

Acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) in the sediment cores of the Pearl River Estuary, South China

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Abstract

The acid volatile sulfide (AVS), simultaneously extracted metals (SEM), total metals and chemical partitioning in the sediment cores of the Pearl River Estuary (PRE) were studied. The concentrations of total metals, AVS and SEM in the sediment cores were generally low in the river outlet area, increased along the seaward direction, and then decreased again at the seaward boundary of the estuary. The amounts of AVS were generally greater in deeper sediments than in surface sediments. SEM/AVS was >1 in the surface sediments and in the river outlet cores. The ratio was <1 in the sediments down the profiles, suggesting that AVS might play a major role in binding heavy metals in the deep sediments of the PRE. The SEMs may contain different chemical forms of trace metals in the sediments, depending on the metal reaction with 1M cold HCl in the AVS procedure when compared with the results of the sequential chemical extraction. The SEM/AVS ratio prediction may overestimate trace metals availability even in the sediments with high AVS concentrations in the sediments.

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1. Introduction

Estuarine and coastal areas are often regions of high population density and intensive human activity. As a result, elevated levels of heavy metals in sediments reflect the impacts of industrial activities and urban development. The Pearl River (Zhujiang) estuary (PRE) was created by the inflow of freshwater from the largest river system flowing into the South China Sea. The river water covers an area of more than 8000 km² during the peak discharge time, with a watershed of 230,000 km². Enriched by the large amounts of river-borne nutrients, the Pearl River estuary supports large populations of marine organisms and contributes significantly to the fisheries in South China (Wong et al., 1995). The massive economic growth and urban development in the surrounding region in the last three decades had led to excessive release of waste into the estuarine and coastal environment. In the past, most studies of metal contamination in this estuary had only focused on metal concentrations in surface sediments (Wen and He, 1985; Huang, 1995; Li et al., 1996). Recently, Li et al. (2000 and 2001), Liu et al. (2003) and Ip et al. (2004) studied the concentrations and chemical forms of heavy metals in the sediment cores of the PRE.

In oxic sediments, metals availability for bioaccumulation is related to binding mechanisms onto organic C (org-C), Fe and Mn oxyhydroxides (Yu et al., 2001). In anoxic sediments, the availability of divalent metals to organisms living nearby has been related to

acid volatile sulfide (AVS) (Di Toro et al., 1990 & 1992; Ankley et al., 1996; Cooper and Morse, 1998). AVS is defined as the fraction of sulfides in sediments, which is extractable by 1 mol/L cold HCl. Several cationic metals, such as Cu, Cd, Pb, Ni, Zn and Ag, can react with sulfides to form insoluble metal sulfides (Di Toro et al., 1992). Therefore, the presence of AVS in sediment provides a mechanism for partitioning metals from the pore water to solid phase, reducing the potential solubility and bioavailability. Simultaneously extracted metal (SEM), the metal extracted by AVS extraction method, are another measure of potentially bioavailable metal concentrations in sediment. When the ratio of the molar concentrations of \sum SEM to AVS is <1 , there may be no acute toxicity for aquatic organisms in terms of heavy metals. On the contrary, the sediment may be considered potentially toxic when the ratio is > 1 . The theoretical consideration of these assessments is that SEM, apart from binding with AVS, can exist in pore water and may be available to benthic organisms (Ankley et al., 1996). However, not all sediments with SEM/AVS ratios >1 can cause increased toxicity because there are many other metal binding phases in sediments such as organic matter, Fe and Mn-oxides (Ankley et al., 1996; Leonard et al., 1996; Chapman et al., 1998).

Sequential extraction procedure (SEP) is also often used to assess the possible chemical partitioning of trace metals, particularly on the mobility and bioavailability of metals in sediments (Tessier et al., 1979; Belzile et al., 1989; Ryssen et al., 1999; Li et al., 2001). A comparison of SEP and SEM results may provide new insights for interpreting the SEM/AVS measurement. Brumbrauh et al. (1994) studied some correlations between SEM and metals associated with particular phases in freshwater sediments. Their results showed

that the oxides and organic fractions probably contained some or all of the AVS-bound metals. However, the distribution of heavy metals among various geochemical phases, including AVS, carbonates, Fe and Mn oxides, and organic fractions has not been elucidated on a quantitative basis (Yu et al., 2001), especially in sediment profiles.

Berner (1980) described diagenetic sulfide formation in sediment as a function of porosity, sediment density, sediment burial rates, mixing intensities, organic matter supply, the rate constant for SO_4^{2-} reduction and the SO_4^{2-} concentration at the sediment-water interface. A comparison of the vertical distribution of AVS, SEM and total metal concentrations and chemical partitioning pattern may yield important information on metal mobility and possible changes overtime. To date, most of sediment core studies in this regard have been carried out in freshwater environments (Christian et al., 1995; van den Berg et al., 1998; Borgmann and Norwood, 2002), while very few have been conducted on coastal and marine sediments.

In the present study, six surface sediment samples were collected from the PRE to investigate the spatial distribution pattern of AVS, SEM and total heavy metals. Three sediment cores at different locations were analysed to evaluate the relationship among AVS, SEM, total heavy metals, and chemical partitioning along the sediment profiles in the dynamic estuarine environment. The major objective of this study was to determine the role of AVS and SEM on metal chemical forms and mobility in the surface sediments and sediment profiles of the PRE.

2. Materials and Methods

2.1. Study area

The Pearl River is the third-longest river in China and the largest river system flowing into the South China Sea. The main Pearl River estuary (also called Lingdingyang) is a north-south bell-shape area, with a N-S distance averaging about 49 km and the E-W width varying from 4 to 58 km (see Fig. 1). The study area is within the sub-tidal zone, with strong fresh water and marine water inter-reactions and circulation currents along the west side of the estuary (Li et al., 2000).

2.2. Sample collection

In the present study, six surface sediment samples and three sediment cores (up to 68 cm in depth) were collected from the PRE in 2002. The sampling locations were arranged in a N-S direction from Site 1 to 7 (see Fig. 1). The sampling programmes were carried out in July 2002 for the surface samples and October 2002 for the core samples. The surface sediments (10 cm) were collected by a grab sampler. The core samples were obtained by a Kajak sediment corer (KC-Denmark Co.). Each sediment core was sliced into sub-sections at 2 cm intervals and stored in sealed plastic bags at 4-6°C immediately after collection until the laboratory analysis.

2.3. Chemical analysis

The process of preparing sediment samples for total metal concentration analysis was described by Li et al. (2000). The chemical partitioning of heavy metals were determined by the sequential extraction procedure proposed by Tessier et al. (1979) with some

modifications. The details are described elsewhere (Li et al., 1995 and 2001). The concentrations of Cd, Cu, Pb, Zn and Ni were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer Optima 3300DV). At least one duplicate was run for every six samples to verify the precision of the analysis. The precision of this method was approximately 10% at the 95% confidence level. Moreover, the recovery rates for heavy metals in the international standard reference materials (NIST1646a) were around 89-96%. The recovery rates of heavy metals of the five sequential extraction steps were around 72-99% of the independent total metal concentrations.

The procedures for AVS and SEM analysis were adopted from the method described by Allen et al. (1993). The experimental setup consists of a round-bottom reaction flask connected to a trapping vessel containing 100 ml of a 0.5 M NaOH solution. About 90 ml of Milli-Q water was added into the reaction flask and was sparged for 10 min with N₂. Then the wet sediment sample (about 10 g) was added in, and sparged for another 10 min with N₂. The sediment suspension was stirred and acidified for 45 min with 20 ml of 6 M HCl at room temperature (cold extraction) to form H₂S, which was subsequently collected in NaOH solution with a continuous N₂ flow. The dissolved sulfide concentration in the NaOH solution was measured spectrophotometrically (using the methylene blue method) at a wavelength of 670 nm (Allen et al., 1993). Calibration curves, matrix spikes, apparatus blanks, and standard recoveries were employed in the analysis. Duplicate measurements showed that concentrations of AVS were reproducible with an analytical precision better than 10%. The acidified sediment suspension in the reaction flask was filtered through a

0.45 μm membrane and the concentrations of heavy metals were determined with ICP-AES. The precision of SEM determined by ICP-AES was similar to that of the total metal analysis.

All glass and plastic ware were cleaned by soaking in 10% HNO_3 (v/v) for 12 h, followed by soaking and rinsing with deionized water (Milli-Q). All the chemicals used in the experiment were in analytical reagent grade or better.

3. Results and Discussion

3.1. Spatial distribution of heavy metals, SEM and AVS in surface sediments

The total metal concentrations, AVS and SEM concentrations of the surface sediment samples of the PRE are shown in Table 2. There was a clear trend of total heavy metals, AVS and SEM among the different sampling locations from the river outlet to the sea. In general, the concentrations of total metals, AVS and SEM were low near the river outlet area, increased in the seaward direction, and decreased again at boundary of the estuary. The highest concentrations of Cd, Ni, Pb and Zn were found at Site 4, and Cu at Site 3. The lowest concentrations of heavy metals were found at Site 7, which was the farthest away from the river outlet. The AVS contents were much higher at Sites 3, 4 and 5 than at other sampling sites. The ΣSEM (SEM-Cd + SEM-Cu + SEM-Ni + SEM-Pb + SEM-Zn) values of Site 4 and 5 were higher than those of other sampling sites. The enrichment of heavy metals at Sites 3, 4 and 5 may indicate that these areas were suitable for heavy metal accumulation with slower water movement and weaker flowing current conditions in the

middle shore sites compared with the river outlet (e.g. Site 1) and strong tidal area (e.g. Site 6 and 7).

3.2. *Heavy metals, AVS and SEM in sediment cores*

The vertical distribution of AVS in the three sediment cores is presented in Fig. 2. The AVS contents were very low at the top 5 cm of the three cores, and then increased gradually with depth. Two peaks of AVS were found, at the 33 and 61 cm layers in Core 1. In Core 7, 2 peaks at 12 and 33 cm were identified. Only 1 peak at 22 cm of the total 24 cm was found in Core 5. From the above distribution patterns, it seemed that the AVS contents generally increased along the profile with peaks at various depths.

The concentration of AVS in sediment is a product of the equilibrium between AVS generation and the loss due to oxidation or diffusion. Consequently, the AVS contents in sediment may vary with those factors affecting the supply of organic matter, the rate of SO_4^{2-} reduction, and the redox status of the sediments (Oehm et al., 1997). The distribution of TOC and AVS in Core 7 are shown in Fig. 3. There was no correlation between AVS and TOC in the sediment core. Therefore, organic matter may not be the major controlling factor for AVS content in the sediments because of the lower TOC concentrations in comparison with freshwater sediments (Song and Müller., 1999). High concentrations of SO_4^{2-} (20-30 mM) in marine sediments, compared with 0.2 mM in freshwater sediments, can be responsible for most of the anoxic oxidation process (Balzer, 1989). Thus, SO_4^{2-} reduction is probably more important for AVS formation than the supply of organic matter in marine sediments.

Upon exposure to air, a significant proportion of AVS can be transformed to other phases (Lasorsa and Casas, 1996). The depth of O₂ penetration in sediment depends on its downward diffusion from overlying water (Song and Müller, 1999). The sedimentation process is dynamic in the PRE, and O₂ can diffuse downwards to several centimeters of the sediment-water interface and cause the depletion of AVS by oxidation. Therefore, the AVS content in the estuarine sediments was very low in the top 5-10 cm of the sediment cores.

The peaks of AVS content in the profiles may be explained by non-steady deposition (Matisoff and Holden, 1995), e.g. a “sudden” change in depositional conditions, particle size etc. Using Statistica for Windows Version 5.0 (StatSoft Inc., USA), the Pearson correlation coefficients of AVS to Fe and Al were calculated, and the results are presented in Table 3. Liu et al. (2003) revealed that Fe was significant correlated to the sand content and Al to the clay content in the PRE sediments. The results in Table 3 suggested that there was close relationship between the AVS distribution pattern and the Fe content (the sand content) in the sediment profile of Core 1 and Core 7, while the AVS distribution pattern was also related with Al content (the clay content) of Core 7. However, AVS concentration was not related to the Fe or Al concentrations in the profile of Core 5. The AVS contents of Core 1 ranged from below detection limits (0.01 µmol/g) to near 1 µmol/g. The maximum AVS contents in Core 7 and Core 5 were 3 µmol/g and 6 µmol/g, respectively. These results were consistent with the spatial distribution pattern of AVS in the surface sediment samples.

The total metal concentrations and SEM in the three sediment cores are presented in Fig. 4, 5 and 6, respectively. The vertical distribution of the total metal concentrations showed large variations in the three cores. In Core 1, the concentrations of Cd, Cu, Ni, Pb and Zn

generally increased in the profile between the depths of 0 – 60 cm and decreased after 60 cm. In the short profile of Core 5, however, no distinct enrichment pattern was found for the heavy metals, but the peak values were recorded around the depth of 12~14 cm. The concentrations of heavy metals were similar among the different depths in Core 7.

In a relatively static aquatic environment, the surface layer enrichment of metals can be expected due to the recent increased inputs from industrial operations and urban development. The PRE, however, is a dynamic depositional environment, and the sediment record at some locations may not reflect a process of stable sedimentation. Instead, the narrow channel areas of the estuary have been subjected to annual dredging activities and typhoon storms. Therefore, the distribution patterns of trace elements in the profiles may reflect natural conditions of dynamic sedimentation and possible disturbance by dredging activities in this area (Li et al., 2000).

The possible associations between heavy metals and sulfides in the sediment cores can be assessed by the SEM concentrations. The vertical distribution of SEM in Core 1 showed the same trend as the concentrations of total metals, indicating a close relationship between the SEM and the total concentrations in the sediments. In addition, the results of the Pearson correlation coefficient in Table 3 confirmed the close relationship, especially for Cd, Pb and Zn. Such a relationship was also observed for Cu, Ni and Zn in Core 5.

The SEM concentrations determined by the cold HCl extraction of the AVS analysis accounted for a relatively large percentage of the total metal concentrations (see Fig 7). Compared with other metals, the SEM/total metal ratio was the highest for Pb in all the three cores, which may indicate a possible close association of Pb with sulfides in the sediments

(from 50% to 95% of the total Pb). On the other hand, the ratio for Ni was the lowest in the cores. The ratios for Cd, Cu and Zn showed similar patterns along the profiles, about 0.2-0.6 in Core 1 and 0.2-0.4 in Cores 5 and 7. These results suggested that heavy metals had different associations with the sulfide phase and/or different solubility during the HCl-extraction.

3.3. SEM/AVS ratios in sediment cores

The distribution of Σ SEM along the sediment cores is presented in Fig. 2. The value of Σ SEM was usually larger than AVS in the whole profile of Core 1. In other two cores, however, Σ SEM was larger than AVS in the top layers, but AVS was larger than Σ SEM in the deeper layer (from 16 cm for Core 5 and from 9 cm for Core 7). The results indicated that AVS was not the major metal-binding phase in the surface sediments or the sediments of the river outlet area (e.g. Core 1). AVS might play a major role in deeper sediments in terms of metal activity. After being fully incorporated into sulfide phase, the remaining SEMs may be selectively bound with other components of sediments or remobilized into pore water.

Although the role of AVS in influencing the potential bioavailability of heavy metals is primarily viewed as that of removing metals from biologically available chemical species into insoluble sulfides, the sedimentary sulfide system is of highly dynamic nature. Bioturbation and bioirrigation of anoxic sediments, as well as reactions between H_2S and oxides, can result in over 90% of the reduced sulfides being oxidized in sediments (Lin and Morse, 1991). Consequently, metals that are associated with AVS may be subsequently

released via oxidation process within sediments. Other processes that lead to sediment resuspension, such as storms, bottom trawling, and dredging activities, can also result in the rapid and complete oxidation of associated AVS. Therefore, metals associated with AVS may potentially be released into the aquatic phase, and subsequently have adverse environmental impacts.

3.4. Heavy metal chemical forms in sediment cores

Many divalent metals with lower K_{sp} than FeS and MnS, such as Cd, Cu, Ni, Pb and Zn, can displace Fe and Mn from their monosulfides on a molar basis of 1:1 to form highly insoluble metal sulfides:



The S^{2-} concentration in this reaction can be roughly estimated as AVS content and Me^{2+} as SEM concentration. When $\sum SEM/AVS < 1$, the Me^{2+} concentrations in pore water are controlled by the K_{sp} of their sulfides, and there are very low dissolved metal concentrations in the sediments. By contrast, when $\sum SEM/AVS > 1$, the metal concentrations in pore water may be high in the absence of other strong binding phases. It is generally assumed that the acute metal toxicity to benthic animals cannot occur when there is sufficient AVS in sediment to sequester all of the available metals, i.e. $\sum SEM/AVS < 1$ (Di Toro et al., 1990; Ankley et al., 1996; Berry et al., 1996; Chapman et al., 1998). However, Lee et al. (2000a) recently demonstrated that AVS-bound metals could be assimilated by clams with as much efficiency as the metals bound with oxic sediments. Furthermore, the bioaccumulation of metals by marine clams was related significantly to SEM of the sediments, not related to the

[SEM-AVS] or pore water metals (Lee et al., 2000b). Metal bioavailability refers to the ability of metals to be accumulated by animals and plants, which is subject to the ingestion habits of animals, e.g. through water (pore water and overlying water), and/or through sediments (Chapman et al., 2002). Although metals bound to AVS cannot be released from sediment into water, they may be ingested by animals. The AVS procedure extracts metals not only from the target sulfide phase, but also from other non-sulfide phases that may be bioavailable.

To have a better understanding of SEM and metals associated with particular geochemical phases, sequential extraction was conducted for selected sediment samples with higher AVS contents in this study. The ratios of different metal fractions to SEM of Cores 5 and 7 are shown in Fig. 8. In Core 5, the Cd in the exchangeable, carbonate, and Fe and Mn oxide fractions accounted for 11-18%, 24-31% and 46-59% of SEM, respectively, except for the surface sediments. The residual Cd was 1.2-1.8 times of SEM-Cd. In Core 7, the Cd in the exchangeable, carbonate, and Fe and Mn oxides fractions was 2-6%, 27-56% and 40-77% of SEM-Cd, respectively while the residual fraction was 1.6-4.3 times of SEM-Cd. The first three non-residual fractions were almost equal to SEM-Cd. Therefore, the SEM-Cd represented the first three non-residual fractions in the sediments.

For Cu, the exchangeable, carbonate, Fe and Mn oxides and organic/sulfide fractions were about 0.6-2%, 12-43%, 33-65% and 46-98% of SEM-Cu, respectively in Core 5, and 0.6-1.6%, 11-34%, 23-58% and 63-120%, respectively in Core 7. About 48-88% SEM-Cu belonged to the first three non-residual fractions in Core 5 and 37-78% in Core 7. The Cu in the first three non-residual fractions and the organic/sulfide fraction was higher than

SEM-Cu. This may indicate that 1 M HCl could not completely extract the organic bound Cu in the sediments. It can be seen from Fig 8 that the organic/sulfides fraction of Cu is the largest non-residual fraction. In addition, Campbell et al. (1988) showed that Cu was far more strongly related to the organic phase than AVS. Therefore, AVS may play a limited role in binding Cu in these sediments.

The Pb in the four non-residual fractions was lower than the SEM-Pb in Cores 5 and 7. The Pb in the carbonate, Fe and Mn oxides, organic/sulfide and residual fractions was 8-24%, 47-70%, 17-22% and 19-30% of SEM-Pb, respectively in Core 5, and 20-33%, 36-50%, 14-18%, 19-27% of SEM-Pb, respectively in Core 7. The Fe and Mn oxide fraction was the largest fraction for Pb. The results indicated that the HCl extraction released not only Pb in the exchangeable, carbonate, Fe and Mn oxides and the organic/sulfide fractions, but also some residual Pb in the sediments. The SEM/total-Pb ratio up to 95% was also observed by van den Berg et al. (2001). These results may reflect that Pb was not strongly fixed in the residual phase of sediments.

The Zn in the exchangeable, carbonate, Fe and Mn oxides, organic/sulfide and residual fractions accounted for 0.1-2%, 12-18%, 78-98%, 14-20% and 80-110% of SEM-Zn, respectively in Core 5, and 0-1%, 15-30%, 64-115%, 19-34%, 100-340%, respectively in Core 7. The Fe and Mn oxides fraction was the major phase for Zn in these sediments. As a result, the Zn in the first three non-residual fractions was generally greater than the SEM-Zn (see Fig 8). The K_{sp} of metal sulfides is $\text{Cu}_2\text{S} < \text{HgS} < \text{PbS} < \text{CdS} < \text{NiS} < \text{ZnS} < \text{CuS} < \text{CoS} < \text{FeS} < \text{MnS}$ (Copper et al., 1998). Therefore, ZnS can dissolve more easily than Pb and Cd in sediment.

Comparing the SEP with AVS extraction procedures, 1 M HCl is a stronger reagent than those used in the exchangeable (1 M MgCl₂) and carbonate fractions (1 M NaOAc) of SEP. Therefore, metals bound by these two fractions could be extracted completely by the AVS extraction procedures. Although 1 M HCl is a stronger reagent than those used to extract the Fe-Mn oxide fraction (0.04 M NH₂OH with HOAc), the latter took place at a much higher temperature. As a result, the first three non-residual fractions were comparable for the SEM concentrations of Cd and Zn. Cu showed great affiliation with the organic/sulfide fraction. The SEM-Cu was generally lower than the four non-residual fractions. The SEM-Pb contained all Pb in the four non-residual fractions.

These results indicated the SEM from the AVS extraction represented different potential chemical forms for different heavy metals, depending on the reactions of the metal with HCl in the AVS procedure. SEM/AVS predictions may overestimate metal availability if a significant quantity of metals bound to other phases can be leached out in the 1M HCl extraction (Allen et al., 1993; Ankley et al., 1996; O'day et al., 2000). When SEM/AVS is > 1, other binding forms for metals in sediments should be considered to assess the bioavailability of metals.

4. Conclusion

The results showed that AVS was not the most important phase for heavy metals in the surface sediments and in the sediments at the dynamic river outlet area of the PRE. However, AVS could play an important role in binding heavy metals in deep layer sediments of the estuary. The 1M HCl extraction (AVS procedure) seemed to have insufficient selectivity on

metal chemical forms, as simultaneously extracted metals (SEM) reflected the possible sulfide phase and other geochemical forms in the sediments. The SEM/AVS prediction may overestimate metal availability even in the sediments with measurable AVS concentrations. The sequential extraction procedure can be used as an additional tool with the AVS method for assessing the potential bioavailability and toxicity of metals in sediment.

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Table 1

The sampling locations in the Pear River estuary (PRE)

Sampling Location	Longitude	Latitude	Water depth (m)	Salinity (NaCl ‰)
1	113° 42' E	22° 41' N	19.6	2.30
3	113° 44' E	22° 32' N	13.8	32.1
4	113° 45' E	22° 27' N	8.5	33.8
5	113° 46' E	22° 21' N	7.0	35.3
6	113° 46' E	22° 16' N	6.9	35.1
7	113° 46' E	22° 12' N	8.6	34.6

Table 2

The total metal concentrations, AVS and SEM of the surface sediments in the Pear River Estuary (PRE)

Sampling Location	Cd (mg/kg)		Cu (mg/kg)		Ni (mg/kg)		Pb (mg/kg)		Zn (mg/kg)		AVS	* Σ SEM
	Total	SEM	μ mol/g	μ mol/g								
1	5.2	4.4	44.9	19.8	17.9	17.8	44.3	34.4	136	59.4	0.21	1.89
3	6.6	4.5	83.2	15.9	21.0	12.9	37.8	26.8	133	23.0	2.77	1.12
4	7.2	5.6	57.8	24.7	22.2	19.0	58.9	49.4	197	92.7	2.18	2.65
5	6.3	6.4	51.8	16.1	18.8	18.1	52.2	46.8	164	87.9	3.89	2.47
6	5.5	3.8	45.6	26.4	18.4	17.6	46.2	39.7	145	64.6	<0.01	1.42
7	5.1	4.3	37.9	14.1	16.5	15.0	36.4	30.2	114	40.6	0.48	2.16
RSD%	14.2	20.0	29.9	26.0	10.0	14.8	18.6	23.9	19.5	43.7	83.6	30.6

* Σ SEM = SEM-Cd + SEM-Cu + SEM-Ni + SEM-Pb + SEM-Zn

Table 3

Pearson correlation coefficients of AVS to Fe, Al, and SEM to total metal (Cd, Cu, Ni, Pb and Zn) concentrations in the sediment cores ($P < 0.05$)

Samples	n	critical <i>r</i>	<i>R</i>						
			AVS-Fe	AVS-Al	Cd	Cu	Ni	Pb	Zn
Core 1	34	0.341	0.57992	-0.3284	0.93585	0.41929	0.34322	0.96461	0.95116
Core 5	12	0.576	-0.3004	-0.1910	-0.0786	0.69785	0.78470	0.23542	0.84626
Core 7	21	0.433	0.55597	0.59185	-0.467	-0.0170	n.a	0.33811	0.42655

Note: n.a. – not available.

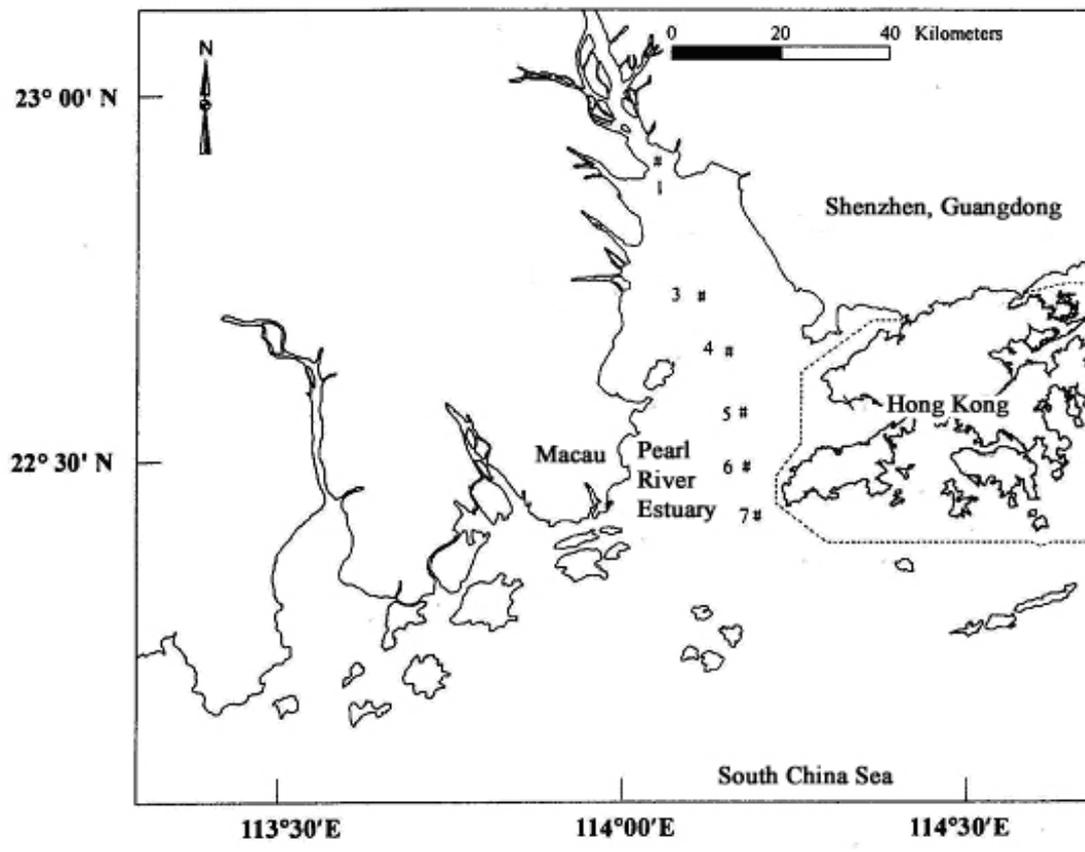


Fig. 1. Location of the sampling sites in the Pearl River Estuary

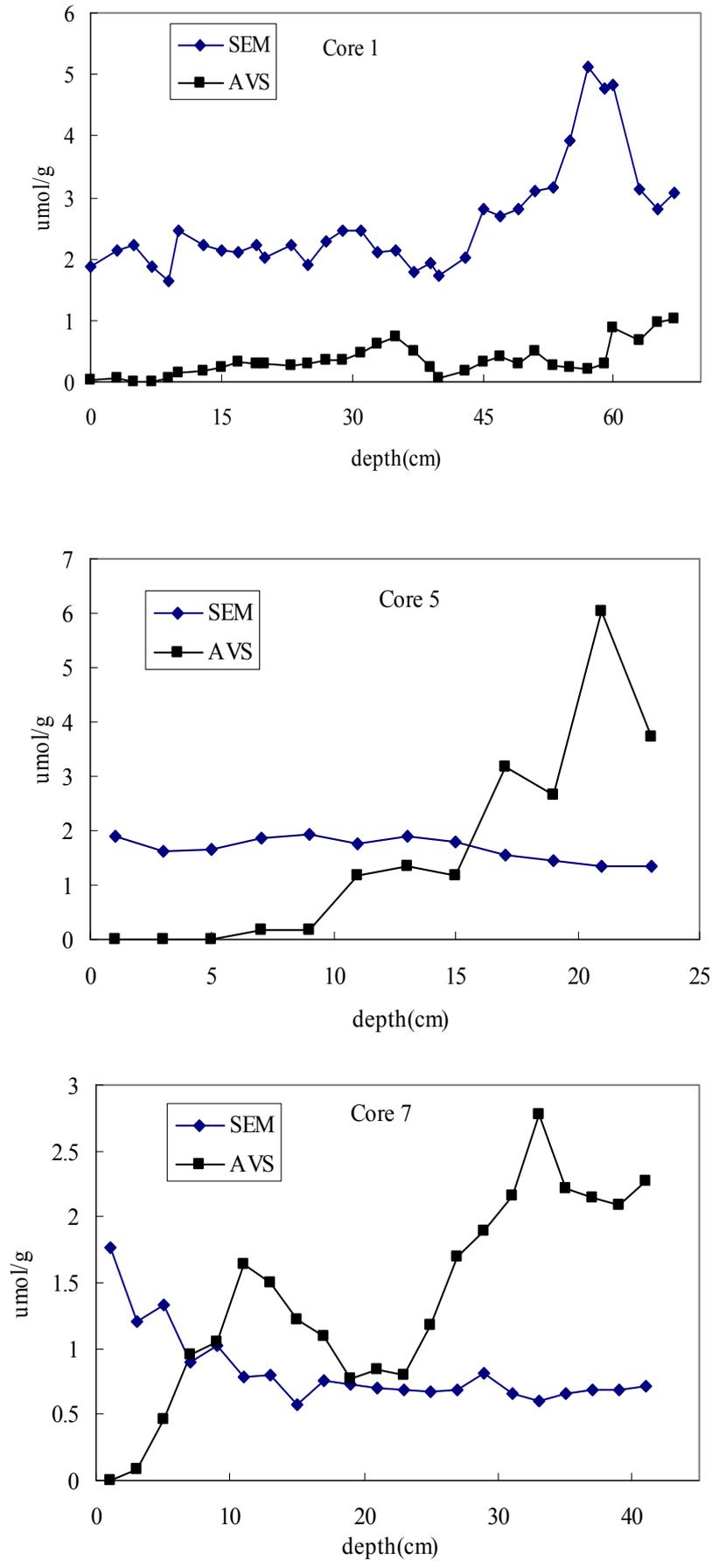


Fig. 2. The vertical distribution of AVS and SEM in the sediment cores

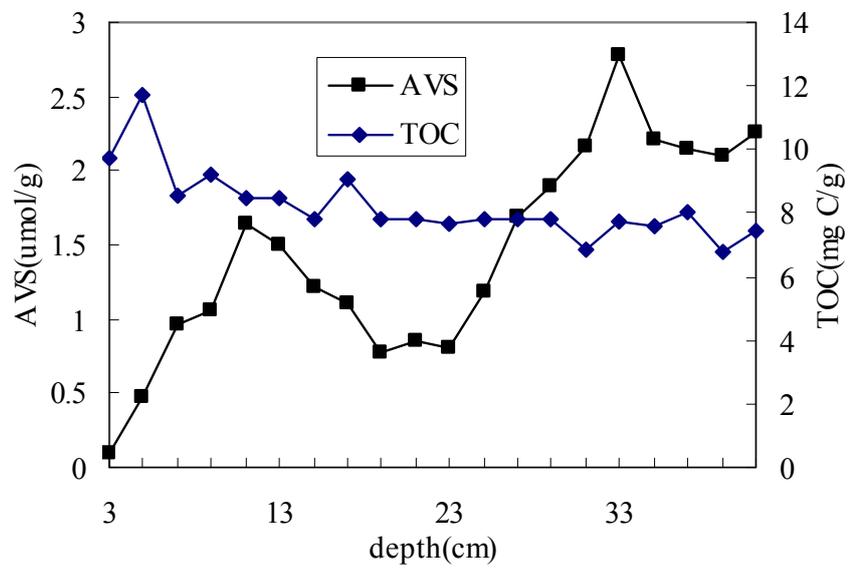


Fig. 3. The variations of AVS and TOC with depth in Core 7

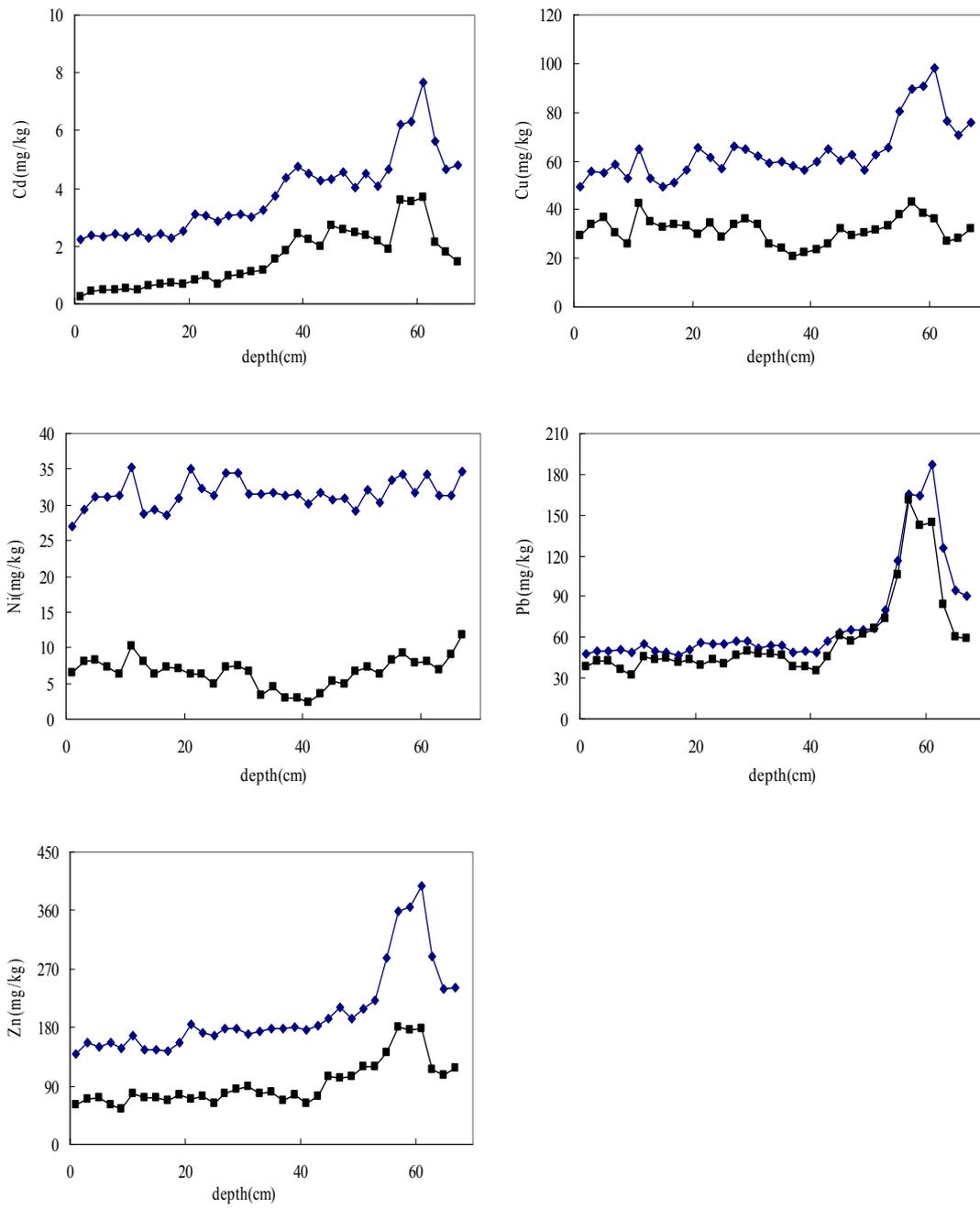


Fig. 4. The total and SEM concentrations of Cd, Cu, Ni, Pb and Zn in the profile of Core 1 (◆ total metal, ■ SEM)

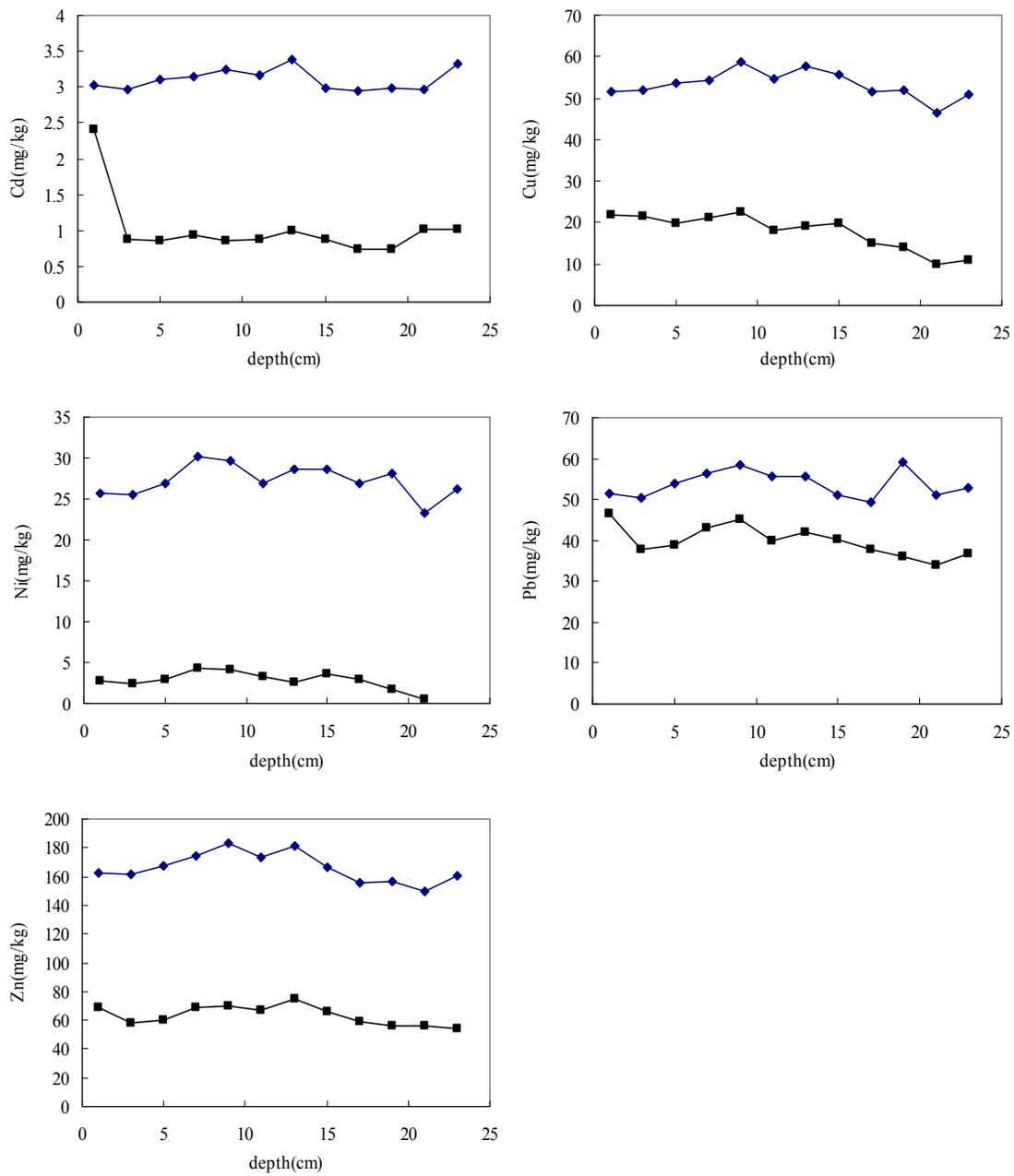


Fig. 5. The total and SEM concentrations of Cd, Cu, Ni, Pb and Zn in the profile of Core 5 (◆total metal, ■SEM)

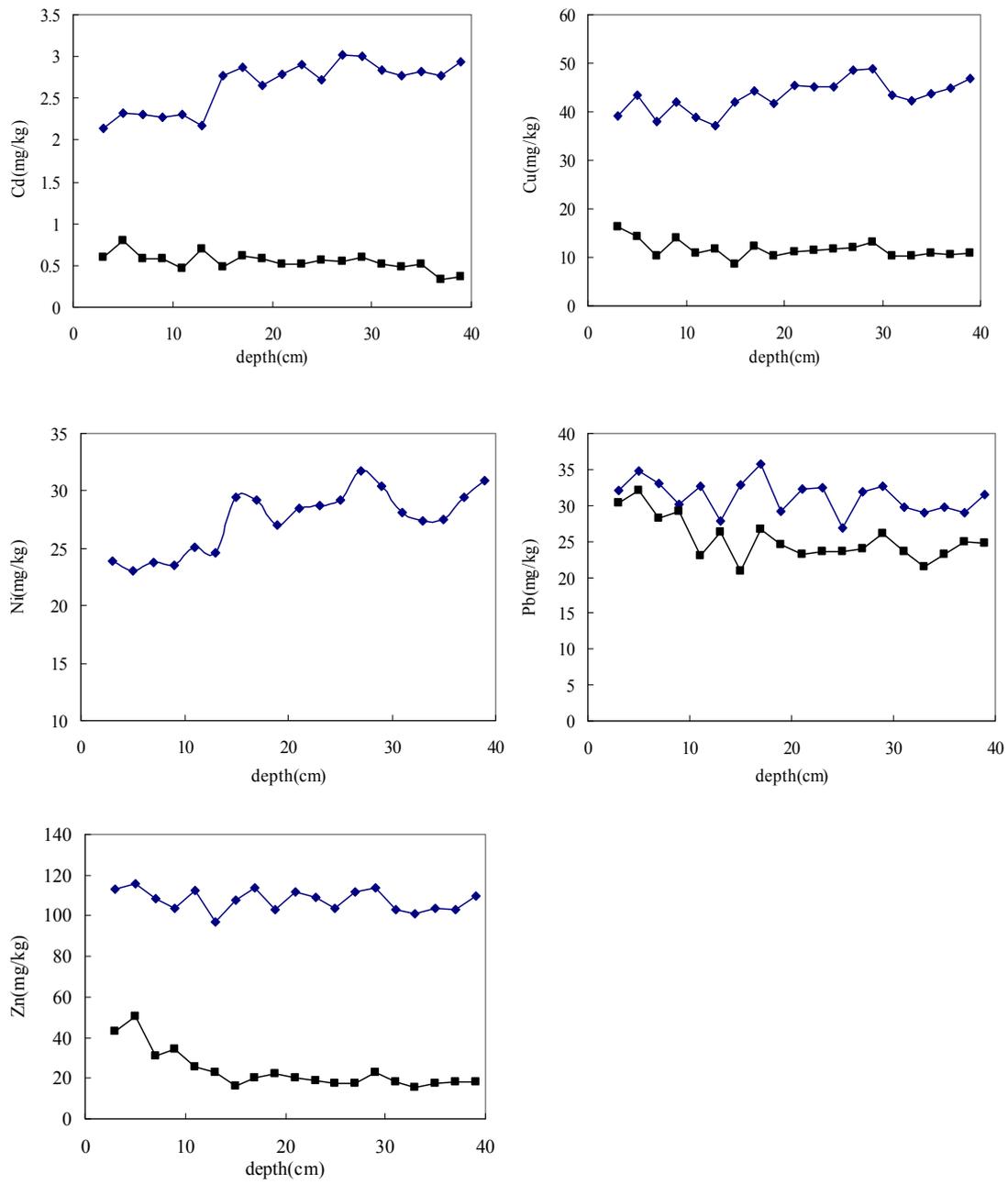


Fig. 6. The total and SEM concentrations of Cd, Cu, Ni, Pb and Zn in the profile of Core 7 (◆ total metal, ■ SEM)

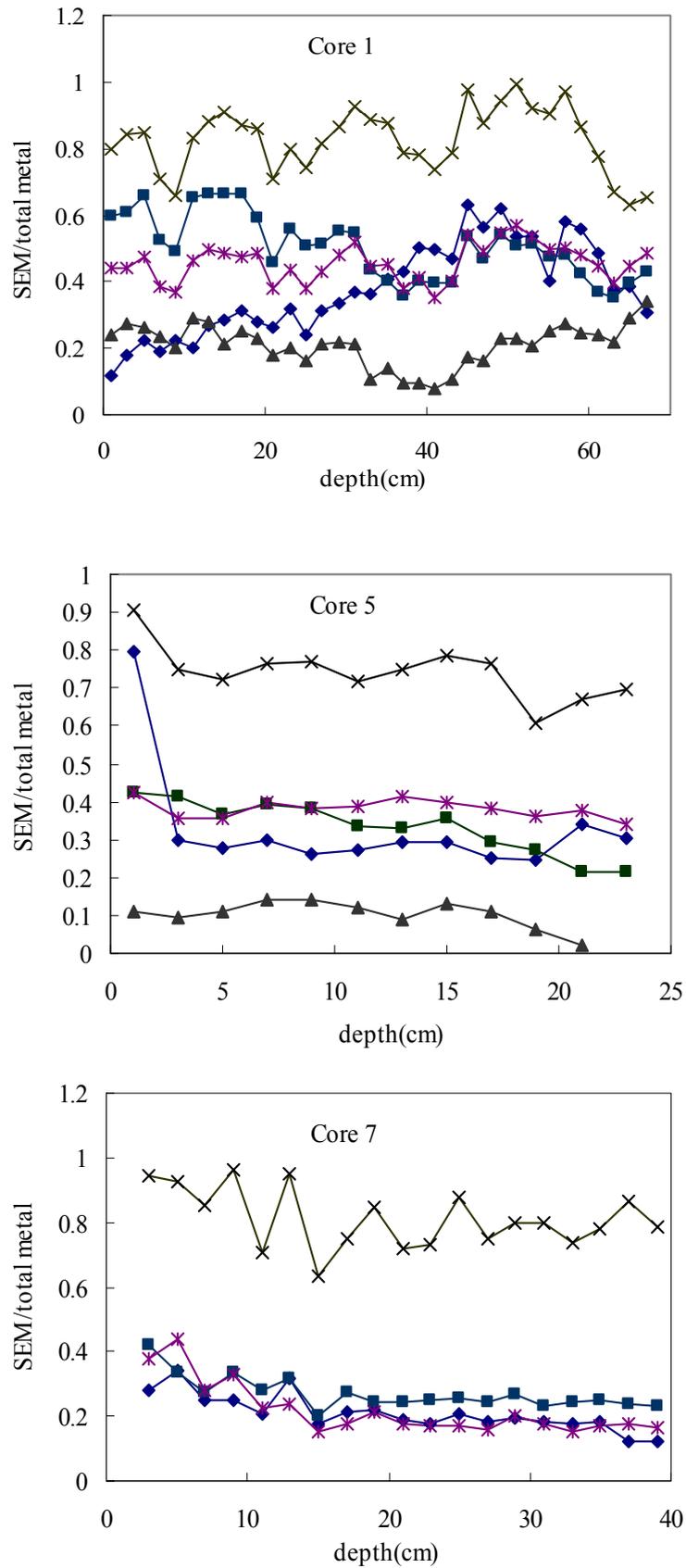


Fig. 7. The ratio of SEM/total metal in the sediment cores (◆Cd, ■Cu, ▲Ni, ×Pb, *Zn)

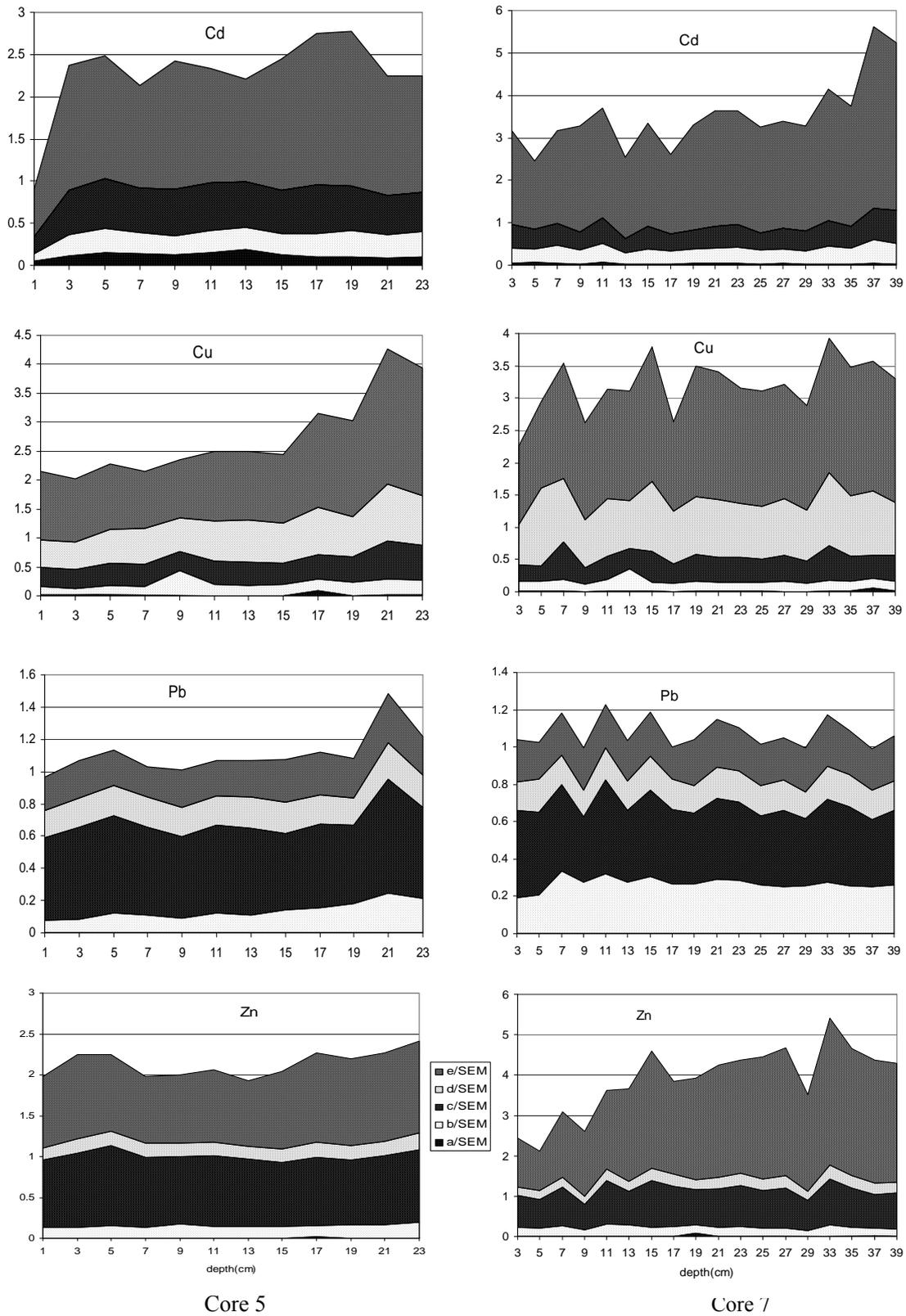


Fig. 8. The ratios of different metal fractions to SEM in the profiles of Core 5 and Core 7 (a: exchangeable, b: carbonate/specially adsorbed, c: Fe-Mn oxide, d: organic/sulfide, e: residual)