

Copper and Zinc in intertidal surface sediment and *Telescopium telescopium* from Lukut River, Malaysia

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Abstract—Lukut River, which is located on the west coast of Peninsular Malaysia, flows into the Straits of Malacca through mangrove areas and receives many kinds of effluent from human activities. Before 1999, Lukut River also received effluent from pig farming activities besides oil palm mills, urbanisation, and agricultural activities. All those activities were reported to elevate copper and zinc in the environment. Now aquacultural activities such as shrimp ponds are developing along the Lukut River. In this study, copper and zinc were analysed in sediment and *Telescopium telescopium* collected from intertidal areas in order to assess the levels of Cu and Zn in the Lukut River. The results show that Copper and Zinc in surface sediments are within the range of 37 to 100 μgg^{-1} and 100 to 210 μgg^{-1} respectively. Twenty to 60% of copper and 40 to 63% of zinc are anthropogenic input and these values are considered high in coastal areas of Peninsular Malaysia. Copper and zinc levels in *Telescopium telescopium* are between 50–60 μgg^{-1} and 35–60 μgg^{-1} respectively. There are some inconsistencies in the correlation of Cu and Zn levels in surface sediments and *Telescopium telescopium* from Lukut River. More studies on the behaviour of Cu and Zn in sediments and *Telescopium telescopium* are needed before recommending *Telescopium telescopium* as a good monitoring agent. High levels of Cu and Zn in the Lukut River may affect the shrimp aquaculture and bioresources of the Lukut estuaries.

Key words: Copper, Zinc, sediment, mollusk, heavy metals, Malaysia

Introduction

Prior to 1999 Lukut area in Negeri Sembilan was known as one of the most important pig farming activities in Malaysia. All pig farming activities have stopped after the outbreak of Japanese Encephalitis (JE) or Nipah Virus. More than a million of pigs were killed in order to stop JE from spreading globally (Chua, 2003). Pig farming activities are known to discharge polluted effluent which usually contain high copper and zinc (Arzul and Maguer, 1980). Studies by Ismail and Ramli (1997) found high concentrations of Cu and Zn in sediment and molluscs collected from Sepang River receiving pig farms effluent. High levels of Cu and Zn in sediment receiving effluent from pig farm may probably due to the addition of these metals in the diet for health treatment. Since 1989–1993, discharged effluent from pig farms is known to be second largest contribution to water pollution after urban sewage in Malaysia (D.O. E, 1993).

After the pig farms were closed, new activities began to develop such as shrimp farming, chicken and cattle rearing and other human activities. Shrimp farms are constructed along Lukut River which formerly received effluent from human activities inland including pig farming activities. Since pig farming activities contributed to the elevations of

copper and zinc in the environment, these contaminants need to be assessed. Elevated levels of copper and zinc in the environment do not only disturb the ecological system but may also affect the shrimp farming activities such as toxicity effect or reduced productivity. Shrimp farming may also increase copper level in the environment since copper might be used in shrimp farm to control algal growth. So far there is no information on copper and zinc contamination in the Lukut River. This study was conducted to assess the level of copper and zinc in intertidal surface sediment and benthic organism from Lukut River. Sediment is known as a final sink for heavy metals in aquatic ecosystem. Trace metals like copper and zinc, are mainly absorbed in the sediment particles (Forstner and Wittman, 1980). Benthic organisms live in the sediments may absorb heavy metals from sediments and surrounding environment. Sediment and benthic organisms can be good indicators for metals pollution. In this study *Telescopium telescopium* was used as a representative of benthic organism.

Materials and Methods

Study area

Lukut River is located between 2°34'45" to 2°36'48"N

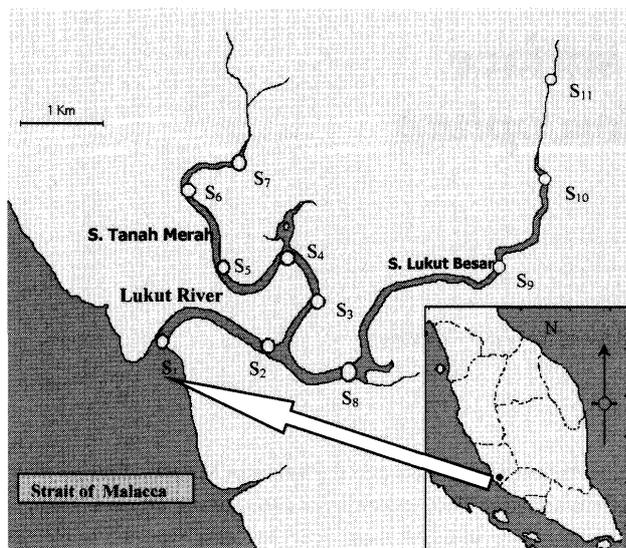


Fig. 1. Location of sampling stations.

and $101^{\circ}47'18''$ to $101^{\circ}50'30''E$ (Fig. 1). It consists of two branches named Sungai Lukut Besar and Sungai Tanah Merah. These two branches are joined together about 1.6 km before the river mouth. The rivers have been receiving effluent from pig farming activities besides oil palm mills, urbanisation, transportation and agricultural activities for many years. In order to assess the distribution of copper and zinc in the river system, 11 stations were chosen along Sungai Tanah Merah and Sungai Lukut Besar. The location of each station is shown in Fig. 1.

Sample collections and analyses

Intertidal sediment was collected from top 5 cm of surface sediment from each station (Fig. 1). Three samples from each station were collected using stainless steel grab, placed in clean plastic bags and deep frozen prior to analysis. In laboratory, samples were dried to constant weight at $80^{\circ}C$ and sieved through $63\ \mu m$ stainless steel sieve. Fifteen samples of *Telescopium telescopium* were collected from the same areas as the sediments were collected. The snails were then placed in clean plastic bags and kept frozen until analyses.

In the laboratory, geochemical fraction of metals in sediment were analysed as described by Badri and Aston (1983) and heavy metals analyses in *Telescopium telescopium* were carried out as described by Ismail and Ramli (1997). All metals were analysed by using air-acetylene flame atomic absorption spectrophotometer model Perkin Elmer 2100. Data from sediments and snails are presented in $\mu g \cdot g^{-1}$.

To avoid any possible contamination, all glassware in the experiment was previously acid-washed and rinsed with milli-Q water ($18.2\ \Omega$). The accuracy of the analysis was checked against the blank and standard addition testing procedure. The percentages of recoveries for the metal analyses in sediments were 93 to 101% for Copper and 94 to 96% for

Zinc. Recovery percentages for *Telescopium telescopium* samples were 98% and 99% for Cu and Zn respectively. A quality control sample was routinely run through during the period of metal analysis.

The quality of the method used was checked with a Certified Reference Material (CRM) for Soil (International Atomic Energy Agency, Soil-5, Vienna, Austria). The agreement between the analytical results for the reference material and its certified values for each metal was satisfactory (90.1% for Zn, 96.4% for Cu). Standard solutions were prepared from $1000\ mg \cdot l^{-1}$ stock solution of each metal (MERK Titrisol).

Results and Discussion

The concentrations of Cu and Zn in all the geochemical fractions of sediments are given in Tables 1 and 2 respectively. Total metal concentrations are computed by summation of the four different fractions. It ranged from 11.27 to $92.77\ \mu g \cdot g^{-1}$ for Cu and 48.24 to $208.68\ \mu g \cdot g^{-1}$ for Zn. Copper levels elevated in station 5, 6 and 7 in Sungai Tanah Merah, and lower levels in main Sungai Lukut Besar at station 8 to 11. Station 1 to 4 which located close to the river mouth show higher level than the samples collected from station 8 to 11. This shows that the main contributor to Cu concentrations in the river mouth are from Sungai Tanah Merah. In general Zn concentrations in surface sediment also show similar pattern as Cu. Both Cu and Zn show significantly higher level in samples from Sungai Tanah Merah compared to main Sungai Lukut Besar ($p < 0.01$). High level of Cu and Zn concentrations in surface sediments from station 6 and 7 may be due to previous pig farming activities. However the total metal levels have more fluctuations in Sungai Lukut Besar than Sungai Tanah Merah. Copper and zinc have been shown to elevate in the areas close to the source.

Yap et al. (2002) reported that the Cu and Zn concentrations in sediments of the Strait of Malacca near Lukut Estuary were ranges from $72.47\ \mu g \cdot g^{-1}$ and $133.53\ \mu g \cdot g^{-1}$. These values are within the range of values measured in this study.

Geochemical fraction analyses of Cu and Zn in surface sediment are shown in Table 1 and 2. In general, the levels of Cu and Zn in resistant fraction of sediment from both Sungai Tanah Merah and Sungai Lukut Besar are consistence. They range from 40–60% for Cu and 38–60% for Zn. High percentages of Cu and Zn are from oxidisable-organic fractions especially for samples from Sungai Tanah Merah and towards the river mouth. This fraction is considered non-resistance fraction and this is usually considered as input from polluted waters (Yap et al., 2003). High input of organic matter into Sungai Tanah Merah probably contributed to these values. Station 4–7 probably received high organic matter

Table 1. Mean Cu concentrations ($\mu\text{g} \cdot \text{g}^{-1}$) in geochemical fractions of sediment samples.

Station	EFLE	Acid-reducible	Oxidisable-Organic	Resistant	Σ (Non-Resistant)	Total (100%)
1	0.44 (1.2)	0.21 (0.6)	17.77 (46.8)	19.52 (51.5)	18.42 (48.6)	37.94
2	0.47 (1.2)	0.28 (0.8)	12.90 (34.5)	23.74 (63.5)	13.65 (36.5)	37.39
3	0.53 (1.1)	0.30 (0.6)	17.80 (37.4)	28.93 (60.8)	18.63 (39.2)	47.56
4	0.51 (1.2)	0.27 (0.6)	20.92 (47.6)	22.24 (50.6)	21.7 (49.4)	43.94
5	0.86 (0.9)	0.33 (0.4)	50.28 (54.2)	41.30 (44.5)	51.47 (55.5)	92.77
6	0.56 (0.6)	0.18 (0.2)	50.28 (57.4)	36.51 (41.7)	51.02 (58.3)	87.53
7	0.56 (1.0)	0.17 (0.3)	30.69 (53.4)	26.00 (45.3)	31.42 (54.7)	57.42
8	0.57 (1.5)	0.18 (0.5)	15.80 (42.7)	20.45 (55.3)	16.55 (44.7)	37.00
9	0.37 (1.7)	0.24 (1.1)	4.72 (22)	16.09 (75.1)	5.33 (24.9)	21.42
10	0.38 (2.5)	0.28 (1.8)	4.17 (27.1)	10.56 (68.6)	4.83 (31.4)	15.39
11	0.9 (8)	0.17 (1.5)	3.50 (31.1)	6.70 (59.4)	4.57 (40.6)	11.27

* Values in parentheses are percentage of the fraction out of total concentration.

Table 2. Mean Zn concentrations ($\mu\text{g} \cdot \text{g}^{-1}$) in geochemical fractions of sediment samples.

Station	EFLE	Acid-reducible	Oxidisable-Organic	Resistant	Σ (Non-Resistant)	Total (100%)
1	1.99 (1.6)	26.5 (21.8)	43.29 (35.6)	49.89 (41)	71.78 (59)	121.67
2	1.41 (1.1)	17.21 (14)	51.24 (41.7)	53.06 (43.2)	69.85 (56.8)	122.92
3	1.98 (1.4)	21.77 (14.9)	63.48 (43.4)	58.87 (40.3)	87.23 (59.7)	146.1
4	1.93 (1.3)	15.94 (10.6)	74.51 (49.5)	58.06 (38.6)	92.38 (61.4)	150.44
5	3.2 (1.7)	22.99 (12.6)	87.49 (47.9)	69.05 (37.8)	113.68 (62.2)	182.73
6	3.86 (1.8)	26.03 (12.5)	93.67 (44.9)	85.06 (40.8)	123.56 (59.2)	208.62
7	1.13 (0.6)	13.07 (7.5)	80.25 (45.5)	81.87 (46.4)	94.45 (53.6)	176.32
8	1.69 (1.3)	18.47 (13.9)	58.25 (43.8)	54.48 (41)	78.41 (59)	132.89
9	0.48 (0.8)	11.7 (19.1)	17.84 (29.2)	31.13 (50.9)	30.02 (49.1)	61.15
10	0.43 (0.6)	8.35 (11.6)	24.92 (34.8)	37.93 (53)	33.7 (47)	71.63
11	0.65 (1.3)	6 (12.5)	12.51 (25.9)	29.08 (60.3)	19.16 (39.7)	48.24

* Values in parentheses are percentage of the fraction out of total concentration.

input from human activities. As a whole the anthropogenic input of Cu and Zn into Lukut River system are about 40–60%. Station 5–7 show more than 60% of Cu and Zn input are from anthropogenic activities. Similar pattern of Cu and Zn levels in sediment were observed by Ismail and Ramli (1997) in Sepang River which received about similar effluent. Ismail and Ramli (1997) showed that sediment of the Sepang estuary which received pig farm effluent, contained high levels of copper ($4\text{--}670 \mu\text{g} \cdot \text{g}^{-1}$) and zinc ($4\text{--}550 \mu\text{g} \cdot \text{g}^{-1}$) which were far higher than this study. Lower levels of Cu and Zn from Lukut River are probably because pig farm activities have been stopped.

Lukut River system basically is an intertidal river which experiences two low and high tides twice daily. This phenomenon may help to reduce the copper and zinc concentrations in the surface sediment through tidal process. Zinc especially, releases easily into the aquatic system compared to copper. If the pollutant input into the river system can be controlled, high levels of Cu and Zn in the surface sediment can be reduced through natural tidal process.

The concentration of Cu and Zn in the soft tissues of

Table 3. Concentration of Cu and Zn in *Telescopium telescopium* (Values expressed in $\mu\text{g} \cdot \text{g}^{-1}$, wet weight).

Station	N	Mean length (mm)	Cu $\mu\text{g} \cdot \text{g}^{-1} \pm \text{S.D}$	Zn $\mu\text{g} \cdot \text{g}^{-1} \pm \text{S.D}$
1	15	78.65	60.3 ± 7.97	53.8 ± 9.82
2	15	81.02	57.1 ± 6.19	58.4 ± 8.43
3	15	82.95	51.5 ± 11.25	51.3 ± 7.14
4	15	78.97	47.4 ± 11.12	49.9 ± 6.23
5	15	91.95	51.5 ± 9.79	49.2 ± 5.78
6	15	86.54	49.9 ± 7.51	41.4 ± 8.59
7	15	72.45	50.8 ± 8.75	36.7 ± 7.72
8	15	100.16	52.4 ± 9.43	50.9 ± 9.39

Telescopium is shown in Table 3. Copper concentration in the soft tissues ranged from 49.9 to $60.3 \mu\text{g} \cdot \text{g}^{-1}$ while Zn ranged from 36.7 to $58.8 \mu\text{g} \cdot \text{g}^{-1}$. The levels of both metals measured in *Telescopium telescopium* are not highly varied in all stations. In most stations copper and zinc level in soft tissues of *Telescopium telescopium* are lower than their total concentration in sediments. No previous data is available on metal

concentration in *Telescopium* in Malaysia to compare with. The only study were done on heavy metals in benthic organisms were in *Cherithedia* and *Nerita* from Sepang River by Ismail and Ramli (1997). The previous data show the levels of Cu and Zn in those gastropods were positively correlated to the levels of Cu and Zn in the surface sediment. This study shows no positive correlation between Cu and Zn in *Telescopium telescopium* and surface sediment. More study is needed in order to understand this phenomenon. There were two studies on Cu and Zn in *Telescopium telescopium* from Australia by Peerzada et al., (1990) and Jones et al., (2000), but they did not discuss in detail on the correlation of Cu and Zn in *Telescopium telescopium* and surface sediment or water column.

Biologically copper is known needed in gastropods as an essential element in their Cu-based respiratory pigment hemocyanin (Langston et al. 1999). The uptake and regulation of copper in gastropods could be related to this biological needs.

The efficiency of metal bioaccumulation in a mollusc species can be estimated from the ratios of the metal concentration in the organism to that in the sediment. Such a ratio has been suggested to form the basis for the introduction of an accumulative index for more objective comparisons between different organisms in their abilities in bioaccumulating of metals in aquatic environment (Lau et al., 1998). The accumulative index (Metal in *Telescopium* / Total metal in sediment) ranged from 0.55 to 1.58 and 0.20 to 0.48 for Cu and Zn respectively. This indicates that metals specially zinc are not highly accumulated by *Telescopium* in Lukut River. Although the accumulation ratio of copper is higher than zinc but the levels are still low.

The accumulative indices provide some indication as to the suitability of using the particular organism for monitoring the level of a certain metal in the aquatic environment (Lau et al., 1998). However from the data can be suggested that some kinds of regulation should be involve in control of Cu and Zn level in soft tissues of *Telescopium telescopium*. Some authors have reported a reasonable ability of molluscs for regulating Cu and Zn in their tissues (Amiard-Triquet et al., 1986). As it is well known, only a few marine organisms are able to regulate metal concentration level in tissues. This ability, however, exists for only a limited range of environmental concentrations for some essential elements such as Cu and Zn (Phillips, 1995).

Several molluscs species, especially bivalves and gastropods have been found to reflect the ambient metal concentration and have been used as biomonitoring agents for heavy metal pollution (Nicolaidou and Nott, 1998; Langston, et al., 1999; Seong et al., 1999; Ismail and Yap, 2001; Cubbada et al., 2001; Campanelle et al. 2001; Yap et al., 2002; Gay and Maher 2003 and Conti and Cecchetti, 2003). In this study show there is no significant correlation in metal concentra-

tion between *Telescopium telescopium* and sediment. This indicate that the changes in sediment metal loading were not the only factor that influenced the level of bioavailability of Zn and Cu into *Telescopium telescopium*. They are many other factors that influence the bioaccumulation of metals such as rates and mechanisms of metal accumulation were taking place between *Telescopium* sp. and the sediment, and other biological and physico-chemical factors (Rainbow, 1997).

Eventhough *Telescopium telescopium* did not show a positive correlation with the level of metals in surface sediment, many other characters such as sessile or sedentary which are representative of the study area, hardy and tolerating high concentrations of pollutants and large ranges in salinity which permitting laboratory studies, abundant in study areas, easy to identify and collected and the tissues are enough for analysis of contaminants, suggested that *Telescopium telescopium* can be used as a good biomonitoring agent.

Conclusion

This study revealed that the levels of copper and zinc are elevated in some stations that received effluent from human activities and these contributed the levels of copper and zinc in the estuaries of Lukut River. Fourty to sixty percents of copper and zinc measured in intertidal surface sediment are from anthropogenic activities and the levels are high in the samples from the sources and declined towards the river mouth. *Telescopium telescopium* can be suggested as biomonitoring agent for assessing copper and zinc in this river. High level of copper and zinc in the river system need to be monitored as the development of shrimp ponds and aquacultural activities are in progress in the area. Continuous contribution of pollutant due to human activities may affect the aquacultural activities as a whole.

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