Heavy Metals in Neuston from the Straits of Malacca

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Abstract
Heavy metals cadmium, lead, copper and zinc in neuston were analyzed from samples collected with a modified neuston net (310 μm mesh size) during an oceanographic cruise from July 29 to August 8, 2000 in the Straits of Malacca. The period of sampling coincided with South-West (SW) monsoon. The heavy metal concentrations in neuston were relatively low: ranging from 1.19-1013.70 μg g-1 wet weight for copper, 16.54-235.78 μg g-1 wet weight for zinc, 3.92-36.08 μg g -1 wet weight for lead and from 0.32-4.09 μg g-1 wet weight for cadmium. The heavy metal concentrations in neuston in this study were within the ranges published elsewhere, except for cadmium, there were significant differences (\(p <0.05\)) in concentrations of Cu, Pb and Zn between northern, central and southern parts of the Straits. However, concentrations of Cu and Zn were significantly (\(p <0.05\)) higher in near-coastal than offshore or neritic areas, whereas those of Pb and particularly Cd were higher in offshore areas though not significantly (\(p >0.05\)). The presence of two groups of stations with high and low heavy metal concentration as revealed by multivariate analyses corresponded mostly to near-coastal and neritic waters, respectively.

Keywords: Heavy metals, Zooplankton, Neuston, Straits of Malacca, Malaysia

1. Introduction
Heavy metals are increasingly being introduced into the environment as contaminants and pollutants and by-products of industry and human civilization (Patin, 1982). Because of this, programs to regularly monitor the levels of these contaminants and pollutants in the environment are important in the environmental management of any country, in order to control anthropogenic sources of pollution and prevent them from rising to level detrimental to human beings.

Marine zooplankton constitute a major component of the total biomass of the marine environment and thereby, play a vital role in the biogeochemical cycling of heavy metals in the sea (Shulz-Blades, 1992). Planktons are capable of concentrating heavy metals from seawater. The average heavy metal content in zooplankton from northwest Mediterranean was reported to be 2.5, 268
and 32.6 μg g\(^{-1}\) dry weight for Cd, Zn and Cu, respectively (Hardstedt-Romeo and Laumont, 1980), where the average metal concentration in water is 0.10-0.22 μg g\(^{-1}\) for Cd, 1.90-7.00 for Zn and 0.20-0.70 μg g\(^{-1}\) for copper (Fukai and Ngoc, 1976). Davies (1978) provided an excellent review of the role of zooplankton in the biogeochemical cycling of metals in marine systems.

Contamination of Malacca Straits marine ecosystems with heavy metals is receiving more attentions (Babji et al., 1978; Law and Singh, 1988; Din, 1992). Knowledge about metal concentration in the surface layer down to 10 cm, inhabited by the neuston communities is very limited. This habitat is directly exposed to atmospheric input, probably the major source of pollution in Malacca Straits. There is significant industrial pollution in the Straits, generated from agro-based and manufacturing industries, such as factories for food, beverage, palm oil, rubber, tapioca and starch and for the manufacture of fertilizers, textiles, pulp and paper, tanneries and sugar (Chua et al., 2000).

Despite its importance, relatively little is known of the effects of heavy metals on zooplankton of Malacca Straits and apparently only one study (Rezai et al., 1999) has been conducted so far in this region. The effects of marine pollution are first and most intensively felt in coastal waters adjacent to the major sources of polluting activities.

This paper describes the distribution of heavy metals in mixed zooplankton and intends to analyze zooplankton for an array of heavy metals to establish baseline heavy metal levels in mixed zooplankton of the Straits of Malacca. In turn, this information can be used to assess the effects on other organisms and man, and to assess the effects of man’s pollution on various micro-organisms. The sampling program was the part of multidisciplinary environmental research program (MASDEC-JICA) in the Straits of Malacca. Such biological monitorings are useful as they provide temporally integrated values of biologically available metal concentrations in a particular habitat.

2. Material and Methods

2.1. Study Area

Zooplankton samples were collected during the R/V \textit{KK. Mersuji} in the Straits of Malacca from 29 July to 7 August 2000 at 15 stations located between 05°59’ N, 99° 59’ E and 01° 10’ N, 103° 29’ E from Langkawi Islands to Johor (Fig. 1). This covered a distance of more than 800 km. Sampling periods during the cruise coincided with post-SW Monsoon.

2.2. Sampling Techniques

Zooplankton samples were obtained by the neuston net (310 μm mesh aperture) towed horizontally for 10-15 minutes at 1.5-2.0 knots beside the ship during the day following procedure of Rezai et al. (2000). The period of sampling coincided with SW monsoon. The net was equipped with a PVC cod end. Heavy metals cadmium, lead, copper and zinc in neuston were analyzed from samples. The risk of contamination were largely reduced by taking any visible debris such as paint chips, tar balls, rust flakes, etc. All samples were shortly rinsed after catch with double-distilled water to remove salts and were placed in acid-cleaned polyethylene bottles, and immediately frozen at –20°C.

2.3. Analytical Analysis

Upon arrival at the laboratory, the frozen samples were immediately lyophilized. Approximately 0.5-2.0 g of zooplankton samples were digested for 3 hrs with a 10 ml concentrated HNO\(_3\) at 140° C. Duplicate digestions were made when the wet weight was sufficiently enough. The digests were then brought to 40 ml with Milli-Q-water and subsequently analyzed by Atomic Absorption
Spectrometer (Perkin-Elmer model 4100). To avoid possible contamination, all glassware and other equipment were acid washed and rinsed with double-distilled water before use. All results were expressed in μg g⁻¹ on a wet weight basis. In order to assess the accuracy of the method, standards and blanks were also employed.

The expression “mixed zooplankton” as the basic unit of observation is used to emphasize that separation of organisms into species for the determination of heavy metals was not possible (Ritterhoff and Zauke, 1997). In order to compare the present data on the metal concentrations with those from various sea areas, wet weight of zooplankton were converted to dry weight by multiplying the wet weights by a factor of 0.12.

2.4. Statistical Analysis

Statistically significant data was represented graphically using cluster analysis and multidimensional scaling (MDS) in conjunction with the Bray-Curtis similarity index (Bray and Curtis, 1957) with square root transformation of the heavy metal concentrations to analyze differences among stations. The extent to which the two-dimensional plot fitted the rank similarity matrix was indicated by a “stress” coefficient (Clark, 1993). These analyses were performed in accordance to the programmes of the PRIMER (Plymouth Routines in Multivariate Ecological Research)(Clarke and Warwick, 1994) computer package, according to the procedures described by Field et al. (1982) and Warwick et al. (1990).

Mann-Whitney U-test was employed to test the difference in concentration of heavy metals between near-coastal and neritic waters. Kruskal-Wallis test was employed to test the difference in metal concentrations between different parts of the Straits. The mixed zooplankton were tested for correlations amongst the metals analyzed using Spearman rank correlation coefficient. Statistical analysis was performed using Statistica version 5.11.

3. Results

Copper varied from 1.19 μg g⁻¹ wet wt. to a high of 1013.70 μg g⁻¹ wet wt., Zn from 16.54 to 235.78 μg g⁻¹ wet wt., Pb from 3.92 to 36.08 μg g⁻¹ wet wt. Fluctuations in Cd concentration in zooplanktons were at a relatively narrow range of 0.32 to 4.09 μg g⁻¹ wet wt.

Surfer plots of heavy metal concentrations in the Straits of Malacca showed high concentrations of Pb in the near-coastal waters, particularly in the vicinity of Port Klang, Penang and in Johor areas (Fig. 2). Copper and zinc presented maximum concentrations in the near-coastal waters of Klang and Lumut areas (Figs. 3 and 4). Cadmium concentrations were, however higher in offshore waters of Lumut and Penang areas compared to other areas (Fig. 5) and slightly increased in offshore water of Port Dickson.

In addition, concentrations of Cu, Zn and Cd were higher in the central part compared to the other parts of the Straits (Fig. 6, a). Except for cadmium, Kruskal-Wallis test presented significant differences (p < 0.05) in concentrations of Cu, Pb and Zn
between northern, central and southern parts of the Straits (Table 1).

Concentrations of Cu and Zn were higher in near-coastal areas of the Straits, whereas those of Pb and Cd were slightly higher in offshore areas (Fig. 6, b). Cadmium concentration increased gradually from near-coastal to offshore waters with the maximum concentration in offshore waters of Lumut. Mann-Whitney U-test showed significant difference \((p < 0.05)\) in Zn and Cu concentrations between near-coastal and neritic areas (Table 2). However, no significant difference in Cd and Pb concentrations was found between these areas. Furthermore, Spearman correlation matrices for various metals showed significant correlations among the metals concerned (Table 3).

Dendrogram plot (Fig. 7a) of stations based on heavy metals determination in mixed zooplankton clustered two main groups of stations: the cluster with low number of stations corresponded to higher heavy metal concentrations, whereas the one with high number of stations contained lower metal concentrations. The multidimensional scaling (MDS) plot obtained from square root-transformed data on heavy metal concentrations confirmed the plot obtained by dendrogram with stations.

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Source of variation</th>
<th>(p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>North vs Center vs South</td>
<td>&lt; 0.05*</td>
</tr>
<tr>
<td>Cu</td>
<td>North vs Center vs South</td>
<td>&lt; 0.05*</td>
</tr>
<tr>
<td>Pb</td>
<td>North vs Center vs South</td>
<td>&lt; 0.05*</td>
</tr>
<tr>
<td>Cd</td>
<td>North vs Center vs South</td>
<td>&gt; 0.05</td>
</tr>
</tbody>
</table>

*: Significant at 5% level.

Table 1. Results of Kruskal-Wallis test based on estimates of heavy metal concentrations in different parts of Malacca Straits \((n = 15)\).

<table>
<thead>
<tr>
<th>Univariate measure</th>
<th>Source of variation</th>
<th>(p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>Near-coastal vs Neritic</td>
<td>0.018*</td>
</tr>
<tr>
<td>Cu</td>
<td>Near-coastal vs Neritic</td>
<td>0.006*</td>
</tr>
<tr>
<td>Pb</td>
<td>Near-coastal vs Neritic</td>
<td>0.066</td>
</tr>
<tr>
<td>Cd</td>
<td>Near-coastal vs Neritic</td>
<td>0.090</td>
</tr>
</tbody>
</table>

*: Significant at 5% level.

Table 2. Results of Mann-Whitney \(U\)-test based on estimates of heavy metal concentrations in Malacca Straits \((n = 15)\).

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Pb</th>
<th>Cd</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>-0.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.70*</td>
<td>-0.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.74*</td>
<td>-0.33</td>
<td>0.90*</td>
<td></td>
</tr>
</tbody>
</table>

*: Significant at 5% level.
Fig. 3: Distribution of Cu concentrations (log transformed) in mixed zooplankton in the Straits of Malacca.

Fig. 4: Distribution of Zn concentrations in mixed zooplankton in the Straits of Malacca.

Fig. 5: Distribution of Cd concentrations in mixed zooplankton in the Straits of Malacca.

Fig. 6: Concentrations of heavy metals in mixed zooplankton in various parts of the Malacca Straits (a), and in near-coastal versus neritic waters (b).

Fig. 7a: Dendrogram plot of stations based on heavy metal concentrations along the Malacca Straits. The goodness-of-fit of bidimensional representation is expressed by the corresponding stress value.
Fig. 7b: Multidimensional scaling plots of stations based on heavy metal concentrations along the Malacca Straits. The goodness-of-fit of bidimensional representation is expressed by the corresponding stress value.

1-3, 7-10, 12, 13, 16 and 24 forming a loose group on the left and the rest of the stations with higher concentrations clustered to the right (Fig. 7b). The MDS plot for heavy metals in zooplankton had low stress value (0.02), indicating that the plot fitted the rank similarity matrices (Bray-Curtis) for metals relatively well.

4. Discussion

In this study, the overall distribution of some metals in mixed zooplankton organisms from the Straits of Malacca yielded an oceanographically meaningful spatial pattern. The present data are in agreement with those by Rezai et al. (1999) in the Straits, in which generally higher heavy metal concentrations were found in the near-coastal versus neritic waters. In addition, two groups of stations as revealed by the dendrogram and MDS plots (Fig. 7) with higher and lower heavy metal concentrations correspond mostly to near-coastal (except for Stn. 19) and offshore areas (except for Stn. 24), respectively.

Heavy metals, including cadmium, copper, lead, mercury and nickel, were reported in the coastal waters of West Malaysia, particularly the coastal waters of Perak and Penang (Choo et al., 1994). There are reports of heavy metal contamination in some locations in Sumatra, such as at Lhokseumawe in North Aceh, and Asahan and Deli Serdang (Dahuri and Pahlevi in Chua et al., 2000). High concentrations of copper, cadmium, cobalt, nickel, lead and zinc were found in the waters of the southern coast of Singapore, especially in Keppel harbor and the main port (Grace et al., 1987).

The significant correlations between Pb and Zn; Cu and Zn; and Pb and Cu (Table 3) indicated that these metals had the same source of pollution, whereas negative correlations between Cd and other heavy metals may indicated a Possible different pollutant source; and as mentioned earlier, cadmium presented a higher concentration in offshore waters, whereas other metals showed high concentrations in near-coastal areas.

In addition, some sort of pollutants may play a role, at least by coupling to other parameters, influencing and/or preventing the normal distribution of zooplankton. This is particularly prominent in the southern part of the Straits where there exist various sources of pollutants such as outflow of factories, refineries and shipping, among others. The results on the status of heavy metals in the zooplankton also indicated relatively high loads from the south. In fact, higher mercury content was also reported from zooplankton samples in the southern part (Rezai et al., unpubl. data). In addition, recently, Law et al. (2001) showed higher levels of petroleum hydrocarbon in the southern parts of the Straits compared with the northern and the central parts. The presence of tar balls occasionally in zooplankton samples from Port Dickson area is again indicative of deteriorating conditions of the Straits waters.

To what extent might the heavy metal concentrations contribute to the overall distribution and abundance of zooplankton is not known. Since copepods of the area were almost equally represented by carnivores and herbivores (Rezai, unpubl. data), they occupied the lower point of entry for pollutant. The present distribution pattern of heavy metals is related to some extent, to spatial distribution of zooplankton. This is despite the fact that no
significant correlation ($p > 0.05$) was found between the heavy metals and zooplankton densities.

Except for Cd, the relatively higher loads of heavy metals in Johor as well as in Klang compared with other areas of the Straits may be partially attributed to the increased industrial development such as shipping activities and/or increased amount of land drainage in these areas. Moreover, it may also be due to the lower water dilution-taking place in the southern compared with the northern part of the Straits. Anti-fouling paints that leach out from transport vessels are probably the main source of Cu and Zn in zooplankton samples collected at stations near Johor and Port Klang areas, although other sources like incidental discharges of diesel oil from ships and boats are also possible.

On the other hand, the reason for relatively high load of Cd in offshore of Lumut is not known, but may be related partially to increased naval activities as well as discharge of pollutants from Perak river into the sea. Furthermore, the distribution pattern of heavy metals may not only be related to the location of the potential metal sources, but also to some extent, to spatial distribution of zooplankton in conjunction with hydrographical characteristics of the area.

Comparison of the present data on the metal concentrations with those from various sea areas led to the following conclusions: the concentrations of copper were in the same order of magnitude as the copper levels from different and similar climatic regions (Table 4). The minimum and maximum value of zinc concentrations in both mixed zooplankton and neuston were considerably lower than in comparable marine environments. The lowest concentrations of lead, measured both in mixed zooplankton and neuston, were lower than that of other tropical regions.

The mean concentrations of cadmium were lower than those reported elsewhere but comparable within the Malacca Straits. It should be understood that the numbers quoted in Table 4 only refer to the biological effects on chemical composition. In addition, partially as a result of this, as well as the statistical techniques employed, the numbers should be viewed as indicators, rather than as absolute values.

There are a few noticeable trends in the neuston samples but they only appear in individual stations and are not universal throughout the area. The problem of discerning any meaningful trends is further compounded by the variations in sample makeup. Thus, it is impossible to make coherent comparisons from station to station. The only significant finding can be reported is that although there are chemical variations between the various samples, they tend to fall within the ranges that have been reported elsewhere for zooplankton (I.O.D.E., 1972). However, plankters are representative for the water body within which they grow and are moved; their short life means that they remain in a given water body for the duration of their life, at least in the open ocean (Schulz-Baldes, 1992). We are confronted with an enormous inter-specific variability for which concise explanations are not at hand, yet. Available information suggests, however, that enhanced metal levels in some organisms do not necessarily imply anthropogenic contamination.

In conclusion, the Straits of Malacca environment does not seem to be heavily contaminated with heavy metals, at least at the zooplankton level. Available information suggests that enhanced metal levels in some organisms do not necessarily imply anthropogenic contamination. Since the obtained data are limited in space and time, further sampling would be needed to see if these trends continue over longer periods or merely reflect short-term local variations. In the absence of similar published data from the Malacca Straits, it is impossible to draw any conclusions about temporal trends of metal concentration in the Malacca Straits zooplankton.

The overall distribution of metals in zooplankton organisms from the Straits of Malacca yielded an oceanographically meaningful spatial pattern.
Table 4. Concentrations of heavy metals in zooplankton collected from various sea areas.

<table>
<thead>
<tr>
<th>Group</th>
<th>Net mesh size (µm)</th>
<th>Location</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Cd</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed zooplankton</td>
<td>-</td>
<td>Off Puerto Rico</td>
<td>41.10 (10.0-207.0)</td>
<td>428 (120.0-1200.0)</td>
<td>49.0 (8.0-107.0)</td>
<td>49.0 (2.0-12.0)</td>
<td>Martin (1970)</td>
</tr>
<tr>
<td>(%75 copepods)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixed zooplankton</td>
<td>250</td>
<td>South Texas Outer Continental Shelf</td>
<td>4.1 (2.8-7.0)</td>
<td>36.0 (34.0-41.0)</td>
<td>8.0 (1.8-18.8)</td>
<td>1.8 (1.2-2.4)</td>
<td>Horowitz and Presley (1977)</td>
</tr>
<tr>
<td>Mixed zooplankton</td>
<td>200</td>
<td>N.W. Mediterranean Sea</td>
<td>31.0 (5.9-129.1)</td>
<td>263 (52.0-742.0)</td>
<td>2.4 (-)</td>
<td>- (-)</td>
<td>Hardstedt-Romeo and Laumond (1977)</td>
</tr>
<tr>
<td>Mixed zooplankton</td>
<td>132</td>
<td>Mediterranean Sea</td>
<td>39.1 (13.3-172.0)</td>
<td>446.0 (224.0-769.0)</td>
<td>-</td>
<td>- (-)</td>
<td>Fowler (1986)</td>
</tr>
<tr>
<td>Neuston</td>
<td>250</td>
<td>South Texas Outer Continental Shelf</td>
<td>8.1 (5.2-9.5)</td>
<td>90.8 (42-156)</td>
<td>12.1 (1.6-24.0)</td>
<td>1.9 (0.4-3.0)</td>
<td>Horowitz and Presley (1977)</td>
</tr>
<tr>
<td>Neuston</td>
<td>310</td>
<td>Strait of Hormuz</td>
<td>0.2 (0.1-0.4)</td>
<td>1.8 (1.1-2.2)</td>
<td>0.7 (0.0-2.3)</td>
<td>0.2 (0.0-0.4)</td>
<td>Rezai et al. (unpubl. data)</td>
</tr>
<tr>
<td>Neuston</td>
<td>310</td>
<td>Malacca Straits (Pre-SW monsoon)</td>
<td>0.3 (0.1-1.3)</td>
<td>4.0 (0.0-23.1)</td>
<td>1.0 (0.4-2.8)</td>
<td>ND (-)</td>
<td>Rezai et al. (1999)</td>
</tr>
<tr>
<td>Mixed zooplankton</td>
<td>140</td>
<td>Malacca Straits (Pre-SW monsoon)</td>
<td>2.3 (0.1-13.3)</td>
<td>3.7 (0.4-15.2)</td>
<td>2.1 (0.6-5.4)</td>
<td>ND (-)</td>
<td>Rezai et al. (1999)</td>
</tr>
<tr>
<td>Mixed zooplankton</td>
<td>310</td>
<td>Malacca Straits</td>
<td>15.9 (0.1-121.6)</td>
<td>9.7 (2.0-28.3)</td>
<td>1.6 (0.5-4.3)</td>
<td>0.2 (0.0-0.5)</td>
<td>Present study</td>
</tr>
</tbody>
</table>

ND=Not detectable

Analysis of heavy metals in plankton organisms thus has been proven as an additional tool for research on water quality, particularly in metal pollution of the Straits.

Acknowledgements

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