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Copper, Lead, Zinc, Cadmium, Mercury, and Arsenic in Marine Products of Commerce from Zhejiang Coastal Area, China, May 1998

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Zhejiang province is located in the southeast coastal areas of China, with the total coastline about 6,321 km in length. There are four bays, i.e. Hangzhou bay, Xiangshan harbour, Sanmen bay and Yueqing bay, and 3,016 islands in this area. The region also includes Zhoushan fishing ground, which is the largest one in China and an internationally important fishing ground that contains many actual and potential maricultural sites. In recent years, the coastal environment was increasingly influenced by rapid economic development as well as a decrease in the productivity of its fish, shrimp and shellfish resources (Ni and Lu 2002). Few studies have been conducted on trace elements in marine organisms along the coastline of Zhejiang Province. In the present account, we provide baseline concentrations on copper, lead, zinc, cadmium, mercury and arsenic in selected species of fish, cephalopod, shellfish and shrimp from eleven stations covering the whole coastal area of Zhejiang Province, China. These data were analyzed and compared with those of others.

MATERIALS AND METHODS

Trace elements were analyzed in tissues from seven fish species (silver pomfret (*Pampus argenteus*), mudskipper (*Periophthalmus sericus*), tapertail anchovy (*Coilia mystus*), Bombay duck (*Harpodon nehereus*), croaker (*Collichthys lucidus*), red tongue sole (*Cynoglossus joyneri)* and mullet (*Mugil cephalus*)), two cephalopod species (long arm octopus (*Octopus variabilis*) and cuttlefish (*Loligo beka*)), four shellfish (ark shell (*Scapharca subcrenate*), oyster (*Saccostrea cucullata*), mud snail (*Bullacta exerata*), razor clam (*Sinonovacula constricta*)), and three species of shrimp (mantis shrimp (*Oratosquilla oratoria*), Chinese shrimp (*Penaeus chinensis*) and coastal mud shrimp (*Solenocera crassicoris*)) collected in May 1998 from eleven stations along the coastal area of Zhejiang Province, China (Fig.1). The organisms selected were dominant, commercially important species consumed by people living in the study area and environs. For every station, ten to fifteen individuals of muscle from each fish, cephalopod (mantle) and shrimp (muscle) species and 30-50 for each shellfish species (whole soft parts) were collected. The sizes of individuals selected for the same species were similar in order to minimize individual differences within and among sampling sites. After collection, samples were cleaned with deionized water,

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wrapped in precleaned polyethylene packets and brought to the laboratory on ice and stored at -18°C until dissected. For each sampling site, a composite sample for each species was prepared by homogenizing the selected in a mixer and kept frozen at -18°C until digestion. A 1-g wet sample was put into a 25 mL Teflon digestion vessel and 3 mL of concentrated nitric acid and 2 mL of hydrogen peroxide (30%) were added to the vessel. The digestion of samples was carried out in a microwave digestion system MK-II (Xinke Microwave Technology Research Institute, Shanghai, China). Five stages of digestion were set with two minutes for each stage. The pressures in five stages were in the order of 0.5, 1.0, 1.5, 2.0 and 2.5 MPa. After digestion, the digest was diluted to 25 mL with Milli-Q water.

Concentrations of the trace elements were determined by flame (Cu, Zn) and graphite furnace (Cd, Pb) atomic absorption spectrophotometer (AA670, Shimadzu). Arsenic was measured using a hydride generator (HG) coupled to an atomic fluorescence spectrophotometer (AF-610A, Beijing BRAIC Analytical Instrument, Inc., China). Total mercury was analyzed using a cold vapor atomic fluorescence spectrophotometer (WGY-SI, Suzhou Optical Instrument Factory, China). The detection limits, calculated as 3 S.D. of the mean of 15 blanks, were 0.08 for copper, 0.005 for lead, 0.10 for zinc, 0.001 for cadmium, 0.004 for mercury and 0.6 for arsenic (μg/g in wet wt.).

Acid washed glassware, ultrapure grade reagents and Milli-Q water were used in all procedures. The accuracy and precision of analytical procedures were assessed by analyzing one blank, 20% digested replicate samples and two samples of standard reference materials (GSBZ-19002-95 oyster tissue, Institute for Reference Materials of SEPA, China) for each batch of fifteen samples. The analytical relative deviations for all duplicate samples were within 10% and the results for standard reference material were within the range of certified values (Table 1). The one-way analysis of variance (ANOVA) was applied to test the differences of trace element concentrations between species and statistical significance was assumed when $P<0.05$.

RESULTS AND DISCUSSION

In 1996, we conducted a baseline investigation of environmental quality status in Zhejiang coastal area which was divided into eight sub-areas, i.e. Yangtze River estuary, Hangzhou Bay, Zhoushan sea area, Zhoushan-Ningbo Port, Xiangshan harbor, Sanmen Bay, Yueqing Bay and Zhejiang central sea area. The ranges of Cu, Pb, Zn, Cd, Hg and As concentrations in seawater (dissolved) from Zhejiang coastal area were 1.12-1.89, 0.44-0.85, 13.8-19.8, 0.051-0.065, 0.018-0.026 and 6.2-7.4 μg/L, respectively, while those in surface sediments were 26.2-32.5 for Cu, 21.1-26.6 for Pb, 69.6-91.6 for Zn, 0.066-0.108 for Cd, 0.042-0.072 for Hg and 7.7-9.5 for As (all values in μg/g, dry wt.). No significant differences of trace elements concentrations in seawater and sediments among eight sub-areas were observed, indicating that geographic patterns in concentrations of trace elements (Cu, Pb, Zn, Cd, Hg and As) in seawater and surface sediments were homogenously distributed throughout the area (ZMEERI 1996). The data from eleven sites in this study were aggregated and mean concentrations ±SD (n=11) and ranges of trace elements in tissues of fish and invertebrates were summarized in Tables 2 and 3.

Table 1. Concentrations of trace elements found in standard reference material GSBZ-19002-95 (oyster tissue) from China (means ± SD, in μg/g dry wt.)

Value	Copper	Lead	Zinc	Cadmium	Mercury	Arsenic
Certified	139.7±20	0.84±0.09	0.19±0.02*	4.56±0.48	0.052	6.67±0.83
Observed	135.8±16	0.81±0.05	0.18±0.01*	4.51±0.20	0.048±0.003	6.2±0.42

* % (w/w)

All elements except As in some fish species were detectable in fish muscle and cephalopod mantle (Table 2). Mercury levels in fish ranged from 0.002 to 0.032 μg/g and concentrations among different fish species were similar. Mercury concentrations ranged from 0.006 to 1.34 μg/g wet wt in fish muscles from some other marine areas of China (Gan and Jia 1997). Mercury levels in fish were lower than those in Australia (Gibbs and Miskiewicz 1995), in which the mercury levels ranged from 0.09 to 1.82 μg/g wet wt, indicating minor mercury contamination. The levels of copper, zinc and cadmium in fish were comparable to those reported for fish from Zhanjiang harbor, Guangdong, China (Chen et al. 1998), while lead concentrations were comparatively much lower.

It is possible to compare metal concentrations in fish muscle with those reported from other marine environments only for *P. arenteus* and *M. cephalus*. Yue (2001) reported mean values of Pb, Zn, Cu, Cd and As in *P. argenteus* collected in a polluted sea area of Hulu Island, Liaoning, China, at 0.13, 21.9, 0.8, 0.14 and 1.74 μg/g wet wt, respectively, which were higher than those in our study. The mercury level in *P. argenteus* in our study was lower than that of conspecifics from Hong Kong (Dickman et al. 1998). Levels of Cu, Pb, Zn and Cd in *M. cephalus* in our study were similar to those of *M. cephalus* from Rio de Aveiro, Portugal (Cid et al. 2001) and from an unpolluted sampling site in Visakhapatnam, India (Sultana and Rao 1998), but much lower than those found in Iskenderun Bay, Turkey (Yilmaz 2003) and the northeast Mediterranean Sea (Canli and Atli 2003). Arsenic levels in *M. cephalus* here were comparable to those reported by Barwick and Maher (2003).

Among fish species studied, the maximum mean concentrations of Cu, Zn and Pb, Cd were found in *P. sericus* and *M. cephalus*, respectively. The interspecific differences in metal accumulation may be associated with varying feeding habits. Balasubramanian et al. (1997) found metal accumulations among fish species in the order of omnivores > phytoplankton feeder > zooplankton feeder > carnivores > macrophyte feeder. In our study, the intertidal fish *P. sericus* and detritivorous fish *M. cephalus* are omnivores, while the others are carnivores. Arsenic levels in *C. joyneri* were noticeably higher than those in other fish species.

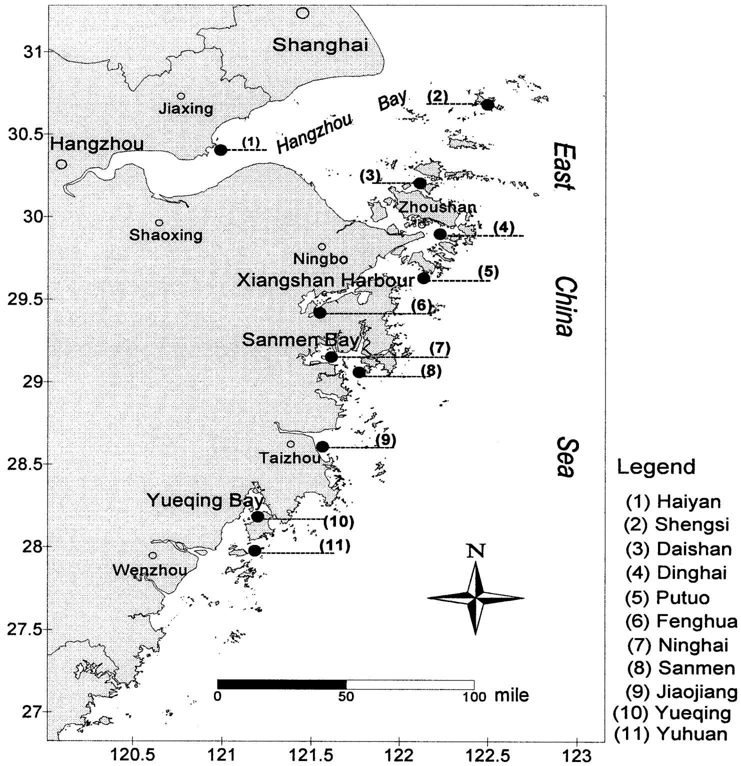

Figure 1. Locations of the eleven sampling sites along the Zhejiang coast.

Only two cephalopod species, *O. variabilis* and *L. beka* were available for analysis (Table 2). The levels of Hg, Pb and Zn in both species were comparable, while concentrations of Cu, As and Cd in *L. beka* were higher than those in *O. variables*. Cui et al. (1996) reported ranges of Zn, Pb, Cu and Cd in *O. variabilis* and *Loligo sp.* from Jiaozhou Bay, Shandong, China of 9.39-11.1, 1.55-1.86, 5.38-5.56, 0.21-0.28 μg/g wet wt and 10.1-14.2, 0.29-2.23, 4.42-8.58, 0.08-0.76 μg/g wet wt, respectively. Our data were similar to those results except for lead, which was lower.

For shellfish, the highest mean concentrations of Hg, Cu, Zn and As were in oyster *S. cucullata*, in which Cu and Zn levels were remarkably elevated when compared to the other three species (Table 3). Oysters were known to have strong abilities to accumulate metals. Blackmore (2001) found higher levels of Cu and Zn in *S. cucullata* when compared to other invertebrates from Hong Kong waters. Cadmium levels in *S. subcrenate* were significantly higher than those in other species. The strong ability of *S. subcrenate* in accumulating cadmium was also reported by He (1996). It can be seen that our data for Cu, Pb, Zn and Cd for four shellfish species were of the same order as values of the same species reported by He (1996). Arsenic contents in *S. subcrenate* and *S. cucullata* were slightly higher than those from northern coast of China (*S. subcrenate*: 0.96μg/g and *S. cucullata*: 0.78 μg/g wet wt) reported by Liu et al. (1996), while mercury levels in *S. cucullata*

Table 2. Trace element concentrations (ranges and arithmetic means ± SD) in fish muscle and cephalopod mantle from eleven stations along the coastline of Zhejiang Province (μg/g, wet wt), May 1998.

Species	Hg	Cu	Pb	Cd	Zn	As
Fish						
Pampus argenteus	0.014±0.002	0.37±0.15	0.026±0.012	0.056±0.033	6.09±1.61	1.0±0.3
	(0.011-0.017)	(0.24-0.61)	(0.011-0.044)	(0.012-0.096)	(4.1-8.4)	(0.8-1.6)
Periophthalmus sericus	0.010±0.001	1.31±0.77	0.064±0.050	0.030±0.022	19.9±15.1	<DL
	(0.01-0.011)	(0.46-1.95)	(0.021-0.135)	(0.017-0.056)	(10.2-42.2)	<DL
Coilia mystus	0.013±0.004	0.29±0.16	0.035±0.020	0.029±0.012	11.8±2.68	<DL
	(0.008-0.017)	(0.20-0.48)	(0.016-0.055)	(0.015-0.038)	(9.68-14.8)	<DL
Harpodon nehereus	0.009±0.006	0.33±0.20	0.020±0.010	0.025±0.012	5.62±3.05	<DL
	(0.002-0.018)	(0.10-0.70)	(0.008-0.033)	(0.013-0.048)	(3.59-13.4)	<DL
Collichthys lucidus	0.010±0.004	0.36±0.11	0.053±0.036	0.021±0.016	5.54±1.59	0.6±0.3
	(0.004-0.014)	(0.26-0.53)	(0.01-0.095)	(0.005-0.048)	(3.27-7.24)	(<DL-1.1)
Cynoglossus joyneri	0.019±0.009	0.24±0.15	0.022±0.007	0.009±0.007	5.89±1.91	3.0±2.2
	(0.01-0.032)	(0.10-0.48)	(0.011-0.029)	(0.001-0.018)	(3.6-8.82)	(1.8-7.6)
Mugil cephalus	0.018±0.010	0.78±0.43	0.092±0.071	0.065±0.066	8.96±5.80	0.7±0.4
	(0.007-0.026)	(0.33-1.19)	(0.021-0.142)	(0.025-0.131)	(4.82-15.7)	(<DL-1.2)
Cephalopod						
Octopus variabilis	0.016±0.010	6.46±2.69	0.041±0.017	0.16±0.11	13.7±4.50	3.8±1.2
	(0.009-0.030)	(3.42-9.97)	(0.024-0.058)	(0.036-0.254)	(9.74-20.1)	(2.1-4.9)
Loligo beka	0.024±0.020	14.1±7.31	0.027±0.003	0.86±0.78	12.9±5.1	7.2±1.8
	(0.011-0.047)	(6.5-21.1)	(0.023-0.040)	(0.084-1.61)	(7.54-17.7)	(5.4-8.9)

Table 3. Trace element concentrations (ranges and overall means ± SD) in shellfish whole soft parts and shrimp muslce from eleven stations along the coastline of Zhejiang Province (μg/g, wet wt), May 1998.

Species	Hg	Cu	Pb	Cd	Zn	As
Shellfish						
Scapharca subcrenate	0.015±0.007	1.67±0.72	0.055±0.028	7.19±3.93	13.9±3.77	1.3± 0.3
	(0.01-0.028)	(0.87-2.62)	(0.029-0.084)	(4.34-13)	(9.32-18.1)	(1.0-1.6)
Saccostrea cucullata	0.027±0.011	76.2±35.5	0.120±0.044	2.43±1.37	139±76.7	1.5±0.5
	(0.013-0.044)	(33.6-135)	(0.051-0.168)	(1.27-4.86)	(24.7-244)	(1.0-2.4)
Bullacta exerata	0.012±0.002	15.7±9.61	0.332±0.023	0.119±0.083	9.61±4.64	1.1±0.3
	(0.009-0.014)	(8.02-26.5)	(0.211-0.348)	(0.067-0.214)	(5.42-14.6)	(0.9-1.4)
Sinonovacula constricta	0.023±0.009	5.06±3.31	0.140±0.043	0.195±0.083	19.3±6.66	1.2±0.4
	(0.014-0.039)	(2.28-11.8)	(0.081-0.210)	(0.101-0.336)	(10-30.7)	(0.7-1.7)
Shrimp						
Oratosquilla oratoria	0.011±0.004	17.0±7.40	0.022±0.006	0.200±0.209	11.8±3.34	2.8±1.6
	(0.004-0.014)	(7.06-23.4)	(0.013-0.029)	(0.053-0.56)	(7.78-15.4)	(1.1-5.0)
Penaeus chinensis	0.015±0.009	6.13±2.14	0.141±0.117	0.606±0.537	10.0±0.93	2.7±1.0
	(0.008-0.028)	(3.72-8.88)	(0.027-0.244)	(0.046-1.12)	(9.4-11.4)	(1.5-3.8)
Solenocera crassicoris	0.010±0.005	3.74±3.30	0.010±0.004	0.146±0.025	10.4±4.51	6.0±2.9
	(0.004-0.013)	(1.43-7.52)	(0.006-0.023)	(0.128-0.223)	(5.49-14.4)	(3.7-9.2)

were similar to those of conspecifics from the coastline of the Northern Territory Australia (Peerzada et al. 1993).

Of the three species of shrimp studied, the metal levels varied among different species except for Zn and Hg (Table 3). Relatively higher Pb and Cd concentrations were found in *P. chinensis*, while higher As and Cu levels were found in *S. sinensis* and *O. oratoria*, respectively. The intraspecific comparison with species from other seas was only available for *O. oratoria* (Yue 2001) wherein mean levels of Pb, Zn, Cu, Cd and As from the polluted inshore of Hulu island, Liaoning, China were 0.065, 63.5, 47.8, 35.4, 4.8 μg/g wet wt, respectively, while Pb, Zn, Cu and Cd in the same species from a relatively uncontaminated area, Daya Bay, Guangdong, China, were 0.04, 28.0, 14.3 and 0.98 μg/g wet wt, respectively (He et al. 2001). Our data for *O. oratoria* were inferior to those values.

Concentrations of Hg, Cu, Pb, Zn and Cd reported in our study appeared to be below the Maximum Permissible Concentrations for human consumption set by the Australia New Zealand Food Authority (ANZFA 1996). Although total As levels in Chinese species frequently exceeded 1.0 μg/g (Max. 9.2 μg/g wet wt), they may not constitute a risk for human health because most arsenic in marine organisms is in the nontoxic organic form (70-95%) (Maher 1983). But care must be taken considering the most coastal people regularly consume large quantities of seafood. A systematic and in-depth research still needs to be conducted to further understand the distribution and accumulation characteristics of potentially toxic trace metal concentrations in different marine organisms from this region.

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