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Heavy metal and Pb isotopic compositions of aquatic organisms in the Pearl River Estuary, South China

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Relative high concentrations of Cd were found in crab, shrimp and shellfish samples while high concentration of Pb was found in fish, particularly from the anthropogenic inputs.

Abstract

The accumulation of trace metals in aquatic organisms may lead to serious health problems through the food chain. The present research project aims to study the accumulation and potential sources of trace metals in aquatic organisms of the Pearl River Estuary (PRE). Four groups of aquatic organisms, including fish, crab, shrimp, and shellfish, were collected in the PRE for trace metal and Pb isotopic analyses. The trace metal concentrations in the aquatic organism samples ranged from 0.01 to 2.10 mg/kg Cd, 0.02 to 4.33 mg/kg Co, 0.08 to 4.27 mg/kg Cr, 0.15 to 77.8 mg/kg Cu, 0.17 to 31.0 mg/kg Ni, 0.04 to 30.7 mg/kg Pb, and 8.78 to 86.3 mg/kg Zn (wet weight). High concentrations of Cd were found in crab, shrimp and shellfish samples, while high concentration of Pb was found in fish. In comparison with the baseline reference values in other parts of the world, fish in the PRE had the highest elevated trace metals. The results of Pb isotopic compositions indicated that the bioaccumulation of Pb in fish come from a wide variety of food sources and/or exposure pathways, particularly the anthropogenic inputs.

Keywords: Heavy metals; Pb isotope; Aquatic organism (fish); Pearl River Estuary; China

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1. Introduction

The mixed regime of the Pearl River Estuary (PRE), with fresh and oceanic water, provides a suitable habitat for a wide variety of aquatic organisms (Chen, 1995; Wang et al., 1995). However, rapid economic development in the Pearl River Delta (PRD) region in the last few decades has led to the excessive discharge of pollutants into the PRE (Li et al., 1997). Hence, great concern has arisen in recent years over environmental pollution in this coastal region. Elevated concentrations of Cu, Pb, and Zn in the sediments of the PRE have been found (Chen and Zhou, 1992; Zheng, 1992; Li et al., 2000a, 2000b, 2001; Liu et al., 2003). Trace metal contamination of the PRE may have a significant impact on aquatic organisms, disturbing the area's delicate ecological balance and potentially contaminating the marine food chain. Trace metal analysis of aquatic organisms from the PRE can provide important information on the degree of environmental contamination, and potential impact of seafood consumption. In addition, the Pb isotopic compositions of aquatic organisms may further assist the identification of possible sources of contamination and biological pathways.

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Aquatic organisms accumulate trace metals from various sources in the environment. The possible sources of trace metals include sediments (Labonne et al., 2001; Goodwin et al., 2003), soil erosion and runoff (Gelinas and Schmit, 1997), air depositions of dust and aerosol (Gelinas and Schmit, 1997; Labonne et al., 2001), discharges of wastewater (Labonne et al., 2001; Goodwin et al., 2003), and so forth (Bryan, 1979; Blackmore et al., 1998; Hoven et al., 1999; Goodwin et al., 2003). The accumulation of trace metals in aquatic organisms can pose a long-term burden on biogeochemical cycling in the ecosphere. Once trace metals enter the food chain, they may accumulate to dangerous levels and be harmful to human health (Manahan, 2000).

Stable Pb isotopic studies have been commonly applied to assess the sources of Pb in various ecosystems, including sediments (Farmer et al., 1996; Ritson et al., 1999; Liu et al., 2003), soils (Sugden et al., 1993; Semlali et al., 2001; Wong et al., 2002), suspended matters (Hinrichs et al., 2002), and atmospheric depositions (Bollhöfer and Rosman, 2000, 2001; Wong et al., 2003). However, only a few studies have focused on stable Pb isotopes in biological samples to trace the anthropogenic origins of Pb (Kurkjian and Flegal, 2003). Previous studies have proven that the Pb isotopic composition of biological samples can provide a fingerprint for sources of Pb (Rabinowitz, 1995; Spencer et al., 2000; Manahan, 2000; Kurkjian and Flegal, 2003).

Aquatic organisms in the PRE are one of the most important sources of seafood for people in the Pearl River Delta (PRD) region (Fu et al., 1995). Extensive studies on the ecosystem in the PRE, such as on sediments (Li et al., 2000a, 2000b, 2001) and water (Ho and Hui, 2001), have recently been carried out. However, only a few of the studies have focused on the aquatic organisms in the PRE (Chen, 1995; Fu et al., 1995), and none on the potential pathway of metal contaminants in this region.

Studies have recently been conducted on the stable Pb isotopic compositions of various ecosystems in the PRD region, such as agricultural soils (Wong et al., 2002), air depositions (Wong et al., 2003), and sediments (Liu et al., 2003; Ip et al., 2004). These environmental media have distinctive ranges of stable Pb isotopic ratios. According to these studies, automobile emissions and industrial discharges are the major sources of anthropogenic Pb in the PRD region. These research projects have provided an important database on Pb isotopic signatures in the PRD region. This database may help in efforts to evaluate the accumulation and biological pathways of heavy metals in aquatic organisms in the PRE. Trace metal accumulation in aquatic organisms depended on several factors, including (i) the environmental concentrations of metals in water and sediments; (ii) the species of organisms; (iii) body size and age of organisms. Different concentrations of trace metals can also be found in different organs in the same biological sample. However, this study mainly focused on the general trace metal burden in aquatic organisms, and the potential major pathways for metal contaminants in the estuarine environment. The common species of seafood in the PRE were collected in the present study. The whole meat tissue of the samples was used in this study in order to examine the general situation of trace metal contamination of aquatic organisms in the PRE. Therefore, the present study aims; (1) to assess the accumulation of trace metals in several groups of common aquatic organisms in the PRE, and (2) to identify possible Pb sources for aquatic organisms using the Pb isotopic signature in aquatic organisms and various environmental media in the region.

2. Materials and methods

A total of 58 samples of aquatic organisms were collected at seven sampling sites in the PRE in April 2003 with the assistance of the South China Sea Institute of Oceanology under the Chinese Academy of Sciences. The seven sampling locations are depicted in Fig. 1. The samples include four common estuarine groups: fish, crab, shrimp, and shellfish. Sixteen species of fish, one species of crab, two species of shrimp, and three species of shellfish were sampled in the present study. The details of the sampled species are summarized in Table 1.

All samples of aquatic organisms were individually stored in polyethylene bags at 4–6 °C immediately after collection prior to the laboratory analysis. After washing with tap water and distilled and deionised water (DIW), the samples were stored frozen at −20 °C prior to freeze-drying. The samples were freeze-dried at −45 °C for 3 days. Whole tissues of the samples were grounded homogeneously. All of the freeze-dried and grounded samples were stored in a dessicator prior to undergoing further chemical analyses.

The samples of aquatic organisms were digested using strong acid digestion according to the method in USEPA (1999) with some modifications. About 0.500 g of grounded aquatic organism samples were weighed and placed in Pyrex test tubes pre-cleaned with high purity nitric acid. The nitric acid used in the present study was in high purity grade, which contained usually less than 0.1 ppb trace metals (except Al, Ca, Mg and Zn in less than 0.5 ppb). High purity nitric acid (5 ml) was added to each tube, and the tubes were left overnight to be slowly digested. Another 3 ml of high purity nitric acid and 1 ml of perchloric acid were added to each tube the next day. Each mixture was gently shaken using a vortex and then placed in an aluminium heating block (FOSS TECATOR 2000). The heating process for the digestion was set up according to the following temperature scheme: 50 °C for 8 h, 75 °C for 2 h,

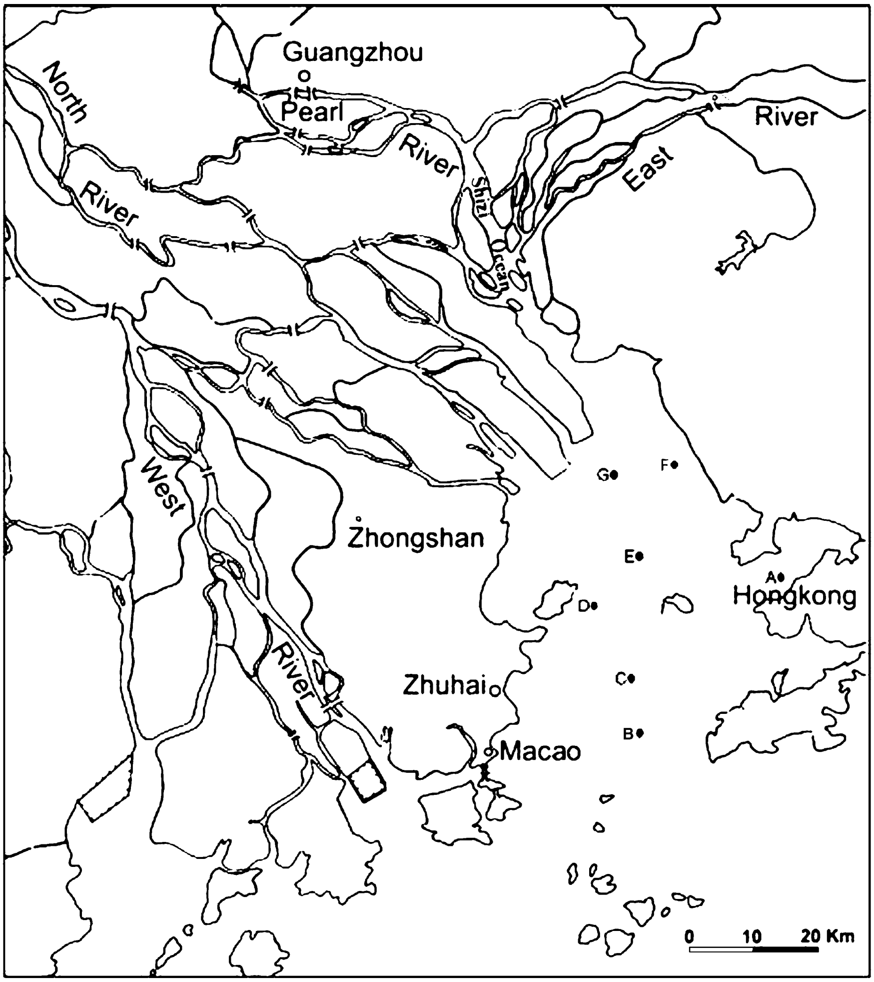

Fig. 1. The location of sampling sites in the Pearl River Estuary (PRE).

100 °C for 2 h, 125 °C for 3 h, and 150 °C until complete dryness was achieved. After the test tubes were removed from the heating block and cooled down, 10 ml of 5% high purity nitric acid were added to the residue. The mixture was then heated at 70 °C for 1 h. The heated mixture was shaken gently and poured into polyethylene tubes. The tubes were centrifuged with centrifugal force around 150 N for 10 min prior to determining the concentration of metals. The concentrations of Al, Ca, Cu, Fe, Mg, Mn, and Zn were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES; *Perkin Elmer Optima, 3300DV*) (Li and Thornton, 1992; USEPA, 1999; Li et al., 2001). Due to the low concentrations of Cd, Co, Cr, Ni, Pb, and V, the concentrations of these elements were determined by inductively coupled plasma-mass spectrometry (ICP-MS; *Perkin Elmer Sciex Elan 6100 DRC^{plus}*). Selected samples of aquatic organisms were also analysed for Pb isotopic composition by ICP-MS. All analytical solutions for Pb isotopic composition were diluted to about 30 μg/L Pb using 5% high purity nitric acid.

The quality controls for the strong acid digestion method included reagent blanks, duplicate samples, and standard reference materials (NIST SRM 1566a and DORM-2). The QA/QC results showed no sign of contamination in all the analysis. The recovery rates for most of the trace metals in the reference materials were around 80–115%, except for Al and Ni (62% and 147%, respectively). To detect whether there was any contamination and drift during the measurements, quality control standards were used during the determination of elemental concentration and isotopic compositions at every 10 samples for the ICP-AES analysis and every 4 samples for the ICP-MS analysis. For the Pb isotopic analysis, an international standard reference material (NIST SRM 981, common lead) was used for calibration and analytical control. The relative standard deviation of each sample measurement was <0.3%. The average measured ratios of ^{204}Pb/^{207}Pb, ^{206}Pb/^{207}Pb, and ^{208}Pb/^{207}Pb of the SRM 981 were 0.0645 ± 0.0003, 1.0931 ± 0.0023, and 2.3718 ± 0.0045, respectively. These values were very

Table 1
Aquatic organisms analysed in this study

Groups of aquatic organisms	Common name	Scientific name of spices	No. of samples	Sampling locations	Sample ID
Fish	Chinese herring	*Iisha elongata*	2	A, F	AY1, FY3
	flat head fish	*Platycephalus indicus*	3	A, F, G	AY2, FY5, GY7
	ray-finned fish	*Odontamblyopus rubicundus*	2	A, C	AY4, CY7
	ponyfish	*Leiognathus bin*	5	A, B, E, F, G	AY5, BY5, EY2, FY4, GY6
	white flower croaker	*Nibea albiflora*	1	B	BY2
	common mullet	*Mugil cephalus*	3	B, C, F	BY3, CY3, FY7
	zebra sole	*Zebrias zebra*	1	B	BY4
	large scaled tongue sole	*Cynoglossus macrolepidotus*	2	C, D	CY2, DY8
	croaker	*Collichthys lucidus*	5	C, D, E, F, G	CY5, DY2, EY1, FY2, GY1
	golden sardine	*Sardinella aurita*	1	C	CY6
	white sea bass	*Lates calcarifer*	1	D	DY3
	hilsa herring	*Macrura reeuesii*	1	D	DY4
	–[a]	*Collicchthys gunther*	2	D, F	DY7, FY6
	sea horse	*Syngnathus linnaeus*	1	F	FY1
	spinefoot	*Siganus oramin*	1	G	GY8
	–[a]	*Ambassidae, siganus forskal*	1	G	GY4
	–[a]	–[b]	3	C, D, G	CY4, DY6, GY2
Shrimp	Mantis shrimp	*Dictyosquilla foveolata*	7	A–G	AX1, BX2, CX1, DX2, EX1, FX1, GX1
	sand prawn	*Metapenaeus ensis*	6	A–F	AX2, BX1, CX2, DX1, EX2, FX2
Crab	redspot swimming crab	*Portunus pelagicus*	7	A–G	AP1, BP1, CP1, DP1, EP1, FP1, GP1
Shellfish	–[a]	*Scapharca subcrenata*	1	A	AB1
	–[a]	*Turritella bacillum keener*	1	B	BB2
	–[a]	*Murex ttrapa*	1	B	BB4

[a] No common name available.
[b] Unidentified fish species.

close to the certified standard values (0.0646, 1.0933. and 2.3704, respectively).

3. Results and discussion

3.1. Trace metal concentrations of the aquatic organisms

The trace metal concentrations of the fish, crab, shrimp, and shellfish collected in the PRE are summarized in Table 2. A comparison between the data of the present study and those of previous studies conducted in Hong Kong (Tam and Mok, 1991) and China (Wei et al., 2002) is presented in Table 3, together with the guidelines for assessing the aquatic organisms in China and the baseline reference values in Norway (Green and Knutzen, 2003). The mean and median concentrations of Cd and Cu in crab, shrimp, and shellfish; and Cr in shellfish exceeded the threshold values recommended by China's assessment guidelines, suggesting that the concentrations of these trace metals in these species from the PRE were elevated. In addition, the mean Pb concentrations in fish also exceeded the China's assessment guidelines, while the median concentration of Pb in fish was below the guidelines. This indicated that a small number of fish samples accumulated high concentrations of Pb in their bodies. The highest concentration of Pb was found in fish, *Siganus oramin* (30.7 mg/kg wet weight). This value was about 30 times higher than the recommended values in the Food Assessment Guidelines of China. According to the present results, the concentrations of Pb in 20% fish samples were above the guideline level. Furthermore, the concentrations of Pb in fish were considerably higher than in other organisms. This group of aquatic organisms needs to pay special attention for their Pb accumulation. Although the mean concentrations of other metals in these species were below the guideline values, some samples also had high concentrations of one or more metals due to the wide ranges of metal concentrations in these aquatic organisms.

Table 2
Summary of trace metal concentrations (mg/kg, wet weight) in different sub-groups of aquatic organisms collected in the PRE

Metals	Concentrations (mg/kg)	Fish ($n = 35$)	Crab ($n = 7$)	Shrimp ($n = 13$)	Shellfish ($n = 3$)
Cd	Mean ± standard deviation (S.D.)	0.0409 ± 0.0289	0.795 ± 0.506	0.835 ± 0.637	0.725 ± 0.305
	Median	0.0306	0.871	0.851	0.791
	Median of absolute deviations (mad)	0.0165	0.322	0.516	0.267
	Range	0.01–0.13	0.2–1.61	0.04–2.10	0.39–0.99
Co	Mean ± S.D.	0.100 ± 0.101	0.128 ± 0.065	0.0775 ± 0.0372	1.51 ± 2.44
	Median	0.0595	0.132	0.0583	0.105
	mad	0.0546	0.0299	0.0300	1.42
	Range	0.02–0.48	0.05–0.26	0.03–0.53	0.09–4.33
Cr	Mean ± S.D.	0.667 ± 0.756	0.411 ± 0.065	0.201 ± 0.131	1.17 ± 0.86
	Median	0.381	0.403	0.152	1.07
	mad	0.347	0.146	0.07512	0.809
	Range	0.11–4.27	0.14–0.76	0.08–0.53	0.37–2.08
Cu	Mean ± S.D.	1.81 ± 1.74	26.1 ± 24.4	28.0 ± 11.0	28.7 ± 42.6
	Median	0.381	24.4	27.8	6.08
	mad	1.01	6.89	3.38	26.4
	Range	0.15–7.55	16.3–41.8	15.2–56.2	2.28–77.8
Ni	Mean ± S.D.	0.653 ± 0.550	0.616 ± 0.359	0.560 ± 0.220	10.9 ± 17.4
	Median	0.428	0.529	0.493	0.890
	mad	0.309	0.124	0.182	10.1
	Range	0.17–2.08	0.26–1.39	0.26–0.99	0.73–31.0
Pb	Mean ± S.D.	2.20 ± 6.02	0.177 ± 0.062	0.135 ± 0.064	0.424 ± 0.234
	Median	0.405	0.176	0.103	0.298
	mad	1.86	0.0299	0.0525	0.144
	Range	0.09–30.7	0.09–0.29	0.04–0.23	0.28–0.69
V	Mean ± S.D.	0.616 ± 0.451	0.315 ± 0.089	0.252 ± 0.102	0.967 ± 1.44
	Median	0.428	0.289	0.268	0.158
	mad	0.308	0.0631	0.0821	0.852
	Range	0.15–1.93	0.17–0.42	0.07–0.41	0.12–2.63
Zn	Mean ± S.D.	18.4 ± 6.25	16.3 ± 2.92	15.8 ± 2.81	41.2 ± 39.0
	Median	18.8	17.7	16.0	19.1
	mad	4.53	1.68	1.85	23.0
	Range	8.78–30.26	12.2–19.9	11.0–20.0	18.3–86.3

Table 3
Trace element concentrations in some aquatic organisms (mg/kg, wet weight) in other regions in China, reference concentrations from Norway, and the assessment guidelines in China

Commodity (city/country)	Cd	Cr	Cu	Ni	Pb	Zn
Shellfish (Hong Kong)[a]	0.49	0.21	–	–	0.254	–
Shellfish (Yangtze River Estuary), 1982–1983[b]	0.42	–	14.9	–	2.08	37.8
Crab (Hong Kong)[a]	0.58	<0.05	–	–	0.04	–
Shrimp (Hong Kong)[a]	0.12	<0.05	–	–	0.08	–
Shrimp (Zhanjiang Harbour Bay), 1990–1994[b]	0.04	–	1.56	0.11	0.42	13.48
Shrimp (PRE), 2000[b]	0.04	0.15	1.28	0.27	0.50	2.60
Marine fish (Hong Kong)[a]	<0.02	<0.05	–	–	0.03	–
Fresh water fish (Hong Kong)[a]	<0.02	<0.05	–	–	0.03	–
Fish (Yangtze River Estuary), 1982–1983[b]	0.14	–	2.29	–	1.68	18.3
Fish (Yellow River Estuary), 1984[b]	0.13	–	0.31	–	0.81	12.0
Fish (Zhanjiang Harbour Bay), 1990–1994[b]	0.08	–	0.68	0.09	0.67	13.1
Fish (Guangdong Coastal waters), 1986–1988[b]	0.03	–	0.77	0.14	0.22	6.26
Fish (PRE), 2000[b]	0.03	0.16	0.18	0.28	0.51	1.01
Reference values						
Fish, *Cod* (Norway), 2003[c] ($n = 1184$)	0.0001	–	0.0075	–	0.00003	0.024
Shellfish, *Blue Mussels* (Norway), 2003[c] ($n = 291$)	0.25	–	1.30	–	0.26	20.29
Assessment guidelines						
Assessment standard in China[b]	0.05	1.00	5.00	–	1.00	–
Action level for fish Canada[d]	–	–	–	–	0.5	–

[a] Tam and Mok (1991).
[b] Wei et al. (2002).
[c] Green and Knutzen (2003).
[d] Canadian Food Inspection Agency (2004).

Among the four groups of aquatic organisms, the concentrations of Cd in shrimp were the highest. The highest concentration of Cd was 2.10 mg/kg wet weight in shrimp, *Metapenaeus ensis*. This value was more than 40 times higher than the assessment standard of China. The concentrations of Cd were also noticeably elevated in both crab and shellfish. However, the concentration of Cd was significantly lower in fish in comparison with other species. Among the species studied, the highest concentrations of Co, Cr, Cu, Ni, V, and Zn were observed in shellfish. The concentrations of these elements in shellfish were 3–20 times higher than that in other species. These findings suggest that shellfish could accumulate trace metals more efficiently from water and sediment.

In general, the average concentrations of trace metals in aquatic organisms in the PRE were higher than the reported values in other parts of China (see Tables 2 and 3). In addition, the concentrations of trace metals in the present study were higher than those in previous studies of the same region. According to Wei et al. (2002), the concentrations of Cd, Cr, Cu, Ni, Pb, and Zn in fish collected in 2000 were 0.03, 0.16, 0.18, 0.28, 0.51, and 1.01 mg/kg, respectively; while those in the fish samples in the present study were 0.0409 ± 0.0289, 0.667 ± 0.756, 1.81 ± 1.74, 0.653 ± 0.550, 2.202 ± 6.02, and 18.4 ± 6.25 mg/kg, respectively. These figures represent increases of 1.4–18 times between the two studies. The results might indicate that concentrations of trace metals in fish in the PRE increased in the last few years.

The concentrations of trace metals in fish from the PRE were generally over 200 times higher than the reference values in Norway (see Tables 2 and 3). The concentrations of Cd, Cu, Pb, and Zn in shellfish in the PRE were generally enriched. The enrichment factors for fish in the PRE were 409, 240, 73 333, and 780 for Cd, Cu, Pb, and Zn, respectively. For shellfish in the PRE, the enrichment factors of the mean Cd, Cu, Pb, and Zn concentrations were 2.9, 22, 1.6, and 2.0, respectively.

At low concentrations, Zn and Cu are essential elements for the growth of organisms (WHO, 1996). They are normally the most abundant trace elements in aquatic organisms (Parsons, 1998; Chien et al., 2002; Wei et al., 2002; Usero et al., 2004). At low concentrations, Co, Ni, and V are probably elements essential to organisms. Cd and Pb are non-essential elements and are toxic even at low concentrations. Cd is usually present in low concentrations in different environmental media; for example, in sediments (Li et al., 2000a, 2000b, 2001; Lin et al., 2002), soils (Wong et al., 2002), and atmospheric depositions (Wong et al., 2003).

The four groups of aquatic organisms collected in the PRE showed quite different patterns of metal accumulation, although the metal concentrations of the aquatic organisms showed large variations within the same group. Crab and shrimp showed similar ranges of metal concentrations and relative orders of mean trace metal concentrations: Cu > Zn > Cd > Ni > Cr > V > Pb > Co for crab and Cu > Zn > Cd > Ni > V > Cr > Pb > Co for shrimp. This exemplified the common feeding habits and living behaviours of these two aquatic organisms. However, fish and shellfish had different patterns of trace metal accumulation. The accumulations of trace metals in fish were: Zn > Pb > Cu > Cr > Ni > V > Co > Cd, while those in shellfish were: Zn > Ni > Co > Cu > Cr > Cd > Pb. The accumulation of Pb in fish was particularly significant in these samples.

The different feeding habits and living modes of shellfish, shrimp, crab, and fish as well as the different aquatic geochemistry of the trace metals significantly affect the intake, bioassimilation, and subsequent bioaccumulation of trace metals in these organisms. Although the trace metal concentrations in different species of aquatic organisms in the same group were in a wide range of variations, the aquatic organisms in different groups also showed significant metal accumulation patterns (see Table 2). This demonstrated that aquatic organisms in different groups had different accumulation mechanisms for trace metals. Shellfish is a filter feeder and mainly filters fine suspended matter as its source of food. Furthermore, shellfish are benthic organisms, and are usually relatively immobile or sessile. Based on the feeding mode and living habits of shellfish, the trace metal content of shellfish most likely reflects the quality of the water and sediment in the aquatic environment, including the accumulation of both dissolved and suspended trace metals. The significantly elevated concentrations of Co, Cr, Cu, Ni, V, and Zn found in shellfish likely resulted from the fact that their primary source of food is suspended matter, in particular, suspended fine sediment near or on the sea floor. It might also be partly attributed to the solubility of these trace metals in an aquatic environment. This is because the ratio of the dissolved metal concentration to the total metal concentration (dissolved/total) generally increases in the following order: Pb < Cd < Cr < Ni < Cu < Zn (Foster and Charlesworth, 1996). Hence, in an aquatic environment, Cr, Ni, Cu, and Zn are more soluble and bioavailable than Pb and Cd.

Similar to shellfish, crab and shrimp are also benthic organisms that generally live on or near the sea floor and are capable of travelling in distance. As scavengers, crab and shrimp have similar feeding patterns. They tend to feed on detritus and, sometimes, small crustaceans and fish on or near the sea floor as well as on floating materials. Among the different aquatic organisms, fish are probably the most mobile and capable of travelling a long distance. However, the fish samples collected in this study mainly live near the sea floor, and with short travelling distance (e.g. *Collichthys lucidus*, *Platycephalus indicus*, *Nibea albiflora*, *Zebrias zebra*, and *Cynoglossus macrolepidotus*). Furthermore, fish is also on a high trophic level in the food chain as compared to other three types of organisms; hence, their diet is probably the most diverse of the species studied here.

Moreover, the comparatively low bioaccumulation of Pb in shellfish, crab, and shrimp showed that the bioassimilation and bioavailability of Pb is limited in the aquatic environment, especially near the sea floor. Pb generally becomes immobile or bound to organic complexes shortly after its deposition in water. Based on the Pb concentrations of the different aquatic organisms (see Table 2), the direct intake and subsequent bioassimilation of Pb by shellfish and even crustaceans, in the form of suspended matter and detritus near or on the sea floor, might be of secondary importance in the PRE. The results suggest that the primary importance of the bioaccumulation of Pb in aquatic organisms could be bioassimilation in the food chain and/or exposure in water. As mentioned previously, fish is situated at a higher trophic level in comparison with other three groups of organisms. Not only are their sources of food most diverse, they also require a large quantity of food compared to other organisms. These factors could lead to the bioassimilation and bioaccumulation of Pb in fish over time (Manahan, 2000; Jacobson et al., 2000). The particularly high Pb concentrations in fish might be due to the bioaccumulation of Pb in some species of fish, such as *S. oramin* (spinefoot), *C. lucidus* (croaker), and *C. macrolepidotus* (large scaled tongue sole) found in the present study. The major food sources of the abovementioned species are small shrimps and fish. A number of studies also revealed that fish have a tendency to accumulate trace metals at high levels (Allen, 1994; Karadede and Unlu, 2000).

3.2. Stable Pb isotope compositions in aquatic organisms

The means and ranges of the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios in the aquatic organisms collected from the PRE are presented in Table 4. The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of the aquatic organisms ranged from 1.161 to 1.193 and 2.438 to 2.494, respectively. The Pb accumulated in aquatic organisms can result from Pb derived from natural processes of weathering, erosion, and transport of bedrocks, as well as from a range of anthropogenic activities in the aquatic environment. According to Zhu (1995), the Pb isotopic ratios of the background geological materials in the PRD region ranged from 1.183 to 1.199 for $^{206}Pb/^{207}Pb$ and 2.468 to 2.497 for $^{208}Pb/^{207}Pb$ ratios. From the present results, a large proportion of the $^{206}Pb/^{207}Pb$ ratios of the aquatic organisms were lower than those of the geological materials. The mean $^{206}Pb/^{207}Pb$ ratios of the aquatic organisms descended in the following order: shellfish > crab > shrimp > fish. This is possibly related to their habits, food sources, and trophic level.

Aquatic organisms are exposed to at least four sources of trace metals in an aquatic system, including water, sediments, plankton, and detritus in the water

Table 4
The means (±standard derivations) and ranges of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios in the aquatic organisms collected from the PRE

Commodity	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
Fish ($n = 35$)		
Mean	1.1789 ± 0.0017	2.4662 ± 0.0123
Range	1.1610–1.1933	2.4383–2.4889
Shrimp ($n = 13$)		
Mean	1.1796 ± 0.0022	2.4842 ± 0.0066
Range	1.1715–1.1908	2.4754–2.4942
Crab ($n = 7$)		
Mean	1.1808 ± 0.0021	2.4766 ± 0.0049
Range	1.1730–1.1875	2.4691–2.4861
Shellfish ($n = 3$)		
Mean	1.1826 ± 0.0034	2.4748 ± 0.0111
Range	1.1791–1.1894	2.4645–2.4865

columns (Kneip and Lauer, 1973; Stokes, 1979; Hare, 1992; Roy and Hare, 1999; Barata et al., 2002). In order to identify the potential pathways of the anthropogenic Pb that had accumulated in the aquatic organisms, the relationship between the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of the selected aquatic organisms in the PRE and the major sources for the input of Pb in the PRD are shown in Fig. 2. The possible sources of Pb include surface sediments in the PRE (Ip et al., 2004), atmospheric deposits (Wong et al., 2003), natural soils (Wong et al., 2002), and some other known anthropogenic sources in the PRD (Zhu et al., 2001). The atmospheric deposition in the PRD was taken into account in the assessment because atmospheric deposition is one of the principal pathways of transport for anthropogenic Pb (Jickells, 1995; Neff, 2002; Reuer and Weiss, 2002). Therefore, the Pb isotopic signature of the atmospheric deposition was used to represent the anthropogenic Pb in the water columns. Lead is usually weakly associated with air particles and can be easily dissolved in water (Foster and Charlesworth, 1996). They are therefore highly reactive and biologically available (Gelinas and Schmit, 1997). The Pb isotopic signature of natural soil is used to represent the Pb derived from natural weathering, erosion, and different processes of transport. In order to examine the significant differences between the $^{206}Pb/^{207}Pb$ ratios of the geological materials and aquatic organism samples, a paired sample t test was preformed. The factors of the paired samples (t test for the $^{206}Pb/^{207}Pb$ ratios of fish, crab, shrimp and shellfish samples) compared with those of the geological materials were 5.844 (degree of freedom, df = 4), 3.913 (df = 4), 8.262 (df = 4), and 4.819 (df = 2), respectively. Therefore, the Pb isotopic signatures of these biological samples had significant differences ($p < 0.05$) in comparison with the geological materials, and provided a useful tool for distinguishing the relative contributions from various natural and anthropogenic sources.

As shown in Fig. 2, all of the Pb isotopic ratios of the aquatic organisms ranged between those of the surface sediments and those of the atmospheric depositions. The Pb isotopic ratios of a small number of aquatic organisms were similar to those of the surface sediments. The Pb accumulated in these aquatic organisms might be derived from the sediments. A large proportion of the aquatic organisms had lower $^{206}Pb/^{207}Pb$ ratios than the surface sediments, indicating that most of the

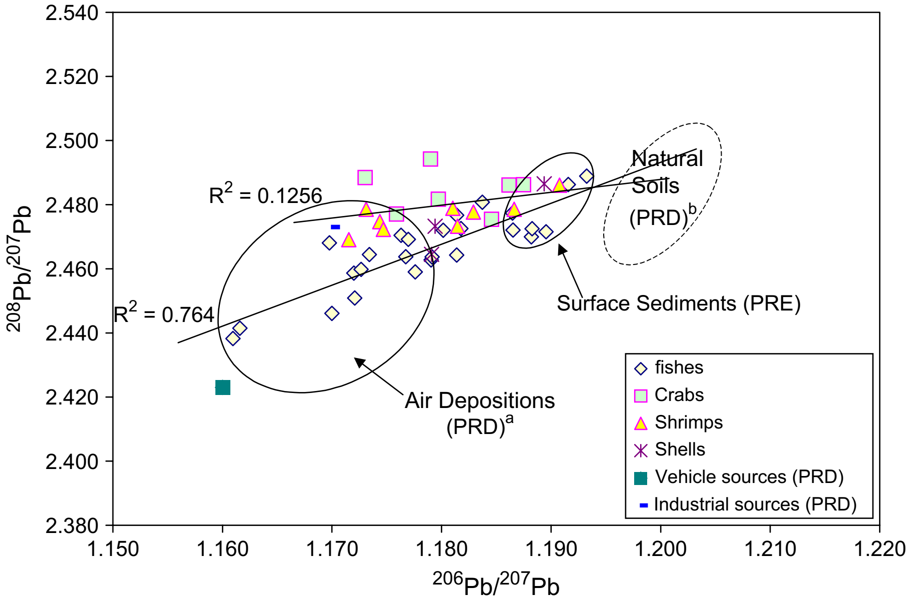

Fig. 2. The correlation between the $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ ratios of aquatic organisms in the PRE. [a] Wong et al., 2003; [b] Wong et al., 2002.

aquatic organisms received contributions from anthropogenic Pb.

In general, three groups of aquatic organisms could be categorized on the basis of their Pb isotopic signatures in the present study. The aquatic organisms in Group 1 possessed Pb isotopic compositions similar to those of the air depositions of the PRD region. Fish were the dominant species in this group. The result indicated that some fish had very similar Pb isotopic signatures as the anthropogenic sources. The aquatic organisms in Group 2 had Pb isotope signatures similar to those of the PRE sediments. The Pb isotopic ratios of the aquatic organisms in Group 3 were in between those of the two groups. Most of the Pb isotopic compositions of shrimp, crab, and shellfish belonged to Group 3, indicating that these aquatic organisms accumulated Pb inputs from various sources, with the Pb being derived from anthropogenic sources (e.g., air depositions) and surface sediments, or food sources. Fish generally received more contributions from Pb derived from anthropogenic sources (e.g., air depositions) than shrimp, crab, and shellfish in the PRE, possibly because their dominant habitat is water and also because of their position in the food chain.

In general, a significant linear relationship between the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios possibly suggests the binary mixing of two end-members with different isotopic compositions (Farmer et al., 1996; Wong and Li, 2004). The Pb isotopic data in this study do not form a single linear correlation (Fig. 2) suggesting that more than two end-members were involved. The different Pb isotopic signatures were mainly due to the different uptake efficiencies of Pb from various sources by the organisms. The ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios in fish were significantly correlated ($r^2 = 0.764$), and those in shrimp and crab were not correlated ($r^2 = 0.126$). Fish can bioaccumulate particle Pb through their gills (Tao et al., 1999). As fishes are more mobile in water columns, they are likely to be more exposed to weakly soluble and potentially bioavailable Pb originating from anthropogenic atmospheric depositions and/or from the inputs derived from the discharges of wastewater. The present study indicated that fish might be bioassimilating Pb from anthropogenic sources such as atmospheric deposits suspended in water columns. Previous studies have also reported that the highest trace metal concentrations in fish were found in their gills (Eisler, 1979; Wang and Fisher, 1996; Barata et al., 2002). This issue can be further investigated in the future by examining the differences in the Pb isotopic composition in the gills, livers, stomachs and fleshes of fish.

4. Conclusions

High concentrations of trace metals were generally found in shellfish, while the highest concentrations of Pb were found in the fish of the Pearl River Estuary. The highly comparable concentrations of Cd and Cu in shellfish, crab, and shrimp were partly attributed to their consumption of detritus materials. The differences in the patterns of accumulation of Pb in these aquatic organisms were mainly attributed to the solubility of the metal in an aquatic environment. In addition, the differences in the feeding habitats of these organisms also affected their physiological responses to different trace metals. The significantly elevated concentrations of Pb and low ^{206}Pb/^{207}Pb ratios in fish compared with other organism samples could be attributed to the bioaccumulation of Pb from weakly soluble and potentially bioavailable Pb originating from anthropogenic sources and a wide variety of food sources.

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