Seasonal variation in the distribution of heavy metals in surface waters from Pulicat lake, Tamil Nadu, India

Dhinamala K, Pushpalatha M, Samuel T, Raveen R

Abstract
Seasonal variation in the distribution of heavy metals in surface waters of Pulicat lake, Tamil Nadu, India was assessed from January 2011 to December 2012. Variation of heavy metals was maximum during summer and minimum during monsoon. The heavy metals investigated were nickel, copper, zinc, chromium, cadmium, mercury, lead and iron. The data revealed that nickel and lead were below the permissible limits, copper, zinc, chromium and mercury were moderately above the permissible limits whereas cadmium concentration was found to be high.

Keywords: Heavy metals, pollution, estuary, Pulicat lake.

1. Introduction
Pollution of the marine environment by heavy metals has become a national and international problem over the years [1]. There are 35 metals that concern us because of occupational or residential exposure. Twenty three of these are the heavy elements or heavy metals [2]. If unrecognized or inappropriately treated, toxicity due to toxic heavy metals can result in significant illness and reduced quality of life [3]. The seriousness of heavy metal contamination was further compounded by the fact that they are generally water-soluble, non-degradable, vigorous oxidizing agents and are strongly bonded to many biochemicals inhibiting their functions. Most metallic elements occur naturally in estuarine environments, and are classified as pollutants only when added by man in quantities sufficient to produce deleterious effects [1]. High quantities of heavy metals are being added to estuarine and coastal regions from agricultural and industrial wastes, hospitals, domestic sewage and from the polluted atmosphere every day [4].

The hydrology of the Pulicat lake is influenced by local climate, the regime of the inflowing rivers, the Buckingham canal that enters the lake, in addition to the effect of the neritic waters of the Bay of Bengal. Pulicat lake harbours many euryhaline species and serves as a nursery for several marine species and a very few secondary freshwater fishes [5]. The industries located around Pulicat lake are discharging effluents indirectly into the lake and the point sources of pollution mainly comes from North Chennai thermal power plant, Ennore port activities, Manali petrochemical industries, other nearby industries and untreated urban wastes from Chennai metropolitan city [6-8]. In view of the above, the present study was undertaken to assess the heavy metal parameters in Pulicat lake, Tamil Nadu, India.

2. Materials and methods
2.1. Study area
Pulicat lake (latitude 13° 24’ and 13° 43’ N and longitude 80° 03’ and 80° 18’ E) is the second largest coastal lake in India located 40 km north of Chennai city, Tamil Nadu, India. The lake is about 60 km in length and 0.2 to 17.5 km in breadth and separated from the Bay of Bengal by an inland split called the Srikarikota Island (Fig. 1). The main source of freshwater is land runoff through three small seasonal rivers that open into the lake viz., Arani, Kalangi and Swarnamukhi. The Buckingham canal, which runs parallel to the Bay of Bengal, brings in the industrial and domestic wastes to the lake and eventually to the Bay of Bengal [8].

2.2. Collection of samples and analysis
Water samples were collected from four stations in the Pulicat lake (Fig. 1) which are suspected sites of possible local and point source pollution. The water samples were collected
undisturbed from the surface water in the study area as the depth of water was very less (< 5m) during early morning throughout the study period. Samples were collected from January 2011 to December 2012 on a monthly basis to study the effects of seasonal variation. The water samples were collected in two litre polyethylene cans which were previously cleaned, rinsed and washed with deionized water and then rinsed with samples several times. The estimation of heavy metal concentration in the collected water samples was done based on the liquid–liquid extraction procedure of Mentasti et al. [9] using Perkin Elmer ICP-MS ELAN DRC equipment. The heavy metals analysed were nickel, copper, zinc, chromium, cadmium, mercury, lead and iron.

3. Results and discussion
The values for heavy metals present in the surface waters of Pulicat lake during the study period from January 2011 to December 2012 are presented in Tables 1 and 2.

3.1. Nickel
In 2011 the amount of nickel varied between 0.003 and 0.009mg/L among the four seasons and in 2012 it varied between 0.017 and 0.046mg/L. High values of nickel in water were recorded during summer and low values during monsoon in both the years. In contrast to the soluble nickel salts, metallic nickel, nickel sulphides, and nickel oxides are poorly water-soluble. Drinking water and food are the main sources of exposure for the general population to nickel. There is a little evidence that nickel compounds accumulate in the food chain. Nickel is a not a cumulative toxin in animals or in humans however, high levels of nickel results in nickel poisoning leading to anorexia, kidney dysfunction, apathy, disruption of hormones, fever, haemorrhages, headache, heart attack, intestinal cancer, muscle tremors, nausea, oral cancer and skin problems [10].

3.2. Copper
Copper ranged between 0.006 and 0.008mg/L during summer and monsoon in 2011 and between 0.008 and 0.009mg/L in 2012 during post monsoon and pre monsoon. Copper in water recorded high values during pre-monsoon and monsoon and lower values during post monsoon and summer. Copper is one of the several heavy metals that are essential to life despite being as inherently toxic as non-essential heavy metals exemplified by lead and mercury. Plants and animals rapidly accumulate it. It is toxic at very low concentration in water and is known to cause brain damage in mammals [11]. The natural inputs of copper to the marine environment are from erosion of mineralized rocks. Anthropogenic inputs of copper are from industries and paints. Copper dissolved in seawater is chiefly in the form of CuCO3 or in reduced salinity as CuOH+. It also forms complexes with organic molecules. Molluscs have a tremendous capacity to accumulate copper from contaminated waters. Reports reveal that the copper concentration factor for oysters growing in contaminated waters was 7500 and may accumulate 2000 ppm of copper in their blood [12].

3.3. Zinc
In 2011 zinc varied between 0.024 and 0.032mg/L among the four seasons and in 2012 it varied between 0.022 and 0.027mg/L. A high value of zinc in water was recorded during post monsoon and low during summer. Zinc is an essential nutrient for the human body and has an importance for health [13]. Zinc acts as a catalytic or structural component in many enzymes that are involved in energy metabolism and in transcription and translation of RNA. However, like other metals, it can be toxic in high concentrations [14]. Symptoms of zinc toxicity are slow reflexes, tremors, paralyzation of extremities, anaemia, metabolic disorder, teratogenic effects and increased mortality in humans [15].

3.4. Chromium
Chromium ranged between 0.014 and 0.051mg/L during monsoon and summer in 2011. In 2012 it ranged between 0.017 and 0.030mg/L during post monsoon and summer. High values of chromium were recorded in water during summer and low values during pre monsoon and monsoon in both the years. Chromium is a naturally occurring compound found in soil, rocks and plants. Normally it exists in an oxidation state ranging from chromium (II) to chromium (VI). However, two major forms, trivalent (III) and hexavalent (VI) are reported to have biological significance. Hexavalent chromium is an extremely toxic metal and is most readily absorbed from the gastrointestinal tract, skin and lungs. Acute poisoning results in symptoms which includes dizziness, intense thirst, abdominal pain, vomiting and shock and sometimes death due to the presence of urea in blood [10].

3.5. Cadmium
In 2011 the cadmium varied between 0.015 and 0.038mg/L among the four seasons and between 0.008 and 0.015mg/L in 2012. High values of cadmium in water were recorded during pre-monsoon and monsoon in both the years where as minimum values were noted during post monsoon. Cadmium is widely distributed in the earth’s crust and is principally used in many industries and in agriculture. Cadmium targets the liver, placenta, kidneys, lungs, brain and bones. Consumption of food or drinking water with very high cadmium levels severely irritates the stomach, leading to vomiting and diarrhoea and sometimes death [10].

3.6. Mercury
Mercury ranged between 0.018 and 0.030mg/L during post monsoon and pre monsoon in 2011. In 2012 it ranged between 0.019 and 0.025mg/L during post monsoon and pre monsoon. In both the years the highest mercury was recorded during pre-monsoon and lowest during post monsoon. Mercury is generated naturally in the environment from degassing the earth's crust and from volcanic emissions. Atmospheric mercury is dispersed across the globe by wind and returns to the earth in rainfall, accumulating in aquatic food chains especially in fish [17]. There are three forms of mercury and among these the most toxic one is the organic form, viz., methyl mercury. Methyl mercury is a microbiologically transformed form of inorganic mercury when it reaches aquatic environments, water bodies or in soils. Inorganic and organic mercury is toxic to the human body in different ways, effecting different organs in different ways [18]. Human population is primarily exposed to mercury via food, where fish is the major source of methyl mercury exposure [19]. Mercury has no necessary function in any living organism and is considered as a non-essential metal, and is among the most toxic elements to man and many higher animals [20, 21].

3.7. Lead
In 2011 the amount of lead varied between 0.022 and 0.029mg/L among the four seasons and in 2012 it varied between 0.024 and 0.029mg/L. Lead is a highly toxic metal
3.8. Iron
Iron ranged between 0.032 and 0.073mg/L during pre-monsoon and summer in 2011. In 2012 it ranged between 0.054 and 0.070mg/L during post monsoon and pre monsoon. Iron is a heavy metal of concern, since ingesting dietary iron supplements may acutely poison the young. Ingestion accounts for most of the toxic effects of iron because iron is absorbed rapidly in the gastrointestinal tract. The corrosive nature of iron seems to further increase the absorption. Sources of iron include drinking water, iron pipes, consumption of clams, oyster and other shellfish [10].

4. Conclusion
The environmental parameters of waters affect toxicity of the metal either by influencing physiology of organisms or by altering chemical form of the metal in water. In general, metals are less toxic at lower temperatures and high salinity than at high temperatures and lower salinity [11]. The heavy metal concentration in water is an important factor to be considered to assess the health of this important water body. There is an increase in concentration of heavy metals in water during the two year study period. This increased ambient heavy metal concentration will result in bioaccumulation in the tissues of commercially important edible species of shellfish as well as in ecologically important species. If this trend of increased pollution in the lake continues, there is an inherent danger of higher bioaccumulation of toxins within the edible species which may result in severe health hazards to the consumers especially human. Most studies on marine environment, which have attempted to determine metals in animals, have focused on animals nearer the lower end of the food web. This is because these animals can be directly harvested for human or livestock consumption, can serve to transfer metals tropically to carnivores, and can modify the speciation, cycling, and transport of metals in marine systems. Observing the changes in accumulation of heavy metals in Pulicat lake waters in the present study is of prime concern to reduce or prevent further pollution by taking urgent and appropriate steps both by the general population and by the authorities to conserve this important lake.

### Table 1: Average concentration of heavy metals in Pulicat lake water in 2011

<table>
<thead>
<tr>
<th>Metals (mg/L)</th>
<th>Post monsoon</th>
<th>Summer</th>
<th>Pre monsoon</th>
<th>Monsoon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>0.005</td>
<td>0.009</td>
<td>0.006</td>
<td>0.003</td>
</tr>
<tr>
<td>Copper</td>
<td>0.007</td>
<td>0.006</td>
<td>0.007</td>
<td>0.008</td>
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<tr>
<td>Zinc</td>
<td>0.028</td>
<td>0.030</td>
<td>0.032</td>
<td>0.024</td>
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<tr>
<td>Chromium</td>
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<td>0.051</td>
<td>0.045</td>
<td>0.014</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.016</td>
<td>0.038</td>
<td>0.035</td>
<td>0.015</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.018</td>
<td>0.026</td>
<td>0.030</td>
<td>0.028</td>
</tr>
<tr>
<td>Lead</td>
<td>0.029</td>
<td>0.025</td>
<td>0.026</td>
<td>0.022</td>
</tr>
<tr>
<td>Iron</td>
<td>0.065</td>
<td>0.073</td>
<td>0.032</td>
<td>0.050</td>
</tr>
</tbody>
</table>

### Table 2: Average concentration of heavy metals in Pulicat lake water in 2012

<table>
<thead>
<tr>
<th>Metals (mg/L)</th>
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<th>Summer</th>
<th>Pre monsoon</th>
<th>Monsoon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
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<tr>
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<td>0.022</td>
<td>0.026</td>
<td>0.024</td>
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<tr>
<td>Chromium</td>
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<td>0.030</td>
<td>0.029</td>
<td>0.023</td>
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<tr>
<td>Cadmium</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
<td>0.015</td>
</tr>
<tr>
<td>Mercury</td>
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<td>0.023</td>
<td>0.025</td>
<td>0.024</td>
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<tr>
<td>Lead</td>
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<td>0.029</td>
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<tr>
<td>Iron</td>
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<td>0.063</td>
<td>0.070</td>
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### References