Thammasat Int. J. Sc. Tech., Vol.2, No.1, January 1997

Distribution of Trace Metals in the Porewaters of Sediments of the Bang Pakong River Estuary, Thailand

Voravit Cheevaporn
Department of Aquatic Science, Burapha University, Bangsaen,
Chonburi 20131, Thailand
M.L. San Diego-McGlone, Gil S. Jacinto
Marine Science Institute, University of the Philippines,
Diliman, Q.C. 1101 Philippines
Phaithoon Mokkongpai
Institute of Marine Science, Burapha University, Bangsaen,
Chonburi 20131, Thailand

Abstract

This paper represents one of the few attempts to understand the behavior of trace metals in the sediments of a tropical estuarine environment. The concentrations of Fe, Mn, Cu, Pb, Zn, Cd, Cr, and Ni in the porewaters of Bang Pakong River Estuary sediments were examined. Porewater Fe and Mn were found to increase with depth and may be due to the recycling of Fe and Mn between solid diagenetic mineral phase and pore solutions. Dissolved Cu, Pb, and Zn in the pore fluids are enriched near the sediment/water interface where they may be released from the reduction of Fe/Mn oxides. The decrease of dissolved Cu and Pb in the oxidized zone may be due to reconsumption of Fe/Mn oxides during recycling and/or sorption by organic materials at the top portions of the sedimentary cores. The results of the chemical partitioning of the sediments show that the reducible phase plays an important role in the transfer of Cu, Pb, and Zn between solid and aqueous phases. In contrast, dissolved Cr and Ni appear to increase with depths as a result of the recycling of Fe/Mn oxides in the oxidized zone and the release of these elements during early diagenesis in the deeper portions of the Bang Pakong sedimentary cores.

1. Introduction

The composition of porewaters reflects the reactions which occur among the various constituents found in the sediments and interaction between the porewaters and the solid phase. The ratio of dissolved to solid components in the sediments is known to be very small [1]. As a result, reactions in the solid phase can have large measurable effects upon the pore solutions. Pore solutions can therefore be sensitive indicators of early diagenetic changes in the solid phase [2].

Various studies [3,4,5,6] have provided information on porewater trace element concentrations of several types of marine sediments. From these studies it was found that porewaters have elevated concentrations of metals relative to values found in overlying water. Such enrichment is most striking for manganese and iron since these elements are very susceptible to dissolution under the reducing conditions generally found in estuarine sediments [7]. The dissolution of the oxides of iron and manganese from decomposition processes will in turn enrich the porewaters with the release of other metals which were adsorbed or coprecipitated with the Fe and Mn under oxidizing conditions [6,8]. This mechanism, as well as organic or inorganic complexation of the metals, may explain the enrichment which has been observed in many porewater samples [4].

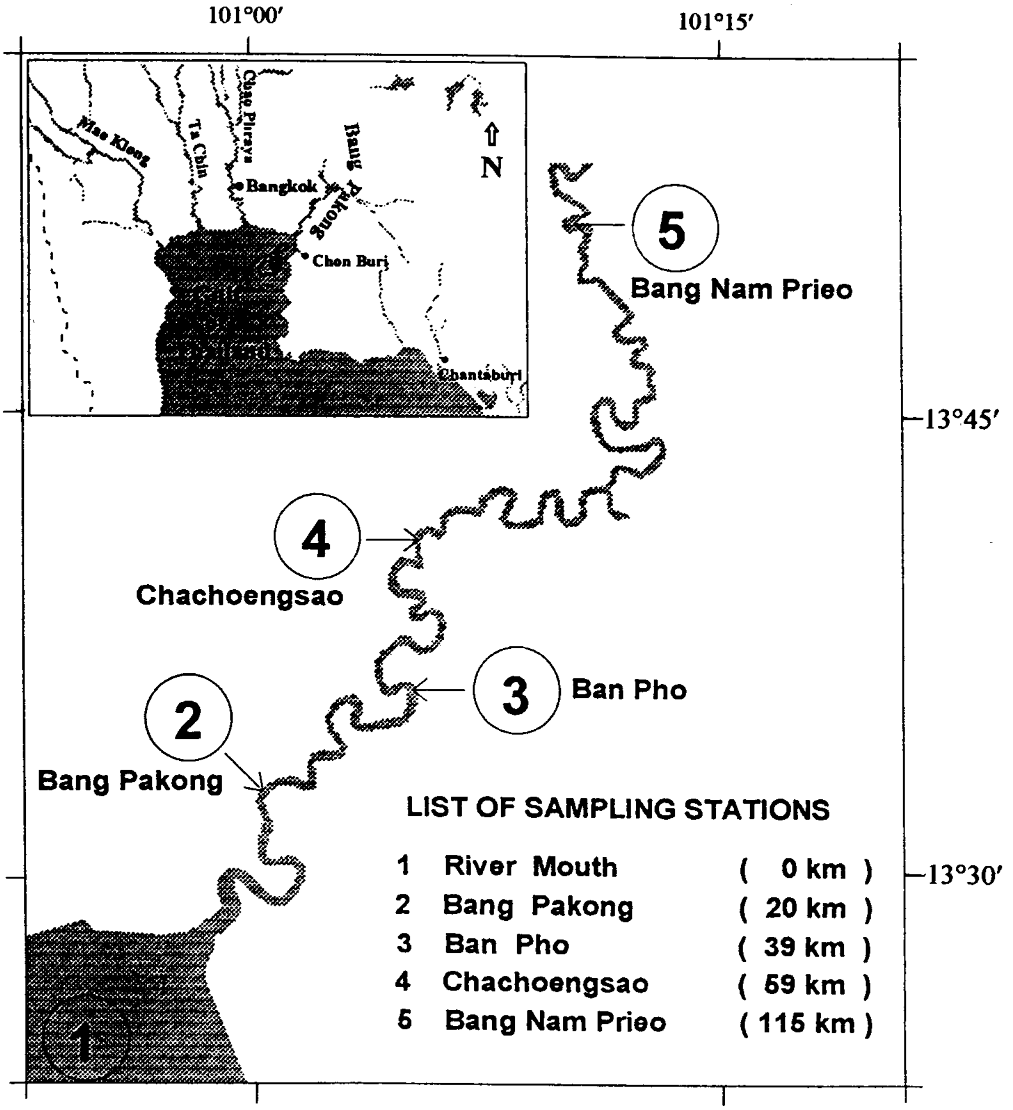
This paper reports on the vertical profile of Fe, Mn, Cu, Pb, Zn, Cd, Cr, and Ni in the pore fluids and solid phase of estuarine sediments of the Bang Pakong River estuary. The Bang Pakong River is one of the most important rivers on the eastern coast of Thailand. The high rate of population growth in the province and the rapid industrial development of the area have significantly degraded the water quality of Bang Pakong River. The purpose of this study is to quantify heavy metal sediment concentration in this estuary and examine chemical processes, such as early diagenesis, which may affect the overlying water concentrations of these metals. To help estimate potentially reactive metals in terms of sediment-water mobility, a sequential leaching scheme was used to partition the composition of the sediments into different fractions.

2. Materials and Methods

The sampling locations for the sediment cores are shown in Figure 1. Core samples were obtained using pre-cleaned PVC tubes. The tubes were immediately sealed at both ends with plastic sheets. The cores were then sectioned under nitrogen atmosphere with a plastic knife at 3-cm intervals up to a depth of 10 cm, and at 5-cm below that depth. The sediment sections were centrifuged at 15,000 rpm at 5 °C for 20 minutes. Porewaters were filtered through 0.4 μm Nuclepore filters into polyethylene vials and acidified with redistilled hydrochloric acid to pH<2. These samples were analyzed for Cd and Pb by direct injection into a flameless atomic absorption spectrophotometer with deuterium background correction (Perkin Elmer 5000). The metals Fe, Mn, Cu, Zn, Cr, and Ni were measured using an air-acetylene flame atomic absorption spectrophotometer (Hitachi 180-30). All the vessels and materials used for metal determinations were cleaned with acid and dried in a laminar flow hood before use. The recovery of the metals using these procedures was determined and the results given in Table 1.

The solid phases of the sediments were dried overnight at 110 °C, ground and homogenized with an agate mortar and sieved through a nylon sieve (2 mm mesh size) to eliminate coarse fragments. The sediment samples (0.3 g) were then digested for total metal analysis in Teflon digestion vessels with 12 ml of a mixture of HF + $HCLO_4$ (5v +v) at 100-150 °C to near dryness. Finally, 2 ml of $HCLO_4$ was added and evaporated until the appearance of white fumes. The residue was dissolved in concentrated HNO_3 (2 ml) and diluted to 25 ml. The resulting solution was then analyzed for trace metals using an atomic absorption spectrophotometer(Hitachi 180-30). The sequential leaching scheme proposed by Tessier *et al.* [9] and later modified by Meguellati *et al.* [10] was adopted to partition the elements of the dry sediments into different fractions. These fractions include the reducible, oxidizable, carbonate, exchangeable and residual phases.

The pH and Eh of the sediment sections were determined by direct insertion of a glass electrode and a platinum electrode respectively into the sediment cores. Hydrogen sulfide in porewaters was measured using the method of Cline [11]. The titration method of Gaudette *et al.* [12] was used for the determination of organic carbon in sediments.



LIST OF SAMPLING STATIONS

1	River Mouth	(0 km)
2	Bang Pakong	(20 km)
3	Ban Pho	(39 km)
4	Chachoengsao	(59 km)
5	Bang Nam Prieo	(115 km)

Figure 1. Sampling stations along the Bang Pakong River Estuary.

Table 1. Percent recovery of heavy metals in porewater (all value in ppb).

	Standard spiked	Average Determined Value(n=3)	C.V. (%)	% Recovery	Mean % Recovery
Fe	100	91.7±2.5	2.7	91.6	92.7
	200	187.7±4.1	2.1	93.8	
Mn	100	91.3±1.7	1.8	91.3	93.1
	300	284.7±2.9	1.0	94.8	
Cu	20	16.7±1.2	7.4	83.3	85.3
	50	43.7±1.2	2.8	87.3	
Pb	10	7.3±0.5	6.4	73.3	75.8
	20	15.7±1.7	10.8	78.3	
Zn	10	9.3±1.2	13.3	93.3	90.8
	20	17.7±0.5	2.6	88.3	
Cd	0.1	0.07±0.01	17.0	73.3	76.6
	0.2	0.16±0.01	5.1	80.0	
Cr	10	8.3±0.5	5.6	83.3	84.1
	20	17.0±0.8	4.8	85.0	
Ni	10	8.0±0.8	10.2	80.0	85.8
	20	18.3±0.9	5.1	91.6	

C.V. = Coefficient of variation

3. Results and Discussion

The sediments consisted mostly of silty clay with 2 % organic carbon in the upper section and decreasing to 1 % at lower depths (Figure 2). Sedimentation rates of the Bang Pakong River Estuary system have been estimated at 0.47 - 0.72 cm/yr [13]. The first few centimeters of the sediments were characterized by a thin oxidized surface layer. The redox potential and hydrogen sulfide profiles given in Figure 2 suggest that the diagenetic sequences of these sediments are within the iron reduction stage (-500 to +50 mv) [14].

Overall, there was a similarity in the heavy metal profiles from all the sampling stations. Results of statistical analysis (ANOVA) indicate that there are no significant differences in the distribution of each element at different stations. Hence, station 1 was selected as a representative station for this discussion. However, the analytical data on dissolved metal concentrations at Station 1, 3 and 5 of Bang Pakong River Estuary are given in Table 2. Metal concentrations in the porewaters were higher than values in the overlying waters of the sediments. Upon comparison with other nearshore sediments (Table 3), porewater metal concentrations in the study area were in the same order of magnitude (except Mn) as concentrations found in the porewaters of Loch Fyne, a shallow water loch in Scotland [6], but one order of magnitude lower than values reported in River Conway Estuary (N. Wales) for Pb, Zn, and Ni [15]. The Conway Estuary is affected by mining of Pb and Zn in the area.

3.1 Fe and Mn profiles

The presence of a surface oxidized layer overlying reduced sediments is illustrated by the profiles of Fe and Mn which are sensitive indicators of diagenetic processes (Figure 3). Minimum values of dissolved Fe and Mn are found in the surface layer with concentrations increasing gradually down each core. Porewater profiles show a concave upward trend in the upper sections which can be attributed to the diffusion of dissolved Mn^{2+} and Fe^{2+} from deeper sections of the sediments across the redox boundary and its consumption in the oxidation zone [16]. The formation of oxidation products such as solid hydrous Fe and Mn oxides would then explain the maxima in solid phase Fe and Mn in the subsurface layer (Figure 3). As solid Fe and Mn oxides are buried below the redox boundary they undergo reduction. Fe^{2+} and Mn^{2+} are released into the porewaters, resulting in their increase with depth. There is a corresponding decrease in solid Fe and Mn with depth. Based on free energy change, Mn oxide reduction should be preceded by Fe oxide reduction. This implies that dissolved Mn should appear in the porewaters at upper sections of the core relative to Fe. However, profiles show the opposite with Fe appearing at a shallower depth than Mn. This may be due to the higher Fe content in the sediments as compared to Mn. It is suggested that complexation of Fe with organic matter in the upper section of the sedimentary column and remineralization processes make Fe more readily available during early diagenesis and eventually releasing this to the pore fluids. Moreover, Klinkhammer [17] suggested that Mn can be produced and consumed in more than one zone which implies that the Mn profiles are probably controlled by other processes and are more complex than what simple oxidation/ reduction reactions can predict.

3.2 Trace metal profiles (Cu, Zn, Pb, Cd, Cr, and Ni)

The porewater profiles of Cu, Zn, Pb, Cd, Cr, and Ni in Station 1,3, and 5 are given in Figures 4, 5, and 6 respectively. Using the behavior of trace elements during early diagenesis as reflected in their porewater profiles, the elements (excluding Fe and Mn) can be divided into three groups.

Table 2. Mean concentration of trace metals in porewaters (ppb), pH and Eh values from Bang Pakong River Estuary sediments.

Depth(cm)	Fe	Mn	Cu	Pb	Zn	Cd	Cr	Ni	pH	Eh (mv)
					Station 1					
1	100	200	22	8.9	26.2	0.15	11.7	9.7	7.3	46
7	120	620	97	21.2	20.8	0.16	14.6	12.6	7.9	-53
15	200	1260	57	11.6	16.8	0.15	15.5	13.5	7.9	-107
25	220	2150	51	10.6	14.6	0.13	15.8	13.8	7.9	-103
35	220	2160	52	11.2	14.3	0.13	15.8	13.7	8.0	-112
					Station 3					
1	80	240	35	19.5	39.4	0.16	13.4	11.7	7.5	21
7	180	1570	100	26.5	31.9	0.15	14.2	12.3	7.9	-83
15	230	5500	62	15.3	18.7	0.14	14.6	12.8	7.8	-150
25	270	6240	56	13.5	15.4	0.14	15.6	13.7	7.6	-116
35	270	6240	54	13.5	15.0	0.13	15.5	13.5	7.7	-124
					Station 5					
1	80	160	22	14.3	31.0	0.15	12.4	10.5	7.4	31
7	180	530	78	17.7	25.7	0.15	12.8	10.7	7.9	-79
15	230	1510	59	14.4	18.9	0.14	13.3	11.4	7.9	-101
25	260	2170	53	12.5	14.7	0.13	14.4	12.4	7.8	-101
35	260	2200	52	12.2	14.1	0.12	14.3	12.5	7.7	-105
L.O.D.	10	10	9	5	1.5	0.01	10	5		
oceanic water*	0.06	0.03	0.26	0.002	0.4	0.08	0.2	0.5		
overlying waters(St.1)	0.05	0.07	4.7	n.d.	8.8	0.03	1.2	1.1		

* Ref [20]

n.d. = not detectable

L.O.D. = limit of detection of trace metals in porewaters

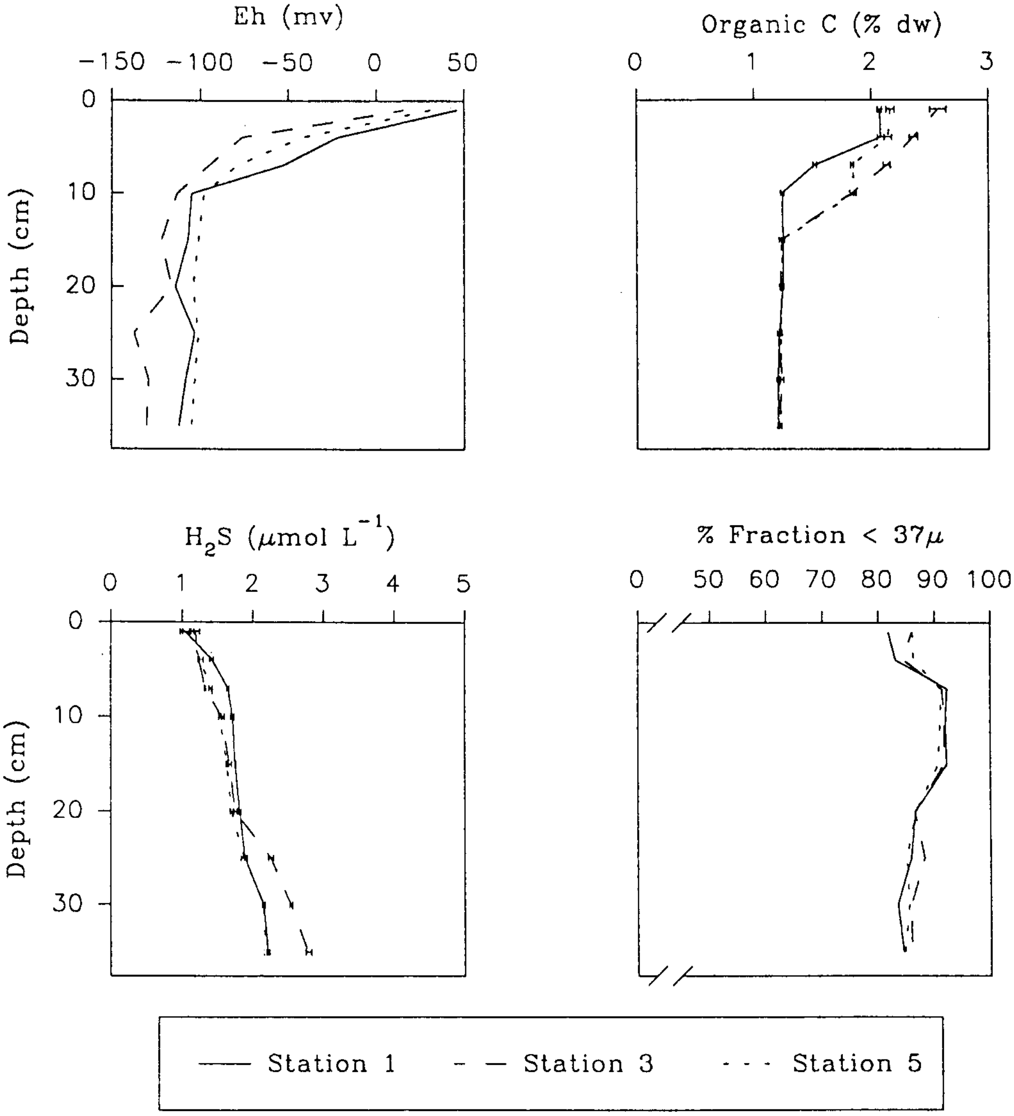


Figure 2. Profiles of Eh, organic carbon (in percent of dry weight), hydrogen sulfide and percent of sediment < 37 μm at Station 1, 3 and 5 of the Bang Pakong River Estuary sediments.

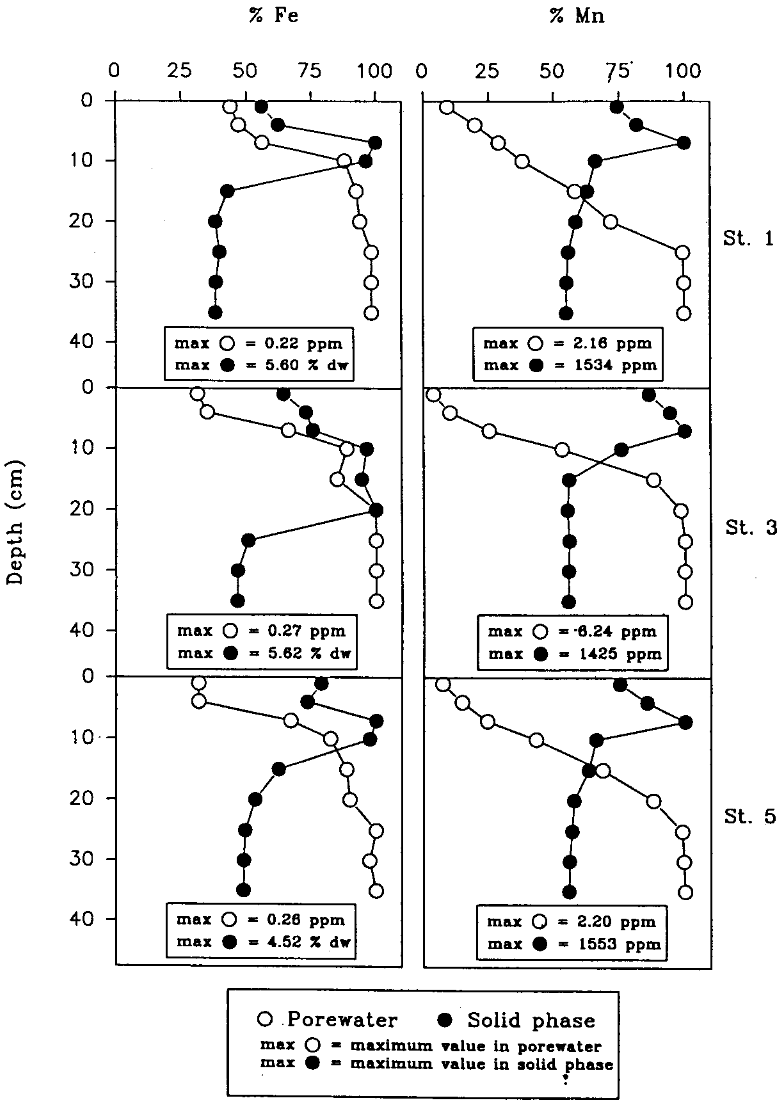


Figure 3. Dissolved Fe and Mn profiles in porewaters and total Fe and Mn profiles in dry sediments of Bang Pakong River estuary. Percentage of trace elements relative to their maximum concentrations in the sedimentary core are expressed as percent trace elements [% trace elements = (concentration/ maximum concentration) x 100]. The concentration of metals in sediments is given on a dry-weight basis.

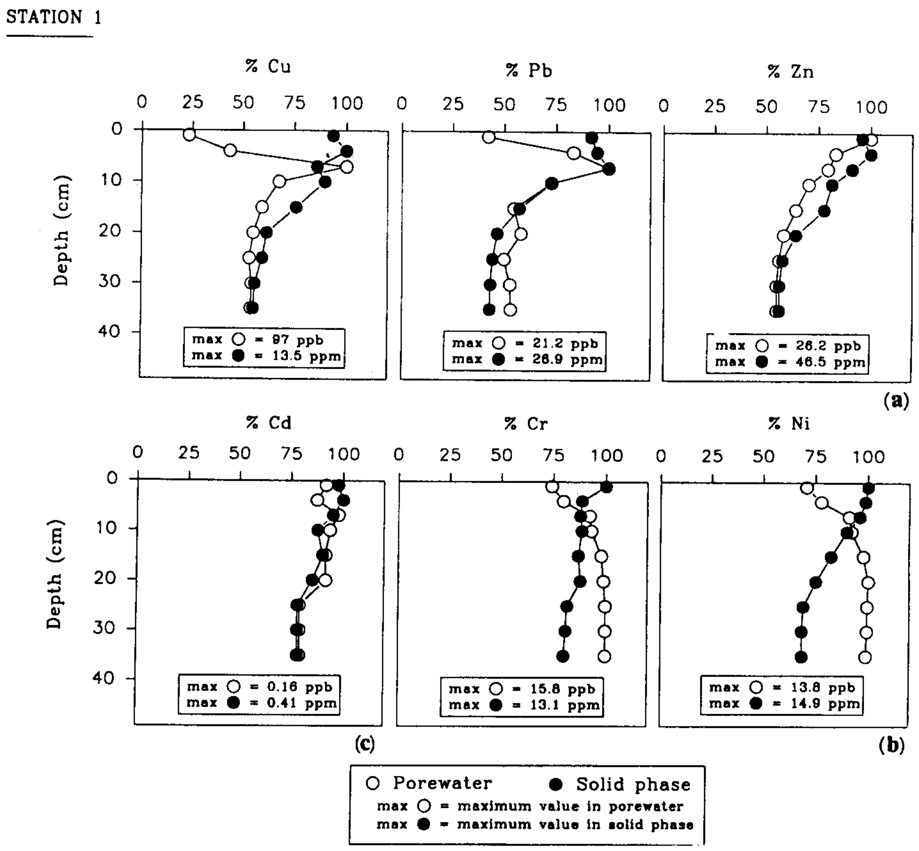


Figure 4. Dissolved Cu, Pb, Zn, Cd, Cr and Ni profiles in porewaters and total Cu, Pb, Zn, Cd, Cr and Ni profiles in dry sediments (Station 1) of Bang Pakong River Estuary. Percentage of trace elements relative to their maximum concentrations are expresed as percent trace elements [% trace elements = (concentration / maximum concentration) x 100]. [a = Group A, b = Group B, c = intermediate group]. The concentration of metals in sediment is given on a dry weight basis.

STATION 3

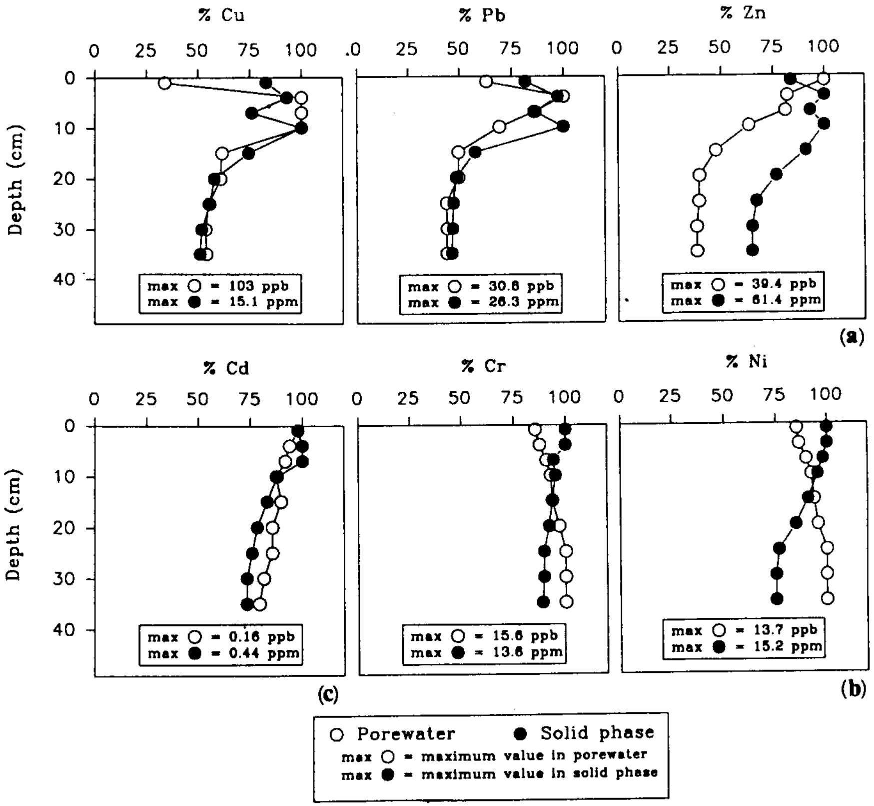


Figure 5. Dissolved Cu, Pb, Zn, Cd, Cr and Ni profiles in porewaters and total Cu, Pb, Zn, Cd, Cr and Ni profiles in dry sediments (Station 3) of Bang Pakong River Estuary. Percentage of trace elements relative to their maximum concentrations are expresed as percent trace elements [% trace elements = (concentration / maximum concentration) x 100]. [a = Group A, b = Group B, c = intermediate group]. The concentration of metals in sediment is given on a dry weight basis.

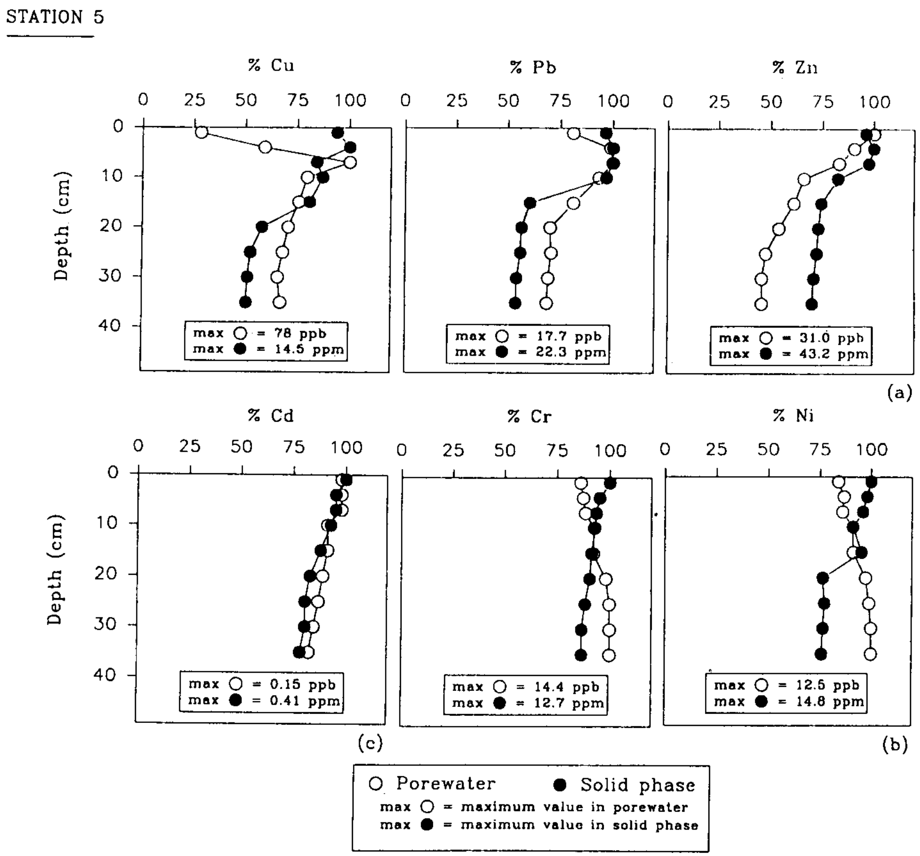


Figure 6. Dissolved Cu, Pb, Zn, Cd, Cr and Ni profiles in porewaters and total Cu, Pb, Zn, Cd, Cr and Ni profiles in dry sediments (Station 5) of Bang Pakong River Estuary. Percentage of trace elements relative to their maximum concentrations are expresed as percent trace elements [% trace elements = (concentration/maximum concentration) x 100]. [a = Group A, b = Group B, c = intermediate group]. The concentration of metals in sediment is given on a dry weight basis.

One group (Group A) is composed of those elements which are more enriched in the upper portions of the sedimentary cores relative to the lower layers. This group includes Cu, Pb, and Zn. Group B is composed of those elements which appear to increase with depth. Cr and Ni belong to this group. Cd seems to be intermediate (Group C) in behavior between elements belonging to Groups A and B appear to have little variation with depth. Statistical analysis (New Multiple Range Test, $p = 0.05$ and 0.01) also indicated that these elements can be divided into three groups.

The results of chemical fractionation of Bang Pakong River sediments show that the highest percentage (60-91%) of elements in group A are found in the leachable fraction (Table 4). This fraction represents the exchangeable, oxidizable, carbonate and reducible phases of sediment. The distribution in different chemical fractions of Group C (Cd) is similar to Group A. Within the leachable fraction, the majority of Cu, Zn, Pb, and Cd were found in the reducible phase, with the organically bound fraction (oxidizable phase) of secondary importance. Within Group B, 60 % of Cr was found associated with the non-leachable fraction (residual phase), but only 44 % was associated with this phase. The discrepancy is probably due to the limitations of the leaching schemes. Overall, these elements can be divided into three groups based on their behavior as reflected in their porewater profiles. Elements in Group A and Group C are mostly associated with the leachable fraction while elements in Group B are generally associated with the non-leachable fraction.

3.2.1 Group A. (Cu, Pb, and Zn)

For this discussion, the first few centimeters (~ 2-3 cm) of thin oxidized surface layer is referred to as the *oxidized zone*. The interval (~ 3-13 cm) where there is curvature in the porewater Mn-depth profile is considered to be the *reduction zone*. The zone below the *reduction zone* is referred to as the *equilibrium zone*. Since the majority of Cu, Pb, and Zn are associated with the reducible phase (Table 4), this phase could play an important role in the transfer of these elements between solid and aqueous phases. In the *oxidized zone* the lower Cu and Pb content in the porewaters may be due to consumption by the oxides of Fe and Mn and/or sorption by organic materials at the top portion of the sedimentary cores. Zn, however, behaved differently. There was no decrease in concentration in the *oxidized zone*. This can be attributed to the preferential coprecipitation of Cu and Pb with Fe/Mn oxides than Zn [18]. Moreover, Cu and Pb are also preferentially sorbed by organic materials such as humic or fulvic acids than Zn [19]. This indicates that the proposed mechanism to explain the behavior of Group A elements applies more for Cu and Pb than Zn. In the *reduction zone*, the elements were enriched due to their release with the reduction of Fe/Mn oxides. Below this zone Cu, Pb, and Zn gradually decrease because the amount of Fe/Mn oxides have reached thier minimum values relative to surface values. This implies that the amounts of Cu, Pb, and Zn which were released by reduction of these oxides may have also reached a minimum value.

3.2.2 Group B. (Cr and Ni)

Both Cr and Ni have almost equal percentages associated with oxidizable, carbonate and reducible phases. Thus, unlike Group A, the reducible phase plays a less important role in the transfer of metals between the solid and aqueous phases. The slight decrease in Cr and Ni at the topmost zone may still be due to consumption by iron and manganese oxides, but the absence of the subsurface maxima seen in Group A metals may be attributed to the smaller fraction of the reducible phase.

3.2.3 Group C. (Cd)

Cd appears to have little variation with depth. Although the majority of Cd was found in the reducible phase, it did not exhibit similar profiles as Group A. This is probably due to the extremely low concentrations of Cd in the porewaters. Thus, the sensitivity of determination cannot detect any significant variations of Cd in porewaters. However, the available data are not sufficient to provide an adequate description. Further investigation is still needed.

Table 3. Porewater metal concentrations (ppb) in nearshore sediments.

	River Conway Estuary*	Loch Fyne (FYC 23)**	Bang Pakong Estuary
Fe	520	70-920	80-270
Mn	4,700	1,600-13,460	200-6,240
Cu	210	40-380	22-124
Pb	300	16-48	8.9-31.4
Zn	260	14-74	14.3-39.4
Cd	---	---	0.12-0.16
Cr	---	---	11.7-16.1
Ni	490	8-24	9.7-14.1

* Ref. [15]

** Ref. [6]

Table 4. Trace element content in different chemical fractions of Bang Pakong River Estuary sediments
(unit in % total).

Elements	Leachable Fraction				% of Leachable Fraction	% of Unleachable Fraction
	Exc	Oxi	Car	Red		
Group A						
Cu	n.d.	24 ± 2.22	2 ± 0.52	34 ± 4.26	60	40
Zn	1 ± 0.28	31 ± 1.21	20 ± 1.21	37 ± 2.36	89	11
Pb	2 ± 0.71	21 ± 2.37	11 ± 1.14	58 ± 2.14	91	9
Group B						
Cr	6 ± 0.99	12 ± 1.58	11 ± 1.24	11 ± 1.39	40	60
Ni	5 ± 0.97	18 ± 1.01	14 ± 1.55	19 ± 1.69	56	44
Intermediate Group						
Cd	n.d.	37 ± 6.25	7 ± 2.06	47 ±8.13	91	9

4. Conclusions

This study is one of the first attempts to understand the behavior of trace metals in the porewaters in estuarine sediments in Thailand and quite possibly among the few studies done in tropical estuarine sediments. Based on the study, trace metals can be divided into three groups. The conceptual model to describe the distribution of trace metals (Group A and B) is shown in Figure 7. Group A elements (Cu, Pb, and Zn) are enriched in the upper portions of the sedimentary cores while Group B elements (Cr and Ni) show an increase with depth. In the oxidized zone, elements in Group A and B have lower concentration due to consumption by the oxides of Fe and Mn and/or sorption by organic materials. The presence of the subsurface maxima for Group A can be attributed to their release with the reduction of Fe/Mn oxides since elements in this group are mainly associated with the reducible fraction. The enrichment of solid phase trace metals at the surface of the sediment column relative to deeper sections may be interpreted as evidence of recent natural and anthropogenic input, and a consequence of sediment diagenesis.

5. Acknowledgements

The authors would like to express their sincere thanks to Ms. P. Tonawanik for the help rendered by her throughout the study. Thanks are due to Professor Ian Brindle of Brock University, Canada for his valuable suggestions.This work was partially supported by the Thai Farmers Bank Fund, Burapha University, Thailand.

6. References

[1] Presley, B.J. and Trefry, J.H. (1980), Sediment-water Interactions and the Geochemistry of Interstitial Waters, In Olausson, E. and Cato, I. (eds.), Chemistry and Biogeochemistry of Estuaries, John Wiley & Sons, Ltd., New York, pp. 187-232.

[2] Berner, R.A. (1980), Early Diagenesis, Princeton University Press, New Jersey.

[3] Presley, B.J., Brooks, R.R. and Kaplan, I.R. (1967), Manganese and Related Elements in the Interstitial Waters of Marine Sediments, Science, Vol.158, pp.906-910.

[4] Brooks, R.R., Presley, B.J., and Kaplan, I.R. (1968), Trace Elements in the Interstitial Waters of Marine Sediments, Geochim. Cosmochim. Acta, Vol.32, pp.397-414.

[5] Li, Y.H., Bischoff, J., and Mathieu, G. (1969), The Migration of Manganese in the Arctic Basin Sediment, Earth Planet, Sci. Lett., Vol.7, pp.265-270.

[6] Duchart, P., Calvert, S.E., and Price, N.B. (1973), Distribution of Trace Metals in the Pore Waters of Shallow Water Marine Sediments, Limnol. Oceanogr., Vol.18, pp.605-610.

[7] Tessenow, V. and Baynes, Y. (1975), Redox-dependent Accumulation of Fe and Mn in a littoral Sediment Supporting Isoetes lacustris, Naturwissenchaften, Vol.62, pp.342.

[8] Presley, B.J., Kolodny, Y., Nissenbaum, A., and Kaplan, I.R. (1972), Early Diagenesis in a Reducing Fjord, Sannich Inlet, British Columbia-II, Trace Element Distribution in Interstitial Water and Sediment, Geochim. Cosmochim. Acta., Vol.36, pp.1073-1090.

[9] Tessier, A., Campbell, P.G.C., and Bisson, M. (1979), Sequential Extraction Procedure for the Speciation of Particulate Trace Metals, Anal. Chem., Vol.52, pp.844-851.

[10] Meguellati, N., Robbe, D., Marchandise, P., and Astruc, M. (1983), A new Chemical Extraction Procedure in the Fractionation of Heavy Metals in Sediments Interpretation, Proc. Int. Conf. on Heavy Met. Environ., Hiedelberg, C.E.P., Consultants Publ., pp.1090-1093.

[11] Cline, J.D. (1969), Determination of Hydrogen Sulfide in Natural Waters, Limnol. Oceanogr., Vol.14, pp.454-458.

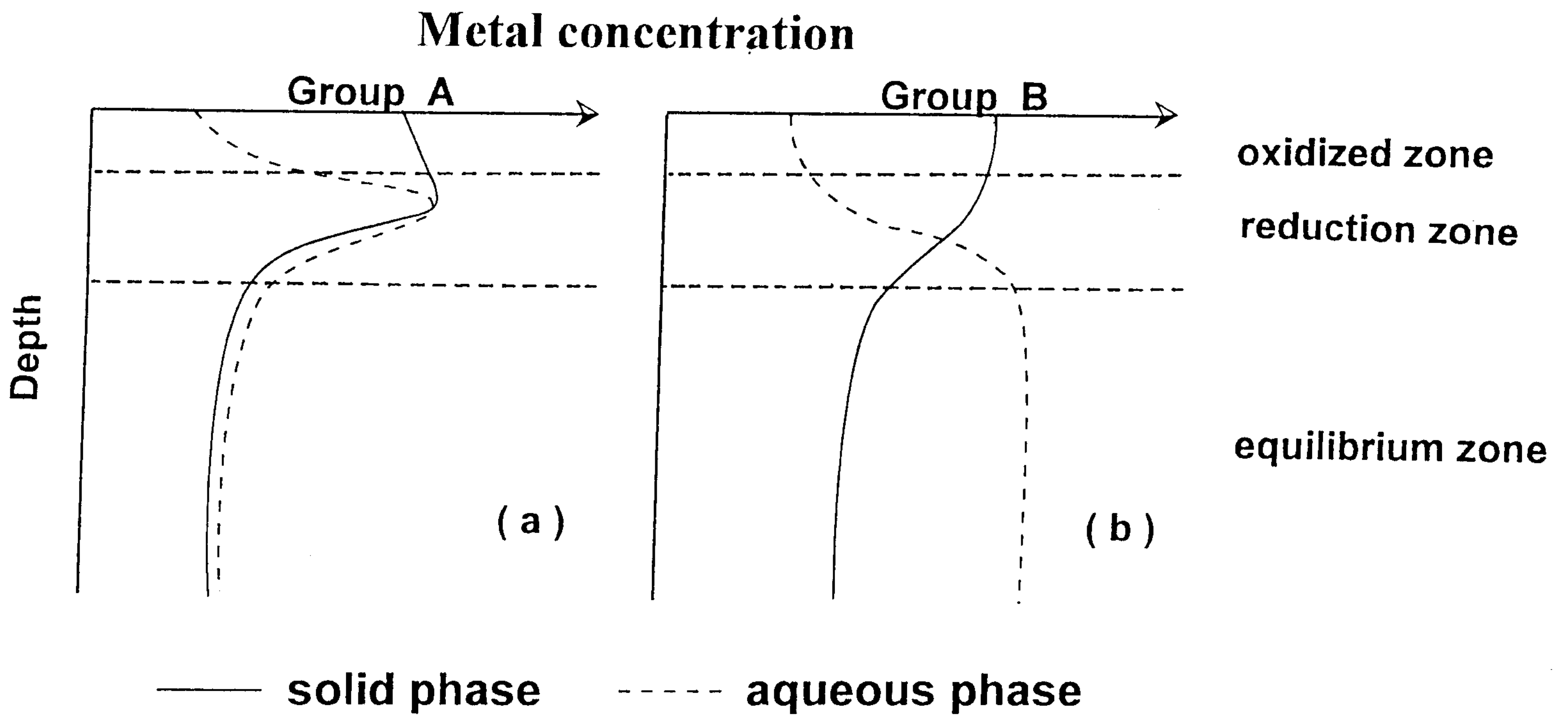


Figure 7. Conceptual model of trace metal diagenesis in estuarine sediments. (a) and (b) Schematic representation of dissolved and solid phase profiles of Group A and B elements.

[12] Gaudette, H.E., Flight, W.R., Toner, L. and Folger, D.W. (1974), An Inexpensive Titration Method for the Determination of Organic Carbon in Recent Sediments, J. Sediment. Petrol,Vol.44, pp.249-253.

[13] Cheevaporn, V., Jacinto, G.S., and San Diego-McGlone, M.L. (1994), History of Heavy Metal Contamination in Bang Pakong River Estuary, Thailand, J. Sci. Soc. Thailand, Vol.20, pp, 9-22.

[14] Stumm, W. and Morgan, J.J. (1981), Aquatic Chemistry, John Wiley & Sons, Ltd., New York, pp.459-460.

[15] Elderfield, H., Thornton, I., and Webb, J.S. (1971), Heavy Metals and Oyster Cultures in Wales, Mar. Pollut. Bull.,Vol.2, pp.44.

[16] Burdige, D.G. and Gieskes, J.M. (1983), A Porewater/solid Phase Diagenetic Model for Manganese in Marine Sediments, Am. J. Sci., Vol.83, pp.29-47.

[17] Klinkhammer, G.P. (1980), Early Diagenesis in Sediments from the Eastern Equatorial Pacific, II Pore Water Metal Results, Earth Planet, Sci. Lett., Vol.49, pp.81-101.

[18] Groth, P. (1971), Untersuchungen Uber Einige Spurenelemente in See. Arch. Hydrobiol., Vol.68, pp.305-375.

[19] Jonasson, I.R. (1977), Geochemistry of Sediment/water Interactions of Metals, Including Observations on Availability, In The Fluvial Transport of Sediment-Associated Nutrients and Contaminants, IJC/PLUARG, Shear, H., Watson, A.E.P. (eds), Windsor/Ont., pp. 255-271.

[20] Chester, R. (1990), Marine Geochemistry, Unwin Hyman, Ltd., London, 698 pp.