Levels of Cu, Pb, Zn, Cd, Hg and As in Selected Marine Organisms from Zhejiang Coastal Area, China

J. Fang,[1] K.X. Wang,[1] J.L. Tang,[2] Y.M. Wang, [2] S.J. Ren, [2] H.Y. Wu, [2] J. Wang [2]

[1]Department of Environmental Engineering, College of Environmental and Resource Sciences, Zhejiang University, Hangzhou 310029, China and [2]Zhejiang Marine Eco-Environmental Research Institute, Zhoushan 316000, China

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 internationally important fishing ground, and contains many actual and potential maricultural sites. In recent years, the coastal environment is increasingly influenced by the activities of rapid economic development. At the same time, decreasing in the productivity of its fish, shrimp and shellfish resources has been observed (Ni and Lu 2002). Up to now, few studies had been conducted on toxic residuals in marine organisms along coastline of Zhejiang Province. In the present study, we provided baseline concentrations concerning trace metals (copper, lead, zinc, cadmium, mercury and arsenic) in selected fishes, cephalopods, shellfishes and shrimps, collected from eleven stations covering the whole coastal area of Zhejiang Province, China. The data were analyzed and compared with those of other studies.

MATERIALS AND METHODS

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 shellfishes, ark shell (*Scapharca subcrenate*), oyster (*Saccostrea cucullata*), mud snail (*Bullacta exerata*), razor clam (*Sinonovacula constricta*); and three shrimps, mantis shrimp (*Oratosquilla oratoria*), Chinese shrimp (*Penaeus chinensis*) and coastal mud shrimp (*Solenocera crassicoris*) were sampled during May 1998 from eleven stations, covering the whole coastal area of Zhejiang Province, China (Fig.1). The marine organisms selected were of dominant, commercially important species and consumed considerably by the people living in the study area and beyond. For every station, ten to fifteen individuals for each fish, cephalopod and shrimp species were collected while the individual number of the shellfish species ranged from thirty to fifty because of their relatively smaller size, especially for *B. exerata*. The sizes of individuals selected for the same species were similar in order to minimize individual difference within and among sampling sites. After collection, samples were cleaned with deionized water, 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 were prepared by homogenizing the muscle tissue (shellfish: whole soft tissue; cephalopod: mantle) in a mixer and kept frozen at -18°C until digestion. A 1-g wet sample was put into a 25 mL PTFE 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 heavy metals 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 for copper, lead, zinc, cadmium, mercury and arsenic were 0.08, 0.005, 0.10, 0.001, 0.004 and 0.6μg/g in wet weight, respectively.

Acid washed glassware, ultrapure grade reagents and Milli-Q water were used in the whole procedure of analysis. 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 SRM were within the range of certified values. All the concentrations were expressed in μg/g wet weight.

RESULTS AND DISCUSSION

Overall mean concentration ±SD (n=11) and the ranges of heavy metals in tissues of fishes, cephalopods, shellfishes and shrimps from coastal area of Zhejiang Province, China were summarized in Table 1 and 2.

As seen in table 1, all elements except As in some fish species were detectable in

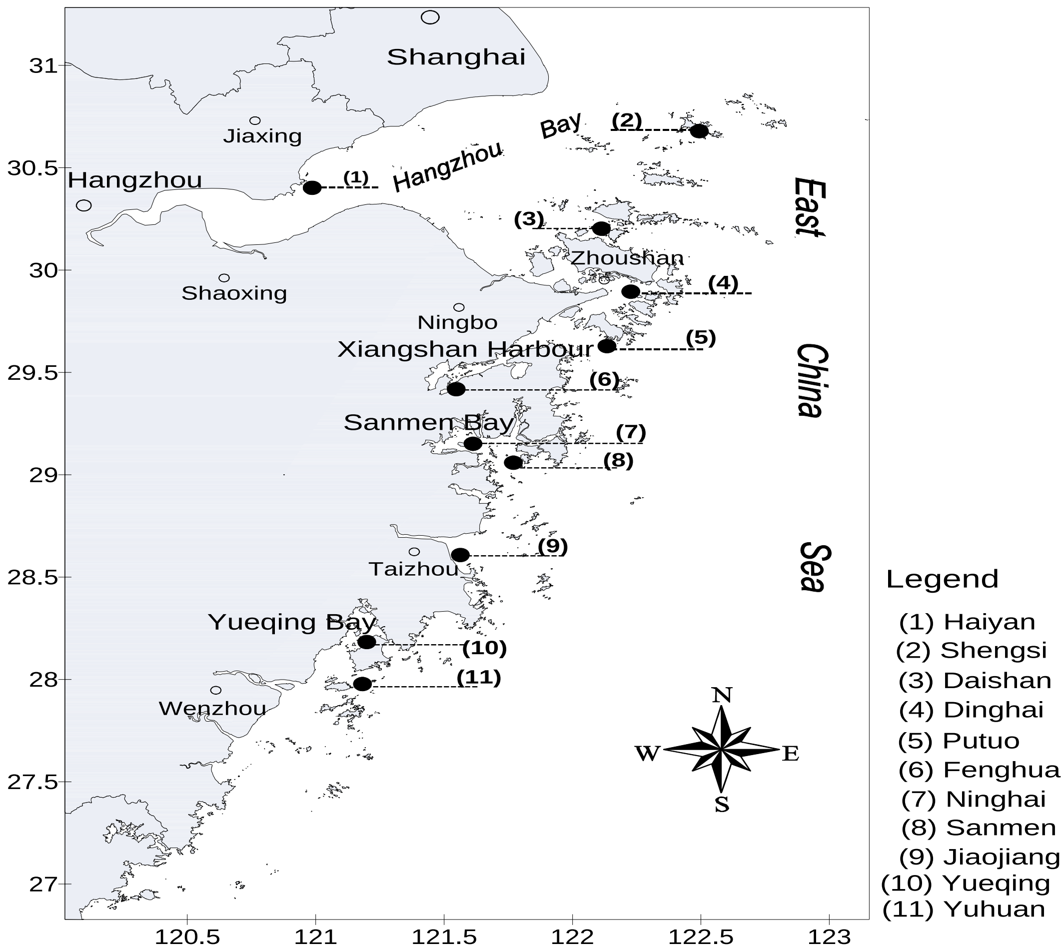

Figure 1. Locations of the eleven sampling sites along the coast of Zhejiang

fish samples. Mercury levels in fish ranged from 0.002 to 0.032µg/g and concentrations among different fish species were similar. Gan et al. (1997) reported concentrations of mercury from 0.006 to 1.34µg/g wet wt in fish muscles from some other sea areas of China. The levels of mercury in fish were lower compared to the study in Australia (Gibbs et al. 1995), in which the mercury levels ranged from 0.09 to 1.82 µg/g wet wt, indicating minor mercury contamination in this area. 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 polluted sea area of Hulu Island, Liaoning, China, were 0.133, 21.88, 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 this study was lower when compared to the value of the same species in Hong Kong (Dickman et al. 1998). The levels of Cu, Pb, Zn and Cd in *M. cephalous* in this study were similar to the values of the same species in Rio de Aveiro, Portugal (Cid et al. 2001) and from unpolluted sampling site (S1) in Visakhapatnam, India (Sultana and Rao 1998), but much lower than those found in Iskenderun Bay, Turkey (Yilmaz 2003) and northeast Mediterranean Sea (Canli et al. 2003). Arsenic levels in *M. cephalus* here were comparable to the values 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. cephalous*, respectively. The interspecific difference in metal accumulation may be associated with varying feeding habits. Balasubramanian et al. (1997) found the heavy metal accumulation in fish species in the order of omnivorous feeder>phytoplankton feeder >zooplankton feeder > carnivorous feeder > macrophyte feeder. In this study, the intertidal fish *P. sericus* and detritivorous fish *M. cephalous* are omnivorous feeders, while the others carnivorous ones. Arsenic levels in *C. joyneri* were noticeably higher than those in other fish species.

Only two cephalopod species, *O. variabilis* and *L. beka* were available for analysis (Table 1). 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. (1997) reported ranges of Zn, Pb, Cu and Cd concentrations in *O. variabilis* and *Loligo sp.* from Jiaozhou Bay, Shandong, China were 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 above results except lead, which was comparatively lower.

Four shellfish species were collected in this study (Table 2). The highest mean body concentrations of Hg, Cu, Zn and As were found in oyster *S. cucullata*, in which Cu and Zn levels were remarkably elevated than those in other three species. Oysters were known to have strong abilities to accumulate metals. Blackmore (2001) found higher levels of Cu and Zn occurred in *S. cucullata* compared to the values of the other invertebrates from Hong Kong waters. Cd 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 other studies (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* were similar to those of the same species from coastline of the Northern Territory, Australia (Peerzada et al. 1993).

Table 1. Estimated muscle tissue metal concentrations (ranges and arithmetic means ± SD) in fish, cephalopod from eleven stations along coastline of Zhejiang Province (μg/g, wet wt)

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 vavriabilis	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 2. Estimated muscle metal concentrations (ranges and overall means ± SD) in shellfish and shrimp from eleven stations along coastline of Zhejiang Province (μg/g, wet wt)

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)

Of the three species of shrimps studied (Table 2), except for Zn and Hg the metal levels in shrimp varied among different species. Relatively higher Pb and Cd concentrations were found in *P. chinensis*, while higher As and Cu levels in *S. sinensis* and *O. oratoria*, respectively. The intraspecific comparison with species from other seas was only available for the species *O. oratoria*. Yue (2001) reported mean levels of Pb, Zn, Cu, Cd and As in *O. oratoria* collected from polluted inshore of Hulu island, Liaoning, China were 0.065, 63.47, 47.77, 35.36, 4.79 μg/g wet wt, respectively, while the amounts of Pb, Zn, Cu and Cd in the same species from a relatively uncontaminated area, Daya Bay, Guangdong, China, were 0.040, 27.98, 14.29 and 0.98 μg/g wet wt, respectively (He et al. 2001). Our data for *O. oratoria* were inferior to those values.

The levels of Hg, Cu, Pb, Zn and Cd in the selected species as reported in this study appeared to be below Maximum Permissible Concentrations for human consumption set by Australia New Zealand Food Authority (ANZFA 1996). Although total As levels in these species mostly exceeded 1.0 μg/g with the highest value of 9.2μg/g wet wt, they may not constitute a risk for human health since most arsenic in marine organisms is in the nontoxic organic form (70-95%) (Maher 1983). But care must be taken considering most coastal people regularly consume large quantities of seafood. A systematic and in-depth research still needs to be carried out in order to further understand the distribution and accumulation characteristics of toxic residuals in different marine organisms in this region.

Acknowledgments. The authors would like to thank a large number of technicians from local environmental monitoring stations in the eleven sampling sites of this study for their participation in the field sampling.

REFERENCES

ANZFA (1996) Australia New Zealand Food Authority, Food Standards Code. Australian Government Publishing Service, Canberra.

Balasubramanian S, Pappathi R, Jayanthi-Bose A, Raj SP (1997) Bioconcentration of copper, nickel and cadmium in multicell sewage fish ponds. J Environ Biol 18: 173-179

Barwick M, Maher W (2003) Biotransference and biomagnification of selenium copper, cadmium, zinc, arsenic and lead in a temperate seagrass ecosystem, NSW, Australia. Mar Environ Bull 56:471-502

Blackmore G (2001) Interspecific variation in heavy metal body concentrations in Hong Kong marine invertebrates. Environ Pollut 114:303-311

Canli M, Atli G (2003) The relationship between heavy metal (Cd, Cr, Cu, Fe, Pb, Zn) levels and the size of six Mediterranean fish species. Environ Pollut

121:129-136
Chen Rong, Xu Zhongxian, Zhang Lin (1998) The assessment on the contents of the heavy metals in the seafoods from Zhanjiang harbor waters. Journal of Oceangraphy of Huanghai & Bohai Seas 16:54-59 (in Chinese)
Cid BP, Boia C, Pombo L, Rebelo. E (2001) Determination of trace metals in fish species of the Rio de Aveiro (Portugal) by electrothermal atomic absortion spectrometry. Food Chem 75:93-100
Cui Yi, Chen Bijuan, Song Yunli (1996) The assessment on the contents of the heavy metal in the organisms in the Jiaozhou Bay. Marine Environmental Science 15: 17-22 (in Chinese)
Dickman, M.D., Leung, K.M.C (1998) Mercury and organochlorine exposure from fish consumption in Hong Kong. Chemosphere 37: 991-1015
Gan Juli, Jia Xiaoping (1997) Hygienic quality for heavy metals of economic fish in coastal waters of China. Marine Science Bulletin 4: 88-93 (in Chinese)
Gibbs P. J., Miskiewicz A. G. (1995) Heavy metals in fish near a major primary treatment sewage plant outfall. Mar Pollut Bull 30: 667-674
He Guangkai (1996) Levels of heavy metals in molluscs from the coastal region of Bohai sea and Huanghai sea. China Environmental Science 16:96-100 (in Chinese)
He Xueqin, Zhang Guanxi, Zheng Qinghua, Du Wancheng, Wen Weiying (2001) Analysis and assessment of the content of four heavy metals in the benthons Daya Bay. Scientia Geographica Sinica 21:282-285 (in Chinese)
Liu Guangyan, Han Mingfu, Chen Zeling (1996) Study and investigations of arsenic in the economic shellfishes in the northern coast of China. Marine Environmental Science 15: 22-27 (in Chinese)
Maher, WA (1983) Inorganic arsenic in marine organisms. Mar Pollut Bull 14:308-310
Ni Haier, Lu Jiehua (2002) Dynamic analysis on fisheries resources in Zhoushan fishing ground. Journal of Fisheries of China 26:428-432 (in Chinese)
Peerzada N, Watson D, Guinea M (1993) Mercury concentrations in oysters from the coastline of Northern Territory, Australia. Bull Environ Contam Toxicol 50: 158-163
Sultana R, Rao DP (1998) Bioaccumulation patterns of zinc, copper, lead, and cadmium in grey mullet, *Mugil cephalus*(L), from harbour waters of Visakhapatnam, India. Bull Environ Contam Toxicol 60: 949-955
Yilmaz AB (2003) Levels of heavy metals (Fe, Cu, Ni, Cr, Pb and Zn) in tissue of *Mugil cephalus* and *Trachurus mediterraneus* from Iskenderun Bay, Turkey. Environ Res 92: 277-281
Yue Lijuan (2001) Monitoring the contaminated situation of the aquatic animals caused by heavy metals in the inshore maritime area of Hulu island. Environmental Monitoring in China 17:45-47 (in Chinese)