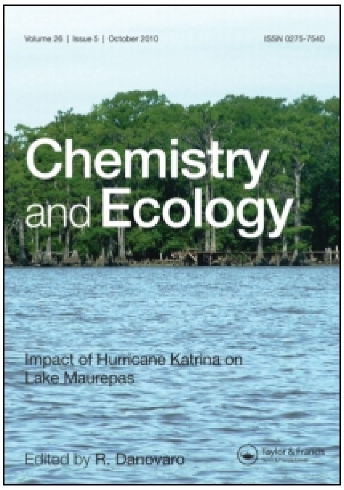

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Sources and Distribution of Heavy Metals in East China Sea Surface Sediments

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SOURCES AND DISTRIBUTION OF HEAVY METALS IN EAST CHINA SEA SURFACE SEDIMENTS

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Box cores and surficial sediments collected from the shelf, slope and Okinawa Trough of the East China Sea were analyzed for loss on ignition, and concentration and speciation of aluminium, iron, manganese, lead, cadmium, copper and zinc. In general, concentrations of these metals are higher in the inner shelf and lower in the midshelf, but the highest LOI, cadmium and manganese levels are found in the Okinawa Trough. Spatial distributions of these metals in surficial sediments indicate that the Yangtze River is the major source for materials deposited in the inner shelf. The results of a six-stage sequential leaching experiment indicate that the fluvial input includes natural (*e.g.*, Al and Fe) and anthropogenic (*e.g.*, Pb) materials. The depletion concentration of these metals in the midshelf sediments reflects the dominance (~ 70%) of coarse, relict sand, while the enrichments in the inner shelf and the Okinawa Trough sediments are due to the fine grained, organic-rich sediments. The speciation of manganese in the sediments of the Okinawa Trough indicates that its distribution is diagentically or hydrothermally controlled.

Keywords: East China Sea; Heavy metal; Sediments

INTRODUCTION

The East China Sea (ECS) is surrounded by the most heavily populated as well as the most rapidly developing regions in the world. With

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*Address for correspondence: 5th FL., No. 2, Jui-Kuang Rd., Taipei, Taiwan. Tel.: 886-2-27948833, Fax: 886-2-27940083, e-mail: hychen@envimac.com.tw estuarine input from one of the largest rivers in the world, the Yangtze River, this marginal sea receives enormous amounts of sediments and associated pollutants from its vast drainage basin. The sediment discharge of the Yangtze River (5×10^8 t yr^{-1}) accounts for more than 30% of the total output from the main land China rivers (Zhao and Yan, 1993). About 40% of the Yangtze River suspended sediments are deposited on the inner shelf of ECS (water depth normally less than 50 m) and the remaining 60% are transported by the coastal current southward alongshore (Milliman *et al.*, 1985). Butenko *et al.* (1985) reported that the grain-sizes of the Yangtze River sediments are relatively fine (average size 8.6 µm). As a result, the inner shelf sediments have equal amounts of silt and clay and very low sand (6%). Due to high specific surface area of fine-grained sediments, particle reactive chemicals transported by the Yangtze River will be enriched in the inner shelf sediments, especially near the mouth of the Yangtze River.

In the midshelf of the ECS (water depth between 50 and 100 m), the sediments are characterized by about 70% sand. This sediment type occupies most of the southern East China Sea shelf (Butenko *et al.*, 1985). It has been suggested that the sea floor beneath the Taiwan Warm Current, which generally flows along the midshelf, is covered by relict sand without fresh deposition to the sea floor (Milliman *et al.*, 1985).

In contrast to the shallow shelves to the west, the eastern part of the ECS is characterized by steep slope areas along the Okinawa Trough. The sediments consist of clay minerals ($>50\%$) and shells of organism ($>40\%$), and high concentrations of organic carbon have also been found in the Okinawa Trough sediments (Qin *et al.*, 1987; Zhao and Yan, 1994).

This study examines the spatial distributions of some heavy metals in the ECS sediments to find out possible sources of natural and anthropogenic metals. A six-stage sequential leaching technique will be applied to identify the phase variations in different areas of ECS.

METHODOLOGY

The sediment samples were collected on five cruises aboard R/V *Ocean Researcher I* (OR-293, 456, 460, 493 and 499) using a box core sampler. The midshelf sediment samples were collected on board R/V *Vinogradov* (July – August, 1992) with a stainless steel Van – Veen grab sampler which sampled only the top sediments (< 3 cm). The sampling locations are shown on Figure 1 and the details for the sampling stations are listed in Table I.

Immediately following the recovery of the box cores, subcores (9.4 cm inner diameter) were taken and sectioned. The subsamples and the grab samples were kept frozen until analysis in the laboratory.

The method of Spliethoff and Hemond (1996) was used to determine the loss on ignition (LOI). In brief, about 1 g of sediment sample was weighed into a crucible and combusted at 550°C for 5 h. From the weight loss, LOI as a percentage of the total weight was calculated.

For the determination of metals, sediment samples of 0.5 g were subjected to total dissolution using mixed acids followed by evaporation

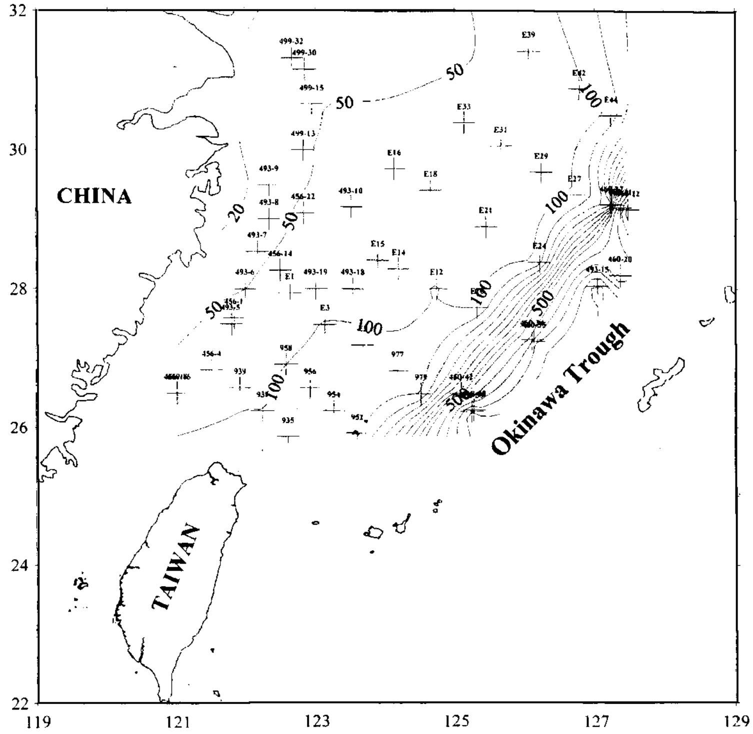


FIGURE 1 East China Sea bathymetric map with location of sampling stations.

TABLE I Station locations and water depths

Station	*Longitude (N)*	*Latitude (E)*	*Depth (m)*	*Station*	*Longitude (N)*	*Latitude (E)*	*Depth (m)*
456 – 1	121°00′	26°30′	68	935	122°36.7′	25°52.4′	104
456 – 4	121°30′	26°50.4′	72	937	122°15′	26°15.1′	100
456 – 6	121°49.8′	27°35.4′	67	939	121°55.1′	26°35.1′	98
456 – 14	122°30′	28°15.6′	68	952	123°35′	25°55′	133
456 – 22	122°49.8′	29°04.8′	59	954	123°15′	26°15.2′	126
460 – 8	121°00.3′	26°30.4′	68	956	122°55′	26°35.1′	118
460 – 17	127°15′	29°12′	232	958	122°35′	26°55′	100
460 – 20	127°22.2′	28°11.4′	586	977	124°09.9′	26°50.1′	129
460 – 21	127°22.6′	29°09.7′	811	979	124°30.2′	26°30.1′	143
460 – 22	127°29.4′	29°08.4′	1012	E1	122°38.2′	27°56.4′	73
460 – 34	126°05.4′	27°16.8′	597	E3	123°07.6′	27°29.4′	103
460 – 35	126°07.1′	27°15.4′	805	E5	123°39.5′	27°11.7′	110
460 – 39	125°14.4′	26°14.4′	1000	E14	124°10.6′	28°17.3′	84
460 – 40	125°15.9′	26°15.6′	811	E15	123°52.7′	28°24.7′	75
460 – 42	125°04.8′	26°30.4′	415	E12	124°44.1′	28°00.6′	104
490 – 5	121°48′	27°30′	65	E10	125°18.5′	27°44.4′	100
490 – 6	122°00′	28°00′	49	E16	124°07.1′	29°43.8′	60
493 – 7	122°49.1′	28°31.8′	37	E18	124°39.3′	29°24.9′	72
493 – 8	122°21′	29°00′	32	E21	125°26.2′	28°53.6′	102
493 – 9	122°21′	29°29.4′	26	E24	126°11.7′	28°22.5′	114
493 – 10	123°30′	29°10.2′	62	E33	125°07.6′	30°23.8′	66
493 – 15	127°02.4′	28°02.4′	1072	E31	125°38.8′	30°03.5′	64
493 – 18	123°31.2′	28°00′	87	E29	126°14.1′	29°41′	90
493 – 19	123°00′	28°00′	77	E27	126°42.4′	29°20.9′	108
499 – 13	122°49.8′	30°00′	48	E36	125°18.1′	32°00.1′	51
499 – 15	122°57′	30°40.2′	49	E39	126°03.5′	31°26′	67
499 – 30	122°50.9′	31°10.1′	46	E42	126°47.9′	30°53.4′	95
499 – 32	122°40.1′	31°19.8′	42	E44	127°14.7′	30°30′	110

(Huh and Chen, 1998). The final condensate was diluted with 2N HNO_3 to bring the total volume to 50 ml for the determination of copper, zinc, cadmium and lead. The solution was further diluted 10 times for manganese analysis and 100 times for iron and aluminium.

A transect of surficial sediment samples (from the inner shelf *via* the midshelf to the Okinawa Trough) was selected to study the partition of metals using a six-stage sequential leaching technique. The principal operationally-defined host components associated with each stage in the sequential scheme are: exchangeable phase (Stage 1), carbonate or surface associations phase (Stage 2), easily reducible or new oxides phase (Stage 3), moderately reducible or aged manganese oxides phase (Stage 4), refractory organic or sulphide phase (Stage 5) and residual or detrital phase (Stage 6). This procedure has been well documented by Chester *et al.* (1988).

For total digestion samples, cadmium and lead were determined on Hitachi Z-8100 Zeeman effect graphite furnace AAS, and iron, aluminium, manganese, copper and zinc were quantified on a Jobin YvonJY-24ICP-AES. The sequential leaching samples were determined using Hitachi Z-8100 flame or graphite AAS. Blanks were processed during each digestion and sequential leaching run to monitor for potential contamination.

RESULTS AND DISCUSSION

Spatial Distributions of Surficial Sediments

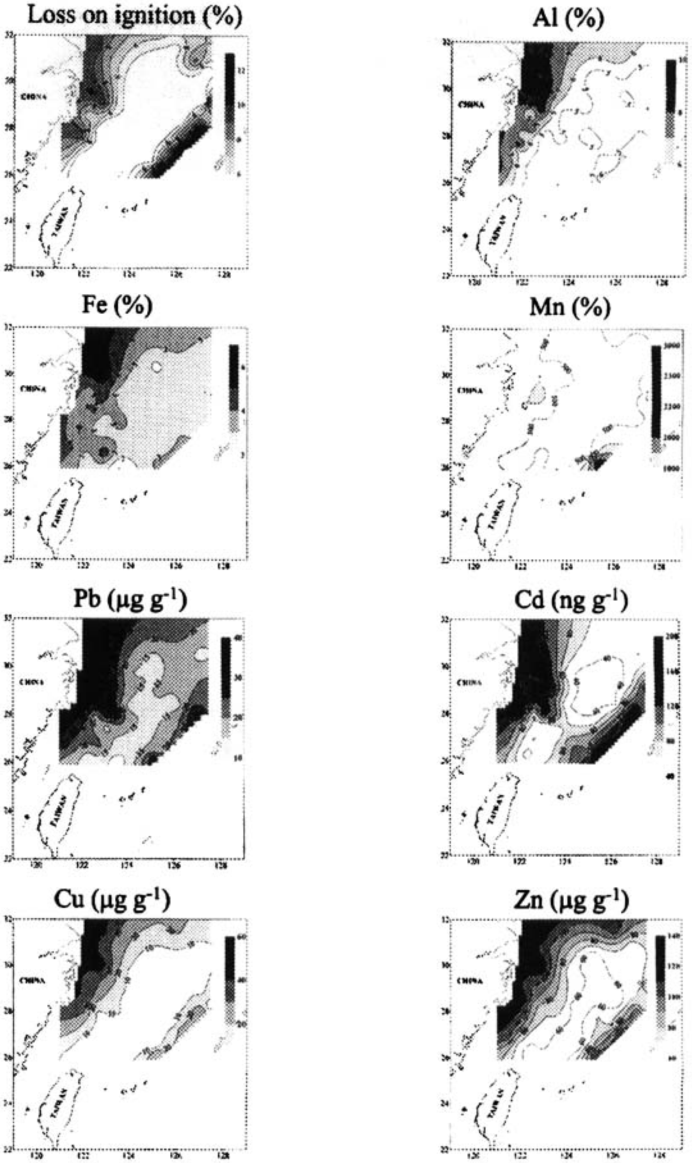
Figure 2 shows the spatial distributions of LOI and the analyzed metals (Al, Fe, Mn, Pb, Cd, Cu and Zn) in the ECS sediments. Each contour plot includes 56 surficial sediment samples and marks with different colour scale.

LOI

LOI varied between 7 ~ 9% near the mouth of the Yangtze River. The values decreased eastward, to 3 ~ 4% in the midshelf sediments. The low LOI concentrations were related to the low organic content and the coarse grained sediments (Sternberg *et al.*, 1985). In contrast, LOI was the highest (9 ~ 12%) in the Okinawa Trough, which is mainly due to the fine-grained and well-sorted sediments (Hung and Chung, 1994).

Heavy Metals

In the ECS sediments, the concentrations of aluminium decreased away from the mouth of the Yangtze River, both southward alongshore and eastward offshore. In general, the concentration of aluminium in sediment is represented as a detrital or background signal, which transmits elements carried in the crystalline matrix of lithogenous minerals (Chester, 1990). For the inner shelf sediments, the Yangtze River contributes large portion of weathering aluminosilicate minerals. Most of these minerals are deposited around the


Loss on ignition (%)

Al (%)

Fe (%)

Mn (%)

Pb ($\mu g\ g^{-1}$)

Cd ($ng\ g^{-1}$)

Cu ($\mu g\ g^{-1}$)

Zn ($\mu g\ g^{-1}$)

FIGURE 2 Concentration distribution maps of LOI, aluminium, iron, manganese, lead, cadmium, copper and zinc in the surface sediments of the East China Sea.

mouth of Yangtze River and, the others are carried southward by the coastal current. In the study area, the concentration distributions of iron show a similar distribution to aluminium and both elements have a strong relationship to each other (see below). Therefore, iron can also be represented as a product of crust weathering in this area.

Like aluminium and iron, the spatial distributions of lead, cadmium, copper and zinc in the inner shelf sediments have a maximum around the mouth of Yangtze River and minimum in the midshelf sediments. This indicates that the Yangtze River is not only a source for the products of crust weathering but also a source for the products of human activities. In the Okinawa Trough sediments, the concentrations increased abruptly which is probably caused by the high organic contents of fine-grained particles.

The concentrations of manganese in the ECS sediments show the different distribution type from the above metals. The maximum concentrations of manganese occurred in the Okinawa Trough and the concentrations in the Trough sediments were about 3 times greater than in the inner shelf sediments. The high concentrations of manganese in the area was probably caused by the diagentic process or hydrothermal activity (Hsu *et al.*, 1998).

Relationships Among LOI and Metals

The regression coefficients between LOI and seven metals (Al, Fe, Mn, Pb, Cd, Cu and Zn) are listed in Table II. Overall, strong correlations are apparent between the concentrations of aluminium and iron ($r = 0.53 - 0.90$), copper and zinc ($r = 0.71 - 0.96$). This is interpreted to be the result of common sources and enrichment mechanisms for these metals. The former is related to the presence of particular crust-derived weathering sources and the latter pair, zinc–copper, is due to a combination of biological process and residual source.

Sequential Leaching Experiment

The results of a six-stage sequential leaching experiment are shown in Figure 3. For aluminium and iron, the phase partition patterns show similar distributions in the inner, midshelf and trough sediments. On average, about 88% of aluminium and 63% of iron in the sediments are present in the detrital phase (Stage 6). For both natural metals, the results indicate that the different environments of deposition do not have a significant effect on the compositional *distribution*.

TABLE II Correlation coefficient (*r*)* matrix for the studied chemical parameters in the surface sediment samples of three different ECS regions

		Al	*Fe*	*Cu*	*Zn*	*Pb*	*Cd*	*Mn*
LOI	inner[a]	0.29	0.08	0.38	0.20	0.14	0.07	0.49
	middle[b]	0.66	0.69	0.80	0.76	0.61	0.40	0.41
	slope[c]	0.67	0.66	0.94	0.92	0.45	0.71	0.43
Al	inner		0.90	−0.28	−0.13	−0.12	−0.24	0.02
	middle		0.88	0.88	0.89	0.81	0.10	0.64
	slope		0.53	0.57	0.83	0.23	0.50	0.39
Fe	inner			−0.37	−0.30	−0.14	−0.33	0.11
	middle			0.87	0.85	0.84	0.25	0.75
	slope			0.50	0.70	−0.11	0.23	0.65
Cu	inner				0.71	0.70	0.78	0.38
	middle				0.96	0.86	0.50	0.64
	slope				0.84	0.66	0.80	0.34
Zn	inner					0.53	0.64	0.38
	middle					0.85	0.40	0.63
	slope					0.38	0.61	0.43
Pb	inner						0.75	0.59
	middle						0.41	0.62
	slope						0.47	−0.29
Cd	inner							0.46
	middle							0.21
	slope							0.54

*Correlations are significant at $p < 0.01$.

[a] $n = 11$.

[b] $n = 33$.

[c] $n = 9$.

For manganese, the highest percentage concentration of detrital phase (~40%) has been found in the midshelf sediments and the minimum in the Okinawa Trough (~5%). The concentration value of detrital manganese in the Trough sediment is very close to those in other surface sediments. Therefore, the percentage concentration of detrital manganese is mainly diluted by large portion of new oxides or easily reducible oxides (Stage 3) which accounts for ~77% of the total manganese. Figure 4 shows a vertical profile of total manganese in the inner shelf (sta. 460-8) and Okinawa Trough (sta. 460-40). The profiles indicate that manganese has a significant enrichment in the Trough surface sediment which is about 10 times greater than the background level. Chester *et al.* (1988) reported a simple model, which is called a "manganese trap" to describe this phenomenon in the Mediterranean sediments. In this model, organic carbon is decomposed or oxidized at or near the sediment surface and manganese oxides are used as

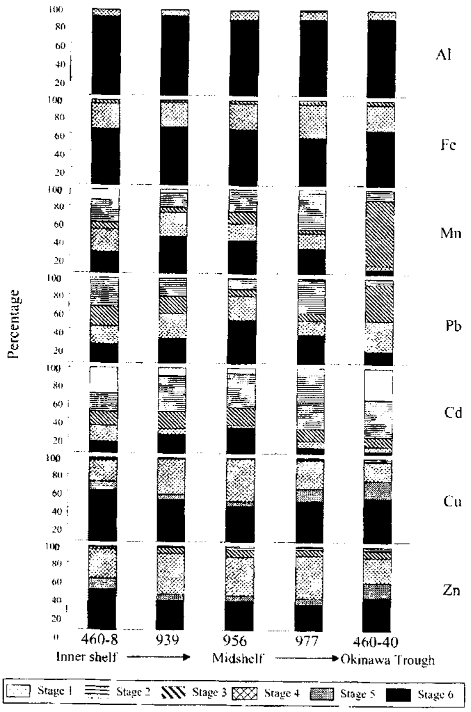


FIGURE 3 Partitioning signatures of the analyzed metals in surface sediments from inner, middle, and outer shelves to Okinawa Trough.

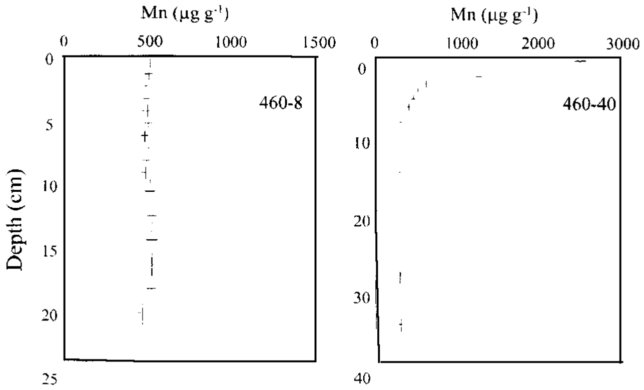


FIGURE 4 Vertical profiles of manganese in the inner shelf (sta. 460-8) and Okinawa Trough (sta. 460-40) sediments.

secondary oxidants during this stage. Manganese (Mn^{2+}) is then released from the sediment into the interstitial water and diffuses upwards. At the top of the sediment, this element is consumed by a small amount of oxygen and manganese oxide (MnO_2) (the new oxide) is then formed in this reaction. Chester (1990) has classified this process into the diagenetic signal to marine sediments.

For lead and cadmium, the fractions of detrital phase have a maximum in the midshelf sediment and minimum in the Okinawa Trough sediments. Overall, lead mainly exists in carbonate, and easily and moderately reducible phases. In the inner shelf sediment, most of the lead is associated with the oxide-carbonate fraction (Stages 2 and 3). El Ghobary and Latouche (1986) suggested that if large portion of lead in the sediment associated with manganese-oxides and -carbonates which seems to be the result of an anthropogenic source. The high proportion of easily and moderately reducible phases ($>80\%$) were found in the Okinawa Trough sediments. This is probably due to the formation of lead with new manganese-oxides on the Trough. Cadmium is a labile metal and mainly exists as exchangeable, carbonate and easily reducible phases in the ECS sediments. In the inner shelf and Trough sediment, cadmium is enriched in the exchangeable and carbonate phases ($\sim 50\%$ and $\sim 85\%$ for the inner shelf and Okinawa Trough, respectively) because of the fine-grained sediments with high organic carbon content and adsorption area.

Shaw *et al.* (1990) pointed out that copper is enriched in the sediments by transport with detrital biogenic material, followed by adsorption onto sediments. Due to the high correlation between copper and zinc, we believe that both metals have a similar fate in the ECS sediments. The copper and zinc fractionation data in different sediment samples indicate that higher percentages (6–21% for Cu and 7–17% for Zn) of both metals are associated with the organic-sulfide fraction (Stage 5) relative to the other metals (*e.g.*, Al, Fe, Mn, Pb and Cd). In the fine-grained sediment area, the results show that organic and detrital phases account for 60% of copper and zinc.

CONCLUSIONS

The spatial distributions of heavy metals show that the Yangtze River is the major source for these metals in the inner shelf sediments.

Another high concentration area was found in the Okinawa Trough sediments. In the ECS sediments, the high concentration areas of high heavy metal concentrations coincide with the areas of fine-grained sediments. The enrichments of the analyzed heavy metals are due to the fine-grained sediments with the high surface area per unit mass and organic matter concentrations. In contrast, the low concentrations of heavy metals were found on the middle shelf where the sea floor is covered by about 70% of coarse sand. Therefore, the sediment particle size is a main factor controlling the distribution of metals in the ECS sediments. The strong aluminium – iron and copper – zinc correlations suggest that the metals of each pair have similar sources and transport mechanisms. The different depositional conditions do not have a significant effect on either series.

The results of a six-stage sequential leaching experiment show that aluminium and iron primarily exist in the residual phase. Both metals are crust-derived weathering products which are mainly located in lattice-held positions. A high concentration of manganese which is chiefly associated with new oxides was found in the Okinawa Trough sediments. From the results of the phase partition and two vertical profiles of the inner shelf and the Okinawa Trough sediments indicate that is related to the diagenetic process of manganese under an oxidizing in surface sediments, but reducing underneath. The data for lead indicate that the anthropogenic input is the main source in the inner shelf sediments. Like manganese, the diagenetic process also plays a key role on the phase partitioning behavior of lead in the Trough sediments. Cadmium is a labile metal and enriched in exchangeable and carbonate phases because of the fine-grained sediments with high organic carbon content and adsorption area. Copper and zinc are enriched in the sediments by transport with detrital and biogenic material, followed by adsorption onto sediments.

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