HEAVY METALS AND ZOOPLANKTON WITH SPECIAL REFERENCE TO MINAMATA (JAPAN) MERCURY POLLUTION - A CASE STUDY

S.N. GAJBHIYE AND R. HIROTA
National Institute of Oceanography
Seven Bungalows, Versova,
BOMBAY - 400 061

Zooplankton samples were collected from nine stations in the three inland sea regions (Minamata bay, Yatsushiro-Kai, and Ariake-Kai) along the western coast of Japan between September 1980 to December 1986 and were analysed for total mercury. Some samples were also analysed for methyl mercury, copper, zinc, iron, manganese, cadmium, lead and nickel. The sediment in Minamata bay still contained high mercury concentrations. The mercury levels in zooplankton suggested that the Minamata bay where mercury was discharged about 30 years ago is still contaminated by mercury.

Concentrations of total Hg in zooplankton decreased with increasing distance from the point of incident. Total Hg varied in the range of 0.037 to 5.40 μg g⁻¹ (dry) whereas methyl mercury content was 0.01 to 0.25 μg g⁻¹ (dry). Among the various groups of zooplankton studied chaetognaths, bivalve, and crustaceans showed higher rate of bioaccumulation.

The distribution of other heavy metals was not abnormal and the values were below the widely accepted limits.

INTRODUCTION

Toxicological aspects of heavy metal especially mercury and mercury compounds in coastal environments as a result of anthropogenic or

1 Aitsu Marine Biological Station (Kum. Univ.) Matsushima, Amakusa, Kumamoto, Japan.
natural processes have been extensively studied and reviewed (Windom et al., 1973. Beers et al., 1977. Kaiser and Tolg, 1980). Many studies have shown an increase in heavy metal concentrations up the food chain. Among the heavy metals, mercury has received considerable attention following of mercury poisoning in human beings after eating mercury contaminated shellfish and fishes. Two major epidemics of methyl mercury poisoning occurred in Japan around Minamata bay and Agano river (Nilgata). The source of mercury was through the waste discharged in Minamata Bay beginning 1952. A severe neurological disorder was recognized among inhabitants of the Minamata Bay region and by 1956 the outbreak had reached epidemic stage. This extensively documented instance (Kurland et al., 1960; Irukayama et al., 1961, 1962(a), 1962(b); Fujiki, 1963; Kiyoura, 1963; Tsubaki et al., 1967, Irukayama, 1967; Matida and Kumada, 1969; Matida et al., 1972; Takeuchi, 1972; Ishikawa and Ikegaki, 1980; gave a new dimension to heavy metal toxicity especially effects upon man of chronic discharges of low level methyl mercury waste into coastal environment.

Although, mercury discharged in the bay has long been discontinued mercury-poisoned fish and shellfish still exist (Ishikawa and Ikegaki 1980) and higher levels of Hg than expected are detected in zooplankton (Hirota et al., 1983).

The present work was undertaken to evaluate whether Hg in zooplankton has decreased over the years. The concentrations of Zn, Mn, Fe, Cu, Cd and Pb were also measured to serve as baseline for future use.

**AREA OF STUDY (MINAMATA BAY)**

Minamata bay is a small bay of Kyushu Island with an area of less than 3 km² and an average depth of 12 m. The bay is open to Yatsushiro Sea which extends between Kyushu and Amakusa Islands covering an area of 400 km² and has averaged depth of 35 m. Yatsushiro sea is connected to the Pacific Ocean by a narrow strait. Minamata port is located at the northeastern end of the bay (Fig. 1). The bay is totally contaminated with mercury discharged from a chemical plant of the Chisso Corporation (Ishikawa and Ikegaki 1980). Sludge containing mercury with a concen-
tation as high as several hundred milligrams per litre of total mercury (per unit dry weight) has been deposited 4 m deep in the innermost part of the bay. The mercury was discharged from a chemical plant manufacturing acetaldehyde and other products for 45 years since 1932, and the total amount of mercury discharged is estimated to exceed 150 tons.
The mercury concentration of the water in the innermost part of the bay is higher than the value specified in the Environmental Water Quality standard (Ishikawa and Ikekaki, 1980). The bay contains several types of fishes and shellfish which contain mercury in excess of the limits specified in the Interim Mercury control standard.

The bottom sediments near the most recessed part of the bay are exposed during low tide and are subject to aerobic action causing methylation of the inorganic mercury. To counteract this the Kumamoto prefecture government has decided to treat the mercury contaminated bottom sediments in Minamata Bay (Ishikawa and Ikekaki, 1980).

The tidal range in the bay is about 3 m with the tidal flow crossing the bay according to the change in tidal levels. The currents are weak about several centimeters per second. Usually the bay is calm, with a wave height of less than 0.7 m, and no erosion is visible along the coastline. The bay bottom is encrusted with soft, silt layer more than 10 m deep, which has no bearing capacity. The water content of the bottom superficial sediments is 200 to 400%.

MATERIAL AND METHODS

Zooplankton samples were collected from 1980 to 1986 at 9 stations (including 3 stations in Minamata Bay, 5 stations in Yatsushiro-Kai and 1 station in Ariake-kai (Fig. 1). Samples were taken by horizontal hauls using a plankton net made from bolting silk (mesh size 0.095 mm). The samples after sorting into different groups in the laboratory were briefly rinsed with distilled water on a silk gauge and dried in an oven to a constant weight at 60°C. The dry materials were stored in a desicator until the time of analysis. Total mercury, methyl mercury and heavy metals like copper, zinc, cadmium, lead, nickel, iron and manganese were measured.

Mercury in zooplankton were analysed on a Rigaku Mercury analyzer (SP2) in which the analytical samples are decomposed by heating to separate mercury from gaseous products and measured by cold flame atomic absorption (Nippon Instruments Corporation Manual).
The analysis of methyl mercury was done by following modified method of Fujiki (1970) in which 10.0 ml of 1 N HCl added in biological sample to soak the sample overnight. Adjust the volume of the HCl to 50 ml by adding 1N HCl and add 50 ml of benzene and shake the solution strongly for 10 minutes. Separate benzene layer and add 5 ml or 10 ml of 0.05% L-cysteine solution, snake the solution for 5 minutes and allow to stand the solution. Add 0.9 ml of conc. HCl to the cysteine layer and add 10 ml of benzene to the cysteine layer and shake the solution for 5 minutes. Transfer the benzene layer into Erlenmeyer flask. Use the benzene for the analysis of methyl mercury by gas chromatography with ECD detector.

For the determination of heavy metals the dried sample (1-2g) was digested with conc. HNO₃ followed by Perchloric acid until a clear solution was obtained. Blanks were maintained along with the samples. The volume of the solution was made to 10 ml with glass distilled water. The solutions were examined for Cu, Zn, Ni, Pb, Cd, Fe and Mn using Plasma Emission Spectrophotometer by following standard procedure.

RESULTS AND DISCUSSION

The food chain in water masses where zooplankton is one of the member is an important process through which mercury and other heavy metals, can be concentrated to hazardous levels. The pathway of Hg through zooplankton is usually considered as one of the most important pathways (Nishimura and Kumagai, 1983). However as stated by Yoshiharu Honma (1977) that the transfer of food organisms contaminated with mercury is not simple, but forms a complicated network or web. It is very much true for Minamata Bay Japan. The pollution was stopped many years ago but many problems remain unsolved. According to a comprehensive review, (Environment Agency of Japan 1973, Nishimura and Kumagai, 1983), in the Minamata Bay, Hg contamination of zooplankton, benthos, fish and sediments still continued though discharge of Hg from the acetaldehyde plant was completely stopped in 1971. The results of the present study suggest that even though the average concentrations of Hg is above the normal values it is gradually decreasing.

Zooplankton samples were dominated by copepods, medusae, si-
phonophores, decapod larvae, fish eggs and larvae, polychaetes, doliolium, cladocora, chaetognaths, bivalve and pteropods. The concentrations of total Hg in whole zooplankton and in different groups of zooplankton ranged from 0.156 to 5.40 µg g⁻¹ (Table 1). The highest content (5.40 µg g⁻¹) was measured in mixed sample during October 1986 whereas lowest mercury content was noticed in medusae and siphonophores. The average mercury content (0.16-2.43 µg g⁻¹) in zooplankton is higher than 0.2 ppm reported in plankton from open ocean (Knauer and Martin, 1972) and in nearshore regions of north Carolina and New York (Cocoros et al., 1973). However, in Minamata bay concentrations of 41.0-100.0 mg Hg/kg have been measured in the crustacean species (Matida and Kumada, 1969). Nishimura and Kumagai (1983) also reported a very high mercury content in zooplankton (collected during 1973 to 1975) of Minamata bay was over 20 µg g⁻¹.

The present distribution of total mercury in the various groups of zooplankton from the same area shows the average values in excess of 1.25 µg g⁻¹ which is very similar to the earlier reports (Hirotta et al., 1974) and Hirotta et al., 1983). Thus the total Hg is relatively high in many groups of zooplankton (Table 1). It varied from 0.446-5.40, 0.485-1.605, 0.156-0.863, 0.258-1.782, 0.130-2.33 and 0.91-2.894 µg g⁻¹ (dry weight) respectively in mixed sample, copepods, siphonophore, decapod larvae, fish eggs/larvae and chaetognaths. Considerable differences in total Hg in mixed samples as compared to individual groups appears to be due to association of the mixed sample with clay particles, detritus etc. which could not be fully separated. Furthermore, whole samples containing various taxonomic groups differing with respect to water contain and therefore mercury contents in such organisms can be varied. In general, the concentrations varied from month to month with relatively higher accumulation during October. This may be due to the removing bottom sediments (which contained higher mercury) as part of the mercury contaminated sludge cleanup project in Minamata bay ( Ishikawa and Ikegaki, 1980).

Zooplankton samples in outer Minamata bay mainly consisted of copepods, fish eggs/larvae and chaetognaths. On a dry weight basis, total mercury concentration in zooplankton collected in April 86 ranged from 0.115 to 0.238 µg g⁻¹. These values agree with those reported earlier (Hirotta et al., 1974; Hirotta et al., 1983) but markedly lower than those reported
Table 1: Total mercury content in zooplankton (µg g⁻¹ dry wt) during 1986.

<table>
<thead>
<tr>
<th>Location &amp; station</th>
<th>Sample, group/species</th>
<th>April</th>
<th>June</th>
<th>August</th>
<th>Oct./Nov.</th>
<th>Dec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minamata Bay (st. 4)</td>
<td>Whole sample</td>
<td>1.32</td>
<td>0.446</td>
<td>1.667</td>
<td>5.40</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td>Copepods</td>
<td>0.485</td>
<td>1.41</td>
<td>0.45</td>
<td>1.605</td>
<td>0.706</td>
</tr>
<tr>
<td></td>
<td>Medusae</td>
<td>-</td>
<td>-</td>
<td>0.156</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Siphonophores</td>
<td>-</td>
<td>-</td>
<td>0.156</td>
<td>0.863</td>
<td>0.523</td>
</tr>
<tr>
<td></td>
<td>Decapod</td>
<td>-</td>
<td>1.782</td>
<td>0.258</td>
<td>3.06</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>Fish Eggs/Larvae</td>
<td>0.26</td>
<td>1.60</td>
<td>0.130</td>
<td>2.33</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>Polychaetes</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.00</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Doliolium</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Cladocera</td>
<td>-</td>
<td>0.635</td>
<td>0.714</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.091</td>
</tr>
<tr>
<td></td>
<td>Bivalve</td>
<td>-</td>
<td>2.43</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Chaetognaths</td>
<td>-</td>
<td>0.94</td>
<td>-</td>
<td>2.894</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>Pteropod</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.70</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Residue</td>
<td>-</td>
<td>0.442</td>
<td>0.824</td>
<td>3.025</td>
<td>0.694</td>
</tr>
</tbody>
</table>

| Minamata Bay (st. 5) | Whole sample            | 0.238 | -    | -      | -         | -    |
|                      | Copepods                | 0.193 | -    | -      | -         | -    |
|                      | Fish eggs/larvae        | 0.115 | -    | -      | -         | -    |
|                      | Chaetognaths            | 0.123 | -    | -      | -         | -    |
|                      | Residue                 | 0.211 | -    | -      | -         | -    |

| Yatsushiro Sea (st. 2) | Whole sample            | 0.207 | -    | 0.083  | 0.145     | -    |
|                       | Copepods                | 0.188 | -    | 0.31   | 0.20      | -    |

| Yatsushiro | Cladocera | -     | -    | 0.044  | -         | -    |
|           | Fish Eggs/Fish larvae  | -     | -    | 0.037  | 0.75      | -    |
|           | Coelenterates/ siphonophores | - | - | 0.045 | 0.041 | - |
Table 1: (Contd...)

<table>
<thead>
<tr>
<th>Location &amp; station</th>
<th>Sample, group/species</th>
<th>April</th>
<th>June</th>
<th>August</th>
<th>Oct./Nov.</th>
<th>Dec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yatsushiro (st. 2)</td>
<td>Whole sample</td>
<td>0.312</td>
<td>-</td>
<td>0.91</td>
<td>1.10</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Copepods</td>
<td>0.172</td>
<td>-</td>
<td>0.625</td>
<td>0.085</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fish eggs/larvae</td>
<td>0.138</td>
<td>-</td>
<td>0.256</td>
<td>0.85</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Coelenterates</td>
<td>0.232</td>
<td>-</td>
<td></td>
<td>0.721</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Cladocera</td>
<td>-</td>
<td>-</td>
<td>0.25-0.812</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Decapods (Lucifer sp)</td>
<td>-</td>
<td>-</td>
<td>0.94</td>
<td>0.120</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Chaetognaths</td>
<td>-</td>
<td>-</td>
<td>0.67</td>
<td>0.089</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Pteropods</td>
<td>-</td>
<td>-</td>
<td></td>
<td>0.80</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Diatom</td>
<td>-</td>
<td>-</td>
<td></td>
<td>0.106</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Residue</td>
<td>-</td>
<td>-</td>
<td>0.202</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Ariake Sea (st.1)</td>
<td>Whole sample</td>
<td>0.083</td>
<td>-</td>
<td>0.214</td>
<td>0.048</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Copepod</td>
<td>0.103</td>
<td>-</td>
<td>0.066</td>
<td>0.67</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Decapod</td>
<td>0.132</td>
<td>-</td>
<td>0.42</td>
<td>0.145</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Noctiluca sp/diatom</td>
<td>0.109</td>
<td>-</td>
<td>0.049</td>
<td>0.083</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Chaetognaths</td>
<td>-</td>
<td>-</td>
<td>0.07</td>
<td>0.176</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Cladocera</td>
<td>-</td>
<td>-</td>
<td></td>
<td>0.53</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fish eggs/larvae</td>
<td>-</td>
<td>-</td>
<td>0.056</td>
<td>0.66</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Coelenterates</td>
<td>-</td>
<td>-</td>
<td>0.086</td>
<td>0.202</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Molluscs</td>
<td>-</td>
<td>-</td>
<td></td>
<td>0.87</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Residue</td>
<td>-</td>
<td>-</td>
<td>0.057</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>
by Nishimura and Kumagai, 1983. Levels of total Hg in most of the zooplankton species were lower than the corresponding species in Minamata bay.

Yatsushiro-kai (st. 2) zooplankton samples were represented by copepods, cladocera, fish eggs/larvae, coelenterates, decapods, polychaetes, chaetognaths, molluscs and by some phytoplankton species. It is evident from Table 1 that total Hg concentrations in zooplankton were relatively low with values ranging from 0.037 to 0.64 µg g⁻¹ (dry weight). Highest concentrations were noticed in polychaetes, fish eggs/larvae and molluscs (bivalve), and the relative bioaccumulations were 3 to 12 times higher than rest of the groups. Comparatively higher values were observed during Oct./Nov. 86. At station (3), zooplankton samples were dominated by copepods, fish eggs/larvae coelenterates, cladocera, decapod larvae (*Lucifer* sp.), chaetognaths, pteropods, and diatoms. However, the mercury contents were relatively higher (Table 1) than at station (2). The highest mercury content was noticed in mixed zooplankton samples collected during Oct./Nov. 1986. Whereas lowest mercury content was measured in copepods during the same month.

At Ariake-kai zooplankton samples contained copepods, decapod larvae. *Noctiluca* sp. diatoms, chaetognaths, cladocera, fish eggs/larvae, coelenterates and molluscs. However, the total Hg were always lower and never exceeded 0.87 µg g⁻¹ (dry weight). Most of zooplankton groups/species of this station were low in Hg content but some species contained high amount of Hg. Among the higher contained groups molluscs, copepods and chaetognaths were recorded highest concentrations. Mixed zooplankton samples (during Nov. 86) had the lowest total Hg content which was lower than any individual groups of zooplankton.

Concentrations of total mercury detected in zooplankton samples (collected from 1980 to 1985) are listed in Table 2. In Minamata Bay, zooplanktons were predominated by *Lucifer* sp, crustacean larvae, chaetognaths, dolioium and meduse whereas samples collected from Yatsushiro-kai were mainly represented by medusae and chaetognaths. From the Table 2, it is apparent that total mercury varied widely depending on the location/station, among the species and the period of collection.
Table 2: Total Mercury (Tot. Hg) content in zooplankton from 1980 to 1985

<table>
<thead>
<tr>
<th>Station</th>
<th>Samples</th>
<th>Station</th>
<th>Periods</th>
<th>Tot. Mercury (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minamata Bay</td>
<td>* Lucifer sp. 6</td>
<td>1980 Dec.</td>
<td>0.703</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* Crustacean larvae</td>
<td></td>
<td>1.368</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* Chaetognaths</td>
<td>1981 Feb.</td>
<td>2.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* Crustacean-L</td>
<td></td>
<td>1.445</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* Chaetognaths</td>
<td>1984 Oct.</td>
<td>0.713</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* Chaetognaths</td>
<td>1984 Dec.</td>
<td>0.637</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* Crustacean-L</td>
<td>1984 Dec.</td>
<td>1.416</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* Doliolium</td>
<td>1985 Aug.</td>
<td>0.539</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* Medusae</td>
<td></td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yatsushiro-Kai</td>
<td>* Medusae 2</td>
<td>1980 Sept.</td>
<td>0.270</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* Chaetognaths</td>
<td>1980 Oct.</td>
<td>0.263</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* Chaetognaths</td>
<td>1980 Dec</td>
<td>0.284</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* Medusae</td>
<td>1980 Dec</td>
<td>0.163</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* Chaetognaths</td>
<td>1980 Dec</td>
<td>0.179</td>
<td></td>
</tr>
</tbody>
</table>

Total Hg in Yatsushiro-kai was considerably lower not exceeding 0.29 ug g⁻¹ (dry wt). Concentrations of mercury in zooplankton near the discharge point (Minamata bay) were as high as 2.20 μg g⁻¹ (dry wt) but decreased with the increase in distance. Highest levels of total mercury were observed in chaetognaths (2.20 μg g⁻¹ dry wt) and in crustacean larvae (1.368-1.416 μg g⁻¹ dry wt).

The zooplankton very often showed lower content of mercury on dry weight basis than the other tropic levels. Mercury, while being a natural trace element in the marine biosphere, is recognised as a potential pollutant of some marine ecosystems principally in coastal regions (e.g. Jernelov, 1974; Kaiser and Tolg, 1980; Goldberg, 1976). In the aquatic environment mercury can be associated with the biota, including the zooplankton, through such avenues as adsorption or absorption, either of dissolved forms in the sea water or from ingested food material. From its entry level, mercury can be passed through connections in the food web, including phytoplankton, zooplankton to organisms consumed by man. Once a part
of any organisms biochemical make-up, mercury has the potential, dependent upon its chemical speciation and concentration. For affecting the physiological well-being of the organisms principally through its action on various enzyme system (Beers et al., 1977). At Minamata bay after mercury incident that mercury which is accumulated in sediment exhibits strong bond with organic substances. The net result of this is a redistribution of particle bound mercury with a higher proportion of the mercury being bound to organic particles. When micro-organisms metabolize such organic substances the mercury is detoxified to the methylated forms so that the redistribution results in an increased rate of biological methylation of mercury. When the organic particles settle, predominantly in coastal regions, the mercury is incorporated in the sediments. When these becomes anaerobic during decomposition and sulphide ions formed, the mercury will becomes bound as sulphide. As a result, mercury transported to the sea via-surface run-off or discharging, will have only a small impact on the open sea; most of it will be retained in the coastal zone. This is very much true for Minamata bay.

Of the total mercury present in an aquatic environment only a small part is generally found in the methylated form. This small proportion, however is very serious from fish contamination point of view as its biological half-life is in years while that for inorganic mercury is a matter of weeks. Furthermore for the human consumer of marine organisms, methyl mercury is far more dangerous than inorganic mercury. Increase in the proportion of the total mercury that exists in the form of inorganic and organic mercury which could result from an increased rate of biological methylation of mercury. In the present study, the distribution of organic mercury in zooplankton also show the similar pattern like total mercury. Organic mercury content on dry weight basis are given in Tables 3. Zooplankton samples were dominated by copepods and fish eggs/larvae at Minamata bay, copepods at Yatsushiro-kai and Ariake-kai. Zooplankton samples collected from Minamata bay contained the highest concentration of organic mercury recorded among all the stations. It varied from 0.042-0.283 μg g⁻¹ (dry weight) with maximum in copepods (during June 1986). Concentrations for other area revealed only small variations, with the values not exceeding 0.049 μg g⁻¹ (dry wt). It is also observed that on many occasions the amount of organic mercury was 0.01 μg g⁻¹ (dry weight). The range
observed in the present study for this regions was almost close to the findings of Hirota et al. (1983). Hirota et al. (1974) and Hirota et al. (1979).

**Heavy metal content**

It is evident from Table 4 that Fe accumulation in zooplankton were high as compared to other trace elements and that substantial variability in Fe content was present. The values ranged from 5.6-148.8 μg g⁻¹ (dry wt). Maximum concentration was detected in mixed zooplankton sample (Nov. 86) collected from Yatsushiro-kai (st.2). Zinc and Copper were the second abundant metals with a variation of 0.23-7.01 and 0.2-4.7 μg g⁻¹ (dry wt). The highest concentration of Zn noticed in mixed shorted zooplankton (round the year). The highest values of Cu accumulation also measured in mixed zooplankton sample (during Nov. 1986) at Yatsushiro-kai. The concentrations of other metal Ni, Cd and Pb were considerably lower with not exceeding 1.4 μg g⁻¹ (dry wt). The concentration
<table>
<thead>
<tr>
<th>Station</th>
<th>Period</th>
<th>Groups</th>
<th>Zinc</th>
<th>Copper</th>
<th>Nickel</th>
<th>Iron</th>
<th>Manganese</th>
<th>Cadmium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minamata bay</td>
<td>Apr. '86</td>
<td>Copepods</td>
<td>3.56</td>
<td>0.9</td>
<td>N.D.</td>
<td>103</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>(st.4)</td>
<td></td>
<td>Dec '86 Whole sample (Copepods, Chaetognaths, Siphonophores, decapods, fish eggs/larvae)</td>
<td>0.67</td>
<td>1.0</td>
<td>0.05</td>
<td>212</td>
<td>0.24</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Round the year Cladocera 50% decapods 50%</td>
<td>5.07</td>
<td>2.6</td>
<td>0.16</td>
<td>515</td>
<td>0.41</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Copepods 50% Fish eggs 50%</td>
<td>3.80</td>
<td>1.4</td>
<td>0.11</td>
<td>82</td>
<td>0.14</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Doliolums</td>
<td>3.05</td>
<td>1.0</td>
<td>0.10</td>
<td>94.4</td>
<td>0.13</td>
<td>N.D.</td>
</tr>
<tr>
<td>Minamata outer</td>
<td>Apr. '86</td>
<td>Copepods</td>
<td>2.64</td>
<td>1.0</td>
<td>0.02</td>
<td>53.2</td>
<td>0.03</td>
<td>N.D.</td>
</tr>
<tr>
<td>(st.5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yatsushiro</td>
<td>Apr. '86</td>
<td>Copepods</td>
<td>2.88</td>
<td>4.5</td>
<td>0.13</td>
<td>73.7</td>
<td>0.97</td>
<td>N.D.</td>
</tr>
<tr>
<td>(st.2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nov. '86</td>
<td>Sample as Whole, 70-80% Copepods 20%, Residue</td>
<td>2.47</td>
<td>4.7</td>
<td>0.14</td>
<td>148.8</td>
<td>1.63</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>Aug. '86</td>
<td>Sample as Whole, 95% Copepods 5%, Residue, Cladocera, Polychaetes, decapods, coelenterates</td>
<td>3.12</td>
<td>2.7</td>
<td>0.07</td>
<td>71.7</td>
<td>0.74</td>
<td>N.D.</td>
</tr>
<tr>
<td>Station</td>
<td>Period</td>
<td>Groups</td>
<td>Zinc</td>
<td>Copper</td>
<td>Nickel</td>
<td>Iron</td>
<td>Manganese</td>
<td>Lead</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------</td>
<td>------------------------------------------------------------------------</td>
<td>------</td>
<td>--------</td>
<td>--------</td>
<td>-------</td>
<td>-----------</td>
<td>-------</td>
</tr>
<tr>
<td>Yatsushiro</td>
<td>Round th year</td>
<td>All plankton (shorted) Copepods, Decapods</td>
<td>5.31</td>
<td>2.6</td>
<td>0.06</td>
<td>31.5</td>
<td>0.32</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>Nov. '86</td>
<td>As whole Copepods, Chaetognaths, Siphonophore, pteropods, decapods, fish eggs</td>
<td>0.23</td>
<td>0.2</td>
<td>0.03</td>
<td>11.2</td>
<td>0.17</td>
<td>N.D.</td>
</tr>
<tr>
<td>Ariake</td>
<td>Apr. '86</td>
<td>Copepods</td>
<td>3.81</td>
<td>2.1</td>
<td>0.12</td>
<td>92.2</td>
<td>1.13</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>Apr. '86</td>
<td>Noctiluca</td>
<td>0.71</td>
<td>2.1</td>
<td>0.02</td>
<td>22.3</td>
<td>0.34</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>Round the year</td>
<td>All plankton (shorted copepods, Cladocera, decapods)</td>
<td>7.01</td>
<td>3.3</td>
<td>0.23</td>
<td>13.3</td>
<td>0.13</td>
<td>0.7</td>
</tr>
</tbody>
</table>
of Nickel varied from N.D. to 0.23 µg g⁻¹ (dry wt) with highest value recorded in mixed zooplankton at Ariake-kai. Very lower accumulations were noted in Pb and Cd concentrations and in most of the samples accumulation of Pb and Cd were below the detection limits.

The present levels of trace elements in zooplankton were found to be far below that are known to affect adversely the aquatic life. The reasons for lower values of these metals may be due to the various environmental factors such as trace metal concentrations in surrounding sea water (Sakino et al., 1980), Salinity, temperature as well as species composition also affect the concentrations of metals in plankton. Also no correlation is evident between the concentrations of mercury in zooplankton and that of Cu, Zn, Fe, Mn, Cd, Pb and Ni.

ACKNOWLEDGEMENTS

The first author is grateful to Ministry of Education of Japan (MONBUSHO), for awarding the fellowship. Also grateful to CSIR (India), Director, NIO for allowing to take the study. Thanks are also due to Dr. M.D. Zingde for critical comments to the manuscript.

REFERENCES


Fuji, M. 1963: Studies on the course that the causative agent of Minamata disease was formed, especially on the accumulation of the mercury compound in the fish and shellfish of Minamata Bay. *J. Kumamoto Med. Soc.*, 37: 494-521.

Fujiki, M. 1970: Gas chromatographic determination of methylmercury compounds from samples containing sulfide. *Japan Analyst (Bunseki kagaku)* 19: 1507-1513.


Honma Hoshiharu 1977: Concentration of methylmercury by organisms, especially fish, in the Agana River in “Minamata Disease” Edited by T. Tsubaki and K Irukayama (Kodansha Ltd., Tokyo), 288-310, contributions from the Sado Marine Biological station, Niigata University No. 267.


Irukayama, K., Fujiki, M., Kai, F. and Kondo, T. 1962a: Studies on the origin of the causative agent of Minamata disease II. comparison of
the mercury compound in the shellfish from Minamata Bay with mercury compounds experimentally accumulated in the control shellfish. *Kumamoto Medical J.*, 15: 1-12.


Kurland T., Faro, S. N. and Siedler, H. 1960: Minamata disease, the outbreak of a neurologic disorder in Minamata, Japan and its relationship to the ingestion of seafood contaminated by mercuric compounds. *World Neurology*, 370-395


