Heavy metal accumulation in commercial fish Species of Bheemili, Visakhapatnam, Andhra Pradesh, India

Chaitanya I, Gayatri Ch vrl and Byragi Reddy T

Abstract
Major sources of toxic metals arising from human activities are domestic and industrial wastewaters and their associated solid wastes. Metals like, arsenic, chromium, mercury, nickel and lead exhibit toxicity at certain levels. Marine fishes exposed to heavy metals have been consumed as seafoods and, hence are a connecting pathway for the transfer of toxic heavy metals into human beings. The temporal distribution of heavy metals in three fish species of Visakhapatnam, east coast of India, determined using flame atomic absorption spectrophotometer. The concentration of heavy metals viz., Cr, Mn, Co, Cd and Pb varied seasonally. The overall mean concentration of metal magnification in pre-monsoon season is Mn>Co>Cr>Pb>Cd, whereas in monsoon season is Mn>Co>Cr>Cd>Pb, while in post-monsoon season, the order of magnification is Mn>Co>Cd>Pb>Cr respectively. This paper makes an attempt to identify the toxicity levels in the three fishes viz., Pampus argenteus, Rastrelliger kanagurta and Upeneus vittatus in the Visakhapatnam coast which is one of the most vulnerable systems for pollution of different types.

Keywords: Heavy metals, bio-accumulation, Bheemili

1. Introduction
Fish constitutes a very important component of the diet for many people and often gives the much needed nutrient that is not provided by the cereal-based diets [1]. Nutrition has been mentioned as one of the most important reasons why consumers are attracted to seafood [2]. As the demand for fish is continuously increasing, making the required protein available to the existing population is a challenge. With an increasing population, the fishing pressure is also increasing in the capture sector [3]. Seafood are an significant fraction of a healthy diet where they have high quality protein and other indispensable nutrients can be low in saturated fatty acids and may contain omega-3 fatty acids [4]. Seafood, especially finfish provides a major source of essential nutrients such as proteins, vitamins, fats and minerals which help in the maintenance of life to man [3]. Basically, tuna meat is considered highly nutritive owing to its content of essential amino acids, protein and fat [5].

India has a long coastal line of more than 8000 km with an associated continental shelf of 0.5 million km2 and an exclusive economic zone of 2.02 million km2. The coastal zone of the country with its wetlands, lagoons, mangroves, sea-grass beds, coral reefs, and shallow bays, creeks, and estuaries is rich in natural sources. More than 300 million people living in the coastal zone of India are considered to generate 1.11 × 1010 m3 of sewage annually; a considerable fraction enters the coastal waters [6]. Marine organisms are exposed to trace elements that are present in their diet and dissolved in seawater. Many marine organisms have the ability to control and maintain internal metal (essential to health) concentrations even when being exposed to significant variations in the chemical composition of the surrounding environment. This double exposure results in element accumulation in their different tissues whether or not these elements are essential to the metabolism [7].

Marine pollution is a global environmental problem. Different human activities on land, water and air contribute to the contamination of seawater, sediments and organisms with potentially toxic substances. Contaminants can be natural substances or artificially produced compounds. After discharge into the sea, contaminants can stay in the water in dissolved form or they can be removed from the water column through sedimentation to the bottom sediments [8]. Contamination with metals on local, regional and global scales, have been intensively studied in recent years, due to the fact that metals are persistent, toxic, tend to
bioaccumulate, and they pose a risk to humans and ecosystems \[7,9\]. Pollution of the aquatic environment and its effects on the living resources, especially the fishery resources, has assumed considerable interest as well as importance in the recent times \[4\]. Trace metals in aquatic systems are distributed over different compartments, such as the dissolved state, colloidal state, and particulate matter (abiotic or biotic), in planktonic and higher organisms. Studies on trace metal distributions and its recycling processes within zooplankton from the Arabian Sea and Bay of Bengal are poorly investigated other than a few reports \[10,11\]. Trace metals in biota natural sources can be used to account for a background exposure, which may be increased by anthropogenic inputs. In assessing environmental quality with respect to heavy metals in seawater, the bioavailable fraction is of major importance, because toxicity depends on the amount absorbed by an organism, itself based on bioavailable exposure concentration. 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. Information about trace metal partitioning and distribution in marine organisms has important implications in understanding both elemental bioavailability and the time scales of cycling \[12\]. Heavy metals are intrinsic, natural constituents of our environment. They are generally present in small amounts in natural aquatic environments. Apart from the natural sources, several anthropogenic ones also contribute to metal concentrations in the environment. In recent times, industrial activities have raised natural concentrations causing serious environmental problems. Marine coastal ecosystems could therefore be endangered by pollutants, such as heavy metals, pesticides and antifoulants that could be easily detected in the water column or in the sediment of harbours and estuaries \[13,14\]. Water and sediment play salient role in regulating the components of the ecosystem. In which, the organisms in the sediments are mostly involved in the mineralization and metabolization of many pollutants. Various studies in the coastal sediments were carried out \[15\]. Toxic elements can be very harmful even at low concentration if consumed over a long period of time. With ever increasing human population and associated rapid industrialization, the problem of environmental pollution have become more critical. Industrial effluents, agricultural run off, transport, burning of fossil fuels, animal and human excretion, geological weathering and domestic waste contribute to the heavy metal pollution of aquatic bodies \[16\].

2. Material and methods

*Pampus argenteus*, *Rastrelliger kanagurta* and *Upeneus vittatus* samples were collected in fresh condition bimonthly from fishing harbors of three regions viz., Visakhapatnam, pudimadaka and Bheemili, east coast of India during the period of July 2015 to June 2016. Samples were soak with marine water and packed in a polyethylene covers to stored in a frozen condition at -20 °C for further analysis. The samples were thawed and dissected on a clean polypropylene board, five grams of each sample was weighed followed by 7ml of pure nitric acid and 3 ml of hydrogen peroxide and kept overnight to dilute the sample. Sample digestion was done by using microwave digester. The digested sample was made up to 100ml with double distilled water and analysed by using Flame Atomic Absorption Spectrophotometer following the AOAC method \[17\]. All of the chemicals used in this work were high purity GR grade. The data generated from the results of the present study were presented as mean ± standard error (SE) and statistically analyzed by one-way ANOVA using MS-Excel to determine the variations among the mean concentrations of heavy metals of three fish species during different seasons at 1% or 5% significant level.

3. Results

During pre-monsoon in *Pampus argenteus* the mean metal concentrations recorded for the fish samples was Cr (2.16 ppm), Mn (15.32 ppm), Co (5.74 ppm), Cd (0.13 ppm) and Pb (1.28 ppm) respectively given in Table 1, Figure 1. The sequence of metal concentrations observed was Mn>Co>Cd>Pb>Cr. During monsoon the mean metal content of the samples was Cr (0.24 ppm), Mn (5.18 ppm), Co (1.71 ppm), Cd (1.30 ppm), Pb (0.49 ppm) respectively (Table 2, Figure 2). The metal sequence followed Mn>Co>Cd>Pb>Cr. During post – monsoon the mean heavy metal concentrations recorded for the samples was Cr (1.56ppm), Mn (6.34 ppm), Co (1.68 ppm), Cd (0.53 ppm) and Pb (1.12 ppm). The sequence of metals observed was Mn>Co>Cd>Pb>Cr (Table 3, Figure 3). During pre-monsoon in the fish species Rastrelliger kanagurta the mean metal concentrations were Cr (1.16 ppm), Mn (19.61 ppm), Co (4.19 ppm), Cd (0.55 ppm) and Pb (1.07 ppm) respectively shown in Table 1 and Figure 2. The sequence of metal accumulations was Mn>Co>Cd>Pb>Cr (Table 1, Figure 1). During monsoon the mean metal content in the samples analyzed was Cr (1.06 ppm), Mn (3.46 ppm), Co (1.16ppm), Cd (0.73 ppm) and Pb (0.51 ppm) as given in Table 1 and Figure 1. The sequence of metal levels was Mn>Co>Cr>Cd>Pb respectively (Table 2, Figure 2). In post – monsoon the mean metal levels in the fish species analyzed was Cr (0.15 ppm), Mn (0.15 ppm), Mn (13.61 ppm), Co (3.53 ppm), Cd (1.03 ppm) and Pb (0.82 ppm) as shown in (Table 3, Figure 3). The overall sequence of metals observed was Mn>Co>Cd>Pb>Cr respectively.

<table>
<thead>
<tr>
<th>Table 1: Metal accumulation in pre-monsoon season</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fish species</strong></td>
</tr>
<tr>
<td><em>Pampus argenteus</em></td>
</tr>
<tr>
<td>Rastrelliger kanagurta</td>
</tr>
<tr>
<td>Upenes vittatus</td>
</tr>
</tbody>
</table>

Note: Values are mean±SE, n=3
Fig 1: Metal accumulation in pre-monsoon season

Table 2: Metal accumulation in monsoon season

<table>
<thead>
<tr>
<th>Fish species</th>
<th>Cr</th>
<th>Mn</th>
<th>Co</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Pampus argenteus</em></td>
<td>0.24±0.08</td>
<td>5.18±0.06</td>
<td>1.71±0.21</td>
<td>1.30±0.12</td>
<td>0.49±0.06</td>
</tr>
<tr>
<td><em>Rastrelliger kanagurta</em></td>
<td>1.06±0.18</td>
<td>3.46±0.33</td>
<td>1.16±0.09</td>
<td>0.73±0.05</td>
<td>0.51±0.08</td>
</tr>
<tr>
<td><em>Upenes vittatus</em></td>
<td>1.05±0.18</td>
<td>1.93±0.45</td>
<td>0.31±0.02</td>
<td>0.05±0.05</td>
<td>0.14±0.13</td>
</tr>
</tbody>
</table>

Note: Values are mean±SE, n=3

Fig 2: Metal accumulation in monsoon season

Table 3: Metal accumulation in post-monsoon season

<table>
<thead>
<tr>
<th>Fish species</th>
<th>Cr</th>
<th>Mn</th>
<th>Co</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Pampus argenteus</em></td>
<td>1.56±0.28</td>
<td>6.34±0.13</td>
<td>1.68±0.40</td>
<td>0.53±0.06</td>
<td>1.12±0.61</td>
</tr>
<tr>
<td><em>Rastrelliger kanagurta</em></td>
<td>0.15±0.15</td>
<td>13.61±0.82</td>
<td>3.53±0.43</td>
<td>1.03±0.46</td>
<td>0.82±0.19</td>
</tr>
<tr>
<td><em>Upenes vittatus</em></td>
<td>1.03±0.91</td>
<td>9.37±0.48</td>
<td>2.49±0.67</td>
<td>0.98±0.32</td>
<td>1.17±0.81</td>
</tr>
</tbody>
</table>

Note: Values are mean±SE, n=3

Fig 3: Metal accumulation in post-monsoon season

In fish species *Upenes vittatus* during pre-monsoon the mean metal content in the samples analyzed was Cr (0.48 ppm), Mn (10.01 ppm), Co (2.02 ppm), Cd (0.05 ppm) and Pb (0.82 ppm) respectively and presented in Table 1, Figure 1. While the sequence of metal concentrations observed was Mn>Co>Pb>Cr>Cd. In monsoon the mean metal levels recorded for the samples was Cr (1.05 ppm), Mn (1.93 ppm), Co (0.31 ppm), Cd (0.05 ppm) and Pb (0.14 ppm) respectively. The metals followed a sequence of Mn>Cr>Co>Pb>Cd which has shown in Table 2, Figure 2. In post-monsoon the mean metal content in the fish samples was Cr (1.03 ppm), Mn (9.37 ppm), Co (2.49 ppm), Cd (0.98 ppm) and Pb (1.17 ppm) respectively. The sequence of metal levels observed was Mn>Co>Pb>Cr>Cd (Table 3, Figure 3).

4. Discussion

Environmental pollution caused by residues of run offs from agricultural areas and other inorganic pollutants has received great importance in developed countries. But in this region research on these aspects has only recently begun and practically very little information on the impact of chemical residues on living aquatic resources of the sea and coastal water is available. Researchers have showed that fishes accumulate heavy metals in their tissues and their concentrations depend on many factors such as concentration and duration of exposure, salinity, temperature and hardness of water and metabolic rate of organisms. According to Lithuanian Standards of Hygiene, the Maximum Tolerable Limit of lead in fish meat is 0.4mg/kg which is same as the value adopted by the European Commission for lead in marine fish muscle while FAO set a limit of 0.5mg/kg. Seafood is good source of dietary copper, which is an essential element available to humans.

Heavy metal like chromium was accumulated either directly from the surrounding water or by ingestion of food in environment. Chromium may be present in domestic waste from various synthetic materials. Through waste incineration it may spread to the environment when protection is insufficient. Manganese is the second most profuse cation in sea water next to sodium. It does not appear to take part in the biological cycle; thereby it behaves as a conventional element in sea water. Therefore, its ratio to chlorinity is more or less constant except in nearshore areas where fresh water and other industrial activities modify the relationship between these two ions. The present study values were comparable with Solai. Cobalt is a biologically important metal although only few cobalt metalloproteins are known. The average value of cobalt was 5.07 μg/l in Visakhapatnam region, 6.37 μg/l was found in rushi konda region and 5.27 μg/l was observed in Bheemili region respectively. The present study values were less than. Cadmium is highly toxic, it is associated with nephrotoxic effects particularly long term exposure may cause bone damage. The threshold concentration of cadmium in fish muscles design for human consumption set by the European Commission is 0.1mg/gw, the guideline limit set for Cd by FAO is 0.05mg/kg for fish. According to Jakimska et al., it is the diet of an animal that dictates its accumulation of metals in its tissue. The more we consume fish that shows the type of results above the more exposed to bioaccumulation and its consequences. Lead is considered as a non-essential and toxic metal which also

4. Discussion

Environmental pollution caused by residues of run offs from agricultural areas and other inorganic pollutants has received great importance in developed countries. But in this region research on these aspects has only recently begun and practically very little information on the impact of chemical residues on living aquatic resources of the sea and coastal water is available. Researchers have showed that fishes accumulate heavy metals in their tissues and their concentrations depend on many factors such as concentration and duration of exposure, salinity, temperature and hardness of water and metabolic rate of organisms. According to Lithuanian Standards of Hygiene, the Maximum Tolerable Limit of lead in fish meat is 0.4mg/kg which is same as the value adopted by the European Commission for lead in marine fish muscle while FAO set a limit of 0.5mg/kg. Seafood is good source of dietary copper, which is an essential element available to humans.

Heavy metal like chromium was accumulated either directly from the surrounding water or by ingestion of food in environment. Chromium may be present in domestic waste from various synthetic materials. Through waste incineration it may spread to the environment when protection is insufficient. Manganese is the second most profuse cation in sea water next to sodium. It does not appear to take part in the biological cycle; thereby it behaves as a conventional element in sea water. Therefore, its ratio to chlorinity is more or less constant except in nearshore areas where fresh water and other industrial activities modify the relationship between these two ions. The present study values were comparable with Solai. Cobalt is a biologically important metal although only few cobalt metalloproteins are known. The average value of cobalt was 5.07 μg/l in Visakhapatnam region, 6.37 μg/l was found in rushi konda region and 5.27 μg/l was observed in Bheemili region respectively. The present study values were less than. Cadmium is highly toxic, it is associated with nephrotoxic effects particularly long term exposure may cause bone damage. The threshold concentration of cadmium in fish muscles design for human consumption set by the European Commission is 0.1mg/gw, the guideline limit set for Cd by FAO is 0.05mg/kg for fish. According to Jakimska et al., it is the diet of an animal that dictates its accumulation of metals in its tissue. The more we consume fish that shows the type of results above the more exposed to bioaccumulation and its consequences. Lead is considered as a non-essential and toxic metal which also
implies that it has no known function in biochemical processes. Lead induces reduced cognitive development and intellectual performance in children and increased blood pressure and cardiovascular disease in adults [19]. Mustafa et al. [27] have found that the levels of Pb in marine fish ranged from 0.33 to 0.86 mg/kg in Trigla gurnardus and Dracunculus vulgaris respectively. Another marine study reveals that the Pb contents were in the range between 0.33 to 0.93 mg/kg in muscles tissues of fish in Black and Aegean seas [28].

As found in the present study, the metal concentrations in the three fishes were in the permissible limits, with the only exception in the case of manganese which is beyond the permissible limits in the edible part of given three fishes. Thus it is essential that the pollution levels in the Bheemili region need to be studied in more detail, to understand the pollution accumulated in different strata of the biota and also the pollution impact on the species breeding in the Bheemili waters.

5. Conclusion
This study was carried out to provide information on seasonal wise heavy metal accumulation of three fish samples from Bheemili region. All results were below the limits of fish for human consumption proposed by International standards of fish. In the present study the elevated concentrations of these heavy metals are apparently indicative of sea water pollution by toxicants, leading to bioaccumulation in aquatic organisms, which may surpass to humans causing ailments and deficiencies. Hence intensive studies to control and maintain the sea parameters for sustainability of the valuable aquatic resources are in need.

6. References
5. Chinnamma G. Biochemical differences between the red and white meat of tuna and changes in quality during freezing and storage. Fish Technol. 1975; XII(1):70-74.