Bull. Environ. Contam. Toxicol. (1995) 55:666–673

Environmental Contamination and Toxicology

Natural and Anthropogenic Trace-Metal Input into the Coastal and Estuarine Sediments of the Straits of Malacca

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Received: 29 July 1994/Accepted: 19 March 1995

One of the concerns of local management authority in Malaysia is the problem of metal pollution in the coastal waters. A survey by the Department of Environment of Malaysia (DOETH, 1985), revealed that, of the total of 220,000 m^3 per annum production of toxic and hazardous wastes in Peninsular Malaysia, approximately 44% was contributed by the metal finishing industries.With regards to this problem, there have been several outcries and finger-pointing, particularly from public awareness group. However, many of the accusations were not substantiated with good, well-interpreted data.

Although studies on heavy metals in the coastal waters of Malaysia have been carried out for more than 15 years, the available data and publications are very limited and patchy. Most of the studies that have been conducted were on metal contents in fish and shellfish (including Babji et al 1978, Jothy et al 1983, and Law and Singh 1988) with less than a handful on metal contents in the environment (Sivalingam et al 1979, Seng et al 1987, and Din 1992). The Department of Environment of the Ministry of Science, Technology and Environment of Malaysia routinely collects trace-metal data from the rivers and coastal areas of the country, but so far, only metal concentrations in the water have been determined (Department of Environment, 1991). While there have been other studies on trace-metal contents in the local marine environment, the data is not easily accessible due to the fact that the studies were conducted under contract with various government as well as private agencies.

With regard to metal contents in the coastal sediments around Malaysia, all the values that have been documented are total concentration of individual metal. Although this kind of information is useful, it has its limitation, and in some cases it may lead to erroneous conclusions. This is because particulate metals from natural and anthropogenic sources accumulate together in the sediment. In order to determine the level of metal pollution in an area we do need to isolate the two metal proportions and this can pose problems because sedimentary metal loads can vary by several orders of magnitude, depending on the mineralogy and grain-size distribution of the area (Loring, 1991). Thus, in order to properly interpret the status of metal pollution in an area, a normalization procedure is recommended so that we will be able to compensate for natural variability of the metals in the sediment, which would then enable us to detect and quantify any anthropogenic metal contribution to the system. In this study, natural and anthropogenic trace metal input into the Straits of Malacca was estimated based on normalization procedures using aluminium as the reference material since it was shown to work for several metals in the area (Din, 1992).

MATERIALS AND METHODS

Twenty four stations were selected along the Malaysian coast of the Straits of Malacca, stretching from close to the Malaysia-Thailand border in the north, to approximately near the Malaysia-Singapore boundary in the south (Figure 1). This covers a distance of more than 800 km. At each site, replicate sediment grabs were taken using a Ponar dredge. Before any sediment sample was taken, the grab samples were each examined to see that a clean grab was accomplished, and that the bottom sediment was not excessively disturbed in the process. Once this was satisfied, a small sample of approximately 100 g wet-weight was taken in the middle of the grab just beneath the top surface using a non-metallic spatula in order to reduce metal contamination from the sampler. The samples were then placed in sealed plastic bags which had been pre-washed with dilute acid, and taken to the laboratory for analysis.

In the laboratory the sediment samples were oven-dried at 80°C for a few days. Each day during the drying period, the sediment samples would be taken out and mixed thoroughly. Upon drying, approximately one-gram portion of the samples was finely ground using a porcelain mortar and pestle. In between samples, the mortar and pestle were cleaned with dilute acid, rinsed with distilled water and dried. About 250 mg of each ground sample was then measured exactly into a 100-mL teflon beaker followed by addition of 10 mL concentrated nitric acid and 10 mL of concentrated hydrofluoric acid. The samples were left to digest in the fume cabinet overnight at room temperature. The next morning, 3 mL of perchloric acid was added into each beaker and the beakers were then placed on hot plates set at 120°C. Once the acid had evaporated to dryness, 2 mL of concentrated nitric acid was added and the samples were reheated to dryness. The beakers were then set aside to cool. Finally, 2 mL of 10% nitric acid was pipetted into the beakers, and after a few swirls to dissolve the residue, the samples were poured into plastic scintillation vials. Each beaker was then rinsed with 18 mL of double-distilled water and this was added into the vials. Prior to analysis of the metals, 10-mL 1/50 dilution for Al , and 1/20 dilution for the other metals were prepared from the sample solutions. Concentrations of aluminium and manganese were determined using a Perkin-Elmer Zeeman 5000 spectrophotometer while a VG Plasma Quad Plus 2 inductively-coupled plasma spectrometer was used for the other metals.

A very strict quality control was maintained during analysis of the metals . The teflon beakers and their covers were cleaned by soaking in concentrated nitric acid for 3 days followed by rinsing with double-distilled water. After each use, the beakers were first wiped with acetone, rinsed with double distilled water before they were soaked in concentrated nitric acid. Before use, the plastic scintillation vials were first soaked in 10% nitric acid and placed on a warm hotplate for 3 days, following which they were rinsed with double distilled water. For the purpose of proper interpretation of metal contamination in the sediments, a total digestion of the sediment samples is required. This was monitored by analyzing a standard estuarine sediment sample (NBS Standard Reference Material 1646) with each batch of sediment, to assess daily performances of the procedure.

Using regression analysis, the concentration of each metal was correlated with the concentration of aluminium. Log-transformation was first carried out for all the data in order to satisfy the assumption of constant variance and normality, as

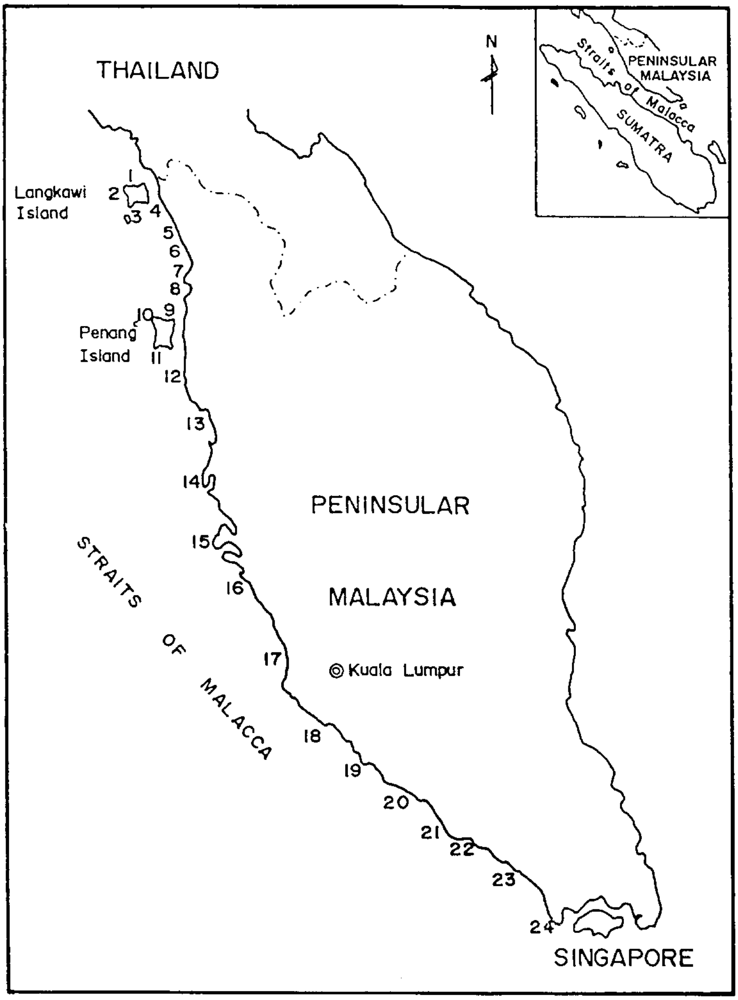

Figure 1. Map of Peninsular Malaysia and the Straits of Malacca showing location of sampling stations

suggested by Schropp and Windom (1988). Stations with data points higher than the 95% pridiction limit of the regression line are considered to have some anthropogenic metal input. For these points, the natural input of the metal was estimated as the upper limit of the 95% confidence band, while the anthropogenic contribution was calculated as the difference between the measured concentration and the estimate of natural input.

RESULTS AND DISCUSSION

Table 1 shows the range of concentrations of trace-metals estimated to be from natural input in the coastal and estuarine sediments along the Straits of Malacca. Only 6 metals are listed because these are the metals that were shown to covary with aluminium (Din, 1992). The difference between the lowest and the highest values ranges from a low of 2 times for lead to a high of 6 times for chromium. Among others, variations in natural concentration of trace-metals in sediments as are seen in this case, can be attributed primarily to 2 main factors; the origin of the sediments and the influence of environmental factors such as wave action which can cause grain-size redistribution of the sediments. With regards to the first factor, the natural concentration of some trace-metals in coastal sediments can vary by an order of magnitude depending on whether they originated from crustal or carbonate rocks. For example, Turekian and Wedepohl (1961) documented that carbonate rocks normally contain 1.0 ppm arsenic, 0.04 ppm cadmium, 4 ppm copper, and 20 ppm zinc while Martin and Whitfield (1983), suggested that crustal rocks typically contains 7.9 ppm arsenic, 0.2 ppm cadmium, 71 ppm copper, and 127 ppm zinc. Based on their origin, the natural input of trace-metals into the coastal sediments of the Straits of Malacca should be quite similar to the values quoted by Martin and Whitfield (1983). This is because these sediments are predominantly composed of river transported debris resulting from weathering of granitic materials. In the coastal areas of Malaysia, carbonate materials are normally associated with the coral islands. Some carbonate materials may accumulate around the coast of Perak (Stations 13 and 14) because of the presence of several limestone hills in that state.

Table 1. Natural input (ppm) of trace-metals in the coastal and estuarine sediments of the Straits of Malacca. Values for typical crustal rocks and deep-sea sediments (from Martin and Whitfield, 1983) are included for comparison.

Metal	Concentration	Crustal Rocks	Deep-Sea Sediments
As	4.0 - 20.0	7.9	13
Cd	0.03 - 0.16	0.2	0.23
Cr	11.2 - 64.6	71	100
Cu	4.1 - 14.1	32	200
Pb	15.8 - 37.1	16	200
Zn	27.5 - 89.1	127	120

In comparing the natural input of trace-metals in the coastal sediments of the Straits of Malacca with values for crustal rocks as documented by Martin and Whitfield (1983), we see that in almost all cases the values in the sediments are lower than in the rocks. This is probably a consequence of wave action resulting in grain-size redistribution of the sediments. Because of their weight, most of the finer sediments, which are predominantly clay materials, will be transported further from shore, leaving behind the coarser quartz material. Since the metals are tightly bound within the aluminosilicate lattice, they will be transported together with the clay materials. This arguement is further supported by the fact that deep-sea sediments are normally enriched in trace-metals, as shown by Table 1.

For the determination of anthropogenic input of trace metals into the Straits of Malacca, only the six metals which were shown to covary with aluminium (Din, 1992) were considered. For convenience, a 20% cut-off point was used in this estimation. On this basis, an anthropogenic input of less than 20% for any metal will be neglected. Table 2 lists the estimated contribution of anthropogenic input of five trace-metals to the sediments of the coastal waters of the Straits of Malacca. Chromium does not appear in the list because, for all the stations, its concentration was almost entirely estimated to be from natural input. Anthropogenic contribution if any, must be negligible.

The results of this study indicate that contamination of cadmium is the most serious trace-metal pollution in the coastal sediments of the Straits of Malacca, both in terms of quantity as well as distribution. At 6 of the 24 sampling stations, the input of cadmium due to human activities was estimated to be between 33 to 84%. This translates to actual concentrations of between about 0.03 to 0.16 ppm. One of the main reasons why the percent anthropogenic contribution of cadmium can be high here is the fact that the natural level of cadmium itself is low. A small addition of the metal from human activities will significantly alter the anthropogenic component. Schropp and Windom (1988) suggested that the "anthropogenic" metal component is usually loosely adsorbed to the sediments, and therefore, may be more available to the biota, or may be easily released to the water column in altered forms when the sediments are disturbed. This will certainly pose problems not only to the coastal marine organisms, but eventually to humans. Furthermore, filter-feeders such as the bivalves, are known to be able to bioaccmulate metals up ten or hundred of times the concentration available in their surrounding. Cadmium, being a highly toxic material, can present long-term risks to human, including renal tubular damage and hypertension (Boiteau and Pineau, 1988). This is especially relevent to Malaysia because culture of bivalves is a multi-million dollar industries and bivalves, particularly the blood cockle *Anadara granosa*, is a major source of protein for the local population.

Table 2. Anthropogenic input of trace-metals in the sediments of the coastal and estuarine waters of the Straits of Malacca

Metal	Station	Anthropogenic Input (ppm)	% of Total Concentration
Cd	05	0.08	33
	07	0.03	50
	15	0.16	52
	16	0.03	36
	23	0.15	84
	24	0.16	52
As	23	5.8	58
Cu	04	3.9	22
	07	2.8	37
	18	5.0	26
Zn	10	27.4	23
	15	19.4	20
	23	10.4	26
Pb	07	6.4	27
	15	9.6	21

The next metal that was found to be of concern in this study is arsenic. However, for this metal, only 1 station ie Station 23, was shown to have an anthropogenic input of more than 20%. At this particular station, the input of arsenic from human activities was estimated to be around 5.8 ppm, which translates to about 58% of the total concentration in the sediment. It is quite surprising to note that the contamination of arsenic is not widespread along the Malaysian coast of the Straits of Malacca. Several activities, such as manufacturing of semiconductors, textile

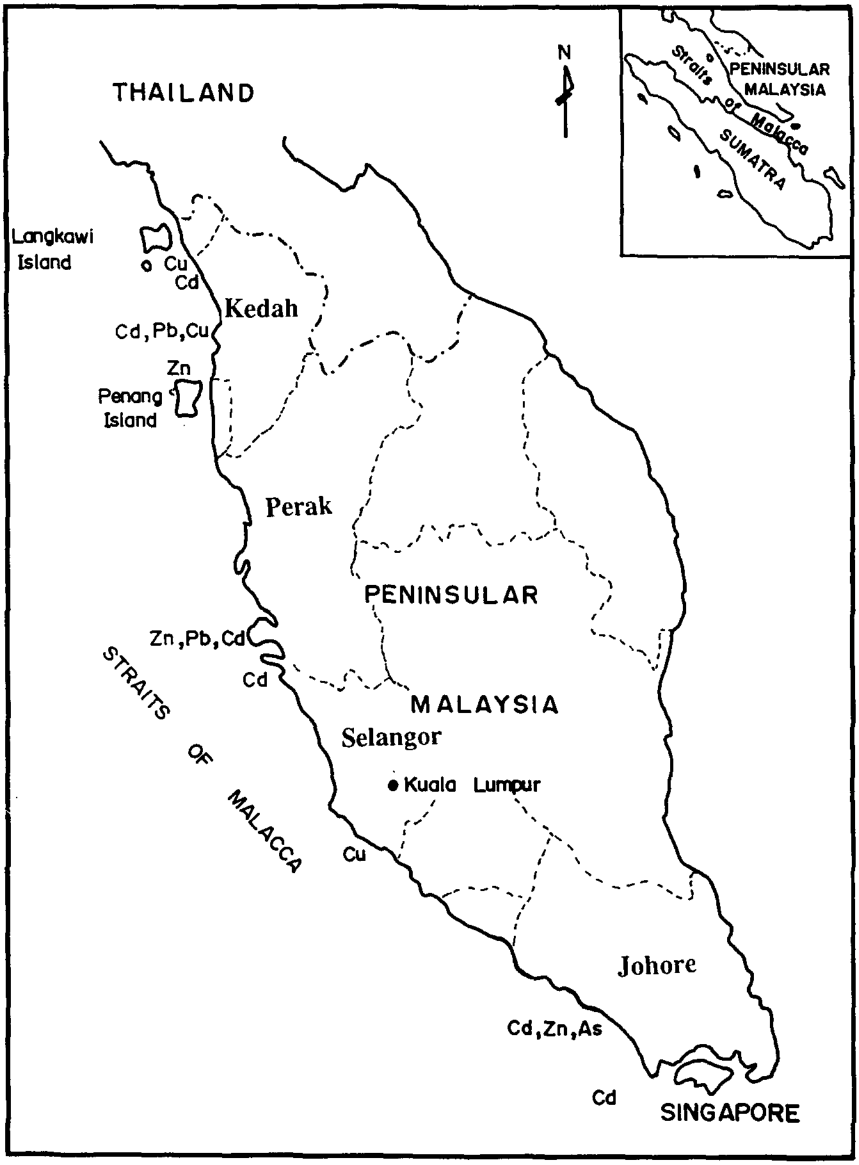

Figure 2. Map of Peninsular Malaysia and the Straits of Malacca showing locations of anthropogenic input of trace-metals into the coastal sediments.

printing, use of antifouling paints, pesticides, and wood preservatives, which may contribute to the arsenic levels in the environment, are quite common along this area.

For the other three metals, the contribution of anthropogenic input to the metal concentration in the sediments was somewhat similar, with values ranging from about 20 to 30%. Of the 3 metals, copper contamination is slightly more serious than the other two. Human input of copper and zinc was found to exceed 20% at 3 of the 24 stations sampled, while only 2 stations were found to have lead contamination of more than 20%.

In comparison with values of anthropogenic input of metals for other coastal areas, for example the southeastern coast of the United States of America as documented by Windom et al (1989), the trace-metal contamination to the coastal sediments of the Straits of Malacca is slightly lower. For example, percentage of anthropogenic input of Cu, Pb, and Zn for the Straits of Malacca was calculated to be about 22 - 37%, 21 - 27%, and 20 - 26%, respectively, while for the coastal areas of southeastern United States, the values estimated were 29 - 37%, 49%, and 25 - 30%, respectively. Comparison of cadmium contamination cannot be made because for the coastal sediments of the southeast of the United States, cadmium concentration do not covary with that of aluminium.

Figure 2 shows the distribution of anthropogenic trace-metal input for the west coast of Peninsular Malaysia, based on data collected in this study. As evident, most of the input were found along the coasts of Kedah, south coast of Perak, and Johore, and to a lesser extent around the south coast of Selangor. Although the presence of trace-metals in the coastal sediments of these 4 states is expected, the author is somewhat surprised to find limited anthropogenic metal input into the coastal areas of the states of Penang and Selangor since these 2 states boast some of the major manufacturing industries in the country. Perhaps, this may be due to the limited number of stations chosen for the study, or maybe the industries in these 2 states have somewhat efficient metal-waste treatment plants. More extensive samplings may identify other "hot-spots".

This study shows the importance of normalizing trace metal data in order to estimate the natural and anthropogenic input of these metals in a particular area. The results of this study indicate substantial anthropogenic trace-metal input along the coast of the states of Kedah, Perak and Johore, and to a lesser extent along the coast of the state of Selangor. Anthropogenic input of five metals, namely cadmium, arsenic, copper, zinc, and lead was estimated to be substantial. Input of cadmium from human activities seems to be quite serious. At one particular station along the southern coast of the State of Johore (Station 23), it was estimated that about 84% of the cadmium concentration in the sediment was from human activities.

Acknowledgments. The author especially thank Dr. Herb Windom of the Skidaway Institute of Oceanography for his invaluable assistance and suggestions and for allowing the use of his laboratory for the analysis of the metals. Thanks also to Dr. Ralph Smith and Debbie Wells for assistance in the chemical analysis and Ahamad Abu and Mohd Zambri Othman for help during sampling. This study was partially supported by grants from the Malaysian Government IRPA Program and the ASEAN-Canada Co-operative Program in Marine Science II.

REFERENCES

Babji AS, Embong MS, Woon WW (1978) Heavy metal contents in coastal water fishes of West Malaysia. Bull Environ Contam Toxicol 23: 830 - 836

Boiteau HL, Pineau A (1988) Chapter 31A: Cadmium. In: McKenzie HA, Smythe LE (eds) Quantitative Trace Analysis of Biological Materials. Elsevier, Amsterdam, p 543

Department of Environment (1991) Environmental Quality Report, Department of Environment, Ministry of Science, Technology and Environment, Malaysia.

Din ZB (1992) Use of aluminium to normalize heavy-metal data from estuarine and coastal sediments of the Straits of Malacca. Mar Poll Bull 24:484 - 491

DOETH (1985) Report on toxic and hazardous waste survey in Malaysia. Dept. of Environment, Malaysia.
Jothy AA, Huschenbeth E, Harms U (1983) On the detection of heavy metals, organochlorine pesticides and polychlorinated biphenyls in fish and shellfish from the coastal waters of Peninsular Malaysia. Arch FischWiss 33:161- 206
Law AT, Singh A (1988) Heavy metals in the Kelang estuary, Malaysia. Malayan Nat J 4:505 - 513
Loring DH (1991) Normalization of heavy-metal data from estuarine and coastal sediments. ICES J Mar Sci 48:101 - 115
Martin JM, Whitfield M (1983) The significance of the river inputs to the ocean. In: Wong CH, Boyle E, Bruland KW, Burton JD, Goldberg ED (eds) Trace Metals in Seawater, Plenum, New York.
Schropp SJ, Windom HL (1988) A guide to the interpretation of metal concentrations in estuarine sediments. Florida Department of Environmental Regulation.
Seng CE, Lim PE, Ang TT (1987) Heavy Metal Concentrations in Coastal Seawater and Sediments off Prai Indsutrial Estate, Penang, Malaysia. Mar Poll Bull 18: 611- 612
Sivalingam PM, Yoshida T, Kosima H, Allapitchay I (1979) Trace metal biodeposition and its extent of pollution in coastal molluscs, sediments and seawater samples from the island of Penang, Malaysia. Proc Fourth CSK Symp, Tokyo. 532 - 544
Turekian KK, Wedepohl KH (1961) Distribution of the elements in some major units of the earth's crust. Geological Society of America Bulletin 72:175 - 192
Windom HL, Schropp SJ, Calder FD, Ryan JD, Smith, Jr. RG, Burney LC, Lewis FG, Rawlinson CH (1989) Natural trace metal concentrations in estuarine and coastal sediments of the southeastern United States. Env Sci Tech 23:314 - 320