Concentration, Distribution and Geochemical Speciation of Copper in Surface Sediments of the Straits of Malacca

C.K. Yap, A. Ismail and S.G. Tan
Department of Biology, Faculty of Science and Environmental Studies, University Putra Malaysia, UPM, 43400 Serdang, Selangor, Malaysia

Abstract: The geochemical partitioning of copper (Cu) in surface sediment of two sampling cruises from the Straits of Malacca have been studied. The results show that the total concentrations of Cu in sediments ranged from 2.48 to 11.95 μg g⁻¹ and 2.59 to 13.3 μg g⁻¹ for the first and second sampling cruises, respectively. Nonresistant fractions (EFLE, acid-reducible and oxidisable-organic) covered 60.43% (first cruise) and 46.21% (second cruise) of total Cu concentration in the sediments. This indicated that although the total Cu concentration in sediments were relatively low, the geochemical study revealed that about 50% of the total Cu found in the sediment could be due to anthropogenic inputs besides natural origins. Among this nonresistant fractions, the oxidisable-organic fraction contributed about 81-86%.

Key words: Geochemical speciation of copper, sediment, the Straits of Malacca

Introduction
Copper (Cu) is ranked the third most toxic metal to aquatic biota, after mercury and silver (Waldeichuk, 1974). In sediment, Cu could be found since it is one of the essential metals for biota, being associated with numerous metalloenzymes and metalloproteins (Thompson, 1990). However, high level of Cu in the sediment could be potentially toxic and this may pose concern because of bioaccumulation once in the food chain. The high level of Cu found in the sediment could be due to both natural origins and man-induced activities which are widely reported in the literature (Christensen and Juracek, 2001). Besides being a source of contamination to the overlying water and to biota, the sediment may act a main sink for heavy metals (Salomons et al., 1987 and Baudo et al., 1990). However, the bioavailability of heavy metals in the sediments could be influenced by the changes of environmental conditions such as pH, sediment redox potential etc. Total metal always receives some arguments that it does not provide information on the bioavailable fraction as well as fraction which is due to anthropogenic activities. This is due to heavy metals are present in different geochemical forms such as easily, freely and leachable fraction, metal carbonates, oxides, ion in crystal lattices of mineral etc., which determine their mobilization capacity and bioavailability (Weisz et al., 2000; Yu et al., 2001). In this study, we used Sequential Extraction Technique (SET) in sediment to fractionate resistant fraction from nonresistant one in addition to total metal analysis by using direct aqua-regia method. The SET is able to reveal fate of contaminant (Lin et al., 1998) which are under different environmentally conditions by differentiating the different types of metal binding (Forstner, 1980). Sequential extraction analysis is a technique applied to study the geochemical partitioning of heavy metals amongst solid mineral and organic phases in sediment or other earth material (Tessier et al., 1979; Calmano and Forstner, 1983; De Souza et al., 1986; Vicente-Beckett, 1992; Howard and Vandenbrink, 1999). Although there are two disadvantages of using sequential extraction technique, namely non-specificity of extractants and metal re-absorption, this technique is still widely reported in the literature (Howard and Vandenbrink, 1999; Walter and Cuevas, 1999). Regardless of using what extractants/chemicals used for the SET, all the different technique is able to provide an estimate of the nonresistant fraction of the total metal which is mainly contributed by anthropogenic sources, not to mention the natural origins.

The Straits of Malacca is an interesting area for scientific studies since it receives a lot of anthropogenic inputs both from land and sea (Thia-Eng et al., 2000). There is a growing concern for the Straits due to its being an important lane in the world and contamination of TBT (Swennen et al., 1997) and hydrocarbons (Zakaria et al., 2000) are reported from the Straits. In Malaysia, most of the studies concentrated at the coastal areas (Sivalingam et al., 1980; Ismail, 1993; Ismail et al., 1993; Ismail and Rosnin, 1997; Yap et al., 2002). Ismail and Rosnin (1997) reported that the polluted Sepang River Besar had Cu concentration as high as 670 μg g⁻¹ and that was due to pig-farm activity. This alarming level is certainly of much...
public concern due to the metal itself is able to pose undesirable hazardous impacts on the biota of the ecosystems. In Malaysia, geochemical fractionations of heavy metals were reported in river sediments (Mushrifah et al., 1995; Lim and Kiu, 1995; Ismail and Rosni, 1997) and coastal sediments (Yap et al., 2002). The geochemical fractions employed in this study are easily, freely, leachable and exchangeable (EFLE), acid-reducible, oxidisable-organic and resistant. The mathematical summation of EFLE, acid-reducible and oxidisable-organic fractions constitutes the nonresistant phase (Badri and Aston, 1983). The objective of this paper is to monitor the distribution and concentration of Cu and its geochemical speciation in the surface sediments of the Straits of Malacca during sampling cruises between 1998-1999.

Materials and Methods
Sample collection: Sediment samples were collected by two sampling cruises. The sampling cruises were a collaborative project of the Japan International Cooperation Agency (JICA) and Universiti Putra Malaysia (UPM). The first cruise was conducted between November and December 1998 while the second sampling cruise was conducted between March and April 1999. The sampling stations established along the Straits of Malacca from Pulau Langkawi to the southern part of Johore are shown in Fig. 1. Samples from each station were collected by using a Smith-McIntyre grab (0.50 m X 0.50 m). The top 3 to 5 cm of each sediment samples was placed in an acid-washed polyethylene bag and they were deep frozen prior to analysis. Samples were brought back to laboratory and were dried to a constant dry weight at 105°C and sieved through a 0.50 mm stainless steel sieve (Yap et al., 2002).

Analytical procedures: Chemical fractions of Cu in the sediments were obtained by the modified SET described by Badri and Aston (1983) and used by Yap et al. (2002). The residue used for each fraction was weighed before the next fraction was carried out. The extraction were conducted in a constant agitation. The supernatant was removed and the residue was washed with 20 ml double distilled water (DDW). They were then filtered through filter-papers Whatman No 1. and the filtrates were stored for metal determination. At each fraction, a blank was employed as the same procedure to check for external contamination. The prepared samples were determined for Cu by an air-acetylene flame atomic absorption spectrophotometer (AAS) Perkin-Elmer Model 4100. The data were presented in μg g⁻¹ dry weight. Direct aqua-regia method was also conducted on the sediments and total Cu levels were determined. The recovery of the sun of four extractions in comparison of direct aqua-regia digestion was 102.08 ± 7.20% with a strong correlation coefficient of r= 0.99 (P< 0.001).

To avoid possible contamination, all glassware and equipment used were acid-washed. A quality control sample, made of standard solution of Cu (MERCK Titrisol), was routinely run though during the period of metal analysis. The percentage of recovery for Cu analysis was 96%. The accuracy of the aqua-regia method was checked with Certified Reference Material for Soil (International Atomic Energy Agency, Soil-5, Vienna, Austria) and about 103.8% (certified value: 77.1 μg g⁻¹; measured value: 80 μg g⁻¹) of Cu recovery had been observed.

To determine the loss on ignition as a proxy of organic matter content (Hakanson, 1980), the dried sediment samples were then ignited for 4 hours at 550°C. The data obtained were analysed statistically by using the Statistical Analysis System (SAS) for Windows, Release 6.12 software. The Pearson’s product moment correlation coefficient on the log_10 (mean + 1) transformed data (Zar, 1996) was applied to determine the strength and levels of significance of the relationships.

Results
The mean values and percentages of four geochemical fractions for each sampling site are presented in Table 1. The EFLE fraction of Cu ranged from 0.08 to 0.28 μg g⁻¹ and 0.13 to 0.33 μg g⁻¹ in the first and second cruises,
Table 1: Geochemical fractions of copper in the sediments of the Straits of Malacca

<table>
<thead>
<tr>
<th>EFLE</th>
<th>Acid-reducible</th>
<th>Oxidisable-organic</th>
<th>Resistant</th>
<th>Total (100%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Cruise (n=3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.11±0.01 (2)</td>
<td>0.25±0.01 (5)</td>
<td>2.70±0.33 (55)</td>
<td>1.81±0.09 (38)</td>
<td>4.86±0.41</td>
</tr>
<tr>
<td>0.23±0.01 (2)</td>
<td>0.30±0.01 (3)</td>
<td>3.27±0.17 (27)</td>
<td>8.15±0.27 (63)</td>
<td>11.95±0.32</td>
</tr>
<tr>
<td>0.17±0.02 (1)</td>
<td>0.36±0.02 (3)</td>
<td>2.63±0.00 (24)</td>
<td>7.90±0.05 (72)</td>
<td>10.99±0.08</td>
</tr>
<tr>
<td>0.15±0.00 (5)</td>
<td>0.36±0.02 (6)</td>
<td>2.20±0.02 (47)</td>
<td>2.05±0.04 (44)</td>
<td>4.69±0.19</td>
</tr>
<tr>
<td>0.15±0.00 (5)</td>
<td>0.29±0.01 (7)</td>
<td>2.14±0.09 (49)</td>
<td>1.78±0.12 (41)</td>
<td>4.63±0.02</td>
</tr>
<tr>
<td>0.15±0.00 (4)</td>
<td>0.27±0.01 (6)</td>
<td>1.94±0.03 (46)</td>
<td>1.88±0.12 (44)</td>
<td>4.24±0.09</td>
</tr>
<tr>
<td>0.16±0.01 (4)</td>
<td>0.28±0.01 (6)</td>
<td>2.75±0.12 (61)</td>
<td>1.31±0.03 (29)</td>
<td>4.49±0.14</td>
</tr>
<tr>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>0.28±0.01 (5)</td>
<td>0.10±0.00 (2)</td>
<td>3.08±0.05 (53)</td>
<td>2.35±0.06 (49)</td>
<td>5.81±0.08</td>
</tr>
<tr>
<td>0.11±0.01 (4)</td>
<td>0.26±0.01 (11)</td>
<td>1.78±0.09 (72)</td>
<td>0.33±0.03 (13)</td>
<td>2.48±0.09</td>
</tr>
<tr>
<td>0.10±0.23 (4)</td>
<td>0.31±0.02 (12)</td>
<td>1.15±0.01 (43)</td>
<td>1.14±0.22 (41)</td>
<td>2.71±0.23</td>
</tr>
<tr>
<td>0.10±0.01 (4)</td>
<td>0.15±0.02 (6)</td>
<td>1.43±0.06 (58)</td>
<td>0.78±0.04 (32)</td>
<td>2.46±0.07</td>
</tr>
<tr>
<td>0.18±0.01 (4)</td>
<td>0.21±0.01 (4)</td>
<td>2.22±0.15 (45)</td>
<td>2.29±0.09 (47)</td>
<td>4.92±0.25</td>
</tr>
<tr>
<td>0.08±0.00 (3)</td>
<td>0.07±0.00 (3)</td>
<td>1.60±0.03 (77)</td>
<td>0.33±0.13 (16)</td>
<td>2.09±0.11</td>
</tr>
<tr>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>0.11±0.02 (5)</td>
<td>0.04±0.01 (2)</td>
<td>1.49±0.12 (62)</td>
<td>0.74±0.07 (31)</td>
<td>2.39±0.17</td>
</tr>
<tr>
<td>0.16±0.00 (6)</td>
<td>0.28±0.02 (9)</td>
<td>1.28±0.06 (50)</td>
<td>0.92±0.11 (35)</td>
<td>2.59±0.17</td>
</tr>
<tr>
<td>0.17±0.00 (4)</td>
<td>0.31±0.01 (7)</td>
<td>2.14±0.22 (49)</td>
<td>1.76±0.23 (40)</td>
<td>4.38±0.03</td>
</tr>
<tr>
<td>0.13±0.02 (2)</td>
<td>0.23±0.02 (4)</td>
<td>2.92±0.04 (55)</td>
<td>2.09±0.18 (39)</td>
<td>5.36±0.21</td>
</tr>
</tbody>
</table>

Table 2: The Pearson's correlation coefficients of total metal with EFLE, acid-reducible, oxidisable-organic, resistant fractions and nonresistant fractions of Cu based on the results of the log_{10}(mean+1) of the sediments of the Straits of Malacca

<table>
<thead>
<tr>
<th>EFLE</th>
<th>Acid-reducible</th>
<th>Oxidisable-organic</th>
<th>Resistant</th>
<th>Non-resistant</th>
<th>Total copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total copper (N=41)</td>
<td>&lt;0.19***</td>
<td>0.36***</td>
<td>0.81***</td>
<td>0.91***</td>
<td>0.43***</td>
</tr>
<tr>
<td>Nonresistant (N=41)</td>
<td>0.72***</td>
<td>0.43***</td>
<td>0.31*</td>
<td>0.49***</td>
<td>-</td>
</tr>
<tr>
<td>Total organic matter (N=15)</td>
<td>0.86***</td>
<td>0.40***</td>
<td>0.34ns</td>
<td>0.82***</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: Values given are the correlation coefficients (r) with their levels of significance
(***P<0.001, **P<0.05, *P<0.01, ***P<0.001).

respectively. The ‘acid-reducible’ fraction of Cu ranged from 0.04 to 0.31 µg g⁻¹ and 0.15 to 0.37 µg g⁻¹ in the first and second cruises, respectively. The ‘oxidisable-organic’ fraction of Cu ranged from 1.15 to 3.27 µg g⁻¹ and 1.6 to 2.76 µg g⁻¹ in the first and second cruises, respectively. The ‘resistant’ fraction of Cu ranged from 0.33 to 8.15 µg g⁻¹ and 0.92 to 10.0 µg g⁻¹ in the first and second cruises, respectively. The total Cu concentrations ranged from 2.48 to 11.95 µg g⁻¹ and 2.59 to 13.36 µg g⁻¹ in the first and second cruises, respectively. No significant differences (F> 0.05) were found for the different geochemical fractions and total Cu of the two sampling cruises.

Fig. 2 shows the comparison of the nonresistant and resistant fractions in the sediments of the two sampling cruises in the Straits of Malacca. It is clearly shown that the nonresistant fractions of almost all stations dominate the total amount of Cu in sediments. The nonresistant fractions covered about 45-60% of total Cu in most sampling stations.

From Fig. 3, the ‘oxidisable-organic’ fraction made up the most (37.7-51.7%) portion of the total Cu. The resistant fraction covered 39.6-53.8% of total Cu. It is followed by ‘acid-reducible’ fraction (5%) and EFLE fraction (3-4%). The distribution of each fraction for both cruises are not much different except for the increased resistant fraction.
Table 2 shows the correlation coefficients of total Cu and total organic matter with the four geochemical fractions in the sediments of the Straits of Malacca. Total organic matter was significantly correlated with EFLE fraction ($R=0.86, P<0.001$), resistant fraction ($R=0.82, P<0.001$) and total Cu ($R=0.83, P<0.001$) of the sediments. Total Cu concentrations significantly correlated with ‘acid-reducible’ ($R=0.36, P<0.05$), ‘oxidisable-organic’ ($R=0.81, P<0.001$), resistant ($R=0.91, P<0.001$) and nonresistant ($R=0.43, P<0.01$) fractions of the sediments. Besides, the nonresistant fraction also highly associated with EFLE fraction ($R=0.72, P<0.001$). This EFLE fraction of Cu, that loosely held on clay surfaces and organic matters, is believed to cause most bioavailable forms although it has shown to cover only about 3-4% of the total Cu concentration in the surface sediments.

Discussion

The present range of total Cu (2.48-13.36 μg g⁻¹) was comparable to Cu levels from the literature (mainly from the offshore sediments of the South China Sea). The total Cu level in the South China Sea offshore from Terengganu was reported as 2.85 to 8.10 μg g⁻¹ (Shazili et al., 1986). Shazili and Mawi (1988) reported that the total Cu level ranged from 2.55 to 24.8 μg g⁻¹ in Sarawak offshore sediments. The total Cu in sediments sampled from South China Sea ranged from 1.94 to 9.21 μg g⁻¹ (Shazili et al., 1987). Copper concentrations in Jakarta Bay was reported as 11.8-82.9 μg g⁻¹ (Hunsperg, 1988). Average Cu concentrations in soils range from 20 to 30 μg g⁻¹ (Scheinberg, 1991). In UK estuaries, concentrations of Cu in sediments ranged from 7.00 μg g⁻¹ in relatively pristine areas to more than 2300 μg g⁻¹ at heavily polluted sites (Bryan and Langston, 1992). In US, Long and Chapman (1985) summarized from several sources and reported Cu concentrations at 34-206 μg g⁻¹ at various Eliott Bay sites. Chapman et al. (1986) reported 30-53 μg g⁻¹ for southern San Pablo Bay, south of Oakland Outer Harbour levels of 43-51 μg g⁻¹ and high levels in Islais Creek Channel of 68-130 μg g⁻¹. Likewise, our Cu concentrations found in the sediment of the Straits of Malacca were much lower compared to the Feder et al. (1990) value of 59 μg g⁻¹ for Port Valdez.

Calmano and Forstner (1983) reported that there was an increase in nonresistant fraction for polluted river ecosystems. In a polluted river in Malaysia, Ismail and Rosniza reported that the resistant fraction of Cu decreased when approaching the source of contamination.
The resistant fractions at stations 2 and 3 covered about 75% of total amount of Cu and reflected these stations were not heavily contaminated with Cu. This may indicate that although the total Cu levels of sediments in these stations were higher than the rest of the stations in terms of total Cu, only a small amount of Cu concentration (25%) were most likely due to anthropogenic input and this seems to pose less impact to living organisms in the sediments since it is mainly due to geological processes under natural field conditions. The similar patterns of the two sampling cruises had further supported the above indication. The resistant fraction of Cu in sediments were probably due to natural sources such as chemical weathering of igneous and metamorphic rocks and decomposition of biota detritus (Badri and Aston, 1983). This natural fraction of sediments contains Cu that strongly incorporated into the crystalline lattice positions of the minerals (Badri and Aston, 1983). Therefore, the resistant fraction is low in biological availability.

The nonresistant fraction of Cu found in the sediments is certainly of much concern from the ecotoxicological point of view. Besides being the fraction that could pose an impact to the living organisms, this nonresistant fraction is most likely due to anthropogenic Cu besides natural origins. The levels of nonresistant fraction of Cu found in the sampling sites could be mostly due to man-induced activities such as dumping, shipping and run-offs from riverine systems. In addition, natural processes such as aerial deposition that brings small particles (haze) due to industrial activities and forest fires are also to be taken into account. However, the nonresistant fraction of Cu in the surface sediments of the Straits was considered low. Geochemical fractionation study of the sediments from the Straits of Malacca showed that most of the total Cu concentrations fall into the ‘oxidisable-organic’ (44.4%) and resistant fractions (46.7%). This conclusion is based on the fact that the different fractions from both sampling cruises did not show significant difference. The dominance of ‘oxidisable-organic’ fraction in nonresistant fractions suggests that the organically-bound materials such as humic and fulvic may be easily available for biological uptake. The geochemical partitioning of Cu provides us with the most useful information on low level of Cu contamination along the Straits of Malacca.

Acknowledgments
The authors wish to thank JICA and MASDEC for organizing the expedition cruises in the Straits of Malacca.

References


