

DETERMINATION AND SPECIATION OF HEAVY METALS IN SEDIMENTS OF THE JURU RIVER, PENANG, MALAYSIA

POH-ENG LIM and MUN-YOON KIU

School of Chemical Sciences, University of Science, Malaysia, 11800 Penang, Malaysia

(Received: September 1993; revised: September 1994)

Abstract. The Juru River flows through largely urbanized areas and is grossly polluted by domestic wastes and discharges from pig farms. Other than carrying highly polluting organic materials, these wastes are also contaminated with heavy metals. To ascertain the extent of heavy metal pollution in the river, total and non-residual concentrations of Cu, Pb, Zn, Mn and Fe in sediment samples collected along the river were determined. The results indicate that both the total and non-residual metal concentrations in sediments can successfully be used to identify heavy metal pollution sources. The speciation of Zn, Mn and Fe in the sediment samples were investigated using a sequential leaching technique which identifies the elements among six operationally defined host fractions: (1) exchangeable, (2) carbonate and surface-associated, (3) easily reducible, (4) moderately reducible, (5) bound to organic matter and sulphides and (6) residual. The results indicate that Zn is mainly associated with the reducible fractions. Zn and Fe found in the moderately reducible fraction are significantly correlated, indicating that iron oxides is the preferred host phase by Zn.

1. Introduction

Heavy metal pollution in a river can best be assessed by analysing the river sediments because they are less susceptible to flow conditions than the water column. They also act as traps for various types of pollutants including heavy metals. Changes in the environmental conditions such as the pH and redox potential, however, may result in the remobilization of some of the trapped metals. In this regard, heavy metals in sediments can become potential sources of pollution.

In recent years, attention has been shifted from the determination of total heavy metals in sediments to other techniques which include a 0.5 M HCl leaching technique for the determination of non-residual heavy metals and sequential extraction techniques for ascertaining the solid state speciation of metals in sediments. Chester and Voutsinou (1981) and Chester *et al.* (1985) had successfully used the 0.5 M HCl leaching technique for pollution reconnaissance survey. For the sequential extraction techniques, various schemes had been proposed, among which the one proposed by Tessier *et al.* (1979) was apparently more widely employed by researchers (Tessier *et al.*, 1980; Rauret *et al.*, 1988; Pardo *et al.*, 1990). The extraction scheme of Tessier *et al.* (1979) separates the elements into five operationally defined host fractions and does not distinguish between an easily reducible fraction associated with 'new' manganese oxides and amorphous iron oxides and a moderately reducible fraction associated with 'aged' manganese oxides and crystalline iron oxides. In view of this, a more comprehensive sequential extraction scheme

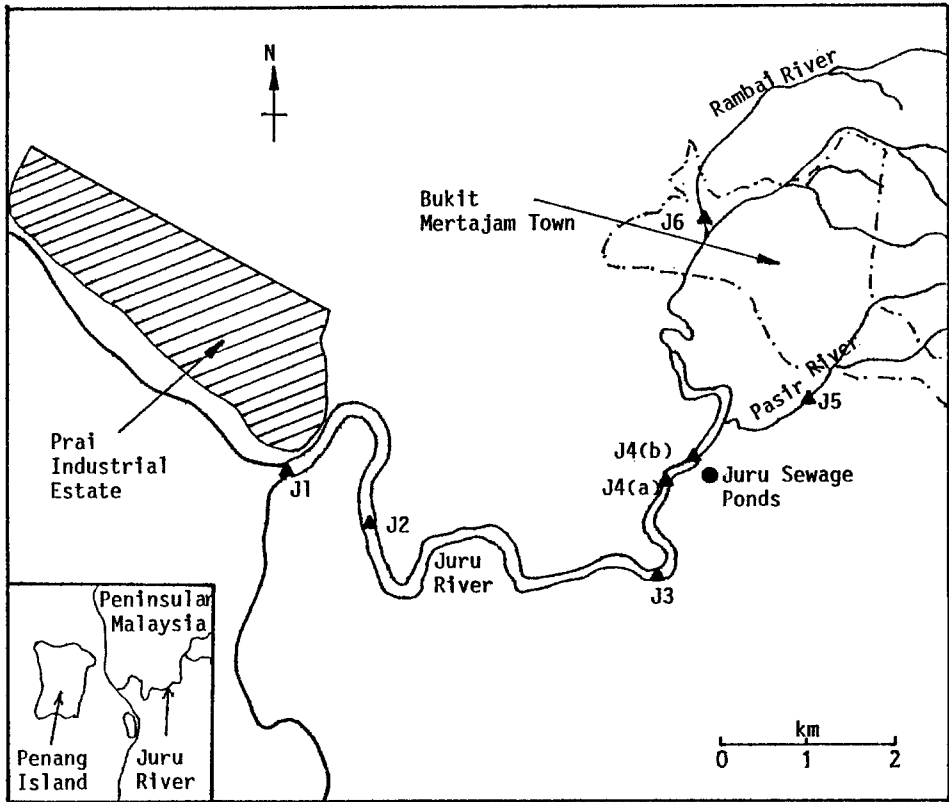


Fig. 1. Locations of sampling stations at Juru River and its tributaries.

used by Chester *et al.* (1985, 1986, 1988) and fully described by Towner (1984) was adopted in this work.

The objectives of this study are: (1) to ascertain the extent of heavy metal pollution in the Juru River by determining the total and non-residual concentrations of Zn, Cu and Pb in the sediment samples and (2) to gauge the remobilization capacity of Zn in the sediments by studying the distribution of the metal among the different operationally defined fractions using a sequential extraction scheme mentioned earlier. Since iron and manganese oxides and hydroxides are excellent scavengers for many trace metals (Hem, 1977; Grieve and Fletcher, 1977; Förstner and Wittman, 1983), the speciation of Fe and Mn in the sediment samples were also studied.

2. Study Area

The Juru River (Figure 1) drains a basin of about 75 km² in area. Its main tributaries are the Rambai, Ara and Pasir Rivers. The river and its tributary, the Rambai, flow

through urbanized areas and are grossly polluted by domestic wastes and discharges from pig farms. Other than carrying highly polluting organic materials, these wastes are also known to be contaminated with heavy metals. The results of a number of studies (Department of Environment (DOE), 1977; Seng *et al.*, 1987; DOE-USM, 1992) conducted at various periods indicate that the river water quality was poor and there was no noticeable improvement over these years.

The tidal stretch of the river extends all the way to Station J3 (Figure 1) and is used for navigation purposes only. However, extensive cockle rearing is found along the mudflats off the estuary of the Juru River, raising the question of the suitability of such an activity in view of the poor water quality in the area.

3. Methods

The top 5 cm surficial sediment samples were collected at the middle section of the river from seven stations, five of which were located at the main Juru River and one each at the Rambai and Pasir (Figure 1). The stations were sampled once in August, September, and December and twice in November 1992. All the stations were sampled in the same trip.

The samples were collected using a PVC corer or a polyethylene scoop where water was shallow. The samples were placed in polyethylene bags and frozen upon reaching the laboratory. For the analysis, the samples were thawed and dried in an oven at 90 °C for about 25 hours. The dried sediment samples were crushed and sieved through a nylon sieve size 1100 μm .

Total metal analysis was conducted using the nitric acid digestion technique. The cold 0.5 M HCl leaching technique (Chester and Voutsinou, 1981) was employed for the analysis of the total non-residual metals. The sequential extraction technique (Towner, 1984) is shown in the flow chart in Figure 2. The extraction reagents used in each stage and the operationally defined host fraction associated with each stage are listed below:

Stage 1. 1 M ammonium acetate (pH 7). Metals released at this stage are classified as being in the exchangeable fraction which contains metals in loosely held surface associations.

Stage 2. 1 M sodium acetate (pH 5). Metals released at this stage are classified as being associated with 'carbonates'.

Stage 3. 1 M sodium acetate + 0.25 M hydroxylamine hydrochloride (pH 5). Metals released at this stage are classified as being associated with the easily reducible fraction which consists mainly of 'new' oxides and oxy-hydroxides of Mn and amorphous Fe oxides.

Stage 4. 0.25 M hydroxylamine hydrochloride + 25% (v/v) acetic acid. Metals released at this stage are classified as being associated with the moderately reducible fraction which consists mainly of 'aged' Mn oxides and crystalline Fe oxides.

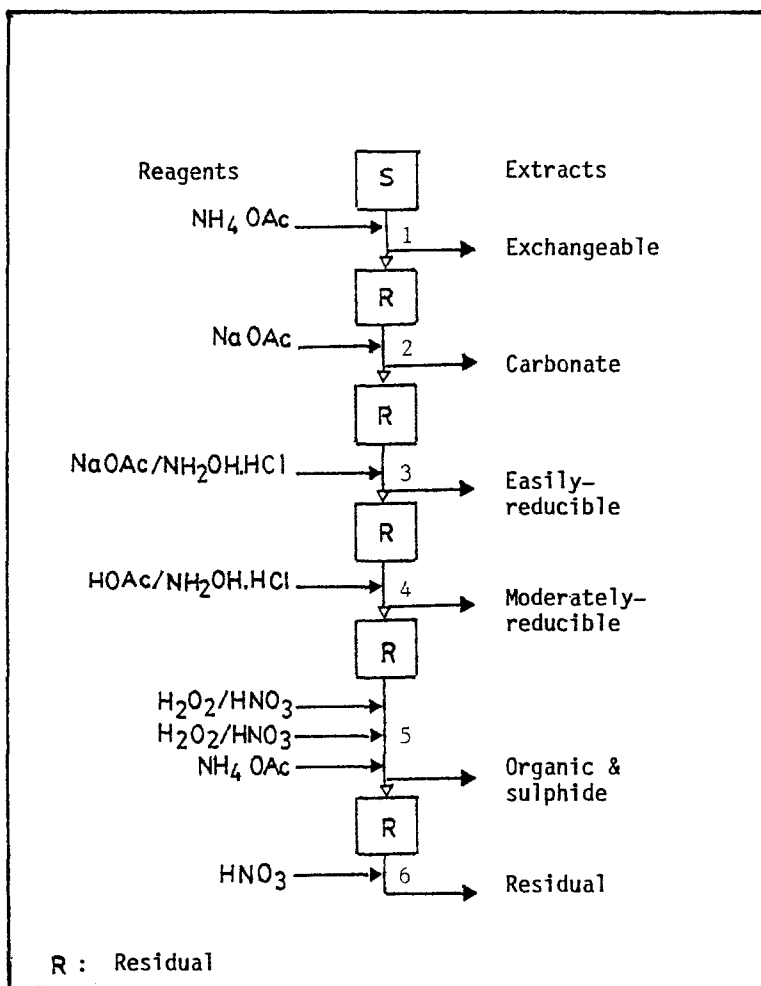


Fig. 2. Schematic representation of the sequential extraction technique used in the present study (after Basaham, 1988). Descriptions of the techniques are provided in the text.

Stage 5. Hydrogen peroxide + 1 M ammonium acetate (pH 2). Elements released at this stage are classified as being associated with organic matter and sulphides.

Stage 6. Nitric acid. Elements released at this stage are classified as being 'residual' in character.

The extractions were carried out in a 50 ml polyethylene centrifuge tube (acid-washed) with a screw cap. Each fraction was then separated by centrifugation at a speed of 3000 rpm for 30 min. All final extracts were stored in preacid-washed 'sterilin' bottles for trace metal determinations.

All reagents used were of analytical grade and double distilled water was used throughout. All trace metal work was performed using a class-100 laminar flow clean bench.

The metal determinations were carried out by using a GBC Model 903 flame and graphite furnace AAS depending on the sample concentrations. The standard addition method was employed to overcome possible matrix interferences. Reference Material GBW 08301 (Institute of Environmental Chemistry Academia Sinica, China) was used to check method accuracies. The results were within $\pm 5\%$ of certified values. For speciation work, the quality of data was assured through comparison of the results of the non-residual metal concentrations and the sum of the metal concentrations in Stages 1 to 5 which agreed within 10% of each other.

4. Results and Discussion

4.1. TOTAL AND NON-RESIDUAL METALS

The mean concentrations and ranges of total and non-residual Zn, Cu, Pb, Mn and Fe in the sediments are shown in Table I. It is observed that both the mean values of the total and non-residual concentrations of Zn, Cu and Pb at Station J6 are consistently higher than those at other stations, indicating that the tributary of the Rambai River is comparatively more polluted. In contrast, Pasir River is the least polluted as seen from the relatively low values of metal concentrations detected at Station J5. Along the main stretch of the Juru River, a peak in the concentrations of Cu, Pb, Zn and Fe is observed at Station J4(a) which is located about 50 m downstream of the discharge point for the Juru Sewage ponds. The metal concentrations at Station J4(b), which is located about 50 m upstream of the discharge point, are significantly lower. In general, there is a gradual reduction in the metal concentrations (except Mn) after Station J4(a) towards the estuary probably due to the flushing action of the tides.

These results are in line with the surrounding land use as the drainage basin of the Rambai River is a predominantly residential area with commercial activities and numerous small manufacturing industries located in between. On the other hand, the drainage basin of the Pasir River is far less populated and no industries are found there. The distribution patterns of the total and non-residual metal concentrations except Mn along the Juru River indicate very strongly that the Juru sewage treatment ponds are the major contributors to the metal pollution in the river.

It is evident based on the data in Table I that the distribution pattern of the non-residual metal concentrations is consistent with that of the total metal concentrations. Since it is the non-residual metal concentrations which truly reflect the extent to which the sediments have been subjected to heavy metal pollution (Chester and Voutsinou, 1981; Chester *et al.*, 1985), the 0.5 M HCl leaching method should, be recommended as the technique to provide an initial assessment of heavy metal pollution in sediments.

TABLE I

Mean concentrations of heavy metals in the surface sediments of Juru River (values in $\mu\text{g g}^{-1}$ dry weight)

Sampling station	Cu	Pb	Zn	Mn	Fe ^a
Total metals					
J1	29 (6-64)	25 (19-32)	84 (35-173)	1164 (326-2507)	1.90 (1.51-2.51)
J2	34 (8-82)	26 (18-35)	129 (38-339)	982 (192-2348)	2.10 (1.69-2.86)
J3	51 (12-115)	30 (29-38)	138 (96-198)	1218 (202-2660)	1.82 (1.44-2.84)
J4(a)	67 (19-136)	46 (42-54)	209 (100-344)	268 (38-834)	3.05 (1.71-5.59)
J4(b)	38 (3-82)	27 (5-42)	107 (36-280)	370 (25-1310)	1.92 (0.91-2.92)
J5	14 (2-43)	9 (0-15)	29 (2-52)	15 (8-34)	0.12 (0.03-0.19)
J6	72 (31-144)	78 (38-117)	316 (51-483)	214 (56-803)	1.80 (1.51-2.65)
Non-residual metals					
J1	17 (3-38)	18 (14-25)	66 (21-150)	725 (173-1577)	0.69 (0.50-0.99)
J2	11 (3-25)	18 (12-31)	82 (23-170)	497 (113-1070)	0.74 (0.62-0.81)
J3	38 (10-91)	22 (17-29)	86 (48-145)	1035 (185-2262)	0.97 (0.76-1.16)
J4(a)	36 (9-87)	32 (24-41)	112 (69-162)	195 (29-657)	1.93 (1.02-3.82)
J4(b)	9 (0-20)	16 (5-21)	74 (28-167)	186 (9-655)	0.75 (0.34-1.87)
J5	10 (1-34)	7 (0-10)	24 (2-40)	10 (2-28)	0.05 (0.02-0.09)
J6	46 (25-105)	60 (20-84)	254 (46-431)	136 (24-564)	0.74 (0.35-1.27)

^a Concentrations in percent.

4.2. SOLID-STATE SPECIATION OF HEAVY METALS

The speciation patterns of Zn, Mn and Fe in the sediments are given in Figure 3. The organic matter and carbonate content in the sediments collected at the various stations are shown in Table II.

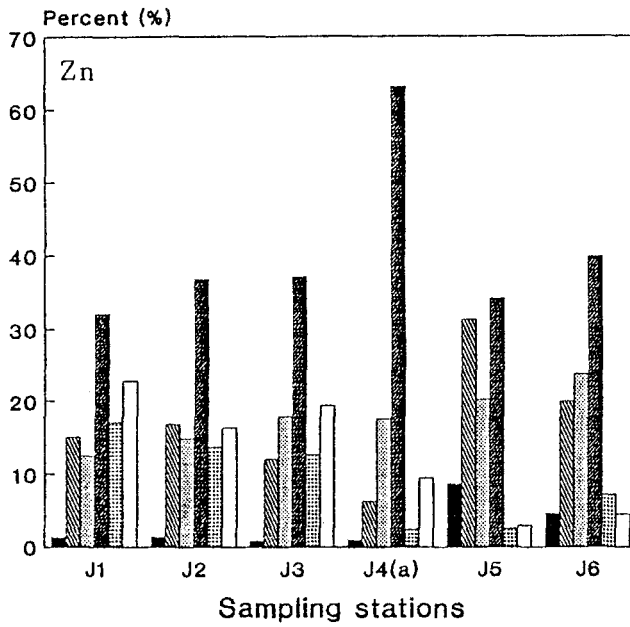


Fig. 3a.

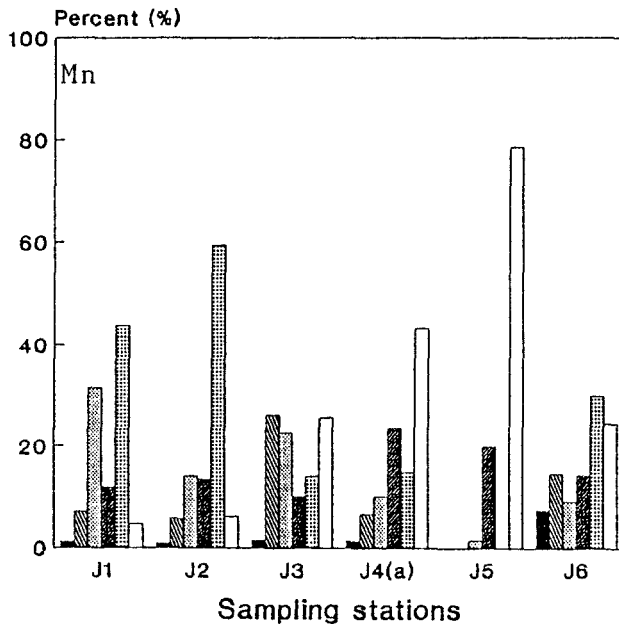


Fig. 3b.

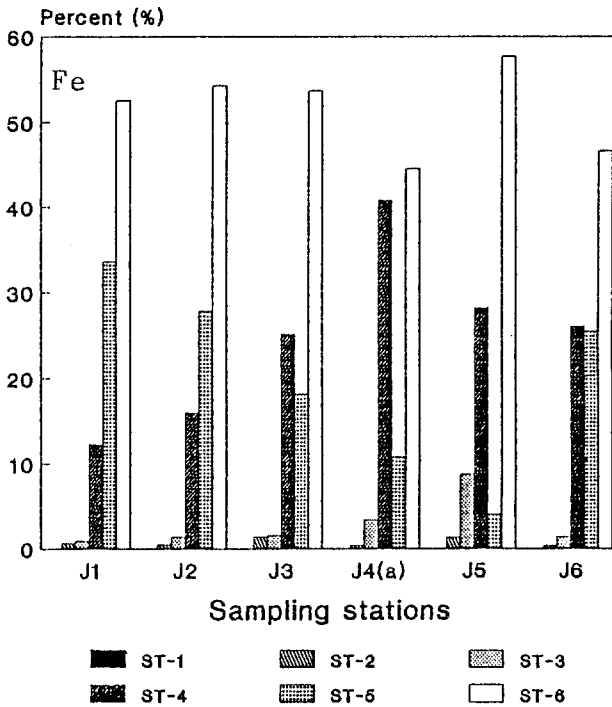


Fig. 3c.

Figs. 3(a)–(c). Percentages of zinc, manganese and iron found in various extraction stages.

TABLE II

Carbonate and estimated organic matter contents in the sediments of Juru River

Sampling station	Carbonate (%)	Organic matter (%)
J1	5.7	9.2
J2	4.8	10.6
J3	3.9	10.4
J4(a)	3.9	20.8
J5	0.0	0.9
J6	0.4	20.7

4.2.1. Iron and Manganese

It is observed that the speciation signatures of the two elements are significantly different from each other. Iron is mainly found in Stages 4, 5 and 6 with Stage 6, i.e. the residual fraction, as the predominant one. In contrast, the speciation signatures

TABLE III

Correlation coefficients between the metals in the various leaching stages

	Sequential leaching stage					
	1	2	3	4	5	6
Zn-Mn	0.396	0.122	0.004	0.052	0.010	0.428
Zn-Fe	-	0.300	0.283	0.819	0.731	0.811
Mn-Fe	-	0.084	0.029	0.240	0.286	0.204

of Mn do not indicate clearly which is the main fraction. For both elements, only very small percentages are found in the exchangeable fraction.

4.2.2. Zinc

Based upon the speciation patterns of Zn, the sampling stations can be roughly divided into three groups, namely, J1, J2 and J3 in one group, J5 and J6 in another group and J4(a) a group by itself. As a group, sediment samples collected at J1, J2 and J3 also have very similar contents of organic matter and carbonate. Sediment samples at J4(a) and J6 show relatively higher content of organic matter, indicating greater input of pollutant load in the vicinity of these sites. This is consistent with the observations discussed earlier that the total and non-residual metal concentrations are higher at these sites.

Irrespective of the sampling sites, the speciation pattern of Zn indicates that more than 50% of the metal is associated with the 'moderately reducible' and 'easily reducible' fractions. These results illustrate the known ability of Fe-Mn oxides to scavenge trace metals from solution through processes such as adsorption and coprecipitation (Hem, 1977). To find the associations between the metals, the correlation coefficients in the various leaching stages were calculated and are shown in Table III. Manganese (Mn) and Zn are found to be not significantly correlated in all the leaching stages. In contrast, significant correlations were observed in Stages 4, 5 and 6 between Zn and Fe with Stage 4 having the highest value. This implies that iron oxide is the preferred host phase by Zn in Stage 4. These results can be explained by the earlier observation that the concentration pattern of Fe along the river was similar to those of other metals studied except Mn, indicating that most of the Fe together with the other metals in the surface sediments originated from the overlying water column. This enables Fe to play the role of scavenger more effectively as opposed to Mn which is more 'indigenous' in origin.

In terms of the remobilization capacity of Zn, it is observed (Figure 3) that a very low proportion of the metal is in the exchangeable fraction which is considered to be readily bioavailable. Nonetheless, more than 70% of the metal are found in Stages 1 to 5 of the sediment samples collected at all the six sites and they

have the potential of being released to the environment if there are changes in environmental conditions such as pH, redox potential or the presence of natural and synthetic chelators (Förstner and Wittmann, 1983).

The results of speciation of Zn at J5 warrants special mention here. This is an interesting case because the total metal concentrations found there were much lower than those at J6, an obviously polluted site, but the speciation patterns are very similar. A likely explanation to this observation is that the sediments at J5 are in the process of being polluted with Zn. This is borne out by the high percentage (>80%) of non-residual Zn in the sediments at J5 and J6 (Table I). In this regard, the solid-state speciation studies provide a more dynamic appraisal of heavy metal pollution in the riverine environment as opposed to those of total and non-residual metal determinations.

4.3. LONG-TERM TREND OF HEAVY METAL POLLUTION IN JURU RIVER BASIN

A recent study (DOE-USM, 1992) has estimated that currently domestic waste contributes about 80% of the BOD load in the Juru River. With the decline of pig-rearing activities because of the country's strict environmental regulations and the projected rapid increase in population in the river basin, the pollution load and its percentage in the river contributed by domestic waste will rise further. Since the Juru sewage ponds are the only treatment facilities available in the river basin, it is anticipated that the heavy metal concentrations in the sediments of Juru River downstream of the sewage ponds will exhibit an upward trend. This could have a serious implication on the cockle-rearing activities found at the river estuary as bioaccumulation of heavy metals by bivalves is now well established.

Although the levels of trace metals in the cockle samples from the Juru estuary indicate no major threat to public health at the moment (Devi, 1986), this situation may change as the metal concentrations in the sediment increase with time. The increase will be predominantly in the non-residual metal fraction with the potential of being remobilized to the environment. In this regard, long-term monitoring of the cockle samples harvested from the area concerning heavy metal levels is recommended.

References

- Basaham, A. S.: 1988, *Elemental Partitioning in Marine Sediments*, Ph. D. Thesis. University of Liverpool, U.K.
- Chester, R. and Voutsinou, F. G.: 1991, 'The Initial Assessment of Trace Metal Pollution on Coastal Sediments', *Mar. Pollut. Bull.* **12**, 84-91.
- Chester, R., Kudoja, W. M., Thomas, A. and Towner, J.: 1985, 'Pollution Reconnaissance in Stream Sediments using Non-residual Trace Metals', *Environ. Pollut. Ser. B.* **10**, 213-238.
- Chester, R., Murphy, K. J. T., Towner, J. and Thomas, A.: 1986, 'The Partitioning of Elements in Crust-derived Marine Aerosols', *Chem. Geol.*, **54**, 1-15.
- Chester, R., Thomas, A., Lin, F. J., Basaham, A. S. and Jacinto, G.: 1988, 'The Solid State Speciation of Copper in Surface Water Particulates and Oceanic Sediments', *Mar. Chem.* **24**, 261-292.

- Devi, S.: 1986, 'Heavy Metal Levels In Some Malaysian Shellfish', *Fisheries Bulletin No. 44*, Department of Fisheries, Ministry of Agriculture, Malaysia.
- DOE: 1977, *Report on Water Pollution Control: Juru River Basin*, Department of Environment, Ministry of Science, Technology and the Environment, Malaysia.
- DOE-USM: 1992, *Development of Water Quality Criteria and Standards Classification-Juru River*, Vol. VIII. Draft Final Report, Department of Environment, Malaysia, Innovation and Consultancy Centre, Universiti Sains Malaysia.
- Förstner, U. and Wittman, G. T.W.: 1983, *Metal Pollution in the Aquatic Environment*, 2nd edn., Springer-Verlag, New York, pp. 486.
- Grieve, D. and Fletcher, K.: 1977, 'Interactions between Zinc and Suspended Sediments in the Fraser River Estuary, British Columbia', *Estua. Coast. Mar. Sci.* **5**, 415–419.
- Hem, J. D.: 1977, 'Reactions of Metal Ions at Surfaces of Hydrous Iron Oxide'. *Geochim. Cosmochim. Acta* **41**, 527–538.
- Pardo, R., Barrado, E., Perez, L. and Vega, M.: 1990, 'Determination and Speciation of Heavy Metals in Sediments of the Pisuerga River', *Wat. Res.* **24**, 373–379.
- Rauret, G., Rubio, R., Lopez-Sanchez, J. F. and Casassas, E.: 1988, 'Determination and Speciation of Copper and Lead in Sediments of a Mediterranean River (River Tenes, Catalina, Spain)', *Wat. Res.* **22**, 479–485.
- Seng, C. E., Lim, P. E. and Ang, T. T.: 1987, 'Physical-Chemical Study' in *Environmental Baseline Studies on the Panang Development Corporation Proposed Land Reclamation in the Prai Industrial Estate*, Consultancy Report Prepared for the Penang Development Corporation.
- Tessier, A., Campbell, P. G. C. and Bisson, M.: 1979, 'Sequential Extraction Procedure for the Speciation of Particulate Trace Metals', *Anal. Chem.* **51**, 844–851.
- Tessier, A., Campbell, P. G. C. and Bisson, M.: 1980, 'Trace Metal Speciation in the Yamaska and St. Francois Rivers (Quebec)', *Can. J. Earth Sci.* **17**, 90–105.
- Towner, J. V.: 1984, *Study of Chemical Extraction Technique Used for Elucidating the Partitioning of Trace Metals in Sediments*, Ph. D. Thesis, University of Liverpool, U.K.