

Heavy metals in oysters, mussels and clams collected from coastal sites along the Pearl River Delta, South China

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Abstract: Concentrations of 8 heavy metals: cadmium (Cd), copper (Cu), zinc (Zn), lead (Pb), nickel (Ni), chromium (Cr), antimony (Sb) and tin (Sn) were examined in 3 species of bivalves (*Perna viridis*, *Crassostrea rivularis* and *Ruditapes philippinarum*) collected from 25 sites along the Pearl River Delta coastal waters in the South China Sea from July to August 1996. In general, Cd, Cu, Zn and Sn concentrations in the three bivalve species collected from the Estuarine Zone were significantly higher than those collected from the Western and Eastern Zones of the Pearl River Delta, which are related to the existence of various anthropogenic activities in the catchment of the Pearl River Delta. The Western Estuarine Zone is mainly impacted by Cr, Ni and Cu contamination. In Victoria Harbor, heavy metal contamination is mainly due to Cu and Pb. Cd, Cu and Zn concentrations in oysters were significantly higher than those in mussels and clams. This could be explained by the fact that oysters live mainly in the Estuarine Zone of the Pearl River Delta which receives most of the polluting discharges from the catchment of the Delta. During turbid condition, heavy metals (soluble or adsorbed on suspended particulates) discharged from the Delta are filtered from the water column and subsequently accumulated into the soft body tissues of oysters. Heavy metal concentrations in the three bivalve species were compared with the maximum permissible levels of heavy metals in seafood regulated by the Public Health and Municipal Services Ordinance, Laws of Hong Kong, and it was revealed that Cd and Cr concentrations in the three bivalve species exceeded the upper limits. At certain hotspots in the Delta, the maximum acceptable daily load for Cd was also exceeded.

Keywords: heavy metals; oyster; mussel; clam; coastal waters

Introduction

Many monitoring programmes such as the “Mussel Watch” recommend the use of bivalve molluscs as indicators of heavy metal pollution in the marine environments (Goldberg, 1975; Phillips, 1985; Lu, 1993; Manly, 1996). As filter feeders, bivalve molluscs accumulate heavy metals in their tissues in proportion to the degree of environmental contamination. The relatively small increase in ambient metal concentration due to pollution will be reflected in measurable amounts in their tissues. Therefore, they can be used as indicators of metal pollution in the marine environment. In addition, analysis of heavy metals in aquatic biota provides important information on the potential impact of seafood consumption on public health.

Many surveys have been conducted on heavy metal levels in green-lipped mussels *Perna viridis*, taken from different locations around Hong Kong coastal waters since 1985 (Phillips, 1985; Chan, 1988a; Cheung, 1992a). The South China Sea Mussel Watch Programme, using the bivalve sentinel organism concept, was also conducted on the northern coast of the South China Sea in 1991 (Jia, 1993; Lu, 1993).

A composite delta in South China was formed by sediments deposited at the mouth of Pearl River by the rivers of West River, North River, East River and their tributaries (Lo, 1988). The Delta covers an area of 40000 km² (Fau, 1988), with 15 million inhabitants (Chen, 1994). The estuary supports large populations of marine organisms and contributes significantly to the fisheries in South China (Fu, 1994).

During the past twenty years, there has been a rapid economic development in Guangdong Province resulting in an over-exploitation of bioresources in the estuary, and excessive release of wastes into the estuarine and coastal environment. It has been estimated that 2400 million t/a of industrial wastewater and domestic sewage are generated in this region (Chen, 1994).

Our previous survey (Fang, 2001) on the levels of heavy metals in edible shellfish obtained from different markets in the Pearl River Delta showed that Cd levels of five species (*Anadara ferruginea*,

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Pinna pectinata, *Chlamys nobilis*, *Babylonia lutosus* and *Hemifusus tertanus*) and Cr levels of seven species (*Anadara ferruginea*, *Paphia undulata*, *Pinna pectinata*, *Babylonia lutosus*, *Hemifusus tertanus*, *Cymbium melo* and *Cipangopaludina chinensis*) were higher than both the human daily acceptable limits and the local regulatory levels. However, the analysis of retail market samples allows no conclusion as to the possible areas of worst contamination. The direct capture method permits the study of samples from known areas and environments, and may therefore be more useful to elucidate possible sources of heavy metal contamination. The main aim of this study was to conduct a comprehensive survey to monitor the heavy metal content of three species of bivalves collected from the coastal waters of the Pearl River Delta. These data will be valuable for water quality and public health assessments in the Pearl River Delta which is under going a rapid socio-economic development.

1 Materials and methods

1.1 Study sites and sampling

From July to August 1996, three bivalve species (*Perna viridis*, *Crassostrea rivularis* and *Ruditapes philippinarum*) were collected from natural or commercial mussel beds from Chanshan Islands in the west to Daya Bay in the east along the Pearl River Delta coastal waters. A total of twenty five sites were chosen for the survey. The sampling sites were grouped into 3 different zones according to their geographic locations: Estuarine Zone, Eastern Estuarine Zone and Western Estuarine Zone (Fig. 1). Mussels, oysters and clams were collected from 13, 10 and 7 sites, respectively along the Delta's coastal waters (Table 1).

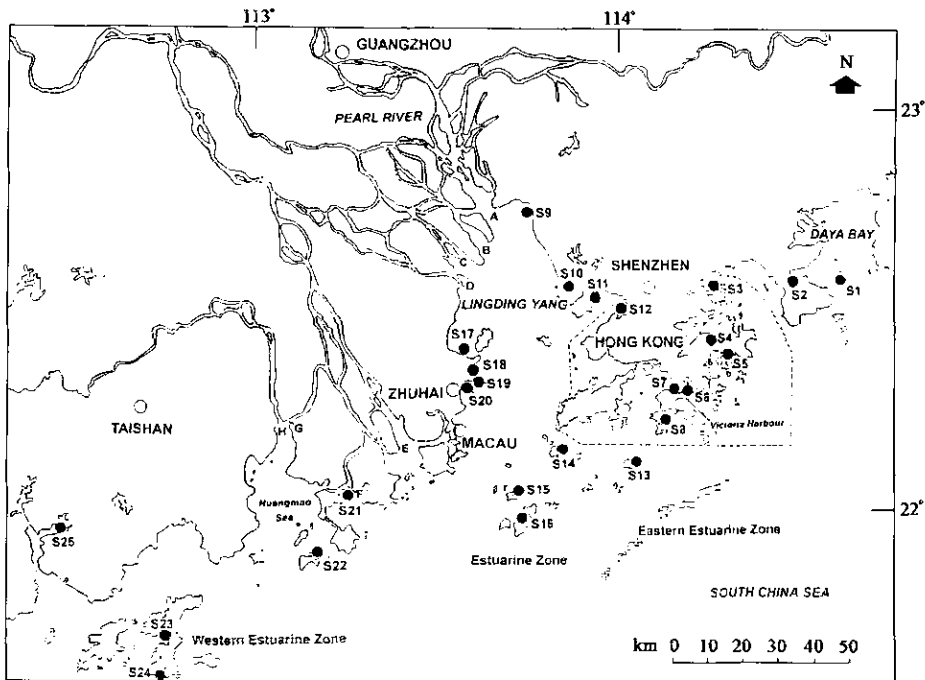


Fig.1 Map showing the Pearl River Delta coastal waters and the locations of sampling sites 1-25 and eight seaports located along Pearl River coast

S1. Lajia Island; S2. Dongshan; S3. Kat O Chau; S4. Lok Wo Sha; S5. Pukuwan; S6. North Point Pier; S7. Tsim Sha Tsui Pier; S8. Lo Tik Wan; S9. Shajing; S10. Baon; S11. Shenzhen Bay; S12. Lau Fau Shen; S13. Wailingding Island; S14. Guishan Island; S15. Dongao Island; S16. Dawanshan Island; S17. Xiashan; S18. Tangjiawan; S19. Yingkeng; S20. Jiuzhouwan; S21. Naoshui Island; S22. Herbao Island; S23. Dawan; S24. Datiewan; S25. Shenjing; A. Humen; B. Jiaomen; C. Hongqili; D. Henmen; E. Molaomen; F. Jitimen; G. Hutiaomen; H. Yamen

1.2 Sample processing and analysis

Samples were stored at -20°C until required for analysis. Twenty-five individuals of mussels and clams, and fifteen individuals of oysters were randomly selected from each sample and combined for analysis. Shell lengths (the longest dimension) were recorded with calipers and the bivalves were shucked with stainless steel instruments. The shells of all species, and the byssus of *Perna viridis* were discarded. The soft parts of all species were then homogenized using a blender(model: Janke & Kunkel IKA-Labortechnik Ultra-Turvax T25).

The homogenized samples were weighed, placed inside clean plastic bottles and stored at -20°C for 24h. They were then freeze-dried in a freezer-drier

(Lyph-Lock 12 Freeze Dryer W/ # 75102 12P ORT Drying Chamber) for about seven days until a constant weight was reached. The dry weight: wet weight ratio of the samples was also determined so that data conversion could be possible. If the freeze-dried samples were not digested immediately, they were kept in an air-tight desiccator below 0°C to prevent re-absorption of moisture.

Approximately 1g of the dried samples(triplicates for each sample) was weighed accurately and then put into a digestion tube. 10 ml of 65% nitric acid was added into each tube which was left to stand for 2h to allow pre-digestion. The digestion tubes were placed in a digestion block (DG-1 Block Digestor Techne), and steadily heated up to 130°C until the brown fumes had disappeared and the solution was clear. Ten ml of 65% nitric acid was added each digestion tube to prevent charring of the contents. The digested solution was filtered through a glass fiber filter paper (Advantec Toyo 5C 90 mm) and diluted to 25 ml with deionized water and stored in acid-treated plastic vials at 4°C before metal analysis.

Cadmium(Cd), copper(Cu), zinc(Zn), lead(Pb), nickel(Ni), chromium(Cr), antimony(Sb) and tin(Sn) concentrations were determined using a flame atomic spectrophotometer(Shimadzu AA-6501Sx atomic absorption spectrophotometer with GFA-6500 graphite furnace atomizer), according to the method described in Allen *et al.*(Allen, 1974).

1.3 Analysis of certified reference material

The analytical methodologies used in this study were confirmed for accuracy by a certified standard reference material (Standard Oyster Tissue 1566a) obtained from the U. S. Department of Commerce, National Bureau of Standards, Gaithersburg, Maryland.

Table 1 Bivalve species (*Perna viridis*, *Crassostrea rivularis* and *Ruditapes philippinarum*) sampled at the 25 locations along the Pearl River Delta coastal waters shown in Fig. 1

Code	Location	Species collected
S1	Lajia Island	<i>Perna viridis</i> , <i>Ruditapes philippinarum</i>
S2	Dongshan	<i>Ruditapes philippinarum</i>
S3	Kat O Chau	<i>Perna viridis</i>
S4	Lok Wo Sha	<i>Perna viridis</i> , <i>Ruditapes philippinarum</i>
S5	Pukuwan	<i>Ruditapes philippinarum</i>
S6	North Point Pier	<i>Perna viridis</i>
S7	Tsim Sha Tsui Pier	<i>Perna viridis</i>
S8	Lo Tik Wan	<i>Perna viridis</i>
S9	Shajing	<i>Crassostrea rivularis</i>
S10	Baoan	<i>Crassostrea rivularis</i>
S11	Shenzhen Bay	<i>Crassostrea rivularis</i>
S12	Lau Fau Shen	<i>Crassostrea rivularis</i>
S13	Wailinging Island	<i>Perna viridis</i>
S14	Guishan Island	<i>Perna viridis</i> , <i>Ruditapes philippinarum</i>
S15	Dongao Island	<i>Perna viridis</i>
S16	Dawanshan Island	<i>Perna viridis</i>
S17	Xiashan	<i>Crassostrea rivularis</i>
S18	Tangjiawan	<i>Crassostrea rivularis</i>
S19	Yingkeng	<i>Crassostrea rivularis</i>
S20	Jiuzhouwan	<i>Crassostrea rivularis</i>
S21	Nanshui Island	<i>Crassostrea rivularis</i> , <i>Ruditapes philippinarum</i>
S22	Hebao Island	<i>Perna viridis</i>
S23	Dawan	<i>Perna viridis</i> , <i>Ruditapes philippinarum</i>
S24	Datiewan	<i>Perna viridis</i>
S25	Shenjing	<i>Crassostrea rivularis</i>

1.4 Statistical analysis

Kruskal-Wallis one way analysis of variance was used to calculate significant differences in metal concentrations between samples from different sites. Three planned comparisons (Student's *t*-test) were then used to elucidate the difference between different zones. Student-Newman-Keuls multiple range test was carried out to establish the ranking of sites with respect to metal concentration. Spearman's rank correlation coefficients (r_s) test was used to ascertain whether any relationships existed between different metals in the bivalve molluscs sampled.

2 Results

2.1 Analysis of certified reference material

The recovery rates obtained from the analysis of the reference material ranged from 91.3% to 99.4% for all metals except Sb and Sn, as no certified values were given for these two metals (Table 2).

Table 2 Certified values of the standard reference material (Standard Oyster Tissue 1566a) and the recovery percentages of different metals

	Cd	Cu	Zn	Pb	Ni	Cr	Sb	Sn
Certified values, $\mu\text{g/g}$ dry wt.	4.15 ± 0.38	66.30 ± 4.30	830 ± 57	0.37 ± 0.01	2.25 ± 0.44	1.43 ± 0.46	NCV	NCV
Concentration found, $\mu\text{g/g}$ dry wt.	3.94 ± 0.13	60.88 ± 2.21	807.8 ± 14.9	0.37 ± 0.64	2.09 ± 0.20	1.43 ± 0.25	0.03	8.10
Recovery percentage	94.85 ± 3.10	91.73 ± 1.73	96.98 ± 1.80	99.40 ± 18.4	92.97 ± 8.63	100.3 ± 17.2	-	-

NCV: no certified value

2.2 Heavy metal contents in the three bivalve species

Data on metal concentrations were based on dry weight, as well as wet weight, in order to compare the observed metal levels with public health standards, most of which are based on wet tissue weights. According to Kruskal-Wallis analysis of variance for each bivalve collected from all sites (except Pb in oyster), significant differences ($p < 0.05$) were observed between the highest and lowest levels recorded for each metal.

2.2.1 Cadmium

There was a 26-fold difference between the highest and the lowest recorded mean values for Cd in oysters. Mussels and clams also exhibited a wide range of Cd concentrations. It was noted that oysters had very high Cd concentrations (46–50 $\mu\text{g/g}$, dry wt.) at sites 17 to 20, whereas mussels and clams exhibited a relatively low Cd levels. For oysters, high Cd levels were found in the western bank of Lingdingyang. For mussels and clams, high Cd levels were found in the estuarine zone. Lower Cd concentrations were found in the bivalves collected from Hong Kong waters. Bivalves collected from the estuarine zone were significantly more contaminated ($p < 0.001$) than those from the eastern estuarine zone (Fig. 2).

2.2.2 Copper

Very high concentrations (up to 2237 $\mu\text{g/g}$, dry wt.) of Cu were found in oysters, in comparison with mussels (23 $\mu\text{g/g}$, dry wt.) and clams (14 $\mu\text{g/g}$, dry wt.). For oysters, higher Cu concentrations were found in samples collected from the western bank than those collected from the eastern bank of Lingdingyang. Mussels collected from Victoria Harbor were generally enriched with Cu. Comparatively higher Cu concentrations in mussels and clams were recorded in samples collected from the western estuarine zone (Fig. 3). Comparison of site ranking showed a significant correlation between Cu and Cd concentrations in oysters (Spearman's rank correlation coefficient $r = 0.8576$, $n = 10$, $p < 0.01$).

2.2.3 Zinc

The zinc profile was similar to that of Cd. All 3 bivalve species exhibited a narrow range, with means for different sites ranging from 2 to 5-fold difference between the highest and the lowest recorded mean

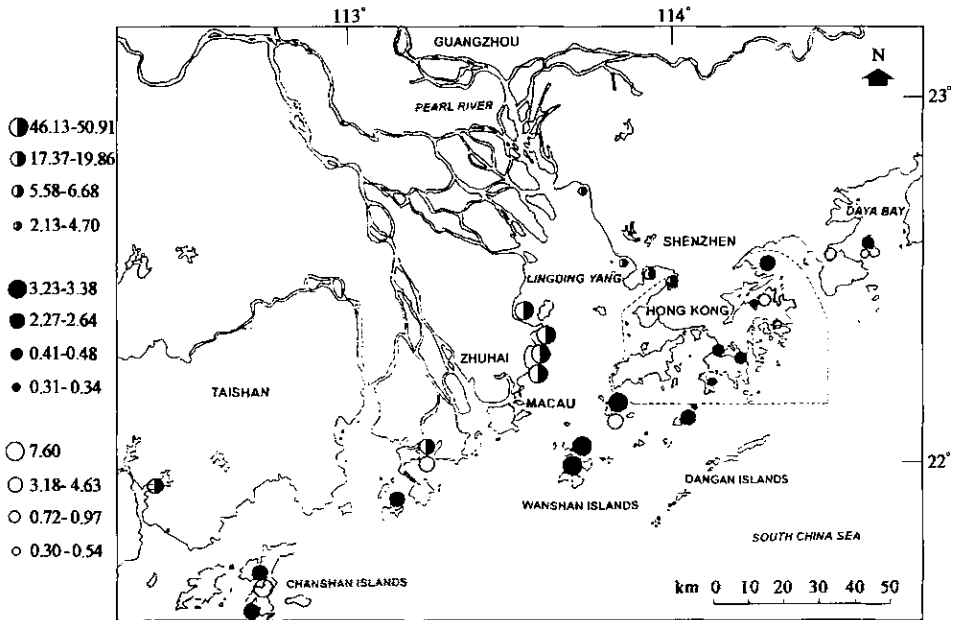


Fig.2 Concentrations of cadmium ($\mu\text{g/g}$ dry wt.) in mussels, oysters and clams from 25 sites in Pearl River Delta coastal waters, sizes of circles denote significant differences between sites. *Perna viridis* (filled circles), *Crassostrea rivularis* (half-filled circles) and *Ruditapes philippinarum* (open circles)

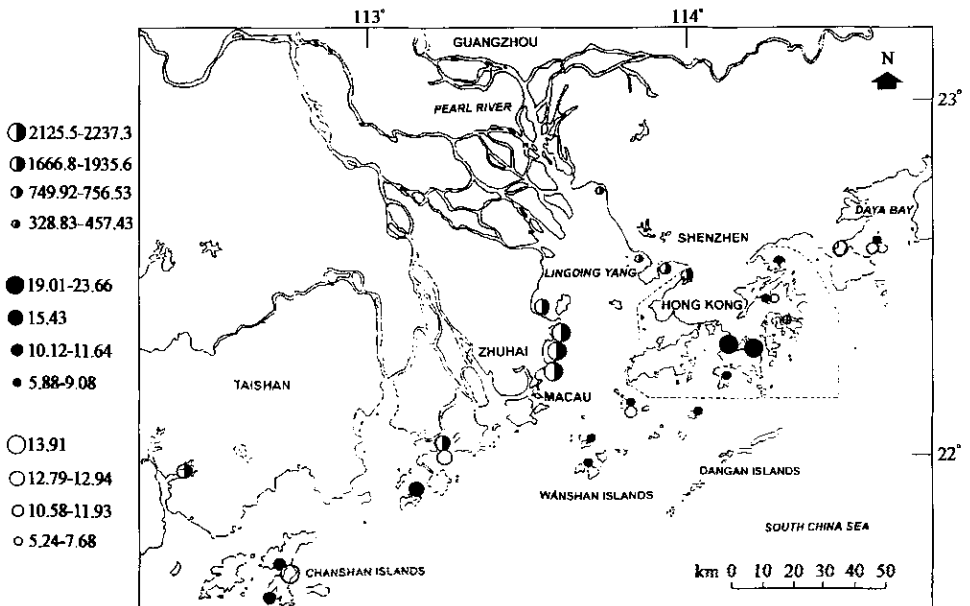


Fig.3 Concentrations of copper ($\mu\text{g/g}$ dry wt.) in mussels, oysters and clams from 25 sites in Pearl River Delta coastal waters, sizes of circles denote significant differences between sites. *Perna viridis* (filled circles), *Crassostrea rivularis* (half-filled circles) and *Ruditapes philippinarum* (open circles)

values. High concentrations (1485 to 6654 $\mu\text{g/g}$, dry wt.) of zinc were also found in oysters. Correlations of the rankings of the concentrations of Zn and Cd by Spearman's rank correlation were significant ($r =$

0.7541, $n = 10$, $p < 0.05$). Zn contents in the three species collected from western estuarine zone were relatively low (Fig. 4).

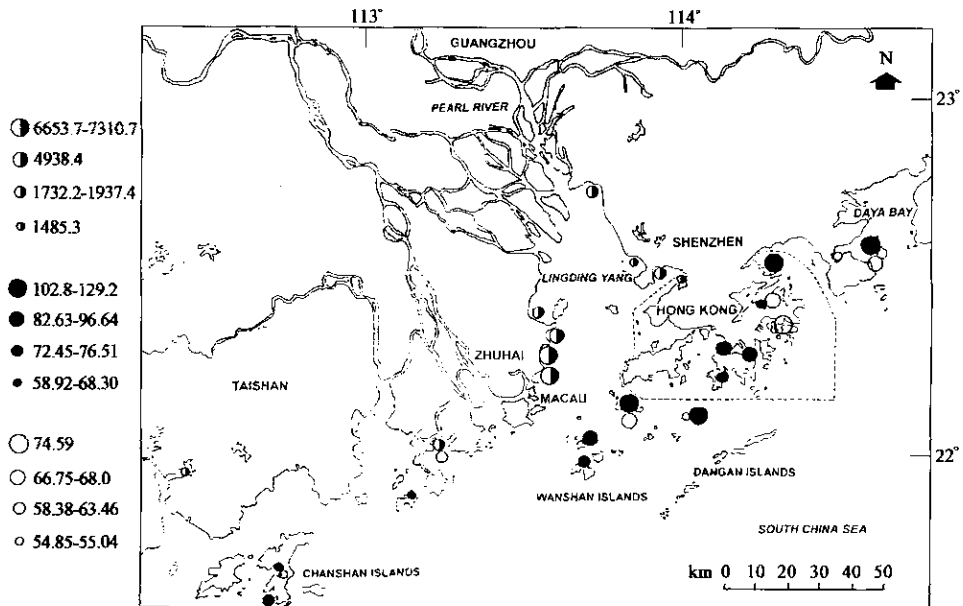


Fig. 4 Concentrations of zinc ($\mu\text{g/g}$ dry wt.) in mussels, oysters and clams from 25 sites in Pearl River Delta coastal waters, sizes of circles denote significant differences between sites. *Perna viridis* (filled circles), *Crassostrea rivularis* (half-filled circles) and *Ruditapes philippinarum* (open circles)

2.2.4 Lead

Lead levels in oyster samples were relatively low. No significant differences ($p > 0.05$) were found between the highest and lowest levels in oysters. The ranges of Pb concentrations in mussels and clams were relatively narrow, exhibiting only a 6-fold difference between lowest and highest levels. For oysters, relatively high Pb levels were found in Shenzhen Bay. Lead concentrations in mussels from Hong Kong waters were relatively higher than those from other sites, with samples from Daya Bay having the lowest Pb concentration. For clams, the highest Pb levels were found in Nanshui Island and Guishan Island (Fig. 5).

2.2.5 Nickel

There was only 5 to 6-fold difference between the highest and the lowest recorded mean values for this metal. Mussels and clams collected from the western estuarine zone (Chanshan Islands and Nanshui Island) had the highest Ni concentrations when compared to other sites ($p < 0.001$; Fig. 6).

2.2.6 Chromium

There was a 5 to 6-fold difference between the highest and the lowest recorded mean values for Cr concentrations in the three bivalve species. For oysters, relatively high Cr levels were found in Jiuzhouwan. High Cr concentrations in mussels and clams were also obtained in samples from western estuarine zone (Chanshan Island; Fig. 7). The spatial distribution of Cr concentrations was similar to that of Ni for all the bivalve species. Comparison of site ranking showed a significant correlation between Cr and Ni concentrations in oysters, mussels and clams (Spearman's rank correlation coefficient: $r = 0.8576$, $n = 10$, $p < 0.01$; $r = 0.9327$, $n = 13$, $p < 0.0001$ and $r = 0.8062$, $n = 7$, $p < 0.05$ respectively). These two metals might share a common source in the Pearl River Delta.

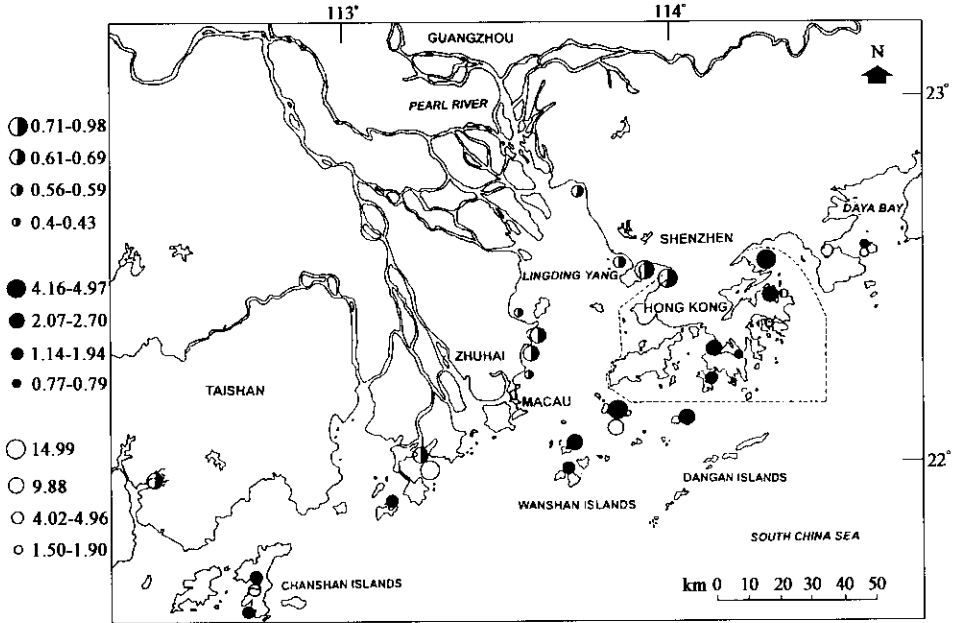


Fig.5 Concentrations of lead ($\mu\text{g/g}$ dry wt.) in mussels, oysters and clams from 25 sites in Pearl River Delta coastal waters, sizes of circles denote significant differences between sites. *Perna viridis* (filled circles), *Crassostrea rivularis* (half-filled circles) and *Ruditapes philippinarum* (open circles)

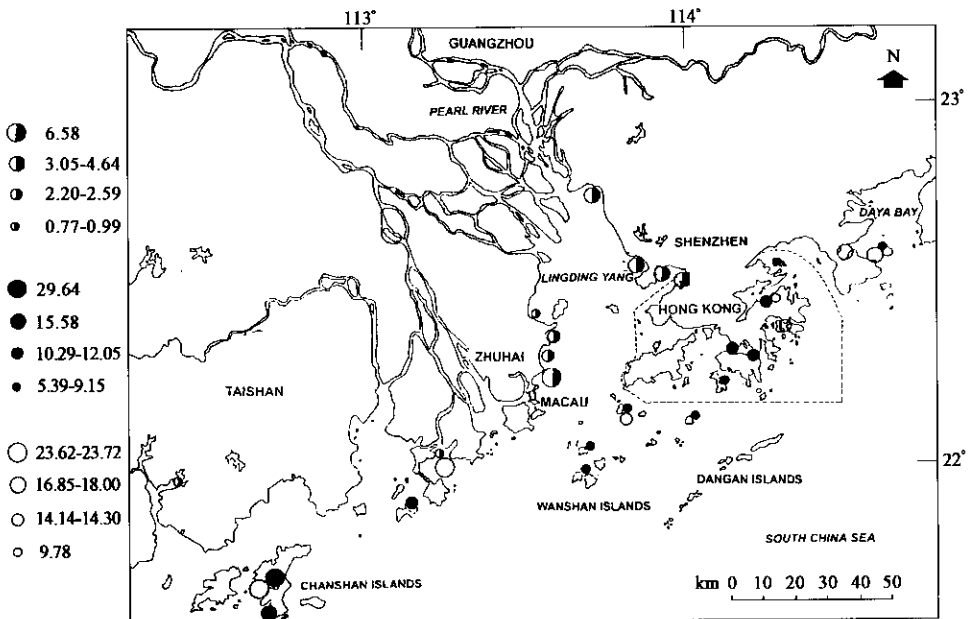


Fig.6 Concentrations of nickel ($\mu\text{g/g}$ dry wt.) in mussels, oysters and clams from 25 sites in Pearl River Delta coastal waters, sizes of circles denote significant differences between sites. *Perna viridis* (filled circles), *Crassostrea rivularis* (half-filled circles) and *Ruditapes philippinarum* (open circles)

2.2.7 Antimony

The tissue levels of Sb in all three species were very low, ranging from non-detectable to 0.83 $\mu\text{g/g}$

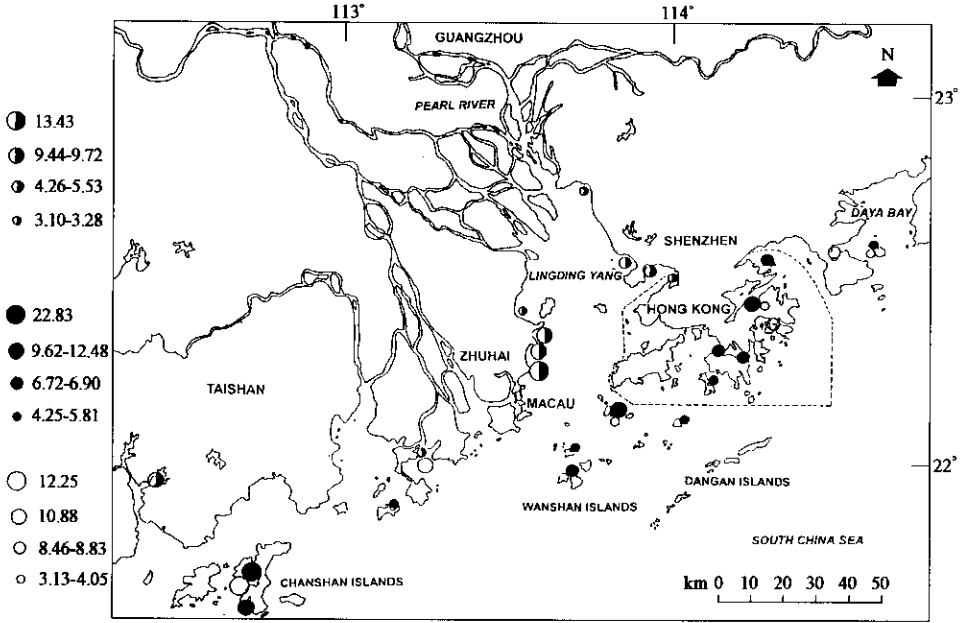


Fig.7 Concentrations of chromium($\mu\text{g/g}$ dry wt.) in mussels, oysters and clams from 25 sites in Pearl River Delta coastal waters, sizes of circles denote significant differences between sites. *Perna viridis* (filled circles), *Crassostrea rivularis* (half-filled circles) and *Ruditapes philippinarum* (open circles)

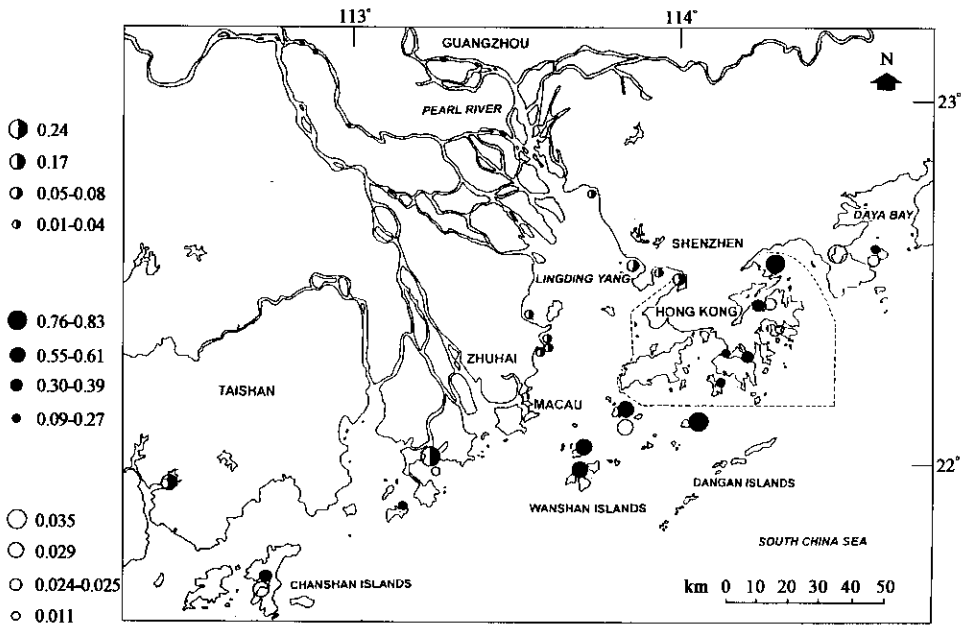


Fig.8 Concentrations of antimony($\mu\text{g/g}$ dry wt.) in mussels, oysters and clams from 25 sites in Pearl River Delta coastal waters, sizes of circles denote significant differences between sites. *Perna viridis* (filled circles), *Crassostrea rivularis* (half-filled circles) and *Ruditapes philippinarum* (open circles)

dry weight. The relatively high Sb concentrations were found in all three species from Kat O Chau and Wailingding Island, while Sb levels of those collected from Hong Kong waters and Daya Bay were low (Fig.

8). The Sb profile in mussels was also similar to that of Pb (Spearman's rank correlation coefficient $r = 0.5938$, $n = 13$, $p < 0.05$).

2.2.8 Tin

A wide range of Sn concentrations was obtained in mussels, the ratio of the highest to lowest value being 11.5-fold. Mussels in the estuarine zone exhibited higher Sn concentrations than those collected from both the eastern estuarine zone and western estuarine zone ($p < 0.01$; Fig.9). The Sn profile was also similar to that of Sb (Spearman's rank correlation coefficient $r = 0.6971$, $n = 13$, $p < 0.001$) in this species.

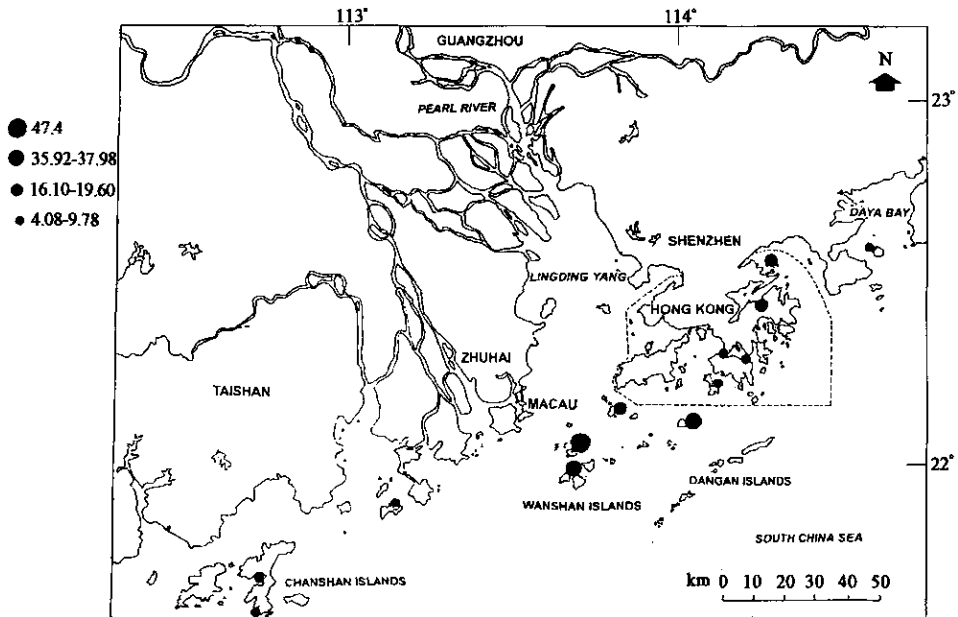


Fig.9 Concentrations of tin ($\mu\text{g/g}$ dry wt.) in mussels, oysters and clams from 25 sites in Pearl River Delta coastal waters, sizes of circles denote significant differences between sites. *Perna viridis* (filled circles), *Crassostrea rivularis* (half-filled circles) and *Ruditapes philippinarum* (open circles)

3 Discussion

3.1 Different capacity of metal accumulation by bivalve species

The analysis of metals in the three species (*Perna viridis*, *Crassostrea rivularis* and *Ruditapes philippinarum*) showed a difference in their capacity of metal accumulation. Each species exhibited different absolute amounts of metals along the Pearl River Delta coastal waters. It was noted that the concentrations of Cd, Cu and Zn in oysters were higher than those in mussels and clams. This could be explained by differences in their ability to accumulate metals. Similar metal contents have been observed in previous surveys of oysters (Wong, 1981; Lu, 1991; 1993; Jia, 1993), mussels (Phillips, 1985; 1988; Chan, 1988a; Cheung, 1992a) and clams (Cheung, 1992b). This suggests that oysters are different from mussels and clams with respect to their net uptake of Cd, Cu and Zn, i.e. the bioavailability of Cd, Cu and Zn of oysters is distinct from mussels and clams. A high Cd level was also found in oysters, *Crassostrea gigas* collected from Lau Fau Shen, Hong Kong (Cheung, 1992c), and it was suggested that Cd was rapidly accumulated by this oyster species, even though a low concentration of Cd was present in the surrounding water. Samples of oysters (*Crassostrea rivularis*) collected from Tangjiawan and Xiangzhou also contained high levels of Cd, Cu and Zn (Lu, 1993). Like other oyster species, such as *Crassostrea*

gigas (Wong, 1981) and *Saccostrea glomerata* (Phillips, 1988), *Crassostrea rivularis* also accumulated Zn to very high concentrations of 1485 to 7310 $\mu\text{g/g}$ dry wt.

Zn concentrations in all three species show a much narrower range (only 2 to 5-fold) than other metals. *Perna viridis* can partially regulate its soft tissue Zn concentration over a wide range of Zn bio-availability (Phillips, 1985). Laboratory evidence which demonstrated that *Perna viridis* maintains a relatively constant Zn tissue concentration over a wide range of external concentrations under otherwise constant conditions was reported by Chan (Chan, 1988b).

The accumulation of heavy metals by different species may be very different from their feeding strategy and habitat. All three species are filter-feeders and all have the capability of suspension feeding. *Crassostrea rivularis* lives mainly in turbulent seawaters in estuarine regions, and is commonly attached to rocks at the bottom. Mussels and clams live mainly in the intertidal zone. Zn uptake and bioaccumulation by zebra mussels were higher in high-turbidity water than in low-turbidity water (Klerks, 1997). During turbid condition, contaminated sediment particles in the estuarine zone become suspended in the water column and may affect metal-uptake by oysters (Eertman, 1995).

3.2 Public health concern

The Cd concentration in oysters collected from the western bank of Lingdingyang, and Cr concentration in all the three bivalve species from most of the sites exceeded the regulatory limits (maximum permitted concentrations according to the Public Health and Municipal Services Ordinance, Hong Kong) (Government of Hong Kong, 1987; Table 3).

Table 3 Cd and Cr in local shellfish and local regulatory (Public Health and Municipal Services Ordinance, Hong Kong) and the Provisional Tolerable Weekly Intake (PTWI) or maximum acceptable daily load levels recommended by FAO/WHO Expert Committee on Food Additive, $\mu\text{g/g}$ wet wt.

Species	Location	Local regulatory		The PTWI or maximum acceptable daily load, mg/(d·adult)	
		Hong Kong limit Cd: 2 $\mu\text{g/g}$ wet wt.	Hong Kong limit Cr: 1 $\mu\text{g/g}$ wet wt.	Recommended daily limit Cd: 0.07—0.08	Recommended limit, National Academy of Science, Cr: 0.05—0.20
<i>Perna viridis</i>	Lok Wo Sha	—	1.83 ± 0.32	—	0.046
	Tsim Sha Tsui	—	1.00 ± 0.13	—	0.025
	Wailingding Island	—	1.07 ± 0.22	—	0.027
	Guishan Island	—	1.45 ± 0.18	—	0.036
	Dongao Island	—	1.14 ± 0.28	—	0.029
	Dawanshan Island	—	1.44 ± 0.32	—	0.036
	Dawan	—	3.76 ± 0.85	—	0.094
	Datiewan	—	1.75 ± 0.21	—	0.044
<i>Crassostrea rivularis</i>	Xiashan	8.21 ± 0.26	—	0.21	—
	Tangjiawan	7.05 ± 0.79	1.51 ± 0.81	0.18	0.038
	Yingkeng	7.53 ± 0.97	1.40 ± 0.32	0.19	0.035
	Jiuzhouwan	6.90 ± 0.18	1.90 ± 0.44	0.17	0.048
	Nanshui Island	2.43 ± 0.16	—	0.06	—
	Shenjing	2.56 ± 0.32	1.26 ± 0.93	0.064	0.032
<i>Ruditapes philippinarum</i>	Lajia Island	—	1.81 ± 0.64	—	0.045
	Pukuwan	—	1.41 ± 0.40	—	0.035
	Nanshui Island	—	1.56 ± 0.72	—	0.039
	Dawan	—	1.47 ± 0.37	—	0.037

When compared with the provisional tolerable weekly intake (PTWI) (FAO/WHO, 1984), based on the consumption statistics provided by the Agriculture and Fisheries Department, Hong Kong Government of an individual that consumed 25g of shellfish daily, only Cd levels in oysters collected from the western

bank of Lingdingyang exceeded the human daily acceptable limits (Table 3). Caution should be taken if these bivalves are consumed in excess.

3.3 Sources of heavy metal pollution

According to the present results, considerable contamination of Cd, Cu, Zn and Sn contamination in Lingdingyang was evident. The western zone of the Pearl River Delta seemed to suffer from Cr, Ni and Cu contamination as judged by metal concentrations in the bivalves. In Victoria Harbor, contamination was mainly due to Cu and Pb.

Heavy metal contamination in the Pearl River Delta region may come from three resources: (1) heavy industrial discharges; (2) traffic activities in urban areas; and (3) metal mine operations and industries related to metallurgy distributed along the upper reaches of the Pearl River. The increasing number of establishments related to paint, enamel, stained glass, TV photoconductor and electroplating are the sources of Cd pollution in this region. Cu contamination mainly comes from smelters and printed circuit board industry. Zn is primarily used for galvanizing iron and steel products and in Zn-based alloys for diecastings. It is also used in large quantities for brass making, and in smaller amounts for batteries, photoengraving (Patter, 1989). In recent decades, Pb is mainly used for making batteries, antiknocking agent in gasoline and anticorrosive paints (Moore, 1984). Nickel is often used in steel making, nickel-cadmium batteries, alloys manufacturing and metal plating (Scott, 1989). Chromium contamination of the aquatic environment mainly comes from the effluent of leather tanning, photography and chromeplating industries. The industrial use of heavy metals in Pearl River Delta is intensive, but the effluent from these industries is seldom treated. Many highways have recently been constructed in the Pearl River Delta, and the automobile exhausts are likely to be another major source of Pb and associated metal pollution; urban storm run-off carries the Pb deposits could be discharged into marine waters. In addition, there are many non-ferrous metal mines (such as lead-zinc, copper, wolfram, tin and antimony) and metallurgical plants distributed along Pearl River.

3.4 Estimation of pollution status in the Pearl River Delta

According to the metal data of the bivalves collected from different locations of the Pearl River Delta, it is apparent that Lingdingyang, Huangmao Sea and Victoria Harbor are of most concern in this region.

3.4.1 Lingdingyang

The Pearl River Delta has eight openings through which the Pearl River waters discharge into South China Sea (Fig. 1). Four seaports (Humen, Jiaomen, Hongqimen and Henmen) which receive water discharges from North River, East River, Pearl River and West River, are located at Lingdingyang, and contributed to 51.6% of the total catchment and runoffs of the Pearl River discharges. There are four other openings (Modaomen, Jitimen, Hutiaomen and Yamen) through which the West River and Tang Jiang waters discharge into Modaomen Shallow Sea Bay and Huangmao Sea (Tang, 1983). More than 170 billion m^3 of freshwater empties into the outer sea through the Lingdingyang annually (Chen, 1992).

3.4.2 North River

The industrial effluents discharged into North River from Shaoguang are about 500 million m^3/a , including Cd 1.838 m^3 , Cr 1.878 m^3 and Pb 24.309 m^3 (Lands Department of Guangdong Province, 1986). Many non-ferrous metal mines and metallurgical plants are distributed along the North River (Fig. 10). The Pb/Zn mine in Fangkuo is the second biggest mining industrial base in China, about 150000t of Pb and 30000t of Zn are produced annually. The Cu mine in Dabaoshan is also one of the biggest mines in Guangdong Province. Cadmium is also found in Pb-Zn and Cu minerals, and metallurgy related industries. The Dabu Sn Mine and Meihua Sb Mine are also located in Shaoguang. Although the mining and industrial sources are some distance away from the Pearl River estuary, their contributions towards the overall metal pollution problem in the Pearl River Delta should not be overlooked.

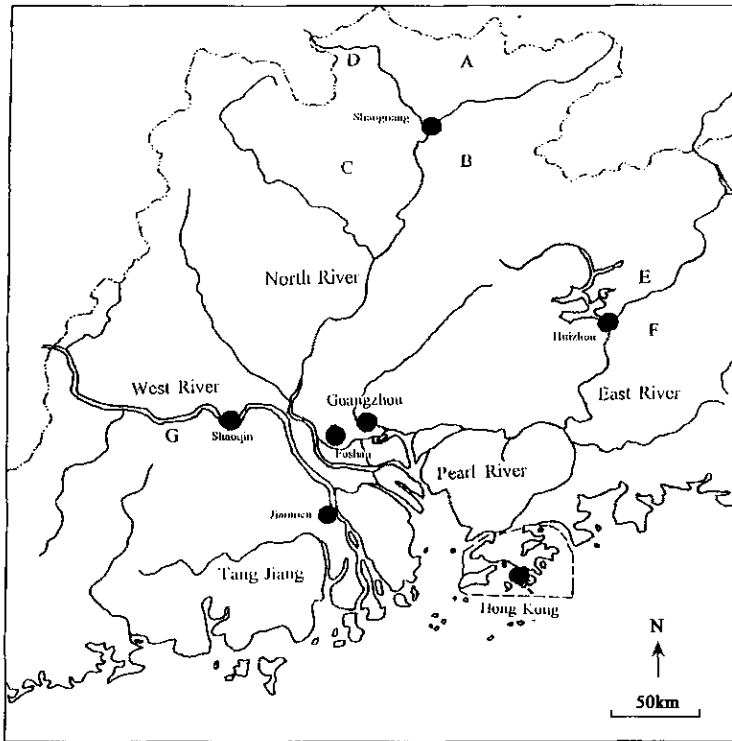


Fig.10 Map showing the Guangdong Province and the locations of the metal mines and metallurgical plants

A. Fankou Lead-Zinc Mine; B. Dabaoshan Copper Mine; C. Dabu Tin Mine; D. Meihua Antimony Mine; E. Guyun Tin Mine; F. Baoshan Steelworks; G. Jinziwo Tin Mine

3.4.3 East River

The discharge volume of industrial effluents from Huizhou is about 3 million m^3/a (The Lands Department of Guangdong Province, 1986), which empties into Lingdingyang by Humen. A Sn mine (Guyun Sn Mine) and a steelwork (Baoshan Steelworks) are also located along the East River.

3.4.4 Pearl River

Guangzhou is one of the most densely populated cities (3.67 million people according to The Planned Committee of Guangzhou and The Lands Planned Office of Guangzhou, 1994) in the region where many factories and industries are located. The annual discharge of industrial effluents into the Pearl River system is about 425 million m^3 , including Cd 0.4025 m^3 , Cr 42.5703 m^3 and Pb 1.6808 m^3 (The Lands Department of Guangdong Province, 1986).

It is likely that in an industrialized estuary such as the Lingdingyang with many urban communities on its banks, that a multiplicity of diffuse and low concentration direct sources may exist. This will tend to confuse any potential source-occurrence matches between homologous profiles. However, high Cd, Cu, Zn and Sn concentrations in the three bivalve species found in this survey were consistent with major inputs of these metals in Lingdingyang. The fact that the cities of Guangzhou, Foshan, Zhongshan, Zhuhai, Macao, Dongguan, Shenzhen and Hong Kong, which support more than 15 million people (Chen, 1994), are located around the western and eastern banks of Lingdingyang. Annually, about 99.68 m^3 of Cd, 704.90 m^3 of Cu and 10304.80 m^3 of Zn (Guangdong Provincial Coast Zone Resource Comprehensive Survey Office, 1986) are discharged into Lingdingyang through Humen, Jiaomen, Hongqili and Henmen.

Although these total annual loads of metals do not represent the amounts of metals actually reaching the Lingdingyang, as some metals are undoubtedly lost in transit to the bays by adsorption and absorption by freshwater biota, and precipitation onto sediments (Phillips, 1976), the effects of these metal discharge can be seen throughout the coastal zone from sites 17 to 20 (western bank of Lingdingyang) and 14 to 16 (Wanshan Islands situated at the mouth of Pearl River) where very high concentrations of Cd, Cu and Zn in oysters, mussels and clams are found. It is noted that the 4 seaports (Humen, Jiaomen, Hongqili and Henmen) are all situated at the western bank of Lingdingyang, and the probable reason why metal levels in oysters from this region were higher than those from the eastern bank of Lingdingyang; in addition, higher metal concentrations in bivalves were associated with the relatively turbulent waters (estuarine zone) containing high suspended solid contents (Chan, 1988a). There are many Sn mine distributing along the Pearl River, such as Jingziwou Sn Mine (West River), Guyun Sn Mine (East River) and Dabu Sn Mine (North River). Tin mining may be one of the major Sn pollution sources but organotin compounds have also been employed as antifouling agents on ships. With a broad economic hinterland, the estuary of the Pearl River is the most prosperous area in China's shipping. Many of the vessels entering the Pearl River estuarine zone are treated with these compounds.

3.4.5 Huangmao Sea

The West River and Tang Jiang receive industrial and domestic wastewaters from many medium-sized cities, which finally discharge into Huangmao Sea and Modaomen Shallow Sea Bay through four seaports (Modaomen, Jitimen, Hutiaomen and Yamen; Fig. 1). Industrial discharges mainly come from Shaoqin (about 7.5 million m³/a, including Cd 0.01, Cr 5.36 and Pb 0.07 m³), and Jianmen (about 162 million m³/a, including Cd 0.0681, Cr 61.95 and Pb 3.4435 m³) (Lands Department of Guangdong Province, 1986). Huangmao Sea and Modaomen Shallow Sea Bay receive about 1148.90 m³ of Cu per annum (Guangdong Provincial Coast Zone Resource Comprehensive Survey Office, 1986) through Modaomen, Jitimen, Hutiaomen and Yamen. Many electroplating factories are concentrated along the West River and Tang Jiang so that it is not surprised that relatively high Ni, Cr and Cu concentrations were obtained in the three species collected from the western estuarine zone. Nickel, Cr and Cu contaminations in the western estuarine zone have also been reported by Liu and Huang (Liu, 1984). Chromium contamination mainly comes from Jianmen, which contributes 43% of the total hexavalent chromium discharge in Guangdong Province (The Lands Department of Guangdong Province, 1986). Our results show that there were relatively high Ni and Cr bio-availability at sites 21 to 24 in the western estuarine zone and a "hot spot" for both elements at Nanshui Island (Jitimen) and Dawan. The strong correlation between site rankings indicates that the sources of bio-available Ni and Cr may be similar.

3.4.6 Victoria Harbor

The eastern estuarine zone mainly consists of Hong Kong waters, which receive a heavy pollution load from over 6 million people and 2000 factories (Phillips, 1989). Victoria Harbor receives the majority of effluents generated from Hong Kong Island and Kowloon Peninsula. Relatively high concentrations of Cu (24.0 µg/g, dry wt.) and Pb (2.0 µg/g, dry wt.) in mussels were found in this survey. In fact, the observed metal levels were of a similar order of magnitude to those reported in Hong Kong earlier on (Chan, 1988a). Cu is an essential element in the mussel as a component of blood proteins and is known to have a typical kinetics in this organism (Scott, 1972). Although Phillips (Phillips, 1976) suggested that mussels should not be used as an indicator of Cu pollution because factors, such as different salinity-temperature regimes, affect uptake regimes. Victoria Harbor is contaminated by Cu, and the major source of Cu includes Kwun Tong and eastern Hong Kong Island (Phillips, 1981; Chan, 1988a). The printed circuit board industry contributes most of the Cu pollution in Hong Kong waters (Environmental Protection Department, 1991). Vehicle emissions may be the main cause of Pb pollution. Areas surrounding Victoria

Harbor are characterized by the congestion of heavy traffic, and Pb compounds from vehicle emissions are deposited in nearby areas, and carried into the sea by urban surface run-off (Chan, 1987). Our data shows that there were low concentrations of Cd in mussels and clams from different sites of Hong Kong waters. Cadmium concentrations were relatively low (around 1 $\mu\text{g/g}$, dry wt.) even in mussels collected from some "hot spots". The results are in line with the comments made by Chan (Chan, 1988a), that there is no major source of Cd pollution in Hong Kong waters. The tissue levels of Sb in the three species collected from different sites are very low. Antimony content is likely to originate from natural sources although there is a small antimony mine (Meihua Sb Mine) located in Shaoguang (North River), some distance away.

4 Conclusions

The concentrations of Cd, Cu and Zn in oysters were higher than those in mussels and clams because of differences in their capacity to accumulate metals. Accumulation of heavy metals by different species may be very different from their feeding strategy and habitat. During turbid condition, metals-contaminated sediment particles become suspended in the water column and may affect filter feeding bivalves, especially oysters which live in the estuarine zone.

Although Cd and Cr concentrations in the three bivalve species exceed the local regulatory levels, only Cd levels of oysters collected from the western bank of Lingdingyang waters are higher than both the human daily acceptable limits and the local regulatory levels; caution should be executed in consuming a large numbers of oysters for extended periods.

In general, Cd, Cu, Zn and Sn concentrations in the three species collected from the estuarine zone were higher than those from the western estuarine zone and eastern estuarine zone. Relatively higher Cr, Ni and Cu concentrations were found in the three species collected from the western estuarine zone. In Victoria Harbor, high Cu and Pb concentrations were found in these bivalve species.

Based on the metal concentrations in the bivalves, considerable Cd, Cu, Zn and Sn contamination and Cr, Ni and Cu contamination were found in Lingdingyang and western estuarine zone respectively.

Comparison of site ranking showed a significant correlation between Ni and Cr concentrations in the three bivalves. The spatial distribution of Cr concentrations was similar to that of Ni in each bivalve species. Significant correlations also occurred between Cd and Cu; Cd and Zn; Sb and Sn. These metal pairs might share a common source in the Pearl River Delta.

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