



Nondetrital and total metal distribution in core sediments from the U-Tapao Canal, Songkhla, Thailand

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Abstract

The U-Tapao Canal is the main source of freshwater draining into the outer part of Songkhla Lake, which is the most important estuarine lagoon in Thailand. Songkhla Lake is located in southern Thailand between latitudes 7°08' and 7°50' N and longitudes 100°07' and 100°37' E. Acetic acid (HOAc)-soluble Cu, Fe, Mn, Pb, and Zn and the total concentration of these metals along with Al concentration, organic carbon, carbonate, sand, silt, and clay contents were determined in 4 sediment cores obtained at selected intervals from the mouth of the canal to 12 km upstream. Readily oxidizable organic matter in the cores varies from 1.52% to 7.30% and is generally found to decrease seaward. Total concentrations of Al (61.7–99.0 g kg⁻¹; 2.29–3.67 mol kg⁻¹), Cu (12.4–28.2 mg kg⁻¹; 195–444 μmol kg⁻¹), Fe (25.2–42.0 g kg⁻¹; 451–752 mmol kg⁻¹), Mn (0.22–0.49 g kg⁻¹; 4.0–8.9 mmol kg⁻¹), Pb (16.7–43.1 mg kg⁻¹; 80.6–208 μmol kg⁻¹), and Zn (48.6–122.7 mg kg⁻¹; 0.74–1.88 mmol kg⁻¹) vary to a certain extent vertically and seaward in the U-Tapao Canal core sediments. These concentrations are at or near natural levels and show no indication of anthropogenic contamination.

Overall, the data show that total metal concentrations in the surface and near surface core sediments are enriched in varying degrees relative to Al in the order of ~Zn>Mn>Pb>Fe>Cu. Chemical partitioning shows that the enrichment in the surface and near surface sediments is related to the relatively high proportion of the total metal concentrations (Mn>Zn>Fe>Cu>Pb) that occur in the acetic acid-soluble (nondetrital) fraction, and they generally decrease with depth. Nondetrital Cu, Pb, and Zn likely derive from those metals held in ion exchange positions, certain carbonates, and from easily soluble amorphous compounds of Mn and perhaps those of Fe. Diagenetic processes involving Mn and to a lesser extent, Fe compounds, as well as the vertical changes in the oxidizing/reducing boundaries, appear to be the most important factors controlling the behavior of the metals in these cores. Organic matter and the aluminosilicate minerals, however, appear to be less important carriers of the metals studied.

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1. Introduction

Sediment is well known as a sink for contaminants such as heavy metals. During the sedimentation process, suspended particulate matter acts as a scavenger of dissolved elements, resulting in the removal of discharged contaminants. Although these adsorbed particulate metals will be trapped in the bottom sediment, it is also possible that the sediments may themselves act as a source of contaminants (Salomon et al., 1987). In addition, the distribution of natural chemicals among different minerals reflects both originic (unchanged from original composition) and authigenic (derived composition in situ) factors. Nevertheless, these are characteristics of the chemical distribution that relate to grain size and mineralogy. Thus, it is necessary to define the two components of chemical abundance in sediments as nondetriral (ND) and detriral. The nondetriral component represents chemical constituents that are associated with sediment particles in a weakly bound form which is more exchangeable with other phases such as water (Bewers et al., 1998). The detriral component represents chemical constituents bound within mineral particles such as the aluminosilicates. Aluminum was measured in this study as a conservative proxy for the variations

of the detriral aluminosilicate fraction and its associated metals.

The U-Tapao Canal is the main source of freshwater draining into the outer part of Songkhla Lake, which is the most important estuarine lagoon in Thailand. The Songkhla Lake is located in southern Thailand between latitudes 7°08' and 7°50' N and longitudes 100°07' and 100°37' E. The outer part of Songkhla Lake is connected to the Gulf of Thailand by a channel that is 420 m wide and 9.5 m deep. It has a surface area of 176 km² and an average water depth of 1.5 m. The salinity of the water is altered by the tidal current and varies over a wide range from nearly 0–31 psu. The sediments inside the lagoon range from clay loam to light clay, but it is sandy in the channel. Kaolin is the dominant mineral in the clay fraction except in the central area where quartz is the main component (Maneepong and Matsumoto, 1994). The sedimentation rate in the Songkhla Lake at the mouth of U-Tapao Canal was 5.3 mm yr⁻¹ (Bhongsuwan and Chittrakarn, 1997).

Maneepong (1996) has reported the concentration of metals in the surface sediment (0–20 cm) of the outer Songkhla Lake. Labile metal concentrations in the surface sediments of the U-Tapao Canal have been previously studied by Maneepong and Angsupanich (1999). The results from both studies showed no

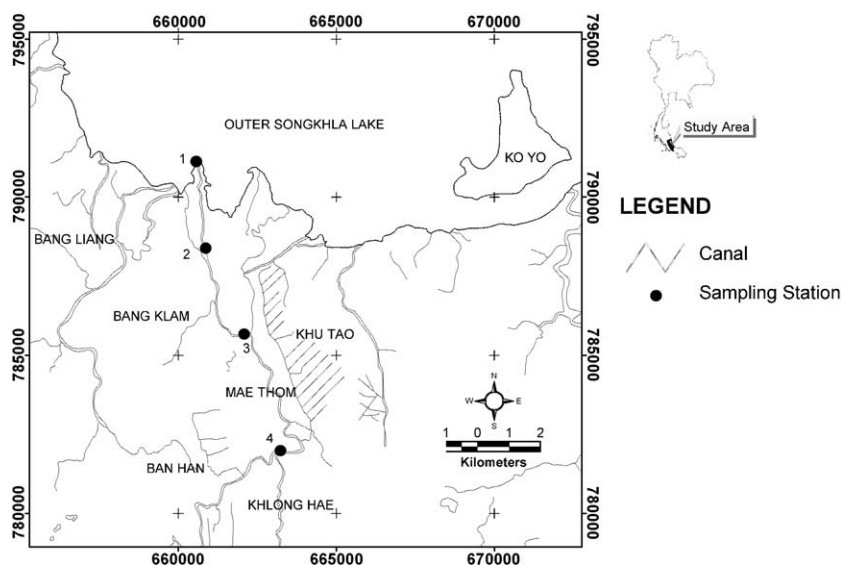


Fig. 1. Location map of the U-Tapao Canal, Songkhla province. Filled circles indicate sampling stations. The first station (U1) was located at the mouth of the canal, and the last station (U4) was at 12 km upstream.

significant enrichment of the metals in sediments collected from this area. However, the behavior of trace metals in the mixing zone is of interest due to the changes of salinity. Metal concentrations in sediments and in pore water at various depths and readily oxidizable organic matter in the U-Tapao Canal have not been studied previously.

We report here the acetic acid (HOAc)-soluble, or so-called nondetriral (ND) concentrations of Cu, Fe, Mn, Pb, and Zn, and the total concentration of these metals along with Al concentrations in four sediment cores obtained at selected intervals from the mouth of the canal to 12 km upstream. A statistical analysis of the data is used to suggest the factors that control the vertical distribution and abundance of the metals.

2. Study site

The U-Tapao Canal is the most important canal in the U-Tapao Basin (with a drainage area of 2305 km²). It is 68-km long and approximately 3–8-m deep. This canal originates from Bantad Mountain and flows through Hatyai Municipality before emptying into the outer part of Songkhla Lake. The discharge ranges from less than 6 m³ s⁻¹ in the dry season to more than 90 m³ s⁻¹ in the rainy season (Jew, 1996). Major sources of waste discharged into the U-Tapao Canal are from rubber, parawood, and seafood processing industries at the rate of 41 000 m³ day⁻¹. The effluents have high organic contents (Environmental Department, Division 12, 2000). Salt intrusion from the Songkhla Lake into the canal has been found to be about 12 km upstream, with partial mixing between fresh and salt water (Pornpinatepong, 1998). Hence, the lower part of the canal is an estuary which connects directly to the outer part of the Songkhla Lake (Fig. 1).

3. Material and methods

3.1. Sample collection and storage

In this study, four core stations (U1–U4) in the canal were investigated (Fig. 1). The first station was located at the mouth of the canal and the last station at 12 km upstream. Undisturbed sediment cores were collected on March 2001 by diving with a 4-in.

diameter, 20-in. long Plexiglas push corer. The cores were taken at each site closest to the centre of the canal where the sediments were least disturbed. After collection, both ends of the cores were closed with plastic caps and wrapped tightly prior to being transferred (vertically) back to the laboratory within 2 h. Immediately after arrival, the cores were subsampled in a nitrogen chamber. This operation was completed within 24 h after core recovery.

3.2. Subsampling

The upper part of each core was inserted into the nitrogen chamber through a lock gate in order to obtain pore water and sediment at different depths. The sediment was carefully pressed out and sliced as follows: 0–1 and 1–2 cm, and then every 3 cm along the full length of the core with an acid-cleaned plastic knife. The pore water from each subsample layer was immediately extracted in the nitrogen chamber. The results of metals in the pore water fraction were reported elsewhere. The sediments retained in the vial were freeze-dried. After removal of material >2 mm, the sediments were separated into two portions. The first portion of dried sediment was sieved through a 58- μ m nylon sieve for geochemical analyses. The second portion was kept for grain size analysis.

3.3. Chemicals

Ultrapure mineral acids (HNO₃ and HCl) were prepared by sub-boiling distillation. Nanopure water (>18 M Ω cm) was obtained from Barnstead (Germany) Systems. All labware was carefully acid-cleaned and stored in plastic bags. All transferal processes and preservation were performed in a class 100 clean bench. Plastic gloves were used at all times. All other chemicals used were analytical grade.

3.4. Microwave digestion for total metal determination

About 0.3 g (weighed to 0.01 g) of the dried sediment (<58 μ m) was digested with 6 ml of hydrofluoric acid and 1 ml of aqua regia in 40-ml LORRAN PTFE bombs (in a domestic type microwave oven), following the digestion technique described by Loring and Rantala (1995).

Total concentrations of Al, Cu, Fe, Mn, and Zn in the sediment were determined by flame atomic absorption (FAAS) using a Varian Spectra-220 and a Shimadzu AA680, respectively. A graphite furnace atomic absorption spectrophotometer (GFAAS) Shimadzu AA-680G equipped with autosampler ASC-60G was used to determine Pb. A mixture of palladium nitrate (0.15%) and magnesium nitrate (0.1%) was used as a modifier for Pb analysis. The relative accuracy for the determination of elements was within the standard deviations of certified values for the National Research Council of Canada (NRCC) sediment reference material PACS-2.

3.5. Acetic acid extraction for nondetriral metal determination

About 2 g (weighed to 0.01 g) of the dried sediment (<58 μm) was extracted for the HOAc-soluble (ND) fractions by adding 25 ml of 4.5 M HOAc (Loring and Rantala, 1995). After shaking slowly for 6 h, the sample was centrifuged at 1000 g for 10 min. The supernatant was poured into a flask. The sediment was washed with 10 ml of nanopure water, and the tube was shaken briefly. The washed water was separated by centrifugation and added to the same flask. The extracted solution in the flask was made up to a volume of 50 ml and stored at 4 °C until analyses. HOAc-soluble concentrations of Cu, Fe, Mn, and Zn in the sediment were determined using FAAS. Pb concentrations were determined by GFAAS.

3.6. Readily oxidizable organic matters and carbonate contents

Readily oxidizable organic matter (OM) in the sediment was determined by the Walkey–Black method (chromic acid method) modified by Loring and Rantala (1995). Carbonate content was determined using an acid-based titration procedure, as described by Sompongchaiyakul (1989).

3.7. Size analysis

The textural classification of the sediment samples was based on wet sieving through a 75- μm sieve. The portion that passed through the 75- μm sieve was later analyzed for its percentage in silt- and clay-sized

particles, using the sedimentation technique described in the Annual Book of ASTM standards (American Society for Testing and Materials (ASTM), 1982). Grain size normalization was used to compensate for the effect of mineralogical variability on metal concentrations.

3.8. Statistical evaluation

Student's Bonferoni t tests ($p \leq 0.05$) were performed to compare population means among data sets. Factor analysis was used to clarify the relationships between the acetic acid-soluble and total metal concentrations, carbonate and organic contents, grain size, and the core depth in each of the cores. Variables are grouped on the basis of their intercorrelations into factors. The factors are the most dominant features of the data variations and are derived from the correlation matrices for each core. For this study, the principle factors (correlation matrices) were rotated to produce normal varimax orthogonal solutions in which three to five factors accounted for most of the total problem variance. The results of the analyses are used to suggest the geochemical processes controlling the accumulation and partitioning of the metals in the cores.

4. Results and discussion

4.1. Sediment characteristics

The top layer of cores U1 and U2 was brownish in colour, while it was grey in cores U3 and U4. Beneath this top layer, the sediments were dark grey. The grain size composition of the four cores is illustrated in Fig. 2. All samples were considered fine (sediments containing <40% of sand material). The core U3 contained less sand fraction than the other three cores.

The concentrations of readily oxidizable OM ranged from 1.52% to 7.30%, with an average of 2.09%, 3.28%, 4.14%, and 2.72% for cores U1, U2, U3, and U4, respectively. It was found that sediments in the surface layers of cores U1 and U2 contained higher OM than those in cores U3 and U4. The enrichment of organic matter was found at a depth of 10–18 cm of cores U2, U3, and U4. A seaward decrease of OM was noted from core U3 to U1. The

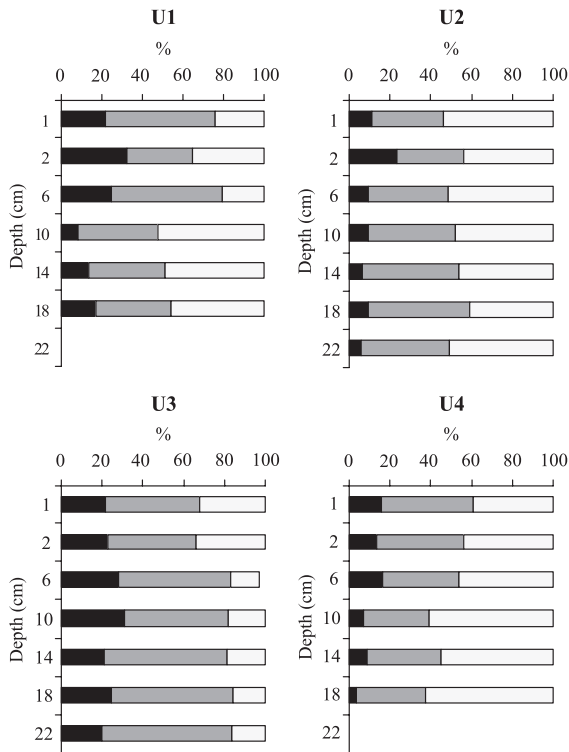


Fig. 2. Grain size composition vs. depth in the sediment cores collected from the U-Tapao Canal. (■: sand, ■: silt, and □: clay).

core sediments also had a relatively high carbonate content ranging from 20–21%.

4.2. Partitioning of total metal concentrations

In sediments, part of the metal load is loosely bound to the particles, and part is locked up physically and/or chemically in detrital particles and minerals. Selective chemical methods using HOAc (Loring, 1978), weak HCl solutions (Luoma and Jenne, 1976), and even sequential extractions (Tessier et al., 1979) have been developed and used to partition the total metal concentrations into their loosely bound (ND) and residual (detrital) phases.

The HOAc method was chosen because it is one of the weakest chemical treatments that can be used to remove effectively the weakly bound part of the total metal concentrations in sediments (Loring, 1978). HOAc (25% v/v or 4.5 M) removes metals held in ion exchange positions, easily soluble amorphous com-

pounds of Fe and Mn, carbonates, and those metals weakly held in OM. It leaves the silicate lattices intact and does not attack the resistant Fe and Mn minerals or organic compounds. The proportion of the metal concentration removed by the HOAc extraction is operationally defined as the nondetrital, acetic acid-soluble (ND) metal fraction of the sediment. The residual metal fraction is referred as the detrital fraction. The proportion associated with aluminosilicate fraction is estimated by metal/Al ratios; that is, constant metal/Al ratios would imply that the metals are associated with the aluminosilicate fraction. Although the extent of metal enrichment relative to Al is not directly known, enrichment factors (EF) may be estimated indirectly by $EF = \text{metal}/\text{Al}_{\text{enriched}}/\text{metal}/\text{Al}_{\text{background}}$. The background level metal/Al ratio is derived from the level in these cores at which the metal/Al ratios is the lowest.

4.3. Total and nondetrital (HOAc-soluble) metals in core sediments

Downcore profiles of ND metals, total metals, and percent contribution of the ND fraction to the total fraction are shown in Fig. 3. The average total Cu, Pb, and Zn concentrations were significantly higher in core U2 than at other stations. The average total Cu, Pb, and Zn concentrations in cores U2 and U4 were higher than at cores U1 and U3, but total Fe and Mn concentration at all stations were relatively constant. Overall, the total average concentrations of Fe, Mn, and Zn show a general decrease seaward (cores U4–U1). Total Al concentrations in the top 10 cm of sediment cores U1 and U2 were slightly higher than in U3 and U4. The total concentrations of Cu, Fe, Mn, Pb, and Zn were found to be at or near natural levels in sediments found in uncontaminated areas of the world (Table 1).

Vertical total metal core profiles show (Fig. 3) that the total concentrations of metals generally decrease (except for Cu in core U4) with depths in all cores. Changes in metal/Al ratios with depth (Table 2) also indicate that total Cu, Fe, Mn, Pb, and Zn concentrations show varying degrees of enrichment in the surface (1–2 cm) sediments. The relative enrichment factor (EF) of each metal for each core profile is shown in Table 2. Total Mn, Pb, and Zn has the highest enrichment factors relative to Al in the cores. Enrichment factors at the surface for Mn

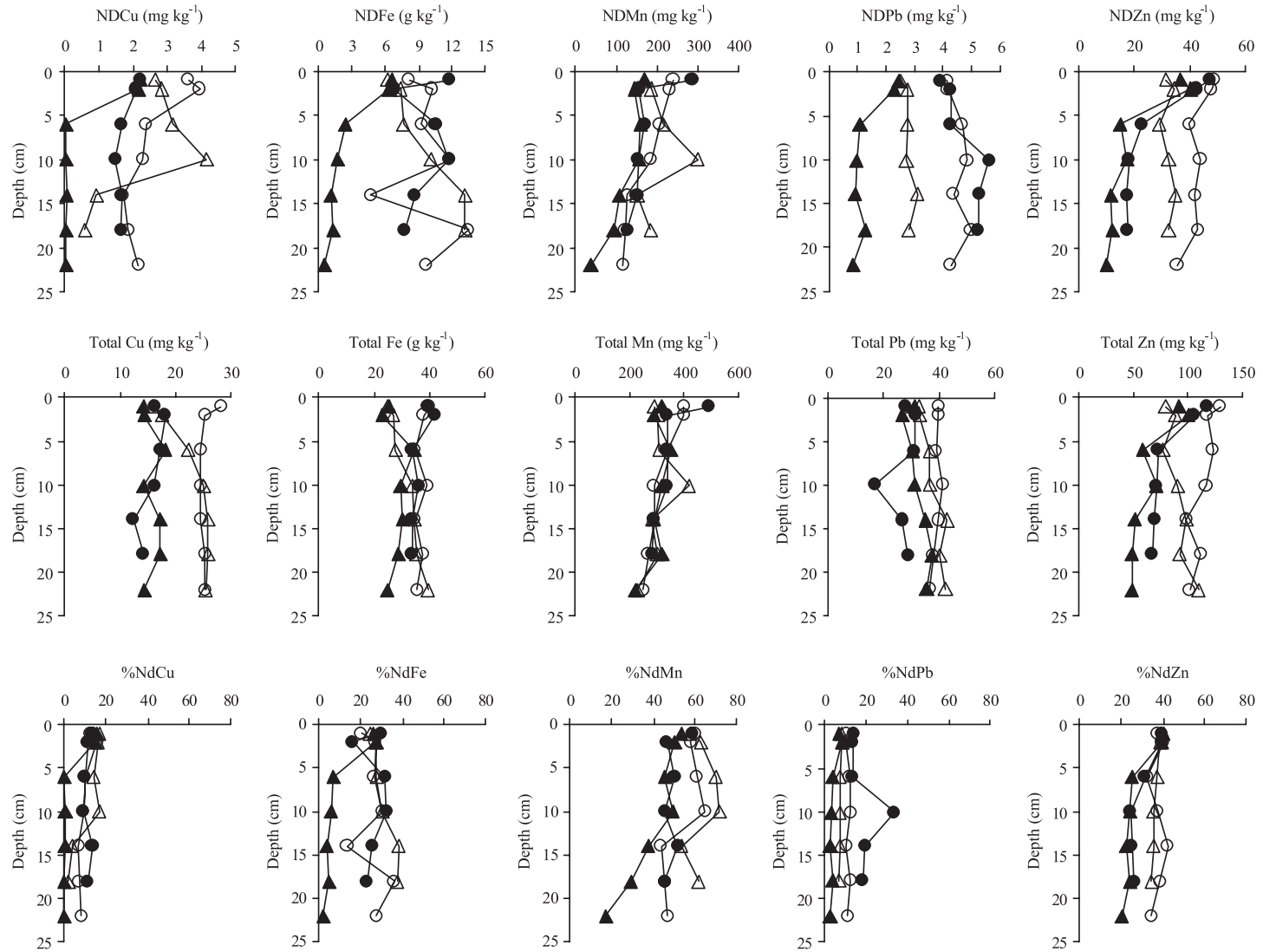


Fig. 3. Vertical depth profiles of nondetrital (ND), total, and percent nondetrital (ND) Cu, Fe, Mn, Pb, and Zn, at U1 (●), U2 (○), U3 (▲), U4 (△).

Table 1

Total concentrations of copper, iron, manganese, lead, and zinc in sediments from various areas of the world

Area	Method	Cu (mg kg ⁻¹)	Fe (g kg ⁻¹)	Mn (g kg ⁻¹)	Pb (mg kg ⁻¹)	Zn (mg kg ⁻¹)
This study	HF/aqua regia	12.4–28.2	25.2–42.0	0.2–0.5	16.7–43.1	48.6–122.7
Gulf of Thailand ^d	NAA ^b	–	16.25–41.96	0.30–1.53	–	–
Songkhla Lagoon (Songkhla) ^c	HNO ₃ /HClO ₄	4–15	8.26–28.02	0.09–0.52	–	22–136
Muvattupuzha River (India) ^d	HF/HNO ₃ /HClO ₄	–	19.4–125.7	0.36–2.06	–	–
Central Vembanad Estuary (India) ^d	HF/HNO ₃ /HClO ₄	–	4.2–82.5	0.12–0.97	–	–
Coastal Wetland (Hong Kong) ^c	HNO ₃ /H ₂ SO ₄	38.6–40.6	–	–	–	175–183
Mai Po (Hong Kong) ^f	HNO ₃ /H ₂ SO ₄	51–87	0.39–3.33	–	69–220	130–308
Rivers in China (Eastern China) ^g	HF/HNO ₃ /HClO ₄	11.5–54.8	24.90–45.6	0.50–1.06	21.5–65.5	60.2–309.0
Mouth of River Asopos (Greece) ^h	HF/aqua regia	11.4–43.0	19.3–50.6	0.33–0.55	7.29–36.70	39.5–129.0
Lena Delta, Laptev Sea ⁱ	HF/aqua regia	1–21	11.8–52.1	0–5.34	9–23	14–134
North–Eastern Irish Sea (UK) ^j	1 M HCl	9–63	3–19	0.4–1.1	40–250	–

^a Sompongchaiyakul, 1989.^b NAA=Neutron Activation Analysis^c Maneepong, 1996.^d Padmalal and Seralathan, 1995.^e Lau and Chu, 1999.^f Ong Che, 1999.^g Chen et al., 2000.^h Angelidis and Aloupi, 2000.ⁱ Nolting et al., 1995.^j Williams et al., 1998.

vary from 1.6 (core U2) to 1.9 (cores U3 and U4), Pb from 1.1 (core U2) to 1.8 (core U1), and Zn from 1.3 (core U2) to 2.6 (core U3). Copper and Fe show the least enrichment in the cores. The enrichment factors for Cu and Fe in the surface sediments vary from 1.0 (Cu: core U4) and 1.1 (Fe: core U4) to 1.3, with the highest enrichment of 1.3 for both metals found in core U3. The enrichment of Mn relative to Fe in the surface sediments is also reflected in three of the four cores by decreasing Mn/Fe ratios with depth (Table 2).

Cu and Fe were most enriched in core U3. High enrichment of Mn was found in the top 10 cm of cores U2, U3, and U4, while in U1, high enrichment was found only at the surface layer. Pb was highly enriched in core U1. The enrichment of Zn was found in the top 10 cm of core U3 and in the surface layer of U1.

Chemical partition data show (Fig. 3) that a significant proportion (~5–70%) of the total metal concentrations (Mn>Zn>Fe>Cu>Pb) occur in the acid-soluble fraction, and that these concentrations generally decrease with increasing core depth. As a result, metals in this fraction are apparently responsible for the metal enrichment in the surface and near surface core sediments. Nondetriral Cu, Pb, and Zn concentrations most likely derive from those held in ion exchange

positions, certain carbonates, and easily soluble amorphous compounds of Mn and perhaps Fe, as they follow, for the most part, with the profiles of acid-soluble Mn, and to a certain extent, with Fe in the cores.

For example, in the surface sediments of core U3, all ND metals are enriched, while sediments at the deeper part contained much lower concentrations of ND metals. The surface enrichment may be partly due to the effect of the scavenging of metals onto Fe and Mn hydroxides (Davis and Leckie, 1978). The control by diagenetic processes of Mn and associated metal profiles whose concentrations decrease with depth is well known (Berner, 1980; Farmer and Lovell, 1984; Jenne, 1968). The decrease in acid-soluble metals with depth is not surprising due to the observation of the dark grey color and the high organic content contained in the deeper sediment of this core (Table 3), which implies that the sediment in the layer beneath 5 cm reflects highly reducing conditions. Thus, available metals may possibly form complexes with sulfides that would not be extracted by 4.5 M HOAc (Loring and Rantala, 1995).

The profiles shown in Fig. 3 also indicate that the concentration of ND Cu, Fe, Mn, Pb, and Zn in the surface sediments slightly increases seaward. NDFe, NDMn, and NDZn found in this study (extracted by

Table 2

Total metal concentrations, metal to aluminum ratios, and metal enrichment factors in various depth of sediment collected from the U-Tapao Canal

Depth (cm)	Cu (mg kg ⁻¹)	Fe (g kg ⁻¹)	Mn (g kg ⁻¹)	Pb (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Al (g kg ⁻¹)	Cu/Al (g/g)	Fe/Al (g/g)	Mn/Al (g/g)	Pb/Al (g/g)	Zn/Al (g/g)	Mn/Fe (g/g)	Cu EF	Fe EF	Mn EF	Pb EF	Zn EF
<i>Core U1</i>																	
1	16.17	39.39	0.49	27.73	118.07	83.08	1.9E-04	0.47	5.9E-03	3.3E-04	1.4E-03	1.2E-02	1.2	1.2	1.7	1.8	1.8
2	18.07	41.97	0.34	31.52	105.35	98.51	1.8E-04	0.43	3.5E-03	3.2E-04	1.1E-03	8.1E-03	1.1	1.1	1.0	1.7	1.3
6	17.12	33.39	0.34	31.06	71.99	87.97	1.9E-04	0.38	3.9E-03	3.5E-04	8.2E-04	1.0E-02	1.2	1.0	1.1	1.9	1.0
10	16.17	36.06	0.34	16.74	71.75	89.77	1.8E-04	0.40	3.8E-03	1.9E-04	8.0E-04	9.4E-03	1.1	1.1	1.1	1.0	1.0
14	12.37	33.56	0.29	26.82	69.11	74.46	1.7E-04	0.45	3.9E-03	3.6E-04	9.3E-04	8.6E-03	1.0	1.2	1.1	1.9	1.2
18	14.27	33.39	0.28	28.59	67.19	73.95	1.9E-04	0.45	3.8E-03	3.9E-04	9.1E-04	8.4E-03	1.2	1.2	1.1	2.1	1.1
<i>Core U2</i>																	
1	28.15	39.77	0.40	39.74	130.28	95.68	2.9E-04	0.42	4.2E-03	4.2E-04	1.4E-03	1.0E-02	1.1	1.1	1.6	1.1	1.3
2	25.34	37.75	0.40	39.89	117.83	91.44	2.8E-04	0.41	4.4E-03	4.4E-04	1.3E-03	1.1E-02	1.0	1.1	1.7	1.1	1.2
6	24.40	34.89	0.34	38.94	122.71	91.69	2.7E-04	0.38	3.7E-03	4.2E-04	1.3E-03	9.7E-03	1.0	1.0	1.4	1.1	1.2
10	24.40	38.94	0.29	41.22	116.38	90.28	2.7E-04	0.43	3.2E-03	4.6E-04	1.3E-03	7.5E-03	1.0	1.1	1.2	1.2	1.2
14	24.52	34.72	0.29	39.73	98.62	88.24	2.8E-04	0.39	3.3E-03	4.5E-04	1.1E-03	8.4E-03	1.1	1.0	1.2	1.1	1.0
18	25.34	37.64	0.27	37.83	111.46	95.81	2.6E-04	0.39	2.8E-03	3.9E-04	1.2E-03	7.2E-03	1.0	1.0	1.1	1.0	1.1
22	25.34	35.57	0.25	36.46	101.62	94.52	2.7E-04	0.38	2.6E-03	3.9E-04	1.1E-03	7.0E-03	1.0	1.0	1.0	1.0	1.0
<i>Core U3</i>																	
1	14.26	25.16	0.32	30.88	91.51	62.28	2.3E-04	0.40	5.1E-03	5.0E-04	1.5E-03	1.3E-02	1.3	1.3	1.9	1.2	2.4
2	14.32	23.02	0.29	26.62	100.84	65.73	2.2E-04	0.35	4.4E-03	4.0E-04	1.5E-03	1.3E-02	1.2	1.1	1.6	1.0	2.6
6	18.14	34.43	0.35	30.17	58.28	62.16	2.9E-04	0.55	5.6E-03	4.9E-04	9.4E-04	1.0E-02	1.7	1.8	2.1	1.2	1.6
10	14.30	29.68	0.32	30.96	71.31	61.65	2.3E-04	0.48	5.2E-03	5.0E-04	1.2E-03	1.1E-02	1.3	1.6	1.9	1.2	1.9
14	17.14	30.47	0.29	34.88	51.40	81.44	2.1E-04	0.37	3.6E-03	4.3E-04	6.3E-04	9.5E-03	1.2	1.2	1.3	1.1	1.0
18	17.13	28.87	0.32	37.43	48.58	61.55	2.8E-04	0.47	5.2E-03	6.1E-04	7.9E-04	1.1E-02	1.6	1.5	1.9	1.5	1.3
22	14.31	24.81	0.22	35.22	48.72	80.99	1.8E-04	0.31	2.7E-03	4.3E-04	6.0E-04	8.9E-03	1.0	1.0	1.0	1.1	1.0
<i>Core U4</i>																	
1	15.74	24.81	0.29	32.41	79.39	59.58	2.6E-04	0.42	4.9E-03	5.4E-04	1.3E-03	1.2E-02	1.0	1.1	1.9	1.3	1.4
2	17.55	27.02	0.30	33.07	88.97	66.73	2.6E-04	0.40	4.5E-03	5.0E-04	1.3E-03	1.1E-02	1.0	1.1	1.8	1.2	1.4
6	22.21	27.67	0.31	36.46	77.69	71.09	3.1E-04	0.39	4.4E-03	5.1E-04	1.1E-03	1.1E-02	1.2	1.1	1.7	1.3	1.2
10	25.04	33.57	0.42	36.67	91.04	84.35	3.0E-04	0.40	5.0E-03	4.3E-04	1.1E-03	1.3E-02	1.1	1.1	2.0	1.1	1.1
14	25.86	34.32	0.28	43.07	98.18	94.47	2.7E-04	0.36	3.0E-03	4.6E-04	1.0E-03	8.2E-03	1.0	1.0	1.2	1.1	1.1
18	25.90	35.17	0.30	40.07	93.03	98.98	2.6E-04	0.36	3.0E-03	4.0E-04	9.4E-04	8.5E-03	1.0	1.0	1.2	1.0	1.0
22	25.44	39.40	0.23	42.06	110.05	90.56	2.8E-04	0.44	2.5E-03	4.6E-04	1.2E-03	5.8E-03	1.1	1.2	1.0	1.1	1.3

Table 3
Readily oxidizable organic content (%) in the U-Tapao sediment cores

Depth (cm)	U1	U2	U3	U4
1	2.13	2.32	1.68	1.52
2	2.42	1.99	1.85	1.97
6	1.73	2.86	4.76	1.86
10	2.17	4.24	7.30	2.48
14	1.93	4.14	6.07	4.56
18	2.14	5.06	3.58	3.93
22		2.34	3.73	

4.5 M HOAc) are in the same range as reported by Maneepong (1996) (extracted by 1 M HCl). The concentrations of NDFe, NDMn, and NDZn in this study are similar to those reported for the Gulf of Thailand (Sompongchaiyakul, 1989; Table 4).

4.4. Geochemical factors derived from the varimax matrices

The study of varimax matrices (Table 5) may reveal a clearer explanation of the geochemical factors controlling the dispersal and accumulation of the metals. The significant relationships between the variables and the associations of the metals with the main sedimentary and chemical components are presented by using factor analyses as the indicators. Because the data base of sediments for each core is statistically small (8 data points), the correlation coefficients are considered significant down to a level of $p < 0.05$. The correlation matrices between the four cores showed no consistent patterns, but the varimax matrices show some significant intercorrelated variables.

Factor analyses of core U1 shows that four factors account for 75.7% of the problem variance (Table 5). Factor 1 (35.4% of the total variance) has significant positive loadings ($p \leq 0.01$) on total Mn, Zn, and ND Cu, Mn, and Zn. These strong loadings suggest that associations with Mn control the abundance and distribution of Zn, NDCu, NDMn, and NDZn in this core. Factor 2 (19.1% of the total variance) is the OM factor in which the amount of OM decreases with increasing silt and clay content. Factor 3 (20.5% of the total variance) indicates that the amount of Pb varies directly with the sand content. Factor 4 (0.68% of the total variance) has significant negative loadings on Al, Cu, and a lesser significant ($p \leq 0.05$) positive loadings on carbonate. This can be identified as the Al factor in which Cu appears to be associated with aluminosilicates, and both are slightly diluted by carbonates. The very low loadings of Al on this factor also shows that aluminosilicates play a relatively insignificant role in the abundance and distribution of the metals in this core.

Factor analyses of core U2 shows that five factors account for 94.8% of the problem variance. Factor 1 (24.5% of the total variance) has significant positive loadings on core depth, total Pb and Zn, and negative loadings on ND Cu and Zn. It indicates that Pb and Zn increase while NDCu and NDZn decrease with increasing depth. This in turn appears to reflect the changes in the decrease in the amounts of acid-soluble Cu and Zn, as the physicochemical environment in the core becomes reducing with perhaps the resulting formation of sulfides at depth. Factor 2 (25.2% of the total variance) has significant positive loadings on total Cu and Mn and ND Mn and Pb. This factor suggests that the association with Mn is the main

Table 4
Nondetrital concentrations of Cu, Fe, Mn, Pb, and Zn in sediments from the U-Tapao Canal and the Gulf of Thailand

Study area	Method	Cu (mg kg ⁻¹)	Fe (g kg ⁻¹)	Mn (g kg ⁻¹)	Pb (mg kg ⁻¹)	Zn (mg kg ⁻¹)
This study	4.5 M HOAc	0.03–4.2	0.5–13.5	0.04–0.36	0.5–5.9	9.4–48.9
U-Tapao Canal ^a	1 M HCl	0.30–17.4	0.34–12.34	0.003–0.36	0.5–21.6	1.7–40.5
The mouth of U-Tapao Canal ^b	0.01 M DTPA	1.8–4	0.6–1.2	0.02–0.06	–	2–12
Upper Gulf of Thailand ^c	1 N HNO ₃	–	7.7–16.6	0.44–0.86	–	13.6–31.4
Lower Gulf of Thailand ^c	1 N HNO ₃	–	5.6–17.6	0.19–0.82	–	11.1–34.6

^a Maneepong and Angsupanich, 1999.

^b Maneepong, 1996.

^c Sompongchaiyakul, 1989.

Table 5

The varimax matrices (factor analyses) of sediment cores U1–U4 collected from the U-Tapao Canal

Factor	Core U1				Core U2					Core U3				Core U4			
	1	2	3	4	1	2	3	4	5	1	2	3	4	1	2	3	4
%	35.4	19.1	20.5	0.68	24.5	25.2	15.0	12.3	17.8	26.9	27.0	26.8	10.03	31.9	26.7	23.6	14.0
Depth	ns	ns	ns	ns	0.83	ns	ns	ns	ns	ns	ns	0.72	ns	−0.88	ns	ns	ns
OM%	ns	0.82	ns	ns	ns	ns	ns	0.87	ns	ns	0.96	ns	ns	ns	ns	−0.83	ns
CO%	ns	ns	ns	0.72	ns	ns	−0.84	ns	ns	0.93	ns	ns	ns	0.79	ns	ns	ns
Al	ns	ns	ns	−0.98	ns	ns	ns	ns	−0.97	ns	ns	0.89	ns	ns	0.92	ns	ns
Fe	ns	ns	ns	ns	ns	ns	ns	ns	−0.76	ns	ns	−0.78	ns	ns	ns	−0.80	ns
Mn	0.87	ns	ns	ns	ns	0.89	ns	ns	ns	ns	ns	ns	0.97	0.88	ns	ns	ns
Pb	ns	ns	−0.99	ns	0.91	ns	ns	ns	ns	ns	ns	ns	ns	ns	0.93	ns	ns
Zn	0.92	ns	ns	ns	0.78	ns	ns	ns	ns	ns	ns	0.78	ns	ns	0.69	ns	ns
Cu	ns	ns	ns	−0.92	ns	0.76	ns	ns	ns	−0.80	ns	ns	ns	ns	0.93	ns	ns
NDFe	ns	ns	ns	ns	ns	ns	ns	ns	−0.72	ns	ns	−0.95	ns	ns	ns	0.67	ns
NDMn	0.89	ns	ns	ns	ns	0.88	ns	ns	ns	−0.88	ns	ns	ns	0.87	ns	ns	ns
NDPb	ns	ns	ns	ns	ns	0.86	ns	ns	ns	−0.83	ns	ns	ns	ns	ns	0.97	ns
NDZn	0.87	ns	ns	ns	−0.91	ns	ns	ns	ns	ns	−0.75	ns	ns	ns	ns	ns	ns
NDCu	0.85	ns	ns	ns	−0.90	ns	ns	ns	ns	ns	ns	ns	0.65	ns	ns	0.75	ns
Sand	ns	ns	−0.82	ns	ns	ns	ns	ns	ns	ns	−0.93	ns	ns	ns	ns	ns	ns
Silt	ns	−0.94	ns	ns	ns	ns	ns	ns	ns	ns	0.94	ns	ns	−0.79	ns	ns	ns
Clay	ns	−0.74	ns	ns	ns	ns	−0.96	ns	ns	0.68	ns	ns	ns	ns	ns	ns	0.94

control on the behavior of Cu, acid-soluble Mn, and Pb in this core. Factor 3 (15.0% of the total variance) is the carbonate and clay factor in which the carbonate content appear to vary directly with the clay content. Factor 4 (12.3% of the total variance) has significant loading on OM alone. Factor 5 (17.8% of the total variance) is the Al factor in which Fe and NDFe vary directly with Al concentration and may indicate that some Fe and its acid-soluble fraction is associated with the aluminosilicate fraction in this core.

Factor analyses of core U3 shows that four factors account for 90.7% of the problem variance. Factor 1 (26.9% of the problem variance) has positive loadings on carbonate and clay content and negative loadings on total Cu, ND Mn, and Pb. This appears to be the factor in which carbonate acts as a diluent for the levels of Cu, NDMn, and NDPb concentrations. Factor 2 (27% of the total variance) has significant ($p \leq 0.001$) positive loadings on OM and silt content and negative loadings on sand but only low loadings ($p \leq 0.05$) on NDZn. This factor suggests that organic matter varies directly with silt content and inversely with sand content. Factor 3 (26.8%) has significant positive loadings on Al, Zn, and core depth and negative loadings on Fe and NDFe. This can be considered as the Al factor in which the concentration of Zn increases, and Fe and NDFe decrease with

increasing Al concentration with core depth. Factor 4 (10.0% of the total variance) has high positive loadings ($p \leq 0.001$) on Mn but weak loadings on ($p \leq 0.05$) on NDCu. This factor suggests that NDCu has a weak association with Mn.

Factor analyses of core U4 shows that four factors account for 96.2% of the problem variance. Factor 1 (31.9% of the total variance) has significant positive loadings on Mn, NDMn, carbonate, and sand content, with negative loadings on core depth and silt content. This appears to be a depth factor in which the concentrations of Mn, NDMn, NDCu, carbonate, and sand decrease and the silt content increases with increasing core depth. It emphasizes again that Mn compounds are the most likely source of NDMn, and that change with core depth from an oxidizing to a reducing physicochemical environment is an important regulator of the behavior of redox sensitive metals such as manganese in this and the other cores. Factor 2 (26.7% of the total variance) has significant loadings on Al, total Cu, Pb, and Zn. This is the Al factor in which the aluminosilicate fraction appears to be a factor controlling the distribution of total Cu, Pb, and Zn. Factor 3 (23.6% of the total variance) has significant positive loadings on ND Cu, Fe, and Pb and negative loadings on OM and total Fe. This apparently is the OM factor in which the concen-

tration of Fe increases and NDCu, NDFe, and NDPb decrease with increasing OM content. Factor 4 (14.0% of the total variance) has significant positive loadings on clay content alone.

Overall, the varimax data suggest that abundance and distribution of Mn, redox changes with core depth, and (to a lesser extent) Al, Fe, organic matter, and carbonate contents are significant factors in controlling the behavior of total and ND Cu, Pb, and Zn in the U-Tapao core sediments.

5. Conclusions

In general, the changes in nondetrital and total Cu, Fe, Mn, Pb, and Zn concentrations in surface (0–1 cm) samples over distance from the Songkhla Lake seem to increase seaward. Cu, Pb, and Zn in sediments of the U-Tapao Canal found in this study were at natural levels and indicate no anthropogenic contamination.

Overall, the data show total metal concentrations in the surface, and near surface core sediments are enriched to varying degrees relative to Al in the order of $\sim\text{Zn}>\text{Mn}>\text{Pb}>\text{Fe}>\text{Cu}$. Chemical partitioning shows that the enrichment in the surface and near surface sediments is related to the relatively high proportion of the total metal concentrations ($\text{Mn}>\text{Zn}>\text{Fe}>\text{Cu}>\text{Pb}$) in these layers that are extracted by a weak acid (HOAc) attack. These acid-soluble or nondetrital concentrations generally decrease with depth. The nondetrital Cu, Pb, and Zn concentrations mostly likely derive from those held in ion exchanged positions, certain carbonates, and easily soluble amorphous compounds of Mn and perhaps those of Fe.

Diagenetic processes involving Mn and to a lesser extent Fe compounds as well as the changes in the oxidizing/reducing boundaries with core depth appear to be the most important factors in controlling the behavior of the metals in these cores. The development of characteristic Mn and its associated trace metal surface enrichment profiles in sediment cores by diagenetic processes is well known where oxic surface sediments become anoxic with depth. The net effect in such environments is believed to result from the upward migration of soluble Mn^{2+} ions from the reducing subsurface layers and subsequent precipitation and enrichment of MnO_2 upon reoxidation in the oxygenated surface layer. Such mobilization and

cycling of Mn would produce metal concentration profiles similar to most of those shown in Fig. 3. In such cases, the main process underlying the recycling of Mn is the microbiological decomposition of organic matter through bacterial utilization of oxygen and inorganic oxidizing agents. These changes in redox potential and pore water chemistry with core depth generate the dissolution, upward flux, and reprecipitation of Mn compounds. These conditions also support the formation of metallic sulfides from the available metal species, as they are buried after being released from the loosely bound and ion exchange positions by reduction of the Mn (and Fe to a lesser extent) oxyhydroxide carrier phases. In addition, Fe is usually separated from Mn during this process because ferrous ion becomes less mobile than Mn^{2+} ions below the redox boundary and tends to form various sulfide compounds. The enrichment of Mn relative to Fe in the surface sediments is reflected in three of the four cores by decreasing Mn/Fe ratios with depth.

Although organic matter plays an important role in the development of the oxidizing/reducing environment within the core sediments, it does not seem to be a major carrier of the Cu, Pb, and Zn. Carbonate, a major component of the core sediments, has little direct influence on the geochemistry of the metals other than to act a diluent. The data also suggest that association of the metals with the aluminosilicate fraction is limited in most cores.

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