**Research Note** 

## A HIGHER BIOAVAILABILITY AND CONTAMINATION OF TRACE METALS IN PANTAI LIDO THAN SUNGAI SEMERAK: EVIDENCE FROM TRACE METAL CONCENTRATIONS IN *Polymesoda expansa* AND SURFACE SEDIMENTS

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Ecotoxicological studies always focused on the pollutant levels in the biomonitors in order to understand better its distribution and abundance over a geographical range. Distribution of metals in the different tissues of bivalves are means to understand the fate and initial transport of metals from the sources to the final storage site of metals in the biomonitors (Yap *et al.*, 2006a; 2006b). This information is important since those metals stored and bioavailable to the biomonitors are of ecotoxicological relevance.

The use of bivalve as a biomonitor of trace metals in the coastal waters are well documented in the literature (Hamed and Emara, 2006; Yap *et al.*, 2006a, 2006b). Marine bivalves are advantageous since the concentrations found in the soft tissues of mussels can provide a time-integrated measurement of metal pollution apart from contamination and bioavailability of metals in the coastal waters (Yap *et al.*, 2006a, 2006b). Since they are sedentary, longlived and widely distributed, their metal body burden can reflect the contamination history of a certain coastal environment (Rainbow, 1995). In Malaysia, Edward *et al.* (2009) and Yap and Azri (2009) had documented the metal levels in *Polymesoda* clams.

In this study, surface sediments were also analyzed because elevated concentrations of metals have been recorded in mangrove sediments all over the world, which often reflect the long-term pollution caused by human activities (Tanner *et al.*, 2000). Moreover, sediments can also act as sinks of trace metals and they are also agents of sources and transportation of heavy metals in the intertidal area (Bryan and Langston, .1992). Previously, Yap *et al.* (2002, 2003, 2004) found that Pantai (P.) Lido was a relatively uncontaminated site in comparison to a metal-contaiminated site at Kg. Pasir Puteh. The objective of this study was to determine the concentrations of Cd, Cu, Fe and Ni in the different tissues of clam *P. erosa* collected from P. Lido and Sg. Semerak besides surface sediments from both sampling sites, with special reference to the reported data from a known metalcontaminated site from Kg. Pasir Puteh.

In this study, surface sediments and about 25-30 of *P. expansa* were collected from P. Lido, Johore



**Fig. 1.** The sampling sites for *Polymesoda expansa* in Peninsular Malaysia (1= Pantai Lido; 2= Sg. Semerak).

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on 3 May 2008 and Sg. Semerak, Kelantan on 14 May 2008 (Figure 1). In addition, some in-situ surface water parameters, namely temperature, conductivity, salinity, total dissolved solids and dissolved oxygen were recorded during the sampling campaigns (Table 1). Measurements of shell length, shell width and shell height of the clams are given in Table 2. In the laboratory, the clams were dissected and pooled into five parts namely: muscle, foot, mantle, gill and remainder. The different pooled tissues were dried at 80°C in an oven for 72 hours until constant dry weights. For the clam samples, three replicates of each different pooled tissue were then digested in concentrated nitric acid (AnalaR grade; BDH: 69%) (Yap et al., 2003). For the sediments, the dried sediment samples were crushed by using a mortar and pestle and sieved through a 63 µm aperture stainless steel sieve and were shaken vigorously to produce homogeneity. For the analysis of total metal concentrations in the sediment samples, three replicates were analyzed by using the direct aqua-regia (AR) method. About 1g of each dried sample was digested in a combination of concentrated HNO<sub>3</sub> (AnalaR grade; BDH 69%) and HClO<sub>4</sub> (AnalaR grade; BDH 60%) in the ratio of 4:1.

The clam tissue samples and sediment samples were put into a hot-block digester first at 40°C for 1 hour and then were fully digested at 140°C for at least 3 hours. For the analytical procedures for four geochemical fractions of the surface sediments, sequential extraction technique described by Badri and Aston (1983) and slightly modified by Yap *et al.* (2002) was used. These four fractions employed were easily, freely, leacheable, or exchangeable, (EFLE), acid-reducible (ARed), oxidisable-organic (OO) and resistant (Res). The summation of first three fractions form the nonresistant fraction which is mostly related to various anthropogenic sources and thus provides an estimate of human-induced fraction (Badri and Aston, 1983; Yap et al., 2002). In this study, the percentages of nonresistant fractions for all metals were calculated. The concentrations of Cd, Cu, Fe and Ni of the digested filtrates of both the clams and sediments were determined using an air-acetylene flame atomic absorption spectrophotometer (FAAS) Perkin-Elmer Model AAnalyst 800. The data are presented in ig/ g dry weight basis. Procedural blanks and quality control samples made from standard solutions with each metal were analyzed once every five samples in order to check for sample accuracy. In addition, the quality of the analytical procedures used for sediment analysis were checked by a Certified Reference Material (CRM) for Soil (Soil-5, IAEA, Vienna, Austria) while for the clam samples were verified by using CRM for Dogfish Liver (DOLT-3, National Research Council Canada). The recoveries for both CRMs were being satisfactory between 80-120%. To compare the metal levels of any two sampling g sites, the t test were generated by using the STATISTICA (99' Edition) software package.

The metal concentrations in the different tissues of *P. expansa* are given in Table 3. In general, the levels of all metals in all the tissues are significant (P < 0.05) higher in P. Lido than in Sg. Semerak except for Cd in all tissues and Fe in remainder. Still, all the Cd levels except for foot were higher (although not significant) in P. Lido than in Sg. Semerak. This general pattern strongly indicated that the metals in P. Lido had higher bioavailability to the biomonitor *P. expansa* when compared to those collected from Sg. Semerak. This suggested that P.

Table 1. In-situ surface water parameters recorded at the sampling sites.

Sampling sites	GPS	Site descriptions	Temp (°C)	Cond (µs/cm)	TDS (g/L)	Sal (ppt)	DO (mg/L)
Pantai Lido	01°28.001′ N 103°43.618 E	Urban area.	30.94 ± 0.01	34570 ± 37	20.19 ± 0.02	19.17 ± 0.02	0.11 ± 0.03
Sungai Semerak	5°51'56.99"N 102°30'27.67"E	Mangrove area.	30.89 ± 0.02	39270 ± 2.89	22.33 ± 0.01	20.87 ± 0.00	0.32 ± 0.01

Note: Temp= temperature; Cond= conductivity; Sal= salinity; TDS= total dissolved solids; DO= dissolved oxygen.

 Table 2. Measurements (mean ±SE, cm) of shell length, shell width and shell height of Polymesoda expansa. N= number of individuals analyzed.

No.	Sampling sites	Ν	Width	Length	Height
1.	Pantai Lido	30	6.75±0.21	6.08±0.78	3.53±0.05
2.	Sg. Semerak	32	6.30±0.12	6.04±0.09	3.55±0.05

		PLido	Semerak	KPPuteh**
Cu	Adductor muscle	4.34 ± 0.25*	3.22 ± 0.16	7.73 ± 2.67
	Foot	4.99 ± 0.28*	$3.59 \pm 0.26$	NA
	Gills	27.27 ± 4.98*	11.34 ± 0.13	$26.2 \pm 0.000$
	Mantle	21.32 ± 2.16*	10.38 ± 1.08	61.6 ± 1.92
	Remainder	15.09 ± 1.35*	$7.65 \pm 0.48$	19.7 ± 0.706
Cd	Adductor muscle	1.43 ± 0.17	1.04 ± 0.16	0.302 ± 0.025
	Foot	1.08 ± 0.12	$1.42 \pm 0.06$	NA
	Gills	2.15 ± 0.11	$1.82 \pm 0.07$	1.21 ± 0.000
	Mantle	2.04 ± 0.15	$1.79 \pm 0.07$	0.706 ± 0.168
	Remainder	1.88 ± 0.12	$1.66 \pm 0.09$	0.585 ± 0.155
Fe	Adductor muscle	396.6 ± 115.7*	101.6 ± 5.19	616 ± 96.2
	Foot	204.9 ± 10.8*	111.5 ± 5.19	NA
	Gills	748.5 ± 281.0*	584.2 ± 13.7	1567 ± 0.000
	Mantle	735.3 ± 42.4*	456.5 ± 25.3	1677 ± 6.84
	Remainder	933.7 ± 196.9	1039.8 ± 185.7	740 ± 267
Ni	Adductor muscle	5.53 ± 0.25*	1.67 ± 0.51	10.4 ± 0.645
	Foot	2.82 ± 0.55*	$0.53 \pm 0.42$	NA
	Gills	14.30 ± 0.85*	5.81 ± 0.23	15.4 ± 0.000
	Mantle	31.18 ± 0.59*	8.32 ± 1.06	11.4 ± 0.053
	Remainder	6.50 ± 1.47*	0.76 ± 0.29	8.58 ± 0.404

**Table 3.** Comparisons of mean trace metal concentrations (µg/g dry weight) in the different tissues of *Polymesoda expansa* between Pantai (P) Lido and Sg. Semerak.

Note:\*\* indicated data of Kg. Pasir Puteh were cited from Edward *et al.* (2009). Those values indicated by \* are significantly higher (P< 0.05) than the other sampling site (between PLido and Semerak).

Table 4. Mean concentrations ( $\mu$ g/g dry weight) of trace metals in the four geochemical fractions of surface sediments collected from Sungai Semerak and Pantai (P) Lido.

		Cd	Cu	Fe	Ni
EFLE	Semerak	0.03	0.22	0.91	0.20
	PLido	0.12*	0.61*	30.05*	0.37*
ARed	Semerak	0.05	0.01	951	0.33
	PLido	0.12*	0.35*	474*	1.12*
00	Semerak	0.08	4.62	3325	2.75
	PLido	0.10	11.12*	6600*	13.18*
Res	Semerak	0.63	14.88*	29596*	6.08
	PLido	0.64	10.66	19059	7.59
SUM	Semerak	0.78	19.73	33872*	9.35
	PLido	0.99*	22.74	26163	22.27*
AR	Semerak	0.75	15.43	29830	7.86
	PLido	0.96*	25.97*	32353*	15.06*
NonR(%)	Semerak	20.25	24.58	12.63	35.04
	PLido	34.69*	53.12*	27.15*	65.90*
Res (%)	Semerak	79.75*	75.42*	87.37*	64.96*
	PLido	65.31	46.88	72.85	34.10

Note: EFLE= easily, freely, leacheable or exchangeable; ARed= acid-reducible; OO= oxidisable-organic; Res= resistant; SUM= summation of EFLE, ARed, OO and Res; AR= direct aqua-regia method; NonR(%)= percentage of non-resistant

 $\label{eq:fraction} \text{fraction} \; [\frac{\text{EFLE} + \text{ARed} + \text{Res}}{\text{SUM}} \times 100\% \; \text{]; } \; \text{Res(\%)= (100-NonR)\%}.$ 

Those values indicated by \* are significantly higher (P< 0.05) than the other sampling site.

Lido as being an active urban area potentially receiving domestic wastes and vehicular runoff while Sg. Semerak as a mangrove area with hardly any observable human activities in the surrounding. However, in comparison to the data reported by Edward *et al.* (2009) in the population from Kg. Pasir Puteh (as cited in Table 3), generally, the concentrations of Cu, Fe and Ni in most tissues of *P. erosa* were higher than those in P. Lido. This indicated that Kg. Pasir Puteh which is located near Pasir Gudang, with many human activities found, was still considered as a metal-polluted site based on metal concentrations accumulated by *P. erosa*.

A few researchers (Dang et al., 2005; Hamed and Emara, 2006; Yap et al., 2006a) had discussed the suitability of the use of molluscs to provide the time-integrated bioavailability and contamination by heavy metals in coastal waters since the bioavailabilities are hardly provided by the analyses of seawater and sediment (Rainbow, 1995; Rainbow et al., 2002). Some explanations can be given to understand the metal distributions in the different soft tissues of P. expansa. In general, the higher metal levels found in mantle and gill indicated the high surface area of contact over total volume which potentially facilitated the metal uptake through these two organs (Yap et al., 2006c; Edward et al., 2009). Some tissues with higher metal accumulation could be a result of more affinities of metals to the binding sites at metallothionein found in the different soft tissues (Roesijadi, 1980; Viarengo et al., 1985). In this study, gill was believed to have high affinities of Cu because the highest concentrations were found in that tissue. According to Gundacker (1999), the differences in the rates of accumulation and depuration indicated that they were the results of internal metal treatment and regulation in the different soft tissues of bivalves.

The metal concentrations in the four geochemical fractions of the surface sediments are given in Table 4. In general, most of the metal levels in the first three geochemical fractions (EFLE, ARed and OO; which are related to anthropogenic inputs) of the surface sediments are significantly (P < 0.05) higher in Pantai Lido and Sg. Semerak. It is also clearly shown that the total concentrations of Cd, Cu, Fe and Ni are significantly (P < 0.05) higher in Pantai Lido than in Sg. Semerak. The non-resistant percentages of all the four metals, which are indicators of anthropogenic input, are also significantly (P< 0.05) higher in Pantai Lido than in Sg. Semerak. Thus, these results indicated that Pantai Lido was more contaminated by metals than Sg. Semerak based on surface sediments.

In conclusion, further study should be conducted to confirm the *P. erosa* as a biomonitor of trace metal pollution based on other recommended criteria for a good biomonitor.

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