Pollution characteristics of the recent sediments in the Hangzhou section of the Grand Canal, China

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Abstract: Spatial distribution of heavy metals, arsenic and organic matter in recent sediments in the Hangzhou section of the Grand Canal and their relationships were analyzed. The results showed that the concentrations of heavy metals and organic matters varied widely along the canal, and the average geological accumulation factors decreased in the following orders: organic carbon(2.6), zinc(2.1), cadmium (2.0), copper(1.5), lead(1.1), nitrogen(0.9), mercury (0.8), phosphorus(0.4), arsenic(0.2) and chromium(0). Content of heavy metals and organic carbon in the top 10 cm layer were lower than that of lower layers, except for mercury and organic carbon in the S9 section. Contents of organic carbon in the top 50 cm layer of the mud sediments are significantly higher than those underneath. In the bottom mud layer, there is a concentration peak of the pollutants. In the mud sediments of the canal, cadmium mainly occurred in the Fe and Mn oxide fraction, copper in the organic fraction, lead in the Fe and Mn oxide fraction, and zinc in the carbonate and the Fe and Mn oxide fraction.

Keywords: sediment; pollution characteristics; Grand Canal; geological accumulation factor; fraction of heavy metals

Introduction

The Grand Canal, connecting Hangzhou in the south and Beijing in the north of China (Fig.1), was built in the seventh century and has a total length of over 1700 km. Crossing several major rivers and many important cities, the Grand Canal served as one of the most important water transportation routes of China for many centuries. Before the industrial development of alongside the canal, its water was the major source for drinking, washing and irrigation of local people.

Since the late 1950s, Hangzhou became one of the most rapidly developing areas of China. More than 100 factories were built near the canal, including power plants, steel plants, chemical plants, textile mills, print and dyeing mills, and pharmaceutical factories. Large amounts of untreated industrial wastewater were drained directly into the canal. Furthermore, the population of Hangzhou increased from 500000 in 1950 to 1600000 in 1998. With a drastic improvement of the living conditions, the production of domestic sewage increased rapidly. Before the first sewage treatment plant(Sibao) was built in 1988, most of the domestic sewage and industrial wastewater were directly drained into the canal. The water quality gradually deteriorated in the canal in the Hangzhou section.

Hangzhou government began to control the pollution of the canal in 1986. First, a channel was dug to connect the canal with the Qiantang River. As a result, water from Qiantang River was introduced into the canal to dilute the contaminants. Soon afterwards, Sibao Sewage Treatment Plant, which could treat 500000 m³ of sewage per day, was built near the canal. As a result, one third of the sewage was treated before being drained into the canal. And industrial wastewater from the large factories must be treated before being released into the canal. Although all these measures prevented the canal from further deterioration, its water quality could not significantly improve. Therefore, Hangzhou government planned to dredge the bottom mud of the canal.

The purpose of this study was to accurately investigate the spatial distribution of the pollutants, such as heavy metals, arsenic, organic carbon, nitrogen and phosphorus, in recent sediments in the Grand Canal(Hangzhou section), and to study the relationships between these pollutants.

1 Study area

Hangzhou is located in the southeast of China(Fig.1). It is in a subtropical, wet climate with an annual precipitation of about 1400 mm. The Grand Canal(Hangzhou section) flows from south to north with a mean current velocity of about 0.07 m/s. At its southern end, water from the Qiantang River is fed into the canal through Sanbao Lock at a rate of 300000 m³ per day. In the study area, the Grand Canal passes three different geographic units from south to north: the urban area of Hangzhou(from S1 to S5, 8.2 km long), an industrial district(from S6 to S10, 10.3 km long) and an agricultural area(S11 and S12, 11.6 km long). The shallow water-bearing strata along both sides of the Grand Canal are composed primarily of clay that was deposited in a variety of sedimentary environments: marine, fluviolacustrine and lake basin bog facies(Weng, 1995).

In 1998, 106 millions m³ industrial wastewater have been released into the canal from 112 factories. Three quarters of the industrial wastewater came from Hangzhou Steel Corporation, which drained 79 millions m³ wastewater into the canal in 1998. The location of factories with wastewater discharge over 0.1 million m³ annually are shown in Fig 1. Entrances of the industrial wastewater were concentrated at the S6-S10 positions. The land in the agricultural area is mainly used for rice cultivation. The rice field holds water from April to September, and the subsiding water is discharged into the canal.

2 Sampling and analysis

Sediment sampling in the Grand Canal was performed in December 1998. According to the distribution of pollution sources and the regime of
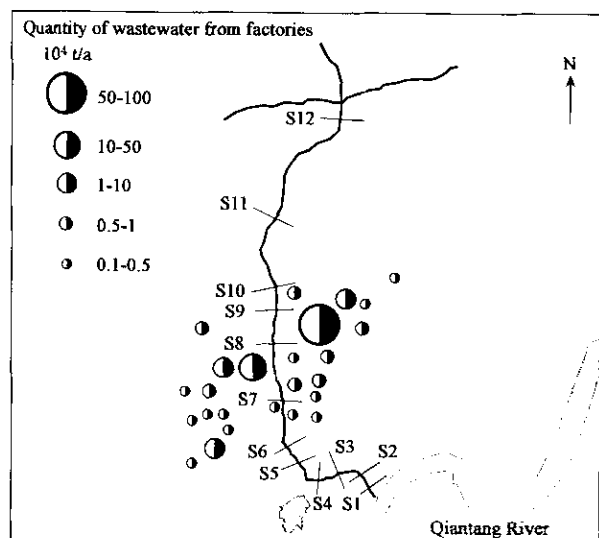
Fig.1   Locations of factories and sampling sites in the Grand Canal(Hangzhou section)

the canal, samplings were carried out in 12 sections of the canal(Fig. 1). In each section, two sediment cores were drilled by a rock-core drilling machine in the left and right side of the main channel of the canal, respectively. The sediment cores were 3 m long with a diameter of 108 mm; each core penetrated the surface mud layer and went into the bottom silt layer of the canal.

The surface mud sediments were black or dark gray, indicating its high organic matter content. The bottom silt is brown, yellow gray, or yellow, and shows a distinct boundary with the surface mud layer. Surface mud and bottom silt of each core were separated in the field. Cores from S6 and S9 section were dissected into 10 cm slices. All samples were sealed in plastic containers and stored frozen(– 5℃) until air-drying and analysis.

The chemical analysis of all the sediment samples was carried out in the central laboratory of Hangzhou Environmental Monitoring Station from January to April 1999. Every sample was air-dried to constant mass, ground in agate mortar, sieved to pass 63 μm and homogenized before chemical analysis.

For the determination of cadmium, copper, lead and zinc, sediment was dissolved on electric hot plate using concentrated HNO_3 and HF followed by $HClO_4$. After complete digestion with $HF-HClO_4$, the samples were taken up in 1% HNO_3. Cadmium, copper, lead and zinc were determined using standard graphite furnace AAS procedures. For mercury determination, sediment were dissolved using concentrated HNO_3 and H_2SO_4 followed by 5% $KMnO_4$ in boiling water bath. Mercury in the solution was determined using cool-vapor AAS. For arsenic determination, sediment was dissolved on electric hot plate using concentrated HNO_3 and H_2SO_4. Arsenic in solution was transformed into AsH_3 by addition of granulated zinc, and gaseous AsH_3 was absorbed by 0.5% silver diethyldithiocarbinate(AgDDC) solution(in pyridine). Then, arsenic in AgDDC solution was determined with Shimadzu UV-1206 spectrophotometer in wavelength of 530 nm. For chromium determination, sediment was dissolved on electric hot plate using concentrated H_2SO_4 and H_3PO_4. After complete digestion, the samples were taken up in 1% H_2SO_4. Chromium in solution was transformed into

hexavalent chromium[Cr(VI)] by adding potassium permanganate and complexed with diphenyl carbazide, and its concentration was determined by colorimetry with the Shimadzu UV-1206 spectrophotometer in wavelength of 540 nm. Cadmium, copper, lead and zinc in samples from S4, S6, S7, S8, S9 were sequentially extracted according to the method of Tessier et al. (Tessier, 1979) modified by Zhang et al. (Zhang, 1999), and the exchangeable fraction(F1), carbonate fraction(F2), Fe and Mn oxides fraction(F3) and organic fraction(F4) were determined.

Samples were air-dried for a month before the determination of organic carbon(OC) to avoid the effect of reducing substances in the sediments. Organic carbon in sediments was quantitatively oxidized by 2% of $K_2Cr_2O_7$ in 10 mol/L H_2SO_4 solution at 180℃ paraffin bathing. The excess $K_2Cr_2O_7$ was titrated by $FeSO_4$ solution. Organic carbon was calculated by the depletion of $K_2Cr_2O_7$. Total N in sediments was determined by Kjeldahl digestion. Total P was extracted with H_2SO_4 H_2O_2-HF and determined by the method of Murphy and Riley (Murphy, 1962).

Statistical analysis of correlation between analyses was evaluated by the Pearson correlation coefficient, and the hierarchical cluster analysis was carried out by Ward method(Euclidean distance) with SPSS for Windows.

ESS-1, a soil CRM provided by Chinese Environmental Protection Bureau, was used to take the analytical quality control. In the determination of the pollutants, twenty-eight samples as a group for elements determination, insert an ESS-1 sample for accuracy control, four samples in each group were triplicate for precision control.

3   Results and discussion

3.1   Longitudinal distribution

The average water depth of the canal is about 2 m, and there is a sharp decline in the section of S6(Fig. 2), which is the site of old port. The average thickness of the surface mud layer of the canal is about 1 m, and varied widely from S1 to S9 section(Fig. 2). There is little mud in S1, due to the flushing action of the inlet of water from Qiantang River. The mud layer in S11 and S12 section is thick, owing to the remarkable increase of the river breadth and the decrease of the fluid velocity in the agricultural section of river, which caused the deposition of a large amount of suspended matter from upstream.
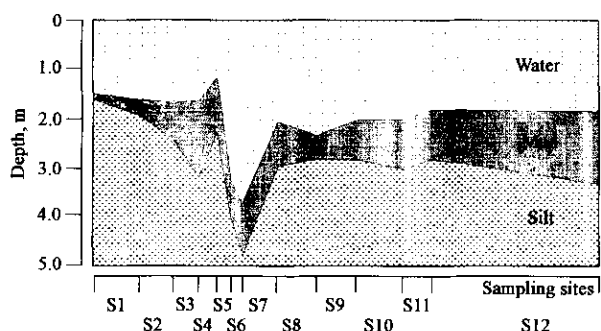

Fig.2   Longitudinal average thickness of the mud layer sediments in the Grand Canal(Hangzhou section)

The longitudinal distribution of organic carbon, total nitrogen, total phosphorus and heavy metals in top mud layer and subjacent silt layer of the canal is shown in Fig.3. It demonstrates that the content of heavy

metals varied drastically along the canal, related to the diversity of the pollution sources. On the other hand, all the peak values of the content of heavy metals occurred in industrial section(S6—S10 section), indicating that industrial wastewater is the major source of heavy metals in the sediments of the canal. Zinc is the most seriously evident element with a peak value(S10 section) of 2560 mg/kg, next is copper, with a peak value of 540 mg/kg (S7 section). Peak values of cadmium, mercury, lead, arsenic, and chromium are 5.3 mg/kg(S8), 1.5 mg/kg (S10), 150 mg/kg(S8), 31 mg/kg(S7) and 136 mg/kg (S7), respectively. Moreover, in the section of S4 and S5(5—10 km from the beginning of the canal), which lie in the urban area, the contents of lead and mercury in the sediments was also quite high, maybe due to the urban surface runoff and atmospheric deposit.
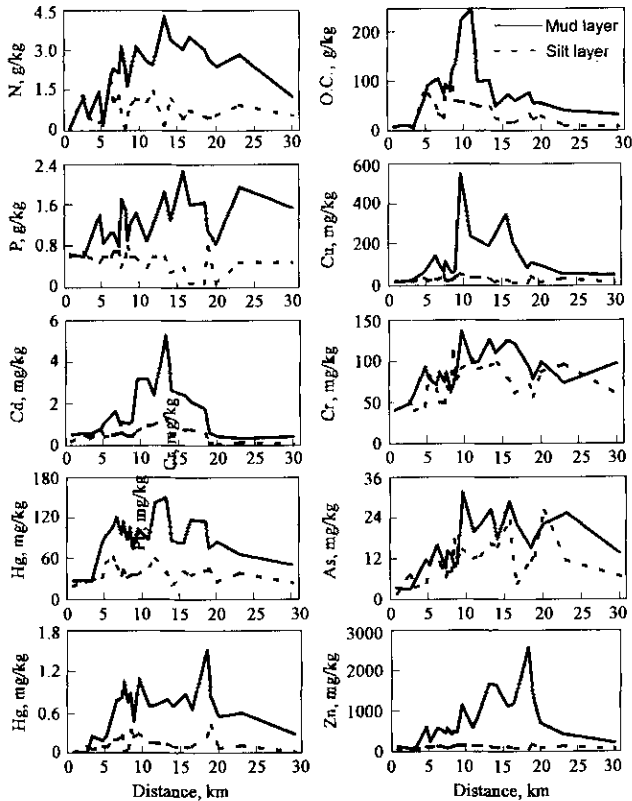

Fig.3 Longitudinal distribution of pollutants in mud layer and subjacent silt layer sediments in Grand Canal (Hangzhou section)

The peak value of organic carbon(246 g/kg) was not located in the urban area, but in industrial area(S7). This is because large amounts of sewage water also drain into the canal in the industrial area. As of the operation of the Sibao Sewage Treatment Plant in 1988, all the sewage has been piped into Sibao Sewage Treatment Plant, but the sewage in the industrial area is still being drained directly into the canal. As a result, the industrial section has nowadays become the most malodorous section of the canal, taking the place of the urban section ten years earlier.

The distribution of nitrogen and phosphorus was quite different from that of organic carbon. Nitrogen and phosphorus content in the mud of the agricultural section (S11 and S12 section) of the canal have not decreased too much compared to the peak value, while that of organic carbon in this section is far below the peak value. This is owing to application of large amount of chemical fertilizer on the cropland. Since the 1980s, application of chemical fertilizer became more and more

popular in China, such as ammonium bicarbonate, urea, superphosphate and so on, that leads serious agricultural non-point source pollution.

3.2 Enrichment of elements

Table 1 shows the mean background concentration of organic carbon, nitrogen, phosphorus and heavy metals in the sediments of the canal (Zhejiang Environmental Protection Institute, un-pub. report). The enrichment of the elements and organic carbon was expressed by geological accumulation factor(I_{geo}) (Müller, 1969), which was calculated as:

$$I_{geo} = \log_2 \frac{C_i}{1.5B_i}.$$

Where C_i is the content of the element in mud, B_i is the background value of the element.

Table 1 Background value of pollutants in sediment of the Grand Canal (Hangzhou section). All values mg/kg, except O.C., total N and total P in g/kg

Element	O.C.	Total N	Total P	As	Cd	Cr	Cu	Pb	Hg	Zn
Background	6.8	0.8	0.6	11	0.20	74	254	264	0.25	87

Fig.4 displays the I_{geo} of organic carbon, nitrogen, phosphorus and heavy metals in the mud of the canal. The I_{geo} varied between ≤0 and 5 (values of ≤0 were expressed by zero), with the largest value of organic carbon(4.6), zinc(4.3), cadmium(4.1) and copper(3.9). The mean I_{geo} of the 24 samples decrease as the follows of organic carbon(2.6), zinc(2.1), cadmium(2.0), copper(1.5), lead(1.1), nitrogen(0.9), mercury(0.8), phosphorus(0.4), arsenic (0.2) and chromium(0).

In the beginning section of the canal(S1 and half of S2 section), I_{geo} of the selected elements and organic carbon, except for cadmium, were ≤ 0. It showed that the content of the selected elements and organic carbon were near, or even lower than, the background value. This is owing to the effect of water from Qiantang River, which flushed the mud to the downstream and brought suspended matter from Qiantang River.

Table 2 shows the correlation coefficients for I_{geo} of metals, nitrogen, phosphorus and organic carbon in the top mud layer of the canal. Except for Cr, all the heavy metals are significantly correlative each other, and significantly correlative with the content of organic carbon and nitrogen. This is related to the sewage-industrial combined pollution characteristic of the canal and the long-term drastic disturbance on the sediments by ships. Because the canal is shallow (Fig. 2), shipping seriously disturbed bottom mud. And the re-suspension caused the absorption equilibrium of heavy metals on organic and inorganic colloid.

Fig.5 is classified analytical result of the geological accumulation factor of the 10 pollutants in the mud layer. Zinc, mercury, cadmium and copper, the most significantly accumulated heavy metals in the mud layer of the canal, are in the same class. Organic matter and lead, which the major pollution sources were sewage drainage and urban surface runoff, are in the other class. Arsenic, chromium and phosphorus, which have the lowest I_{geo}, were in the third class.

3.3 Vertical distribution

Fig.6 shows the vertical distribution of the content of organic carbon

and heavy metals in top mud layer in S6 and S9 section of the canal(the bottom 10 cm layer represent the bottom silt layer). The content of heavy metals and organic carbon in the top 10 cm layer was lower than that of the underlying, except for mercury and organic carbon in S9. This is due to the prohibition of drainage of wastewater since 1994. From bottom to top of the mud layer, there is an increasing trend for zinc and cadmium, except for top 10 cm layer. In S6, content of organic carbon in top 50

cm layer of the mud is significantly higher than that of the underlying mud layer, this is owing to the rapid increase of the population and the lagging behind of the municipal sewage treatment in Hangzhou. The average increasing rate of population of Hangzhou is near 2% since 1950, but until 1988, the first sewage treatment plant(Sibao Sewage Treatment Plant) have been brought into use.
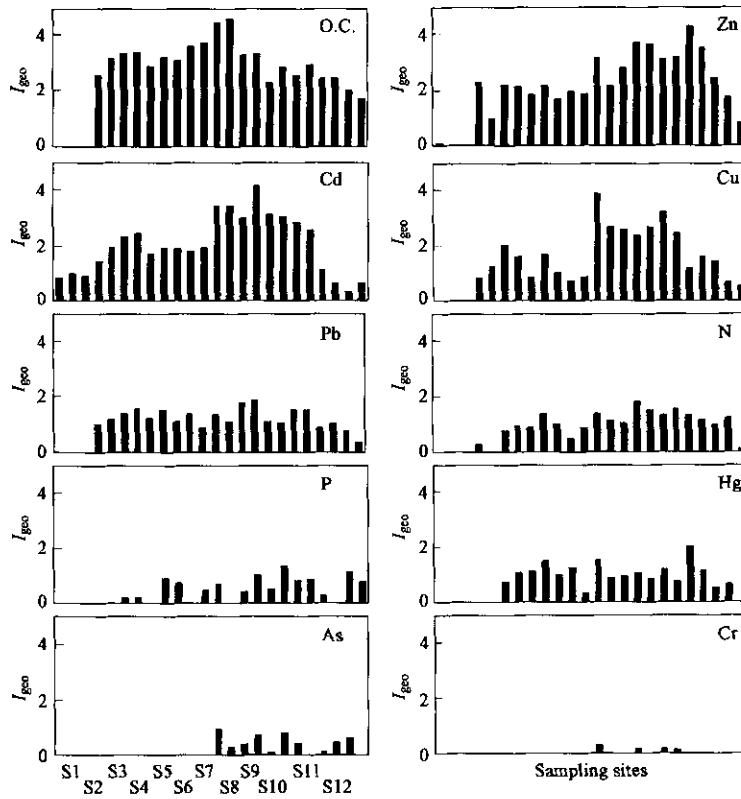

Fig.4 I_{geo} of pollutants in mud layer sediments in 12 sampling sites of the Grand Canal

Table 2 Pearson's correlation of I_{geo} of pollutants in sediments

	O.C.	N	P	As	Cr	Hg	Cd	Pb	Zn	Cu
O.C.	1.000									
N	0.564**	1.000								
P	0.205	0.666**	1.000							
As	0.296	0.586**	0.550**	1.000						
Cr	0.305	0.483*	0.501*	0.819**	1.000					
Hg	0.596**	0.763**	0.468*	0.318	0.347	1.000				
Cd	0.644**	0.641**	0.331	0.434*	0.585*	0.543**	1.000			
Pb	0.816**	0.688**	0.307	0.292	0.299	0.690**	0.704**	1.000		
Zn	0.603**	0.860**	0.499*	0.447*	0.412*	0.756**	0.646**	0.750**	1.000	
Cu	0.667**	0.735**	0.428*	0.687**	0.675**	0.562**	0.815**	0.650**	0.726**	1.000

* Correlation is significant at the 0.05 level(2-tailed) ; ** Correlation is significant at the 0.01 level(2-tailed)
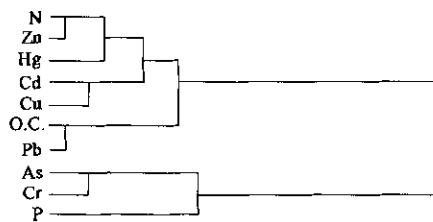

Fig.5 Classification of pollutants in mud layer sediments of the Grand Canal (Hangzhou section) on basis of their I_{geo}

In S6, the trend of all pollutants from the bottom to the top mud layer is the same, while the trend in S9 is quite different, especially for mercury and lead. The difference is partly due to the different type of the pollution sources between two sections. Sewage and wastewater from small-scale factories were the major source of pollution at the S6 section, while wastewater from large size factories was the major pollution source at the S9 section.

In the 10 cm layer near the bottom silt layer, there is a polluted peak value. This shows that it is difficult for all the pollutants to get through the mud-silt interface and to permeate to the bottom silt layer.
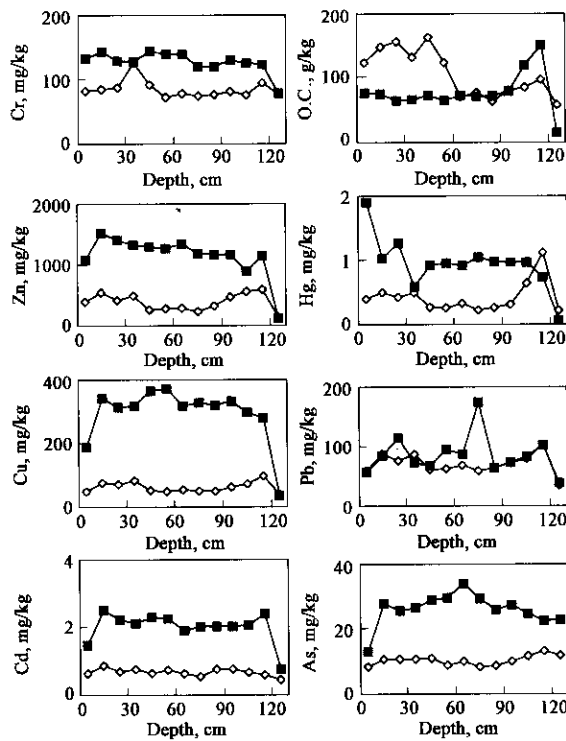
3.4 Fraction of heavy metals

Fig.6   Vertical distribution of organic carbon and heavy metals in S6 and S9 sediment cores

(23.9% ± 4.8%), organic fraction(11.7% ± 3.7%), the content of the exchangeable fraction(1.5% ± 1.3%) is low. This indicates that the mobility of lead is low, which is consistent with the relatively high variability of lead in mud cores (Fig. 6). Both carbonate fraction (42.2% ± 3.0%) and Fe and Mn oxide fraction(40.9% ± 2.9%) are the major fraction of zinc in mud; the amount of organic fraction(14.6% ± 4.7%) is about one third of them; exchangeable fraction(2.2% ± 1.1%) is also low.

Rates of exchangeable fraction of the four heavy metals to the sum of the four fractions are different in five sections of the canal(Table 3). This indicates that the total amount is not the control factor of the mobility of the heavy metals in sediments of the canal. The factors influence the rate of exchangeable fraction in the mud of the canal may be partly due to the different physicochemical conditions of the mud, such as redox potential, organic matter content, sulfide content, and so on.

Table 3   Percentage of exchangeable fraction of Cd, Cu, Pb, Zn in total amounts of the four fractions   Unit: %

Element	S4	S6	S7	S8	S9
Cadmium	2.6 (1.9)	12.7 (5.1)	11.0 (9.2)	8.4 (4.5)	3.2 (1.2)
Copper	4.7 (1.5)	8.8 (4.6)	8.2 (4.8)	8.6 (3.0)	4.1 (2.2)
Lead	0.4 (0.4)	1.2 (0.7)	2.6 (1.6)	0.0 (0.3)	3.1 (1.9)
Zinc	2.3 (0.8)	3.0 (0.4)	1.1 (0.3)	1.1 (0.5)	3.7 (0.7)

4   Conclusions

The results of this work on the Grand Canal (Hangzhou section) represent the typical environmental quality of urban canals in China today. The pollution characteristics of sediments in these canals is high organic matter content combined with high heavy metals content. The concentrations of heavy metals and organic carbon investigated were quite high, especially in the industrial section. The pollution extent of the sediments in different sections of the canal is highly different. It is partly due to the large industrial and domestic wastewater input, but low flow velocity and shallow water depth of the canal.

Organic matter is the most serious pollutant in the sediments of the canal, and it causes deterioration of water quality and difficulty on ecological restoration. This is the most common problem in the urban area in China today, and dredging is the popular measure of dealing with this kind of problem. Since the serious pollution of heavy metals, the treatment of the dredged sediments from the canal must be carefully planned to avoid causing a second pollution.

Fractions of cadmium, copper, lead and zinc were quite different with in the top mud layer(Fig. 7). Cadmium mainly occurred in the Fe and Mn oxide fraction, occupied 46.0% (± 8.2%) of the total amount of the four chemical fractions. Next is the carbonate fraction (37.6% ± 4.4%). Percentage of organic fraction(8.9% ± 9.1%) and exchangeable fraction(7.6% ± 4.5%) is low. Copper is mainly presented in organic fraction(59.7% ± 14.0%), next is the carbonate fraction(25.2% ± 9.5%). The content of Fe and Mn oxide fraction (8.3% ± 5.4%) and exchangeable fraction(6.9% ± 2.3%) is quite low. This indicates that copper tends to be absorbed by organic matter or formed metal sulfide complex compound, and the absorbing potential with inorganic colloid is low in the mud of the canal.
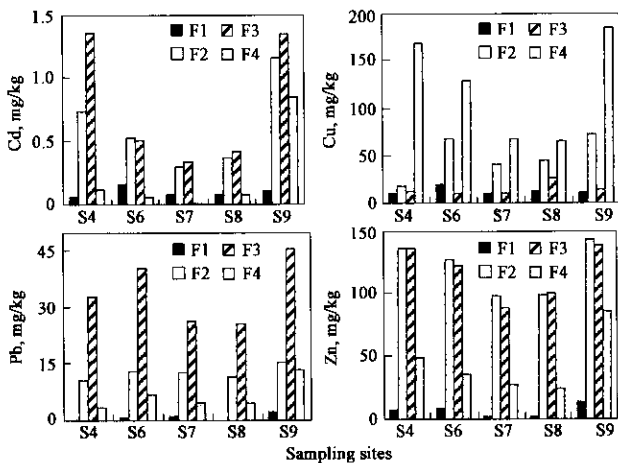
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Fig.7   Contents of exchangeable(F_{ex}), carbonate(F_{ca}), Fe/Mn oxide(F_{fe}) and organic fractions(F_{oc}) of Cd, Cu, Pb and Zn in mud layer sediments from different sampling sections

Most of the lead in the mud of the canal is presented in Fe and Mn oxide fraction (62.9% ± 4.8%), followed by carbonate fraction

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Water Pollution Control Technology Group

Brief introduction

This group is focusing on research and application of theory and technology on water pollution control and wastewater reuse. On the basis of innovation and integration of technologies and equipment, the purposes of this group are to research and develop new cost-effective and cleaning processes/systems for wastewater treatment and reuse.

Research interests

● New cost-effective biotechnologies for wastewater treatment, including novel integrated oxidation ditch with vertical circle (IODVC), membrane bioreactor (MBR), biological nitrogen and phosphorus removal, and biodegradation of persistent organic pollutants (POPs).

● Mechanism and new reactor for biological VOC and odour treatment.

● Sewage sludge treatment, including sludge reduction by grazers and biohydrogen production from sewage sludge.

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