

Trace metal dynamics in fishes from the southwest coast of India

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Abstract

The concentration of Fe, Co, Ni, Cu, Zn, Cd and Pb in the muscle tissue of marine fishes like *Lates calcarifer*, *Nemipterus japonicus*, *Caranx melampygus*, *Rastrelliger kanagurta* and *Cyanoglossus macrostomus* was estimated from samples collected in the continental shelf waters off Kochi and Mangalore on southwest coast of India. Species-specific and spatially heterogeneous patterns of tissue metals loads were apparent within the pelagic and demersal fish species for the two regions. The concentration ranges of Fe (541.60 to 649.60 ppm), Ni (12.12 to 13.92 ppm) and Cu (3.09 to 3.62 ppm) were higher in the demersal species *Caranx melampygus*, whereas Co (9.10 to 11.80 ppm) and Zn (79.30 to 84.30 ppm) were higher in the pelagic species *Lates calcarifer* and Cd (4.35 to 6.38 ppm) were higher in the demersal species *Nemipterus japonicus*, possibly due to enhanced bioavailability of these metals from ecological processes associated with upwelling during the summer monsoon. The fish species showed a great capacity to accumulate metals, with highest bioaccumulation for the essential element iron and lowest bioaccumulation for the non-essential element lead. Among the demersal species, *Caranx melampygus* and *Nemipterus japonicus* had high concentration factors for the metals Fe (280268 to 322808), Ni (88252 to 96891), Cu (2351 to 2600) and Cd (29637 to 32404). In contrast, the pelagic species *Lates calcarifer* and *Rasterelliger kanagurta* had high concentration factors for the metals Zn (40812 to 46892), Co (280285 to 423037) and Pb (854 to 1404).

Key words southwest coast of India. fish. food. trace metals. bioaccumulation.

1. Introduction

Trace elements occur in minute concentrations in biological systems. They may exert beneficial or harmful effects on plant, animal and human life depending upon the concentration (Forstner and Whittman 1981). Metallic elements from natural and anthropogenic sources are environmentally ubiquitous, readily dissolved in and are transported by water. They are taken up by aquatic organisms due to bioaccumulation and biomagnification in the food chain as elements or their metabolites, thus causing a concern for the potential concentrations in animals at the top of the food chain (Papagiannis et al. 2004). Non-essential metals (e.g. Pb, Cd and Hg), are held to be the most dangerous, since continuous exposure of marine organisms to their low concentrations may result in bioaccumulation, and subsequent transfer to man through food web. Fishes are widely consumed in many parts of the world by humans due to high protein content, low saturated fat and sufficient omega fatty acids known to support good health (United States Environmental Protection Agency 2004). Since most harvested fishes are located high in aquatic food chains, they accumulate metals from direct absorption from water (minor) and through trophic transfers (major), exposing human beings through food. The accumulation of metals in fish depends on an equilibrium between absorption and depuration rates (Hadson 1988; Fowler et al. 1993; Mansour and Sidky 2002; Karadede et al. 2004), and thus may reflect localized bioavailability of these substances.

Metal pollution of the sea is less visible and direct than other types of marine pollution but its effects on marine ecosystems and humans can be intensive and extensive. In assessing environmental quality with respect to trace metals in seawater, the bioavailable fraction is of major importance, because toxicity depends on the amount absorbed by an organism. This bioavailable fraction cannot be detected directly by measuring metal concentrations in the soluble phase but can be assessed only by determining the amount of metal incorporated into organisms. Thus the abundance and bioavailability of metals in the marine environment, assessed as the bioaccumulation of metals by the tissues of marine organisms, is of great concern.

Fish have been widely used as bio-indicators of marine pollution by metals (Evans et al. 1993). Bioaccumulation of trace metals in fish is dependent on both the bioavailable concentration and species-specific physiological and ecological characteristics. Metal distribution between the different tissues within an organism depends on the mode of exposure and can serve as a pollution indicator (Maheswari et al. 2006). The bioaccumulation of metals is therefore an index of the pollution status of the relevant

water body and is a useful tool for studying the biological role of the metals present at elevated levels in fish. Due to their different roles in the bioaccumulation processes, the tissue flesh (muscle), liver and gills are those most frequently used for analysis. Flesh is preferred because it is a major target tissue for metal storage and is the main edible part of the fish. Therefore, its study constitutes a tool for environmental assessment and for determining public health risk (Reinfelder et al. 1998).

India is endowed with 2.02 million km² of Exclusive Economic Zone (EEZ) along with a coastline of 8129 km and 0.5 million km² continental shelf, occupying a very important strategic position in the north Indian Ocean and with a catchable annual fishery potential of 3.93 million tones. Among the Asian countries, India ranks second in aquaculture, is the fourth largest producer of fish and one of the top leading exporters of sea foods (Sampath 1998). The marine environment of India consists of unique ecosystems known for their aesthetic beauty and provides habitat for numerous biological species especially shrimps and fishes. Anthropogenic metal inputs have influenced the bioavailable metal supply in these aquatic ecosystems. Due to coastal upwelling, the coastal waters of the southwest coast of India are among the most productive regions in the world, supporting abundant invertebrate and fish populations, many of which are harvested as food. This area will presumably be even more exploited in the future as its potential productivity is realized by this developing country. Random reports on the metal concentrations in some species of fishes from the selected portions adjacent to the Indian Seas are available (Kureishy et al. 1981,1983; Singbal et al. 1982; Maheswari et al. 1997; Asha and Vijayalakshmy 1999; Maheswari et al. 2006), but spatial variations of trace metal bioaccumulation patterns in the pelagic and demersal fishes from the continental shelf waters of the southwest coast of India have been poorly investigated. In this study, we describe and discuss the concentration levels as well as bioaccumulation factors of trace metals in some pelagic and demersal fishes collected from southwest coastal waters of India at off Kochi and Mangalore.

2. Materials and methods

As part of Marine Research-Living Resource Programme (MRLR), trace metal concentrations in the muscle tissue of various fish species like *Lates calcarifer*, *Nemipterus japonicus*, *Caranx melampygus*, *Rastrelliger kanagurta* and *Cyanoglossus macrostomus* were studied. The selected species are economically important and are abundant in the study area. The investigation in the southwest coast of India (Cruise No.217 of Fishery and Oceanographic Research Vessel (FORV) Sagar Sampada, September-October, 2003), was based on the samples collected along the two transects, off Kochi

(Latitude. 10°N, Longitude. 75.60°E), and off Mangalore (Latitude.13°N, Longitude.73.92°E). Fish samples were collected using Expo bottom trawl nets and were subjected to close visual observation under a binocular microscope to ensure the absence of any foreign particle. Each fish sample was placed in a small nylon sieve and thoroughly rinsed with Milli-Q water for removing salts. Water adhering to the samples was removed by placing the sieve on good quality contaminant-free filter paper. Subsequently, dissected muscle of the fish samples was dried in an oven at 65°C and stored in a vacuum desiccator.

The dried muscle was powdered and aliquots of about 300mg were digested for 3 hours at 80°C with 300µl HNO₃ (65%, suprapure, Merck) in tightly closed 2 ml Eppendorf reaction tubes. The digests were diluted to 25ml with HCl (0.1N) and metals were analyzed using Flame Atomic Absorption Spectrophotometer (*PE A Analyst100*). The precision and accuracy of analysis was checked by replicate measurements (n = 5) of target metals in a standard reference material of marine biota sample (Defated Lobster Tomalley; TORT-2, Lobster Hepatopancreas, National Research Council, Canada). The values obtained for the reference material were in excellent agreement with the certified values (Table 1).

Bioaccumulation factors (concentration factors), were calculated for each metal and fish as the ratio of the metal concentration in the organism's body and its concentration in the ambient medium. All metal concentration in the muscle tissue of various fish species are reported in ppm dry weight, since dry weights rather than wet weights provide a more stable basis for comparison.

Pearson's correlation coefficients were used to examine relationships between the elements in the muscle of the fish species.

3. Results

3.1. Trace metals in fishes

Trace metal concentrations (ppm) in the muscle tissue of various fish species from the coastal waters off Kochi and Mangalore are presented in Tables 2 and 3. Even though each individual fish species collected from the two regions are of same length, weight and size, metal content in the muscle tissue of fishes off Kochi is higher than off Mangalore.

3.1.1. Iron

Fish is a major source for iron in adults and children. Iron deficiency causes anemia. Iron is the most abundant element examined in the muscle tissue of the various fishes. In the muscle, the metal iron (Tables 2 and 3), showed large intra-specific variation and ranged from 333.3 to 541.6 ppm and 438.3 to 649.6 ppm for the fishes collected at off Mangalore and off Kochi respectively. The maximum Fe content was observed in the species *Caranx melampygus* and minimum in the species *Nemipterus japonicus*. The iron content for all the species of fish is higher than the reported iron content 127.6 ppm for the muscle tissue of *Rasterelliger Kanagurta* from the near shore waters off Cochin (Maheswari et al. 1997).

3.1.2. Cobalt

Cobalt is beneficial for humans because it is a part of vitamin B₁₂. However, exposure to high levels of cobalt can result in lung and heart defects and dermatitis (Agency for Toxic Substances and Disease Registry 2004). Cobalt content (Tables 2 and 3), in the muscle tissue of different species of fish collected from off Mangalore ranged from 3.64 to 9.10 ppm, whereas that off Kochi ranged from 5.68 to 11.8 ppm respectively. The cobalt content in different species of the fish show wide fluctuations except in the two species *Rasterelliger kanagurta* and *Caranx melampygus*, which is found to be almost constant. The maximum cobalt content is observed in the species *Lates calcarifer*.

3.1.3. Nickel

Nickel concentration is generally low in the aquatic environment. Nickel concentrations (Tables 2 and 3), in the muscle tissue ranged from 6.06 to 12.12 ppm and 7.89 to 13.92 ppm for the fish species collected at off Mangalore and off Kochi respectively, with a maximum observed for the species *Caranx melampygus* and minimum for the species *Nemipterus japonicus*. The nickel content for all the species of fish is higher than the reported nickel content of 0.30 ppm for the muscle tissue of *Lates calcarifer* from the near shore waters off Mumbai (Asha and Vijyalakshmi 1999). The elevated nickel content in the various fish species might be attributed to the extensive upwelling occurring in the area, which brings nickel rich subsurface waters to the surface (Rejomon 2005).

3.1.4. Copper

Copper levels (Tables 2 and 3), in the muscle tissue ranged from 2.06 to 3.09 ppm and 2.66 to 3.62 ppm for the fish species collected at off Mangalore and off Kochi, with a maximum observed for the species

Caranx melampygus and a minimum for the species like *Lates calcarifer*, *Nemipterus japonicus*, *Rasterelliger kanagurta* and *Cyanoglossus macrostomus*. Copper, like zinc, is an essential element in fish and is thought to be strictly regulated in the muscle tissue, although the data presented here questions the rigidity of this statement (Phillips 1980). For instance a generally high mean copper concentration levels in fish axial muscle (> 1.0 ppm) have been reported for species taken from waters suspected of being relatively enriched in this element (by virtue of their proximity to the coast, major rivers, urban and industrial growth centers etc.) both in Indian Seas (Zingde et al. 1976) and overseas (Plasket and Potter 1979). Copper content obtained for the various species of fishes agrees well with the reported copper content of 2.01 ppm for the muscle tissue of *Rasterelliger kanagurta* from the off Cochin near shore waters (Maheswari et al. 1997). However, the values were higher than the reported copper content of 1.40 ppm for the muscle tissue of *Lates calcarifer* from the near shore waters off Mumbai (Asha and Vijyalakshmi 1999).

3.1.5. Zinc

Zinc is an essential element in our diet. Zinc is the next abundant element followed by iron in the different species of the fish examined. Zinc content (Tables 2 and 3), in the muscle tissue of different species of fish show wide fluctuations and ranged from 24.4 to 79.3 ppm and 37.4 to 84.3 ppm for the fishes collected at off Mangalore and off Kochi respectively, with a maximum concentration observed for the species *Lates calcarifer* and a minimum for the two species *Rasterelliger kanagurta* and *Cyanoglossus macrostomus*. It is generally believed that fish actively regulate zinc concentrations in their muscle tissue and as a result they do not reflect to changes in ambient levels of this element in their environment (Phillips 1980). Zinc content in the various fishes is higher than the reported zinc content of 21.7 ppm for the muscle tissue of *Lates Calcarifer* from the coastal waters off Mumbai (Asha and Vijyalakshmi 1999). Zinc concentrations for the various fish species investigated are higher than the reported value of 15.0 ppm for the muscle tissue of *Rasterelliger kanagurta* obtained from the off Cochin coastal waters (Maheswari et al. 1997). The occurrence of extensive upwelling in the area which carries zinc rich sub-surface waters to surface might explain why zinc concentrations are elevated in the muscle tissue of the various fishes in the present study (Rejomon 2005). Therefore, it is noteworthy that the generally higher ranges of zinc concentrations to those presented here have also been reported for species from relatively polluted areas of the world (Halcrow et al. 1973; Eustace 1974; Roth and Hornung 1977; Plaskett and Potter 1979), which in turn infers that fish body regulates zinc concentrations at an elevated level when exposed to high ambient zinc concentrations.

3.1.6. Cadmium

Cadmium is a non-essential toxic metal, and elevated concentrations are often a threat to marine biota. In humans, cadmium may accumulate from food chain magnification and may induce kidney dysfunction, skeletal damage and reproductive deficiencies (Commission of the European Communities 2001). Cadmium content (Tables 2 and 3), in the muscle tissue of various fishes was detectable and ranged from 1.25 to 4.35 ppm and 3.25 to 6.38 ppm for the fishes collected at off Mangalore and off Kochi respectively, with a maximum concentration observed for the species *Nemipterus japonicus* and a minimum observed for the species *Caranx melampygus*. Cadmium content in the fishes investigated is relatively higher than reported cadmium content of 0.06 ppm for the muscle tissue of *Lates Calcarifer* from the Thane creek off Mumbai waters (Asha and Vijyalakshmi 1999).

Indeed, the elevated cadmium concentrations in the fish muscle of various species highlight exposure of the fish to the metal. Even though the elevated cadmium levels in muscle of the various fish species is a matter of great concern, the source of this cadmium enrichment in fish from the continental shelf waters of the sea off the southwest coast of India is conjectural. Anthropogenic contamination cannot be ruled out, but is unlikely given in the whole oceanic water column conditions. Cadmium could originate from water, sediment and food. Cadmium concentrations in seawater are known to be enhanced in areas of upwelling and cadmium has been shown to maintain a one to one relationship with phosphorus in upwelled waters (Bruland 1983). This cadmium could be readily bioaccumulated in the lower portion of the food chain and bioconcentrated by trophic transfers to high levels in the fish. The apparent enrichment of cadmium in the muscle tissue of fishes is likely due to food chain transfer of high levels of cadmium brought into surface waters through the strong upwelling of nutrient-rich waters that was occurring during the summer monsoon (Rejomon 2005). Indeed, such a pathway has been implied to explain the elevated cadmium in fish (4.67 to 51.0 ppm) from the Mauretania (Romeo et al. 1999). The increase of cadmium bioavailability in the southwest coast of India by upwelled deep waters might be at the origin of an increase of cadmium concentrations in the marine biota on a local scale. Whatever the source, the local concentration of this toxic element in organisms is a cause of concern.

3.1.7. Lead

Lead belongs to the group of non-essential and toxic metals, which implies that it has no known function in biochemical processes. It is generally acknowledged that human activities influence the lead content of marine fishes. Lead is known to induce reduced cognitive development and intellectual performance

in children and increased blood pressure and cardiovascular disease in adults (Commission of the European Communities 2001). Lead is the least abundant element examined in the muscle tissue of the various fishes. Lead concentration levels (Tables 2 and 3), in the muscle tissue of various species of fishes was detectable and ranged from 0.23 to 0.34 ppm and 0.51 to 0.56 ppm respectively, with a maximum concentration observed for *Rasterelliger kanagurta* and a minimum concentration for *Nemipterus japonicus*. Lead content in the various fish species analysed is higher than the reported lead content of 0.04 ppm for the muscle tissue of *Lates calcarifer* from the shelf waters off Mumbai (Asha and Vijyalakshmi 1999).

4. Discussion

Metal levels in the muscle tissue of various fishes (Tables 2 and 3), average concentration of dissolved trace metals in the water column (Table 4; Rejomon 2005), and the corresponding bioaccumulation factors (Tables 5 and 6), were compared from the off Kochi and off Mangalore regions. As the different species collected from these two regions were more or less of same size, weight and length the effect of these factors were less apparent. The concentration of Fe, Co, Ni, Cu, Zn and Cd in the water and fishes were found to be higher in off Kochi than from off Mangalore region whereas the ranked order of the corresponding bioaccumulation factors showed an opposite trend. This suggests that regional wise trace metal absorption in the pelagic and demersal fishes from the prey (planktonic and benthic organisms), were not uniform in the continental shelf waters of the southwest coast of India. For instance, the ranges of concentration values for the metals like Fe-541.60 to 649.60 ppm, Ni-12.12 to 13.92 ppm and Cu-3.09 to 3.62 ppm is found to be higher in the demersal species - *Caranx melampygus*, Co-9.10 to 11.80 ppm and Zn-79.30 to 84.30 ppm is found to be higher in the pelagic species - *Lates calcarifer* whereas Cd-4.35 to 6.38 ppm is found to be higher in the demersal species - *Nemipterus japonicus*.

4.1. Factors controlling trace metals in fishes

4.1.1. Enhanced concentration of metals in the upwelled waters

During the summer monsoon period, at the sediment-water interface of the western continental shelf of India, high rates of benthic oxygen demand ($O_2 < 10\mu M$) result in a net flux of trace metals being mobilized out of the reducing sediments into the overlying water column, which subsequently mixes up into the surface waters by upwelling (Rejomon 2005). The enrichment of trace metals in the coastal waters from low-oxygenated waters and upwelling increase both the concentration of metals and the biological productivity that concentrates them. Increased ambient metals concentrations are absorbed by

the increased primary as well as secondary production (phytoplankton & zooplankton). This productivity increases growth and trophic transfers of both benthic and pelagic organisms, increasing biomagnification, though the benthic environment may see more enhancement than the pelagic, leading to different metals enrichment patterns in pelagic and benthic fishes.

4.1.2. Absorption and bioavailability of metals

The multifaceted effects of upwelling plays a prominent role in structuring of phytoplankton and zooplankton communities in the upper ocean and consequently affect to the recruitment of pelagic and demersal fishes due to higher food availability in the mixed layer (Madhupratap et al. 1990; Muraleedharan et al. 2007). Exposure to metals in the fish is mainly through their food and to a limited extent by direct absorption from the water column. Thus, the high concentrations of Fe, Co, Ni, Cu, Zn and Cd in the fishes from off Kochi than off Mangalore was likely to be due to high bioavailability of these elements arising in the fishes by a high metal absorption from the food chain as a consequence of high prey availability during the upwelling of the southwest monsoon.

The demersal species are expected to contain higher concentration of metals than the pelagic species, which may be related to the greater exposure to metal enriched bottom sediments and its interaction with benthic organisms (Campbell et al. 1988). Of the five species, only the *Caranx melampygus* and *Cyanoglossus macrostomus* are mainly bottom-dwelling in habitant (Lieske and Myers 1994; Sommer et al. 1996), and thus have direct contact between gills and the near bottom waters with an increased propensity for uptake of trace metals through the gills (Campbell et al. 1988). Thus, the higher concentrations of Fe, Ni and Cu noted in *Caranx melampygus* than *Cyanoglossus macrostomus* which mainly feeds on benthic invertebrates (Rainboth 1996), even though both one inhabits in a similar bottom habitant, suggesting a different accumulation strategies of the two species for these metals which may be due to variable bioavailability resulting from a variable competence for metal absorption from their feeding food habits at these ecological regimes. The cobalt enrichment in the benthic-pelagic and non-migratory species *Cyanoglossus macrostomus* (Menon 1984; Talwar and Jhingran 1991), when compared to other species like *Nemipterus japonicus*, *Caranx melampygus*, and *Rastrelliger kanagartha* may be due to the high bioavailability of this metal by absorption from prey in the pelagic zone than at the sediment-water interface (Nelson and Donkin 1985). However, the high enrichment of Fe, Ni and Cu in the demersal fish *Caranx melampygus* when compared with all other species is likely to be due to the resulting high bioavailability of these metals from extensive feeding on a variety of planktonic and

benthic prey (Lieske and Myers 1994; Smith 1995) by a high metabolism, highly mobile species that travels through out the water column from surface to bottom (Uchida and Uchiyama 1986; Sudekum et al. 1991). Likewise, the high Co and Zn enrichment found in the pelagic fish *Lates calcarifer* is likely to be due to high bioavailability resulting from the metal absorption by feeding on small fishes and crustaceans (Tait 1981). The high Cd enrichment noted in the demersal, non-migratory fish *Nemipterus japonicus* may be due to high bioavailability of this metal arising out by feeding on small fishes, crustaceans, mollusks (cephalopods), polychaets and echinoderms (Russell 1990; Kapoor et al. 2002). Indeed, cephalopods have been reported as a vector of the transfer of cadmium to top marine predators of the Atlantic Ocean (Bustamante et al. 1998).

The Fe, Co, Cu and Zn content in the pelagic fish *Rastrelliger kanagurta* which mainly feeds on phytoplankton (diatoms) and zooplankton (Collette 2001), appears to be not much significantly enriched when compared with other species. However the Ni and Cd content in the pelagic fish *Rastrelliger kanagurta* appears to be significantly enriched, when compared with other species like *Lates calcarifer*, *Nemipterus japonicus*, *Rastrelliger kanagurta* and *Cyanoglossus macrostomus* were possibly linked with the high bioavailability of these elements absorbing from the phytoplankton food web in the pelagic zone of the southwest coast of India.

4.2. Bioaccumulation of trace metals in fishes

The bioaccumulation of trace metals in fishes includes complex processes, which are controlled by exogenous and endogenous factors. Exogenous factors are reflected to environmental parameters such as metal bioavailability, temperature and alkalinity of ambient aquatic surroundings, whereas endogenous factors include species, age, size, physiological state and type of feeding of fish (Moiseenko and Kudryavtseva 2001).

The metal content in *Rasterelliger kanagurta*, *Cyanoglossus macrostomus* and *Nemipterus japonicus* followed an order Fe > Zn > Ni > Co > Cd > Cu > Pb, whereas for *Caranx melampygus* it followed another order Fe > Zn > Ni > Co > Cu > Cd > Pb. However the metal content for the species *Lates calcarifer* followed the order Fe > Zn > Co > Ni > Cd > Cu > Pb. Thus, for the metals like Fe, Zn and Pb all the species followed the same order whereas Ni, Co, Cu and Cd followed a different order. Metabolic requirements for specific trace metals in the individual species, or differences in diet preferences may account for the differences.

The bioaccumulation factor (concentration factor) is evaluated in relation to the concentration of the soluble metal in the seawater in which the different fish species inhabits. The muscle tissue as an active bioaccumulator organ for all the metals in several fish species since fish have a large mass of tissue in which the concentrations of most metals may be regulated (Reinfelder et al. 1998). In general the non-essential element lead is bioaccumulated least efficiently, while the essential element iron is bioaccumulated with a higher efficiency in the various fishes (Tables 5 and 6). Of the fishes examined, the *Caranx melampygus* species showed a higher range of bioaccumulation factors for Fe (280268-322808), Ni (88252-96891) and Cu (2351-2600). The species *Lates calcarifer* showed a higher range of bioaccumulation factors for Zn (40812-46892) and Co (280285-423037). The species *Nemipterus japonicus* and *Rasterelliger kanagurta* showed a higher range of bioaccumulation factors for Cd (29637-32404) and Pb (854-1404) with respect to the dissolved metal concentrations (soluble fractions) from the southwest coast of India. These values were quite comparable with the ranges of bioaccumulation factors reported for the metals like Fe (4.4×10^3 - 2.5×10^5), Ni (2.0×10 - 1.0×10^3), Cu (8.3×10^2 - 2.4×10^4), Zn (1.0×10^4 - 3.6×10^4), Cd (9.0×10^2 - 1.1×10^5) and Pb (3.0×10 - 1.7×10^3) in the fishes of Antarctic waters (Honda et al. 1987).

The concentration factor of the elements in the species *Lates calcarifer* and *Nemipterus japonicus* followed a same order Co > Fe > Ni > Zn > Cd > Cu > Pb, whereas for the species like *Rasterelliger kanagurta* it followed an order Fe > Co > Ni > Cd > Zn > Cu > Pb. Similarly the concentration factor for the elements in the species *Caranx melampygus* followed another order Fe > Co > Ni > Zn > Cd > Cu > Pb, whereas for *Cyanoglossus macrostomus* it is Co > Fe > Ni > Cd > Zn > Cu > Pb.

Bioaccumulation factors and metal content in different species of fish appreciably vary with the bioavailability of metals in seawater, as well as to inter-specific differences of fish species. Thus, the metal content and bioaccumulation factors in the species *Lates calcarifer* followed a same order for the elements like Cd, Cu and Pb except Fe, Co, Zn and Ni. Similarly for the species *Nemipterus japonicus* the metal content and bioaccumulation factors vary for the elements like Fe, Co, Ni and Zn but remained the same order for Cu, Cd and Pb. However the metal content and bioaccumulation factors for the elements like Cu and Pb followed the same order for the two fish species *Rasterelliger kanagurta* and *Cyanoglossus macrostomus* except Fe, Ni, Co, Zn and Cd. But for the species *Caranx melampygus* the metal content and bioaccumulation factors vary with element like Co, Cu, Zn and Cd except Fe, Ni and Pb. Thus bioaccumulation factors and metal content in different species of fish appreciably vary with most of the elements except lead. This points to the importance of bioavailability of metals in seawater

and prey, as well as to interspecific differences of fish species for potential trace metal accumulation. The differences in bioaccumulation factors of trace metals in different fish species might be attributed to different physiological states and inter-specific differences of the fish studied.

4.3. Inter-Elemental Relationships in fishes

Possible association among the elements (inter-element correlations) which were common in the muscle tissue of five fish species were assessed by means of Pearson's correlation coefficients (Table 7). The correlations between the different elements noted in the same tissue of fishes may result from the similar accumulation behaviour of trace elements in the fishes and their interactions (Kojadinovic et al. 2007). Thus, the significant correlations found among most of the elements may reflect a common source of occurrence and its subsequent accumulation to the muscle tissue of fishes. These inter-elemental relationships for essential and non-essential elements noted in the muscle tissue has been regarded as indicative of similar biogeochemical pathways for metal accumulation in fishes. In the present study, the essential element Fe showed a high correlation between Ni, Cu and Pb whereas Co showed a high correlation between the non-essential elements Cd and Pb. Cu showed a high correlation for the toxic element Pb. A high inter-elemental correlation between the toxic metals Cd and Pb is also noteworthy. Pourang et al. (2005) also noted a similar inter-elemental correlations between the essential and non-essential elements in the muscle tissue of fishes from the Persian Gulf waters.

4.4. Hazard level

Among the different metals analyzed, lead and cadmium are classified as toxic metals, which causes chemical hazards and therefore maximum residual levels have been prescribed for human consumption by various agencies of food standards (FAO 1983; EC 2001). Metal concentrations in the fish tissue during the present study (Table 8) given in dry weight can be converted into wet weight by dividing them by factors ranging from 4 to 6 (Khan et al. 1987; Parsons 1999; Romeo et al. 1999; California Environmental Protection Agency 2002; Lewis et al. 2002) for comparing with food standards. Levels of Zn, Cu, and Pb were well below thresholds of concern, whereas for Cd it was slightly above the acceptable limits for human consumption (i.e. 40.0, 30.0, 0.5 and 0.5 $\mu\text{g/g}$, wet weight for Zn, Cu, Cd and Pb respectively) set by the FAO (1983) food standards for fish. A comparison with the European food standards (EC 2001), for fish (Pb: 0.2-0.4 $\mu\text{g/g}$ and Cd: 0.05-0.10 $\mu\text{g/g}$, wet weight), also show that Pb and was lower than the guidelines for the edible part of the examined fish whereas for Cd it was slightly above the acceptable limits for human consumption. On the basis of the recommended daily

dietary allowances (RDA) for safe consumption of the fish muscle, the allowed intake was regulated at 50-350 mg of metal per 100 g serving of the muscle (National Research Council 1980). From the results of this report, the examined fishes were not associated with vulnerable metal content in their muscle and were safe within the limits for human consumption although Cd and Ni enrichment in the fish from the food web of the southwest coast of India is a matter of concern.

5. Conclusion

The origins of locally elevated metal levels in fishes along the southwest Indian coast likely reflects the associated food chain bioaccumulation of metals from the enhanced bioavailability of metals in upwelled waters during the summer monsoon. This study fills a gap by providing an information on the elevated trace metal concentrations in the pelagic and demersal fishes from upwelling zones of the southwest coast of India and therefore provides an essential baseline data with which future levels may be compared and evaluated.

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Table 1 Accuracy (given as recovery) and precision (given as standard error) of standard Lobster Hepatopancreas (TORT-2), analysed according to the procedure used for fish metal analysis

Metal	Metal Concentration (ppm \pm standard error)		Recovery (%)
	Certified	Measured	
Fe	105 \pm 13	106.5 \pm 3.13	101
Co	0.51 \pm 0.09	0.50 \pm 0.08	98
Ni	2.50 \pm 0.20	2.52 \pm 0.22	100
Cu	106 \pm 10	105 \pm 5.03	99
Zn	180 \pm 6	181.2 \pm 4.78	100
Cd	26.7 \pm 0.6	26.9 \pm 0.8	100
Pb	0.35 \pm 0.13	0.36 \pm 0.11	102

Table 2 Trace metal concentrations (ppm) in the muscle tissue of various fish species from the coastal waters off Kochi

Fish Species	Fe (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Cd (ppm)	Pb (ppm)
<i>Lates calcarifer</i>	604.75	11.80	9.88	2.66	84.30	5.79	0.53
<i>Nemipterus japonicus</i>	438.30	8.01	7.89	2.69	73.40	6.38	0.45
<i>Caranx melampygus</i>	649.60	5.68	13.92	3.62	76.00	3.25	0.51
<i>Rastrelliger kanagurta</i>	604.75	5.69	10.87	2.75	37.40	5.18	0.56
<i>Cyanoglossus macrostomus</i>	602.75	10.28	9.98	2.76	38.10	4.59	0.53

Table 3 Trace metal concentrations (ppm) in the muscle tissue of various fish species from the coastal waters off Mangalore

Fish Species	Fe (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Cd (ppm)	Pb (ppm)
<i>Lates calcarifer</i>	500.75	9.10	7.58	2.06	79.30	3.73	0.31
<i>Nemipterus japonicus</i>	333.30	5.46	6.06	2.06	61.00	4.35	0.23
<i>Caranx melampygus</i>	541.60	3.64	12.12	3.09	64.00	1.25	0.28
<i>Rastrelliger kanagurta</i>	500.75	3.64	9.09	2.06	24.40	3.11	0.34
<i>Cyanoglossus macrostomus</i>	500.75	7.28	7.58	2.06	26.40	2.49	0.32

Table 4 Average dissolved trace metal concentrations (ppb) in the water column of the coastal areas off Kochi and off Mangalore (Rejomon, 2005)

Trace metal	Fe (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	Cd (ppb)	Pb (ppb)
<i>Off Kochi</i>	2.318	0.042	0.144	1.392	2.066	0.197	0.400
<i>Off Mangalore</i>	1.678	0.022	0.137	1.314	1.691	0.147	0.400

Table 5 Bioaccumulation factors for trace metals in the various fish species from the coastal waters off Kochi

Fish Species	Fe	Co	Ni	Cu	Zn	Cd	Pb
<i>Lates calcarifer</i>	260918	280285	68770	1911	40812	29407	1312
<i>Nemipterus japonicus</i>	189104	190261	54919	1932	35535	32404	1122
<i>Caranx melampygus</i>	280268	134917	96891	2600	36794	16507	1277
<i>Rastrelliger kanagurta</i>	260918	135154	75661	1975	18107	26309	1404
<i>Cyanoglossus macrostomus</i>	260055	244181	69466	1982	18445	23313	1312

Table 6 Bioaccumulation factors for trace metals in the various fish species from the coastal waters off Mangalore

Fish Species	Fe	Co	Ni	Cu	Zn	Cd	Pb
<i>Lates calcarifer</i>	298460	423037	55194	1567	46892	25413	779
<i>Nemipterus japonicus</i>	198656	253822	44126	1567	36071	29637	575
<i>Caranx melampygus</i>	322808	169215	88252	2351	37847	8516	700
<i>Rastrelliger kanagurta</i>	298460	169215	66189	1567	14428	21188	854
<i>Cyanoglossus macrostomus</i>	298460	338430	55194	1567	15612	16964	787

Table 7 Pearson product-moment correlation coefficients between trace metals in the muscle tissue of fishes

Metal	Fe	Co	Ni	Cu	Zn	Cd	Pb
Fe	1.000						
Co	0.232*	1.000					
Ni	0.828**	-0.210*	1.000				
Cu	0.668**	-0.070	0.898**	1.000			
Zn	0.023	0.364*	0.135	0.368*	1.000		
Cd	-0.049	0.598**	-0.275*	-0.036	0.283*	1.000	
Pb	0.754**	0.462**	0.520**	0.564**	0.071	0.582**	1.000

Significant levels are indicated by * at $p < 0.05$ and ** at $p < 0.001$

Table 8 Comparison of trace metal concentrations in the muscle (Concentrations are in ppm, dry weight) of different fish species from the Indian coastal waters, Pakistan coastal waters Antarctic waters and maximum allowable concentrations of trace metals in sea food for human consumption (* Concentrations are in ppm, wet weight)

Geographical areas/Standards	Fish Species	Fe	Co	Ni	Cu	Zn	Cd	Pb	References
Southwest coast of India	<i>Lates calcarifer</i>	500.75-604.75	9.10-11.80	7.58- 9.88	2.06-2.66	79.30-84.30	3.73-5.79	0.31-0.53	Present study
Southwest coast of India	<i>Nemipterus japonicus</i>	333.30-438.30	5.46-8.01	6.06-7.89	2.06-2.69	61.00-73.40	4.35-6.38	0.23-0.45	Present study
Southwest coast of India	<i>Caranx melampygus</i>	541.60-649.60	3.64-5.68	12.12-13.92	3.09-3.62	64.00-76.00	1.25-3.25	0.28-0.51	Present study
Southwest coast of India	<i>Rastrelliger kanagurta</i>	500.75-604.75	3.64-5.69	9.09-10.87	2.06-2.75	24.40-37.40	3.11-5.18	0.34-0.56	Present study
Southwest coast of India	<i>Cyanoglossus macrostomus</i>	500.75-602.75	7.28-10.28	7.58-9.98	2.06-2.76	26.40-38.10	2.49-4.59	0.32-0.53	Present study
Off Cochin coastal waters	<i>Rastrelliger kanagurta</i>	127.59			2.01	14.99			Maheswari et al., 1997
Off Mumbai coastal waters	<i>Lates calcarifer</i>			0.30	1.4	21.7	0.06	0.04	Asha and Vijyalakshmi, 1999
Gulf of Cambay, India	Commercial fishes	94.35	0.24		2.37	38.24	0.23	1.09	Reddy et al., 2007
Pakistan coastal waters*	<i>Thunnus tonggol</i>	0.43			0.16	3.49	0.03	0.09	Jaffar and Ashraf, 1988
Pakistan coastal waters *	<i>Thunnus thynnus</i>	2.18			0.21	1.27	0.02	0.08	Jaffar and Ashraf, 1988
Antarctic waters*	Myctophid fishes	10.80-13.80		0.11-0.12	1.92-2.65	9.35-10.10	0.22-0.23	0.05-0.13	Honda et al., 1987
FAO*					30	40	0.5	0.5	FAO,1983
EC*							0.05-0.10	0.2-0.4	EC,2001