each sample was taken for digestion process. The sample along with the digestion mixture was taken into the beaker and then heated at 110-120 °C on Bunsen burner until a clear solution was obtained. The 10mL sample mixture was digested for 15 minutes, 20mL sample mixture for 30 minutes, 30mL for 60 minutes and 50mL sample mixture for 90 minutes. The digested portions were filtered through normal filter paper.

2.4 Heavy Metal Analysis

After filtration the samples were determined for heavy metals using Energy Dispersive X-ray Fluorescence (EDXRF). The filtrate was poured into the sample cup. The cup was covered with X-ray film to prevent the instrument from rusting. The sample cups were placed in the sample changer system; the shutter was closed and then irradiated with an X-ray beam. The sample irradiation was controlled with a software provided with the system.

3. RESULT

The seawater fish samples were collected from the local fishermen from 5 states and 1 union territory in India which are Gujarat (33), Maharashtra (33), Goa (22), Karnataka (22), Kerala (28) and Daman(11). The mean of each metal concentration of five prawns, three Bombay duck and three pomfret were calculated from each location (district). The mean for the Kerala state also included three mackerel fish samples. The metal concentration of Arsenic, Mercury, Tin and Antimony in the fish samples were below the detection limit of the instrument and thus were not taken into consideration for the calculation.

The mean of concentration of each fish samples from the selected districts of the states were established through the spectral report from EDXRF, wherein the measurement conditions were as follows- Instrument: EDX-7000, Atmosphere: Air, Collimator: 10 (mm).

Standard regulatory limits of heavy metals in fish samples have been reported by many organizations. Table 1 gives the holistic representation of limits from all organizations.

Table 1: Standard Regulatory Limits (ppm/mg/kg) Of Heavy Metals In Fish Samples Reported In Literature

Sr. No.	Organization/ Country	Heavy Metals				References
		Cr	Zn	Cu	Pb	
1	FAO	-	30	30	0.5	FAO (1983)
2	FAO/WHO	-	40	30	0.5	FAO/WHO (1989)
3	BIS	-	5	-	0.05	BIS (2010)
4	European Commission	-	30	-	0.3	EC (2008;2014) ^[1]
5	Fssai	12	-	-	0.3	Fssai (2015)
6	Codex Stan	-	-	-	0.3	Codex Stan (1993-1995)
7	Turkey Guidelines	-	50	20	1	Dural et al. (2007)
8	England	-	50	20	2	MAFF (2000)

9	FDA for crustaceans	-	-	-	1.5	FDA (2001)
10	EU limits	-	-	10	0.1	EU (2001)
11	Saudi Arabia	-	-	-	2	SASO (1997)

Note: All tissue concentrations are in (gm) wet weight. Data that was not available in publications was not studied.

Heavy metal residues in the muscle tissue of different sea water fish samples were compared statistically using one-way ANOVA. The significance of the results was ascertained at $P < 0.05$.

The heavy metal concentrations from Daman, India were analyzed using T-test statistics ($P < 0.05$). The concentration of Cr, Zn, and Cu were in the safe levels. However, the lead concentration was found to be higher than the permissible standards. Therefore, it can be ascertained that fishes from Daman are not safe for consumption.

Table 2. Concentration Of Heavy Metals (in Ppm)

State	F. indicus (Indian prawn)			
	Chromium	Zinc	Copper	Lead
Gujarat	3.698	9.68	5.36	0.96
Maharashtra	1.35	1.22	1.08	1.50
Goa	70	7.93	1.33	0.103
Karnataka	5.1	1.59	ND	3.88
Kerala	2.26	1.13	2.52	ND
	H. neherus (Bombay duck)			
	Chromium	Zinc	Copper	Lead
Gujarat	1.09	7.24	0.193	4.73
Maharashtra	1.14	0.41	0.89	0.82
Goa	4.57	1.5	ND	8.898
Karnataka	6.57	1.65	8.72	8.72
Kerala	2.26	0.02	0.016	ND
	P. argentus (Silver pomfret)			
	Chromium	Zinc	Copper	Lead
Gujarat	3.02	1.21	0.133	1.02
Maharashtra	1.02	1.81	0.997	0.2
Goa	0.11	0.71	ND	1.87
Karnataka	2.65	0.74	ND	0.35
Kerala	0.596	1.3	ND	0.047
	R. kanagurta (Indian mackerel)			
	Chromium	Zinc	Copper	Lead
Kerala	0.72	4.19	1.73	2.04

ND-Not Detected

4. DISCUSSION

This study was undertaken to investigate heavy metal concentrations in edible parts (muscle) of four commercially important fish species from the five states of Western Coast of India because this region is highly polluted due to industrial effluents and human activities.

This investigation showed that the different fish species contained different mean concentrations of heavy metals in their muscles. Many researchers indicated that heavy metal bioaccumulation of fish is species-dependent.

Among fish species studied, the maximum mean concentrations of heavy metals were found in *P. argentus* and *H. nehereus* while the lowest concentrations were observed in *F. indicus* and *R. kanagurta*. In the research conducted so far, the species we have taken into consideration were not studied. Hence, the results of the previous related literature could not be used to compare the findings of this study.

It is well known that copper, manganese, nickel and zinc are essential elements, required by a wide variety of enzymes and having vital functions in all living organisms, but very high intakes can cause adverse health problems. On the other

hand, Cr and Pb have no biological role and hence they are harmful to living organisms even at considerably low concentrations. In this study, the overall average concentrations of metals were found to accumulate in the order of $Zn > Cr > Cu > Pb$, with concentrations of essential elements being higher than non-essential elements. These results may confirm the essential role of the former metals to fish species.

The higher levels of Cr may lead to irregular heartbeats, sleep disturbances, headaches, mood changes and allergic reactions. Excessive Zn intake is detrimental to human health and can cause poisoning, diarrhoea and fever. Cu plays a vital role in enzymatic processes and is necessary for the synthesis of haemoglobin. However, in high doses it will cause health problems. Lead is considered as a non-essential element in the human body. Chronic exposure can result in birth defects, mental retardation, autism, psychosis, allergies, paralysis, weight loss, dyslexia, hyperactivity, muscular weakness, kidney damage, brain damage, coma.

5. CONCLUSION

Western coast of India is the major consumer of seafood items, the assessment of heavy metals is an important safety measure for fish consumers. The heavy metal elucidation is a consequence of effluent discharges like increased industrialization, urbanization, anthropogenic activities, and illegal dumping and burning of wastes along the beaches.

The purpose of this investigation is to detect the concentrations of heavy metals i.e. Cr, Zn, Cu and Pb from various regions of Western coast of India. Results showed that the Arabian Sea is highly contaminated with the heavy metals accumulated in water as well as fish. In fishes it can be inferred that lead is the metal of concern as the concentration of lead in all states under study was more than the maximum permissible limits when compared with National and International Organizations.

Therefore, results suggested that lead is accumulating in the tissues of fish through contaminated seawater and thus, it might be passing on to higher trophic level. So, it is crucial to monitor the quality of water as well as concentration of heavy metals at regular intervals to establish a healthy seawater ecosystem and to prevent health problems for the consumers.

REFERENCES

1. A. Velusamy, P. Kumar, A. Ram and S. Chinnadurai. (2014). Bioaccumulation of heavy metals in commercially important marine fishes from Mumbai Harbor, India. *Marine Pollution Bulletin*, vol. 81, pp. 218-224.
2. A. Arulkumar, S. Paramasivan and R. Rajaram. (2017). Toxic heavy metals in commercially important food fishes collected from Palk Bay, Southeastern India. *Marine Pollution Bulletin*. 1-6.
3. H. Ali, E. Khan and M. A. Sajad. (2013). Phytoremediation of heavy metals- Concepts and applications. *Chemosphere*, vol. 91, no. 7, pp. 869-881.
4. M. A. Hashem, M. S. Nur-A-Tomal, N. R. Mondal, and M. A. Rahman. (2017). Hair burning and liming in tanneries is a source of pollution by arsenic, lead, zinc, manganese and iron. *Environmental Chemistry Letters*. vol. 15, no. 3, pp. 501-506, 2017.
5. F. U. Khan, A. U. Rahman, A. Jan, and M. Riaz. (2004). Toxic and trace metals (Pb, Cd, Zn, Cu, Mn, Ni, Co and Cr) in dust, dustfall/soil," *Journal of the Chemical Society of Pakistan*, vol. 26, no. 4, pp. 453-456.
6. E. Merian. (1984). Introduction on environmental chemistry and global cycles of chromium, nickel, cobalt beryllium, arsenic, cadmium and selenium, and their derivatives. *Toxicological & Environmental Chemistry*, vol. 8, no. 1, pp. 9-38, 1984.
7. S. Rezanian, S. M. Taib, M. F. Md Din, F. A. Dahalan, and H. Kamyab, "Comprehensive review on phytotechnology: heavy metals removal by diverse aquatic plants species from wastewater," *Journal of Hazardous Materials*, vol. 318, pp. 587-599, 201.
8. M. S. Afzal, A. Ashraf, and M. Nabeel. (2018). Characterization of industrial effluents and groundwater of Hattar industrial estate, Haripur. *Advances in Agriculture and Environmental Science: Open Access (AAEOA)*, vol. 1, no. 2, pp. 70-77.
9. G. Rajaei, B. Mansouri, H. Jahantigh, and A. H. Hamidian. (2012). Metal concentrations in the water of Chah nimeh reservoirs in Zabol, Iran. *Bulletin of Environmental Contamination and Toxicology*, vol. 89, no. 3, pp. 495-500.
10. H. Ali and E. Khan. (2018). Trophic transfer, bioaccumulation and biomagnification of non-essential hazardous heavy metals and metalloids in food chains/webs: concepts and implications for wildlife and human health. *Human and Ecological Risk Assessment: An International Journal*.
11. B. Mansouri, M. Ebrahimpour, and H. Babaei. sss(2012). Bioaccumulation and elimination of nickel in the organs of black fish (*Capoeta fusca*). *Toxicology and Industrial Health*. vol. 28, no. 4, pp. 361-368, 2012.
12. A. Khaled. (2009). Trace metals in fish of economic interest from the west of Alexandria, Egypt. *Chemistry and Ecology*. vol. 25, no. 4, pp. 229-246.
13. B. Kumar, K. Senthil Kumar, M. Priya, D. Mukhopadhyay, and R. Shah. (2010). Distribution, partitioning, bioaccumulation of trace elements in water, sediment and fish from sewage fed fish ponds in eastern Kolkata, India. *Toxicological & Environmental Chemistry*, vol. 92, no. 2, pp. 243-260.
14. FAO, 1983. Compilation of legal limits for hazardous substances in fish and fishery products. FAO Fish. Circ. vol. 464.
15. FAO/WHO, 1989. National Research Council Recommended Dietary Allowances. 10th ed. National Academy Press, Washington, DC, USA.
16. https://old.fssai.gov.in/Portals/0/Final_Regulations_2010.pdf
17. Commission Regulation (EC), 2008. No 629/2008 of 2 July 2008 amending Regulation (EC) No 1881/2006 setting maximum levels for certain contaminants in foodstuffs.
18. Commission Regulation (EU), 2014. No 488/2014 of 12 May 2014 Amending Regulation (EC) No 1881/2006 as regards maximum levels of cadmium in foodstuffs.
19. Safety, Food, Standards Authority of India (FSSAI), 2015. Proposes Standard Limits of Metal Contaminants in New Food Articles. <http://foodsafetyhelpline.com/2015/06/fssai-proposes-standard-limits-of-metal-contaminants-in-new-food-articles>
20. Codex General Standard for Contaminants and Toxins in Food and Feed, 193-1995a. http://www.fao.org/fileadmin/user_upload/agns/pdf/CXS_193e.pdf.
21. Dural, M., Goksu, M., Ozak, A. (2007). Investigation of heavy metal levels in economically important fish species captured from the Tuzla lagoon. *Food Chem.* 102, 415-421.
22. MAFF (Ministry of Agriculture, Fisheries and Food), 2000. Monitoring and surveillance of non-radioactive contaminants in the aquatic environment and activities regulating the disposal of wastes at sea, 1997. Aquatic Environment Monitoring Report no. 52. Center for Environment, Fisheries and Aquaculture Science, Lowestoft, UK.
23. FDA, 2001. Fish and fishery products hazards and controls guidance. Center for Food Safety and Applied Nutrition's, third ed. USA, US Food and Drug Administration.
24. EU, 2001. Commission Regulation as regards heavy metals, Directive, 2001/22/EC, No: 466.
25. SASO, 1997. Saudi Arabian Standards Organization. Maximum limits of contaminating metallic elements in foods. Riyadh, Saudi Arabia.