Int. J. Chem. Sci.: 13(1), 2015, 53-62
ISSN 0972-768X
www.sadgurupublications.com

DETERMINATION OF SOME HEAVY METALS IN FISH, WATER AND SEDIMENTS FROM BAY OF BENGAL

SIJI THOMAS* and J. ABBAS MOHAIDEEN[a]

Research Scholar, Sathyabama University, CHENNAI (T.N.) INDIA
[a]Maamallan Institute of Technology, CHENNAI (T.N.) INDIA

ABSTRACT

Concentrations of five heavy metals, arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb) and mercury (Hg) were determined in water, sediments and in marine species, the Indo-Pacific king mackerel popularly known as Spotted Seer fish (Scomberomorus Guttus). The samples were collected near the seashore of the Bay of Bengal from five different locations in North Tamilnadu Pulicat, Ennore, Marina, Mahabalipuram and Kalpakkam during the period September-November 2012. The maximum concentrations of heavy metals observed in fish were arsenic (0.382 mg/Kg-Pulicat), cadmium (0.441 mg/Kg-Ennore), chromium (0.711- mg/Kg-Marina), lead (0.673 mg/Kg-Marina), and mercury (0.08 mg/Kg-Kalpakkam). Maximum heavy metal concentrations in water are arsenic (0.03 mg/L-Kalpakkam), cadmium (0.022 mg/L-Ennore), chromium (0.046 mg/L-Ennore), lead (0.015 mg/L-Pulicat) and mercury (0.016 mg/L-Marina). Highest concentrations of arsenic (2.518 mg/Kg), cadmium (1.815 mg/Kg), chromium (3.082 mg/Kg) and lead (1.273 mg/Kg) in sediment was observed in samples collected from Ennore, while mercury was found in the highest concentration (0.668 mg/Kg) from Marina.

Key words: Heavy metals, Concentration, Atomic absorption spectrophotometer (AAS), Chennai, Spotted seer fish.

INTRODUCTION

Heavy metals occur naturally in the ecosystem with larger variations in the concentration. Eventhough some heavy metals form the part of our daily life activities, they are subjected to potent toxics, contaminating ecosystems. Some heavy metals like iron, cobalt, copper, manganese, molybdenum, and zinc are essential to the human body to maintain the metabolism, but its excessive levels can be damaging to the organism. Unlike other pollutants, such as petroleum hydrocarbons and wastes that invade the environment, heavy metals accumulate surreptitiously, eventually reaching toxic levels. The problems associated with the contamination by heavy metals was first highlighted in the industrially

*Author for correspondence; E-mail: sijithomas76@yahoo.com

advanced countries because of their large industrial spills, especially after accidents caused by the pollution of metals like mercury and cadmium. Iron, cobalt, copper, manganese, zinc, etc. are required by humans, but excessive levels can cause a grave damage to the organism[1]. It is the estuary of the Seine[2], an ecological association and a representative of the water police that bring their testimony to this worrying situation. However, there has been a growing awareness of the need for sound management of water resources[3] and in particular to control the dumping of waste in the environment. With industrialization and urban activities happening at a faster pace, the study of heavy metal contamination becomes more relevant in this regard. Heavy metals such as mercury, plutonium and lead are toxic[4] and their accumulation, over a period of time in the bodies of animals can cause serious illness. In natural aquatic ecosystems, metals are found at lower concentrations, typically in the nanogram or microgram. However, the presence of heavy metal contaminants[5], especially higher than natural filler metal concentrations, has become an issue of increasing concern. Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver and other vital organs.

The elevated heavy metal contamination rate can be attributed to rapid population growth, increased urbanization, expansion of industrial activities, exploration and exploitation of natural resource. Factors such as expansion of irrigation, spread of other modern agricultural practices and the absence of environmental regulations have also contributed to the increased contamination. Long-term exposure[6] may affect in the physical, muscular, and neurological degenerative processes. For the sound management and control of water pollution, a detailed study of the inputs, distribution and fate of contaminants, including heavy metals from a land flowing into aquatic ecosystems become relevant. It is particularly important to study the quantity and quality characteristics, and the routes they travel when they disperse their destiny and their effects. Many of our rivers, lakes, and oceans have been contaminated by pollutants. The natural sources such as volcanic activity, weathering of rocks and forest fires, also contribute in contamination. The contribution of volcanoes can be in the form of large, but sporadic emissions from explosive activity, or continuous emission of low volume, resulting in particular, from geothermal activity and magma degassing. Over the past decade[7,] sampling and analytical techniques applied to heavy metals have also improved considerably.

These advances, coupled with the realization of international intercalibration exercises brought together more reliable data. Efforts have been made in this document, to collect and analyze the available information on the presence of heavy metals in marine waters, in order to contribute to the sound development policies for managing water resources. Some of these pollutants are directly discharged by industrial plants and municipal sewage treatment plants, others come from polluted runoff in urban and agricultural areas, and some are the result of historical contamination. The decision to review the data on marine water comes from the need to adopt a holistic approach, which can inspire future strategies. The pollutants that enter the water cause undesirable changes, which affect the ecological balance of the environment. Among all the pollutants, accumulation of heavy metals is of global importance due to its adverse impact on human health. Fish is a valuable food item and source of protein. The concentration of heavy metals in aquatic organisms is higher than that present in water through the effect of bio concentration and bio magnification and eventually threaten the health of human by sea food consumption[8]. Fishes are widely used as bio indicators of marine pollution by metals[9]. Heavy metals cant enter the aquatic environment from both natural sources and anthropogenic sources. Their input can be the result either of spills made directly in marine ecosystems and freshwater, or an indirect path as in the case of dry and wet landfills and agricultural runoff. So the determination of heavy metal concentration in fishes is very important as far as human health is concerned. The objective of this study is to determine the concentration of some trace metals in Seer fish, water and sediments collected from Bay of Bengal in North Tamilnadu.

Literature survey

In the last twenty years, many studies have been devoted to metal toxicity[10]; on the basis of these results, several international and national organizations have developed criteria for water quality for aquatic life. Some heavy metals such as Zn, Cu, Mn and Fe[11] are essential to the growth and well-being of living organisms, including humans. It might nevertheless be expected to have toxic effects when organisms are exposed to concentration levels higher than they normally require. Other elements, such as Pb, Hg and Cd, are not essential for metabolic activities and exhibit toxic properties. The contamination of the aquatic environment[12] by metals from localized sources can have deleterious effects, on aquatic life within the area concerned. The published data so far on the effects of metals on aquatic organism indicate, that these adverse effects occur at higher than those typically found in environmental concentrations. The metals can be absorbed in an inorganic form or organic form. For some elements, such as arsenic and copper, inorganic form is the most toxic. For others, such as Hg, Pb and Sn, organic forms are the most toxic. The main routes of absorption of heavy metals by man are food, water and air.

One of the sources through which mercury and arsenic enters the human system is through consumption of fish. Several methods have been used to find the elements present as traces in environmental matrices. Data on dissolved metals in inland water bodies (lakes and rivers) and in marine and coastal areas were presented. As already mentioned, most studies on the levels and distribution of heavy metals focused on urban and industrial areas. The method[13] most commonly used for the determination of heavy metals is the atomic absorption spectrophotometry (AAS). It has the advantage of being rapid, sensitive, simple and can help analyze complex mixtures without prior separation. For some heavy metals, atomization using graphite furnace or cold vapour is done for better accuracy. In view of the importance of fish as a human diet, it is necessary that biological monitoring of the water and fish meant for consumption should be done regularly to ensure continuous safety of the seafood. Safe disposal of domestic sewage and industrial effluents should be practiced and where possible, recycled to avoid these metals and other contaminants from going into the environment. Laws enacted to protect our environment should be enforced.

EXPERIMENTAL

Methodology

Study area

The study area consists of 5 different locations (Pulicat, Ennore, Marina, Mahabalipuram and Kalpakkam) along the coast of Bay of Bengal in North Tamilnadu.

Pulicat (Pazhaverkadu) is a historic seashore town in Thiruvallur District, of Tamil Nadu. It is about 60 km north of Chennai and 3 km from Elavur, on the barrier island of Sriharikota, which separates Pulicat Lake from the Bay of Bengal.

Ennore is situated on a peninsula and is bounded by the Korttalaiyar River, Ennore creek and the Bay of Bengal. The creek separates Ennore from the Ennore Port. Ennore creek carries a high load of heavy metals. The treated effluents of the Madras Refinery Ltd., through the Buckingham canal and the Madras Fertilizers Ltd.[14-16], through the Red Hills surplus channel, reach the Ennore backwater[17].

Marina beach is an urban beach in the city of Chennai, India, along the Bay of Bengal, part of the Indian ocean. The beach runs from near Fort St. George in the north to Besant Nagar in the south, a distance of 13 Kms, making it the longest urban beach in the country and the world's second longest.

Mahabalipuram lies on the Coromandel Coast which faces the Bay of Bengal. It is around 60 Km south from the city of Chennai. It is an ancient historic town and was a bustling seaport during the time of Periplus (1st century CE) and Ptolemy (140 CE).

Kalpakkam is a small town in Tamil Nadu, situated on the Coromandel Coast 70 kilometers south of Chennai Nuclear facilities. The Madras Atomic Power Station is located at Kalpakkam. It is a comprehensive nuclear power production, fuel reprocessing, and waste treatment facility that includes plutonium fuel fabrication for fast breeder reactors (FBRs). It is also India's first fully indigenously constructed nuclear power station. It has two units of 220 MW capacity each[18-20].

Materials and methods

The water, sediment and spotted seer fish samples were collected during September – November 2012 from all the 5 locations within 500 meters from the seashore. The physico-chemical parameters like temperature, pH, salinity and dissolved oxygen are measured. The fish samples were washed thoroughly with distilled water to remove the sediments and debris. The length and weight of each sample were measured. Then the edible parts were separated and frozen at -20^o for the analysis. The fish samples were thawed, and then dried in a hot air oven at 60^{o}C. After removing the moisture content, the weight was taken again.

Digestion procedure for fish samples

15 g of fish sampled was taken and the ashing was done at 500^{o}C for 16 hrs. After cooling, 2 mL of nitric acid (HNO_3) and 10 mL of 1 molar hydrochloric acid (HCl) were added. After digestion, samples were filtered using Whatman filter paper No. 41, and the filtrate is made up to 25 mL with distilled water.

Digestion procedure for water samples

For As, Cd, Cr and Pb: 100 mL water sample was taken in a beaker and 0.5 mL nitric acid (HNO_3) and 5 mL hydrochloric acid (HCl) were added. Then it is kept in a hot plate for digestion. After digestion, it was made up to 10 mL. Heavy metal concentrations were determined by Atomic Absorption Spectrophotometer (AAS).

For Hg: 100 mL water sample was taken in a beaker and 5 mL sulphuric acid (H_2SO_4), 2.5 mL nitric acid (HNO_3) and 15 mL potassium permanganate ($KMnO_4$) were added. Then it was placed on a hot plate for 15 min for digestion. Then 8 mL potassium persulphate ($K_2S_2O_8$) was added and heated in 100^{0}C water bath for 2 hrs.

After cooling, 6 mL sodium chloride hydroxylamine sulphate was added. After decoloration, 5 mL stannous chloride ($SnCl_2$) was added.

Digestion procedure for sediment samples

2 g of dry sediment was taken in a digestion vessel, 10 mL of 1:1 nitric acid (HNO_3) was added and covered with a watch glass. It was heated at 95 ± 5^{o}C for 10-15 min without boiling. After cooling, 5 mL concentrated HNO_3 was added and refluxed for 30 mins. The step was repeated until no brown fumes come. The solution was allowed to evaporate to nearly 5 mL by heat without boiling. After the sample has cooled, 2 mL of water and 30% H_2O_2 were added. Heated until effervescence subsides and the vessel was cooled. 30% H_2O_2 was added in 1 mL aliquots with warm until the effervescence is minimal. The sample was covered with a ribbed watch glass and continued until the volume has been reduced to 5 mL. 10 mL HCl was added and refluxed for 15 min at 95 ± 5^{0}C. The digest was filtered through Whattman filter paper No. 41 and was collected in 100 mL standard flask. Heavy metal concentrations were determined by Atomic Absorption Spectrophotometer (AAS).

RESULTS AND DISCUSSION

Fish

The maximum and minimum concentrations of selected heavy metals (H. M.) in fish caught from different locations are given in Table 1 and the graphical representation of the maximum concentration in Fig. 1. It is observed that the maximum concentration of arsenic (0.382 mg/Kg), cadmium (0.441 mg/Kg) and lead (0.673 mg/Kg) are observed in fish samples collected from Pulicat, Ennore and Kalpakkam, respectively. The maximum concentrations of chromium (0.711 mg/Kg), and mercury (0.08 mg/Kg) are observed in samples collected from Marina.

Water

The concentrations of heavy metals in water collected from 5 different locations are given in Table 2 and the graphical representation in Fig. 2. The maximum concentration of arsenic (0.03 mg/L), lead (0.015 mg/L) and mercury (0.016 mg/L) are observed in water samples collected from Kalpakkam, Pulicat and Marina, respectively. Maximum concentration of cadmium (0.022 mg/L) and chromium (0.046 mg/L) are observed in samples collected from Ennore.

Sediment

The concentrations of heavy metals in sediments collected from 5 different locations are given in Table 2 and the graphical representation in Fig. 3.

Table 1: Concentrations (Minimum and maximum values) of H. M. in fish caught from different locations (mg/Kg)

Location	As		Cd		Cr		Pb		Hg	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Pulicat	BDL	0.382	0.083	0.417	0.036	0.518	BDL	0.368	BDL	0.064
Ennore	BDL	0.247	BDL	0.441	BDL	0.463	BDL	0.375	BDL	0.06
Marina	BDL	0.24	0.032	0.423	BDL	0.711	BDL	0.203	BDL	0.08
Mahabalipuram	BDL	0.334	BDL	0.417	BDL	0.465	BDL	0.286	BDL	0.062
Kalpakkam	BDL	0.358	BDL	0.308	BDL	0.415	0.071	0.673	BDL	0.072

Table 2: Concentration of H. M. in water and sediment collected from different locations

HM/ Location	Water (mg/L)					Sediment (mg/Kg)				
	As	Cd	Cr	Pb	Hg	As	Cd	Cr	Pb	Hg
Pulicat	0.02	0.021	0.032	0.015	0.008	1.548	0.831	1.387	1.083	0.286
Ennore	0.029	0.022	0.046	0.014	0.007	2.518	1.815	3.082	1.273	0.483
Marina	0.01	0.012	0.02	0.006	0.016	0.572	1.034	1.664	0.574	0.668
Mahabalipuram	0.01	0.011	0.022	0.012	0.012	0.926	0.872	0.423	0.952	0.386
Kalpakkam	0.03	0.015	0.02	0.013	0.007	1.351	1.147	0.736	0.904	0.242

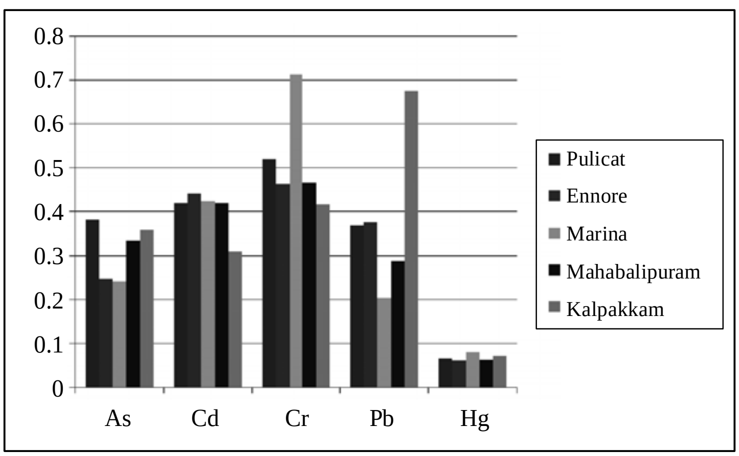

Fig. 1: Maximum concentration of H. M. in fish caught from different locations (mg/Kg)

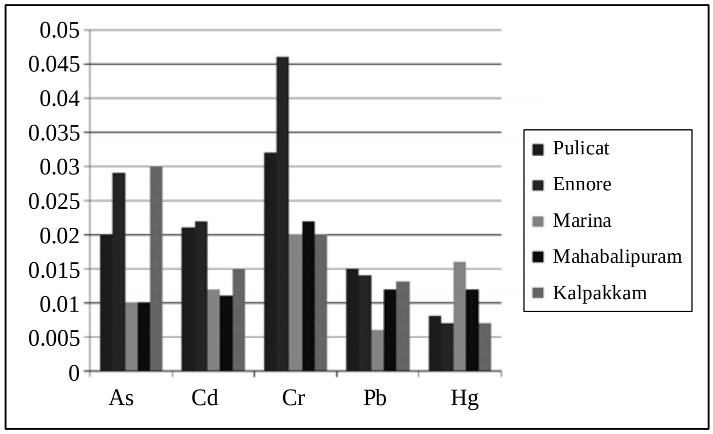

Fig. 2: Concentration of H. M. in water collected from different locations (mg/L)

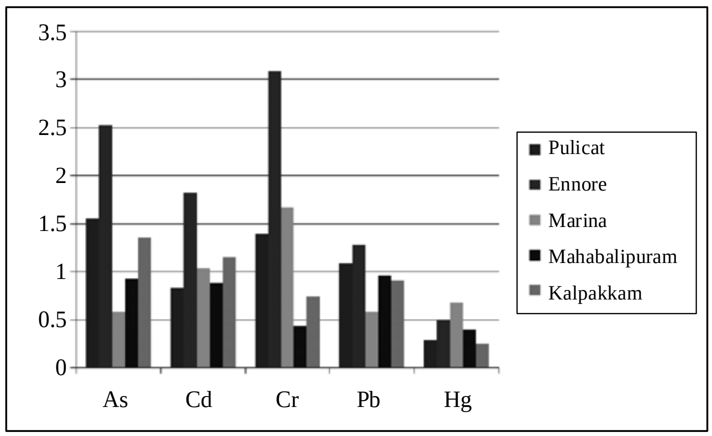

Fig. 3: Concentration of H. M. in sediment collected from different locations (mg/Kg)

The maximum concentration of arsenic (2.518 mg/Kg), cadmium (1.815 mg/Kg), chromium (3.082 mg/Kg) and lead (1.273 mg/Kg) is observed in sediment samples collected from Ennore. Maximum concentration of mercury (0. 668 mg/Kg) is observed in samples collected from Marina.

CONCLUSION

It is observed from this study, that the maximum concentrations of all the five heavy metals in the fish and water are observed in samples collected from different locations. But, the maximum concentrations of four heavy metals (arsenic, cadmium, chromium and lead) in sediment are observed in samples collected from Ennore. It may be due to the discharge of untreated effluent from various industries located near Ennore. As far as the importance of fish in the human diet is concerned, it is necessary that the biological monitoring of water and fish should be done periodically to ensure the safety of seafood consumption. The safe disposal of industrial effluents and domestic sewage should be practiced to avoid such contamination. Also, the laws enacted to protect the environment should be enforced effectively.

REFERENCES

1. S. Martin and W. Griswold, Human Health Effects of Heavy Metals, Center for Hazardous Substance Research, Kansas State University, 15 (2009).
2. O. Chabrerie, I. Poudevigne, F. Bureau, M. Vinceslas-Akpa, S. Nebbache, M. Aubert and D. Alard, Biodiversity and Ecosystem Functions in Wetlands: A Case Study in the Estuary of the Seine River, France, Estuaries, **24(6)**, 1088-1096 (2001).
3. C. Pahl-Wostl, Transitions Towards Adaptive Management of Water Facing Climate and Global Change, Water Res. Manag., **21(1)**, 49-62 (2007).
4. R. U. Ayres,. Toxic Heavy Metals: Materials Cycle Optimization, Proceedings of the National Academy of Sciences, **89(3)**, 815-820 (1992).
5. T. Duxbury, Ecological Aspects of Heavy Metal Responses in Microorganisms, In Advances in Microbial Ecology, Springer US (1985) pp. 185-235.
6. K. E. Giller, E. Witter and S. P. Mcgrath, Toxicity of Heavy Metals to Microorganisms and Microbial Processes in Agricultural Soils: A Review, Soil Biol. Biochem., **30(10)**, 1389-1414 (1998).
7. A. L. Martin-Del Pozzo, F. Aceves, R. Espinasa, A. Aguayo, S. Inguaggiato, P. Morales and E. Cienfuegos, Influence of Volcanic Activity on Spring Water Chemistry at Popocatepetl Volcano, Mexico. Chemical Geology, **190(1)**, 207-229 (2002).
8. I. S. Eneji, R. Sha'Ato and P. A. Annune, Bioaccumulation of Heavy Metals in Fish (Tilapia Zilli and Clarias Gariepinus) Organs from River Benue, North–Central Nigeria, Pakistan J. Analytical Environ. Chem., **12**, 25-31 (2011).
9. E. Padmini and M. Kavitha, Contaminant Induced Stress Impact on Biochemical Changes in Brain of Estuarine Grey Mullets, Poll. Res., **24(3)**, 647-651 (2005).
10. W. Wang, Literature Review on Duckweed Toxicity Testing, Environ. Res., **52(1)**, 7-22 (1990).
11. S. P. McGrath and C. H. Cunliffe, A Simplified Method for the Extraction of the Metals Fe, Zn, Cu, Ni, Cd, Pb, Cr, Co and Mn from Soils and Sewage Sludges, J. Sci. Food Agri., **36(9)**, 794-798 (1985).

12. J. P. Sumpter and S. Jobling, Vitellogenesis as a Biomarker for Estrogenic Contamination of the Aquatic Environment, Environ. Health Perspectives, 103 (Suppl 7), 173 (1995).

13. S. Vellaichamy and K. Palanivelu, Preconcentration and Separation of Copper, Nickel and Zinc in Aqueous Samples by Flame Atomic Absorption Spectrometry after Column Solid-Phase Extraction onto MWCNTs Impregnated with D2EHPA-TOPO Mixture, J. Hazard. Mater., **185(2)**, 1131-1139 (2011).

14. M. Jayaprakash, S. Srinivasalu, M. P. Jonathan and V. R. Mohan, A Baseline Study of Physico-chemical Parameters and Trace Metals in Waters of Ennore Creek, Chennai, India, Marine Pollution Bulletin, **50(5)**, 583-589 (2005).

15. E. Padmini and B. Geetha, A Comparative Seasonal Pollution Assessment Study on Ennore Estuary with Respect to Metal Accumulation in the Grey Mullet, Mugil Cephalus, Oceanological and Hydrobiological Studies, **36(4)**, 91-103 (2007).

16. J. S. I. Rajkumar, M. C. John Milton and T. Ambrose, Distribution of Heavy Metal Concentrations in Surface Waters from Ennore Estuary, Tamil Nadu, India, Int. J. Curr. Res., **3(3)**, 237-244 (2011).

17. V. Shanthi and N. Gajendran, The Impact of Water Pollution on the Socio-economic Status of the Stakeholders of Ennore Creek, Bay of Bengal (India): Part I, Indian J. Sci. Technol., **2(3)**, 66-79 (2009).

18. B . P. D. Batvari, S. Kamala Kannan, K. Shanthi, R. Krishnamoorthy, K. J. Lee and M. Jayaprakash, Heavy Metals in Two Fish Species (Carangoidel m Alabaricus and Belones Tronglurus) from Pulicat Lake, North of Chennai, South East Coast of India, Environ. Monitoring Assess., **145**, 167-175 (2008).

19. M. K. Ahmad, S. Islam, M. S. Rahman, M. R. Haque and M. M. Islam, Heavy Metals in Water, Sediment and Some Fishes of Buriganga River, Bangladesh, Int. J. Environ. Res., **4(2)**, 321-332 (2010).

20. R. K. V. Murthy and B. K. Rao, Survey of Meiofauna in the Gautami-Godavari Estuary, J. Mar. Biol. Assoc. India, **29**, 37-44 (1987).

Accepted : 27.11.2014