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Lead in surface sediments of the Straits of Malacca

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The chemical fractionation of lead (Pb) was determined in surface sediments collected during two cruises in the Straits of Malacca. Total Pb (not included the terrigenous silicate) concentrations in the sediments range from 8.2 to 28.5 μg/g. Nonresistant fractions [easily or freely leachable and exchangeable (EFLE), acid-reducible and oxidisable-organic] contribute 74% (December 1998) and 71% (April 1999) of the total Pb concentration of the sediments. Among the nonresistant fractions, the oxidisable-organic fraction contributes 75-80%. This may indicate that although the total Pb concentrations in the sediments are relatively low in comparison with other regional data and established sediment quality guidelines, the chemical fractionation shows that most (about 70%) of the total Pb found in the sediment could be mostly related to anthropogenic sources although further validation is required.

[**Key words**: Chemical fractionation, sediment, the Straits of Malacca]

Environmental contamination by Pb arises from various sources such as manufacturing processes, paints and pigments, emissions from motor vehicles, incineration of municipal solid waste, combustion of coal, and hazardous wastes[1]. In biosphere, the metabolic requirements of Pb is not understood yet[2]. The Pb may interfere with several enzymes that participate in the heme synthesis pathways. Due to its toxic nature, the ubiquitous Pb has been studied in biological samples[3], coastal sediments[4,5] etc.

Environmental concerns are growing in the Straits of Malacca (Fig. 1) because of activities such as shipping and fishing wherein the region provides relatively easy sites for hazardous waste disposal[6]. The coastal and estuarine sediments have been extensively used to monitor the marine environmental degradation due to anthropogenic activity[4,5]. In Malaysia, fractionation of heavy metals between carrier phases have been reported for river[7-9] and intertidal sediments[10]. The objective of this study is to determine the association of Pb with different sedimentary fractions (EFLE, acid-reducible, oxidisable-organic and resistant) and to estimate Pb contamination in the Straits of Malacca.

In this study, the sequential extraction technique (SET) was used to approximately differentiate the anthropogenic metals from those of natural origin. The chemical fractions employed in this study are easily or freely leachable and exchangeable (EFLE), acid-reducible, oxidisable-organic and resistant. However, the possibility of non-selectivity of extractants and readsorption/redistribution of heavy metals among different phases during extraction[11,12] are two difficulties associated with the SET. Despite these problems, the SET still represents one of the few tools available for examining the sedimentary fractionation of metals. Moreover, several previously published works have used the SET in comparative studies of metal contamination in the coastal areas[12-15].

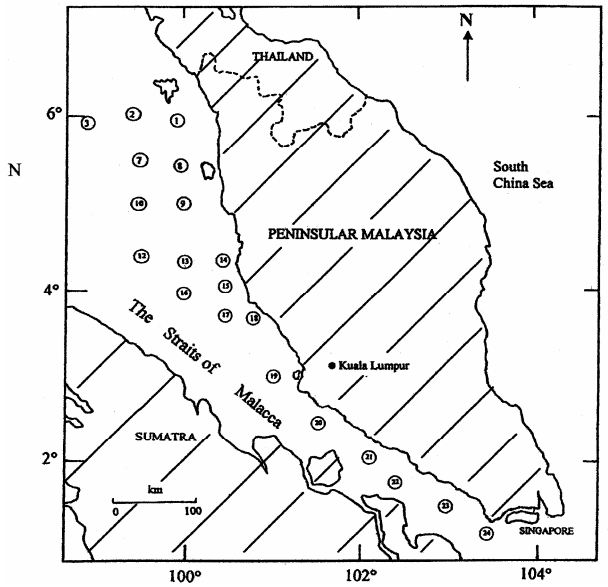


Fig. 1 — Sampling locations along the Straits of Malacca

Materials and Methods

Surface sediment samples were collected during two cruises. The first cruise was conducted between November-December 1998 on board *RV K. K. Mersuji*, and the second cruise was conducted between March-April 1999 on board *RV K. K. Jenahak*. The sampling stations of the two cruises were in the Straits of Malacca from the Pulau Langkawi to the southern part of Johore (Fig. 1). One sediment sample from each station was collected using a Smith-McIntyre grab (0.5 m × 0.5 m). The top 3 to 5 cm thick sediment sample from each grab was placed in an acid-washed polyethylene bag and preserved at –10°C to prevent oxidation of organics[4,5]. The samples were transported to laboratory and were dried at 105°C and ground.

Triplicates from each sampling site were analysed. For the SET of Pb from the sediments, the modified SET described by Badri & Aston[16] was followed. The four fractions extracted are as follows:

1. EFLE: Around 10 g of powdered sample was agitated for 3 h in 50 ml of 1 *M* ammonium acetate (NH_4CH_3COO), maintained at *p*H 7 under room temperature.
2. Acid-reducible: The residue from (1) was agitated for 3 h in 50 ml of 0.25 *M* hydroxylammonium hydrochloride ($NH_2OH.HCL$), maintained at *p*H 2 under room temperature.
3. Oxidisable-organic: The residue from (2) was first oxidized with H_2O_2 (30% v/v) in a water bath at 90-95°C. After cooling, the reaction mixture was agitated for 3 h after adding 50 ml of 1 *M* ammonium acetate (NH_4CH_3COO) acidified to *p*H 2.
4. Resistant: The residue from (3) was digested in a mixture of concentrated nitric acid (69%) and perchloric acid (60%).

The residue used in each leaching step was weighed before the next fractionation was carried out. The residue was washed with 20 ml double distilled water, then filtered through Whatman No 1 filter-paper, and the filtrate was stored until metal determination. At each leaching step, a reagent blank was also subjected to the extraction and finally used as calibration blank to account for any external contamination. Pb content in each extracted nonresistant fraction of the sediment was measured using a flame atomic absorption spectrophotometer (Perkin-Elmer Model 4100). The Pb concentrations are presented in μg/g on dry weight basis.

A quality control sample, made from standard Pb solution (MERCK), was routinely run through during the period of analysis. The accuracy of the analysis was checked with the standard addition testing procedure. The percentage of recovery of Pb in each extraction step was better than 92 %.

In addition, the sediment from each sampling site was analysed for total Pb (not included the terrigenous silicate) by direct digestion method [concentrated nitric acid (69 %) and perchloric acid (60 %)]. The sum of all extraction steps was compared with that found by using the direct digestion method. Values of SET are acceptable since satisfactory recovery (with a high correlation coefficient of $R= 0.94$, $P < 0.001$ between the sum of four fractions [mean: 22.60 μg/g] and direct digestion [mean: 21.87 μg/g]) for Pb was found in the analytical results, by using the SET when compared to those of the direct digestion method. The direct digestion method was also checked with a Certified Reference Material (CRM) for Soil (International Atomic Energy Agency, Soil-5, Vienna, Austria). The percentage of the Pb recovery checking with the CRM was 103 % (Measured: 133 μg/g dry weight; Certified: 129 μg/g dry weight).

Results

The results for all the fractions are presented in Table 1. The Pb concentration ranges in different fractions of samples collected during December 1998 and April 1999 are; in the EFLE, from 1.0 to 1.9 μg/g and 0.4 to 2.5 μg/g; in the acid-reducible, from 0.4 to 2.7 μg/g and 0.3 to 2.4 μg/g; in the oxidisable-organic, from 5.4 to 16.3 μg/g and 5.3 to 16.7 μg/g and in the resistant, from 0.8 to 9.4 μg/g and 1.7 to 14.4 μg/g, respectively. The total Pb (terrigenous silicate not included) concentration ranges from 8.2 to 26.6 μg/g and 9.4 to 28.5 μg/g, respectively in the samples of December 1998 and April 1999. Generally, no significant differences ($P > 0.05$) were found between results of the two periods of sampling.

The fractionwise distribution of Pb in the sediments representing two periods of sampling are summarised in Fig. 2. The oxidisable-organic fraction contributes the most of the total Pb (> 55 %). The contribution from the resistant phase is < 30 % and the acid-reducible and EFLE fractions together contribute < 15%.

From the Fig. 3, it is evident that > 70 % of the sedimentary Pb is associated with nonresistant phase

Table 1 — Pb concentrations in four sedimentary fractions of the Malacca Straits

St no.	December 1999					April 1999				
	EFLE	Acid-reducible	Oxidisable-organic	Resistant	Total (100%)	EFLE	Acid-reducible	Oxidisable-organic	Resistant	Total (100%)
1.	1.2 (8)	1.4 (9)	8.6 (58)	3.7 (25)	14.8	NA	NA	NA	NA	NA
2.	1.8 (8)	2.7 (11)	10.3 (42)	9.4 (39)	24.2	1.8 (9)	1.9 (9)	9.2 (45)	7.7 (37)	20.7
3.	1.4 (8)	2.2 (13)	5.8 (34)	7.5 (45)	16.9	1.6 (8)	1.7 (8)	9.3 (45)	8.1 (39)	20.7
7.	1.3 (7)	2.6 (14)	9.9 (52)	5.1 (27)	18.8	1.0 (6)	1.6 (9)	9.3 (53)	5.4 (32)	17.3
8.	1.4 (9)	2.0 (14)	8.2 (57)	2.9 (20)	14.5	1.1 (7)	1.1 (7)	11.9 (75)	1.7 (11)	15.8
9.	1.5 (6)	2.1 (8)	16.3 (63)	5.9 (23)	25.7	1.2 (6)	1.2 (6)	14.1 (66)	4.8 (22)	21.3
10.	1.5 (9)	2.6 (14)	8.2 (46)	5.7 (31))	17.9	0.9 (6)	1.7 (10)	11.0 (70)	2.3 (14)	15.8
12.	NA	NA	NA	NA	NA	1.6 (8)	1.6 (7)	10.8 (50)	7.7 (35)	21.6
14.	1.9 (7)	0.8 (3)	15.1 (57)	8.6 (32)	26.3	2.5 (9)	1.6 (6)	16.7 62)	6.2 (23)	26.9
15.	1.2 (8)	2.2 (15)	8.0 (54)	3.4 (23)	14.8	1.5 (11)	1.0 (7)	8.5 (62)	2.8 (20)	13.7
16.	1.0 (6)	2.7 (16)	6.4 (37)	7.0 (41)	17.0	1.6 (14)	1.9 (17)	6.3 (54)	1.8 (15)	11.7
17.	1.3 (11)	1.6 (15)	7.0 (64)	1.1 (10)	11.0	1.2 (8)	1.4 (11)	7.9 (59)	2.9 (22)	13.4
18.	1.6 (6)	1.7 (7)	15.2 (58)	7.5 (29)	25.9	1.4 (5)	2.4 (8)	10.4 (37)	14.4 (50)	28.5
20.	1.2 (14)	0.9 (11)	5.4 (65)	0.8 (10)	8.2	NA	NA	NA	NA	NA
21.	NA	NA	NA	NA	NA	0.7 (8)	0.3 (4)	5.3 (56)	3.1 (32)	9.4
22.	1.0 (9)	0.4 (4)	6.9 (69)	1.8 (18)	10.1	0.4 (4)	0.7 (6)	7.7 (66)	2.7 (24)	11.6
23.	1.0 (5)	1.7 (8)	14.7 (69)	3.8 (18)	21.2	1.2 (5)	1.4 (6)	13.8 (58)	7.2 (31)	23.5
24.	1.1 (4)	1.9 (8)	16.0 (67)	4.9 (21)	23.9	0.5 (2)	1.3 (6)	7.5 (34)	12.9 (58)	22.2

Note: The values in parentheses represent the fractions in percentages. NA: Not available. Total Pb does not include the terrigenous silicate of sediment in the present study. EFLE is easily or freely leachable and exchangeable.

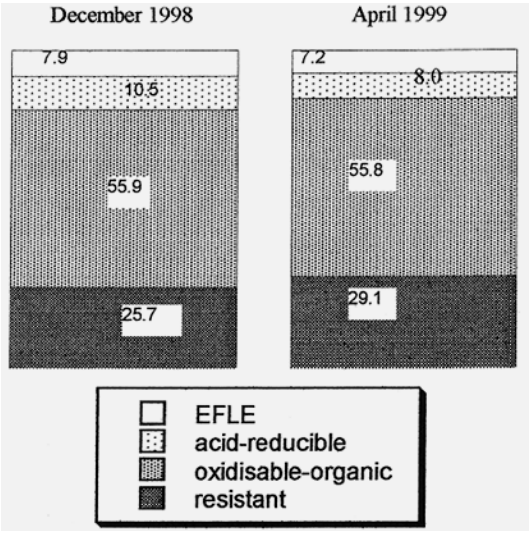


Fig. 2 — The concentrations (μg/g) of Pb with resistant and non-resistant phases in the sediments of the Straits of Malacca (N = 96).

in almost all the stations. Few stations, in particular, sts. 17 and 20 from first cruise samples and sts. 8 and 10 from second cruise samples exhibit extremely high levels of Pb content (about 90 %) associating with nonresistant phase.

Only strong and significant correlations among the different chemical fractions are shown in Fig. 4. The total Pb concentrations are significantly correlated with resistant ($R = 0.98$, $P < 0.001$), oxidisable-organic ($R = 0.92$, $P < 0.001$) and EFLE ($R = 0.81$, $P < 0.001$) fractions of the sediments. In addition, the relationships among the four sedimentary fractions were found to be positively significant between EFLE-oxidisable-organic ($R = 0.80$, $P < 0.001$) while the rest are poorly associated.

Discussion

The measured total Pb range in the Straits of Malacca sediment (8-29 μg/g) is much lower than the ranges of sedimentary Pb reported from various offshore regions in Southeast Asia (2-450 μg/g)[17-20]. The concentrations of Pb in sediments of the United Kingdom range from 20 μg/g in relatively pristine areas to more than 2700 μg/g in heavily contaminated sites such as Gannel Estuary[21]. The recorded Pb levels in the present study when compared to near shore and open ocean sedimentary Pb range (20-320 μg/g)[22], the total Pb levels in the sediments of the Malacca Straits are considerably low regardless of anthropogenic pressure on the Straits.

As compared to the reported sediment quality guidelines for Pb in other areas, our results are considered as 'No Effect Level' (23 μg/g) to 'Lowest Effect Level'[23] (31 μg/g) and within the 'Effect Range Low' (47 μg/g) as proposed by Long *et al*[24]. The above comparisons of our results with international sediment quality guidelines show that the Pb contamination level in the Straits of Malacca is not

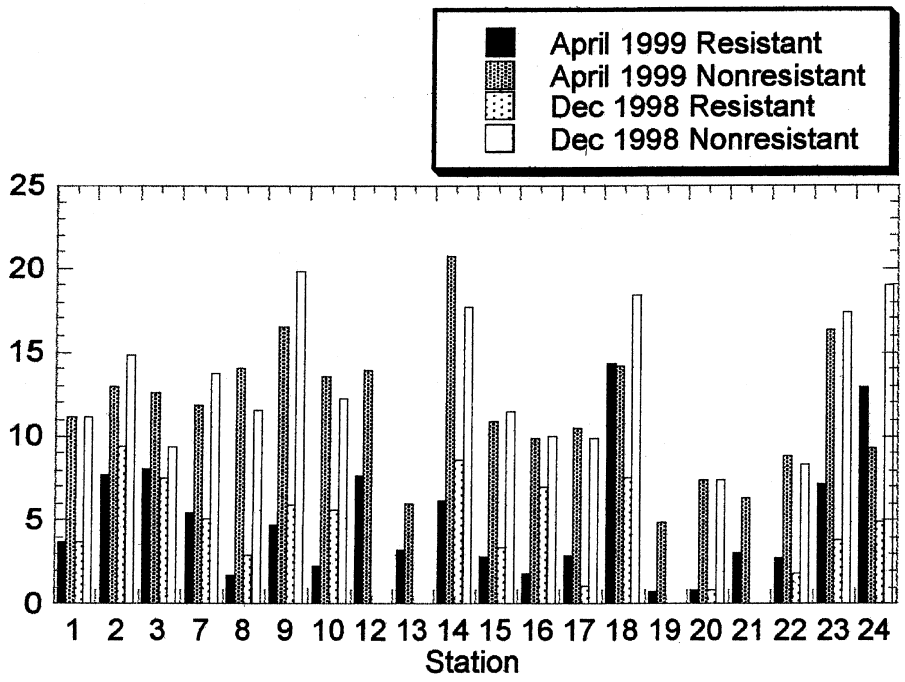
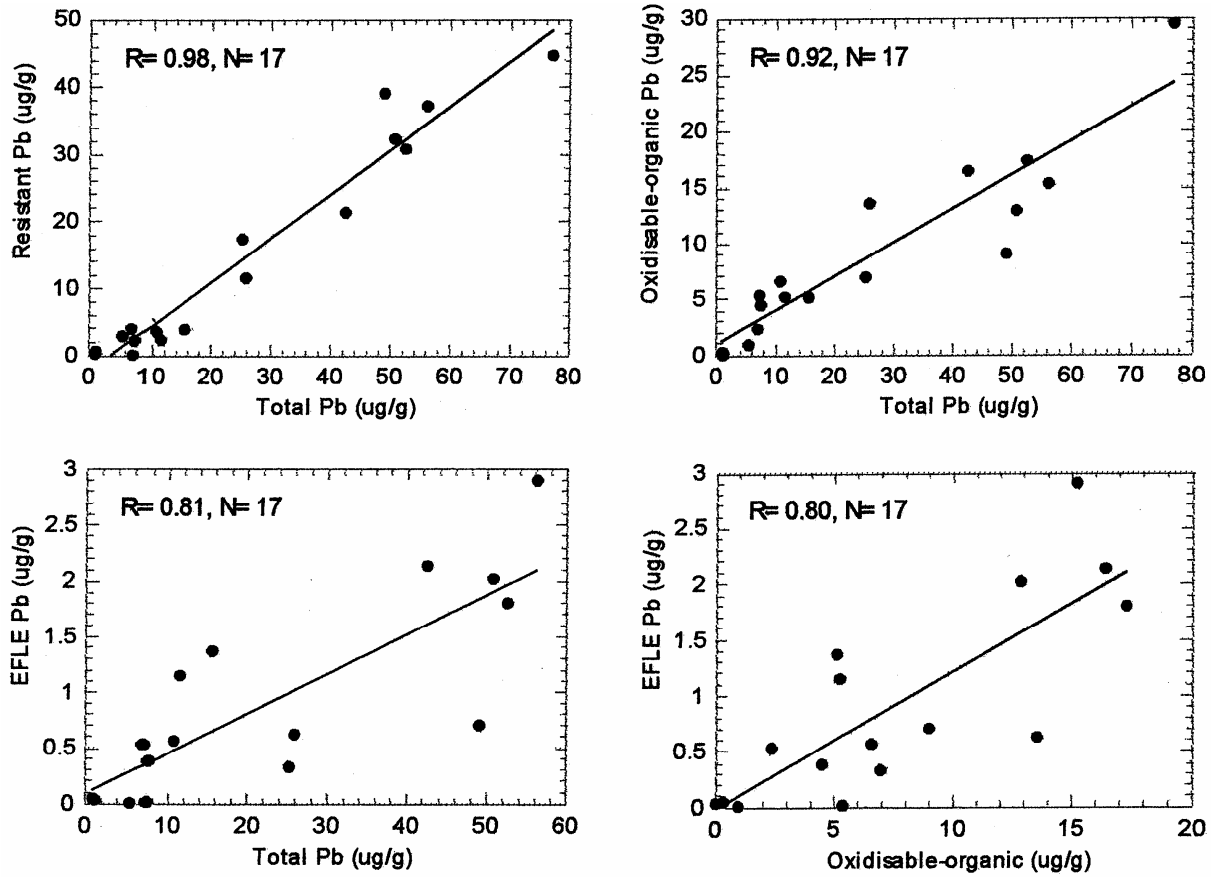


Fig. 3 — The concentrations (μg/g) of Pb with resistant and nonresistant phases in the sediments of the Straits of Malacca (N= 96).



serious. Although the established sediment quality guidelines for metals were obtained from the temperate region, it is still the few available information to approximately compare the status of metal levels from other areas including the Malacca Straits[25]. As the background level of Pb in the sediments of the Straits is not established, it is difficult to conclude whether or not Pb contamination has taken place as a result of anthropogenic activities. Additionally, the obtained Pb values are well within the established 'environmentally tolerant levels', it may be assumed that the results of the present study form the nearly pristine levels in the Malacca Straits. This could be due to the through-flow between the South China Sea and the Andaman Sea continuously cleans up the Malacca Straits preventing accumulation of anthropogenically introduced chemical compounds but this occurrence/assumption should be further investigated. The second possibility is that our sampling (upper 3-5 cm thick sediment from the grab surface) has averaged the high Pb levels in surface few mm sediment. This could be due to the anthropogenic activity was limited to last one century. Last one century contamination signals can be obtained only in the upper few mm thick sediment. Below that, the sediment shall not have anthropogenic signals. Since we sampled 3-5 cm thick sediment, the Pb contamination signals in the upper few mm could have mixed up with several tens of mm of natural signals. This could yield the Pb values been averaged for upper 5 cm which may correspond to thousands of years deposition.

Since the mathematical summation of EFLE, acid-reducible and oxidisable-organic fractions constitutes the nonresistant phase[16], this nonresistant fraction is closely related to anthropogenic inputs while the resistant form exists in nature and is derived from geological processes[14]. Anthropogenic-derived metals as well as from natural origins might contribute to the nonresistant fraction in the sediments[16] and this fraction is influenced by physico-chemical properties of the sediments[11]. In the Malacca Straits, we found about 70 % of the sedimentary Pb could be related to anthropogenic sources.

It should be noted that although EFLE fraction only contributes < 10 % of the total Pb, this fraction is significantly correlated with oxidisable-organic fraction. This agrees with the fact that EFLE fraction is associated with the amount of exchangeable surfaces of clays and organic matter[16]. More organic matter content will provide larger surfaces of the Pb binding onto this EFLE fraction.

The poor relationship between acid-reducible and oxidisable-organic indicates that the low association between organically-bound component of the sediment and the Mn and Fe oxides and hydroxides, and carbonates. Also, the acid-reducible is poorly associated with the total Pb and fractions of EFLE and resistant.

Total Pb exhibits strong positive relationship with oxidisable-organic Pb, indicating the main fraction carrying Pb in the sediment is organic matter. The oxidisable-organic fraction contributes 34 to 75 % of the Pb and is the major carrier phase of Pb in the Malacca Straits. This indicates that the reducing conditions in the sediment is mainly caused by the decomposition of organic matter[12] and poor ventilation of the deep water. The oxidisable-organic component which carries the major portion of the bulk sedimentary Pb could be due to the Pb enriched synthetic binding material (paints/pigments) used for ships. The contribution of Pb by various fractions to the bulk sedimentary Pb is nearly similar to both the sampling periods, indicating insignificant variation through time. The present study also suggests that the oxidisable-organic matter is an important sink for the Pb in the Straits.

The nonresistant fractions indicates that about 70 % of the total Pb found in the present study could be due to the contribution of anthropogenic activities from the shipping activities, offshore dumping of the wastes and riverine inputs although further validation is required. However, the relatively low level of sedimentary Pb indicates that the overall Pb contamination in the Straits is not serious. Since Pb is a hazardous metal in the marine environment and most (70%) of the total Pb in the sediments was nonresistant fraction that could be accumulated in the food chain, further biomonitoring programme for heavy metals in the sediment and living resources from the Straits of Malacca is needed.

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