

Assessment of PCBs and PCDD/Fs Along the Chinese Bohai Sea Coastline Using Mollusks as Bioindicators

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Received: 12 June 2004/Accepted: 3 February 2005

Abstract. Mollusk samples such as bivalves and gastropods were collected from eight sampling sites along Bohai Sea coastline from northeastern China. The samples were analyzed for polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC-HRMS) to elucidate bioaccumulation of persistent organic pollutants in benthon. Residue levels of Σ PCBs and Σ PCDD/Fs were in the ranges of 66.1 to 583.6 ng/g and 0.9 to 15317 pg/g on a lipid-weight basis, respectively. The pollution source was identified using principal component analysis (PCA) in some coastal areas. It indicated that the typical pollution sources were characterized by PCB₃, which was one Chinese technical product of PCBs. PCA also revealed the similarity patterns of PCBs between identical species collected from the different sites. The higher gastropod PCB concentrations were related to a former capacitor factory and the paint factories in some coastal areas, but this was not the case with the bivalves. The results of this study suggest that some gastropod species may be a potential bioindicator or “sentinel” organism for marine PCBs monitoring.

Polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) continue to be a topic of concern in aquatic ecosystems because of their persistence and toxicity. The ocean is a major “sink” for persistent organic pollutants, which are transported from continental areas by atmospheric and oceanic current. Traces of PCBs and PCDD/Fs have been reported in aquatic organisms (Lung *et al.* 2003; Cai *et al.* 1994). In numerous field studies, special attention has been focused on the concentration and distribution of PCBs, especially the coplanar congeners. The World Health Organization (WHO) assigned toxic equivalency factors (TEFs) for 12 coplanar PCBs to evaluate their toxic potencies in the

environment. Several countries have been chosen to monitor PCBs, as a set of seven indicator PCBs, to avoid the complexity involved in determining more congeners. Quantification of the indicator PCBs may be used to determine whether PCB levels in food products and environmental samples comply with the maximum levels permitted by legislature (Everaarts *et al.* 1993).

Bivalves such as mussels have been suggested as a suitable bioindicator for monitoring trace toxic contaminant levels in coastal waters because of their wide distribution, sessile behavior, and ability to bioaccumulate environmental pollutants (Abad *et al.* 2003; Cope *et al.* 1999; Monirith *et al.* 2003). Monirith *et al.* (2003) studied PCB levels in bivalves from the coastal waters of some Asian countries (including some regions of China) with the gas chromatography–electron-capture detection (GC-ECD) method. Nakata *et al.* (2002) reported the PCBs levels in shellfish of some coastal areas of China with the lower-resolution mass-detection method, and Chen *et al.* (2002) also determined the PCBs levels in Chinese foodstuffs with the GC-ECD method. Lower concentrations of PCBs were detected in mollusks from China. However, a few researches reported that the PCBs pollutions in some regions of China were related to Chinese technical products of PCBs (Chu *et al.* 1999; Bi *et al.* 2002). The domestic products of technical PCBs were named PCB₃ and PCB₅, the compositions of which are similar to that of Aroclor 1242 and 1254, respectively (Jiang *et al.* 1997). Total production of PCBs from 1965 to 1974 in China was 10,000 tons (9,000 tons PCB₃ and 1,000 tons PCB₅) (Qin *et al.* 2003). Most PCB₃ products had been used as dielectric fluids in electric capacitors, and most PCB₅ products had been used as paint additive (Jiang *et al.* 1997).

China has the highest fish catch in the world, accounting for 12% of total production, and one third of its haul comes from the Bohai and Yellow Seas. The peripheral area of the Bohai Sea is an economically and socially developed region in China. The objective of this study was to evaluate the status of PCBs and PCDD/Fs in Bohai Sea using mollusks as bioindicators and to study the patterns of PCBs in bivalves and gastropods; moreover, to identify the pollution source of PCBs using PCA based on the levels of individual PCB congeners in bivalves and gastropods.

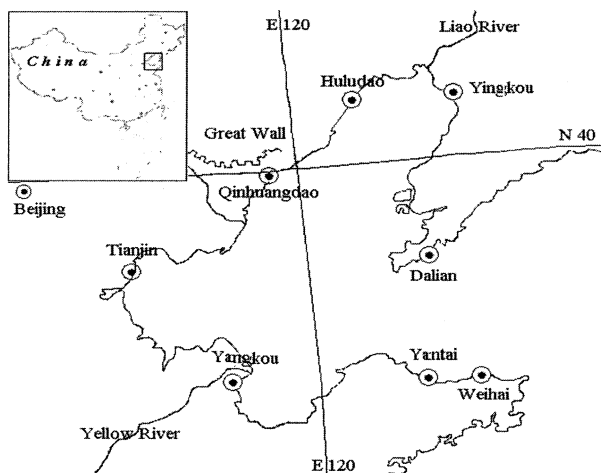


Fig. 1. Sampling sites of mollusk samples along the Chinese Bohai Sea.

Materials and Methods

Sample Collection

Bivalves and gastropods were collected from each of the eight sampling stations along the Bohai Sea. The details of sampling stations are shown in Figure 1. The collected bivalves and gastropods—including *Rapana venosa*, *Neptunea arthritica cumingii*, *Neverita didyma*, *Solen grandis*, *Scapharca subcrenata*, *Meretix meretrix*, *Sinonovacula constricta*, *Chlamys farreri*, *Amusium* spp., and *Clinocardium californiense*—are routine seafood for most Chinese people. Mollusk samples were individually wrapped in aluminum foil, kept in ice boxes, and stored in deep-freeze immediately after reaching the laboratory. In the laboratory, the frozen mollusk samples from each location (120 to 150 specimens) were thawed and shucked, and then the whole soft tissues of mollusks were pooled, homogenized, transferred into clean glass bottles, and frozen at -20°C until chemical analysis.

Chemical Analysis

PCBs and PCDD/Fs were analyzed following the method USEPA 1668A and USEPA 1613B modification. The samples were spiked with known amounts of a $^{13}\text{C}_{12}$ -PCB mixture (EPA 68A-LCS mixture; Wellington Laboratories, Canada) and a $^{13}\text{C}_{12}$ -PCDD/F mixture (EPA 1613-LCS mixture; Cambridge Isotope Laboratories) and mixed with anhydrous sodium sulfate. The samples were allowed to equilibrate for 24 hours and then were Soxhlet extracted with methylene chloride and hexane (1:1,250 ml) for 18 to 24 hours. The extracts were evaporated to 1 ml, and subsequently a constant weight was obtained under a nitrogen stream for each sample; then the lipid contents were determined with gravimetry method. After the extracts were redissolved with hexane, the lipids were removed by anthropogenic isolation columns, which were prepared by packing a glass column (15 mm i.d.) with a series of layers of silica gel in the following order: 2 g silica gel, 2 g potassium silicate, 2 g granular anhydrous sodium sulfate, 10 g acid silica gel, and 2 g granular anhydrous sodium sulfate. Then the extracts were purified with a multilayer silica gel column. Afterwards, the extracts were fractionated by a basic alumina column. The first fraction, eluted with 130 ml methylene chloride to hexane 5:95 (v/v), contained PCBs. The second fraction, eluted with 50 ml methylene chloride to hexane 50:50 (v/v), comprised PCDD/Fs. Then each

fraction was concentrated, the extract quantitatively transferred to a 0.3-ml conical vial for final concentration, and the volume decreased to approximately 100 μl . We then added 20 μl nonane to the vial and evaporated the solvent to the level of nonane for injection into HRGC-HRMS. Identification and quantification of individual PCB and PCDD/F congeners were accomplished with a 6890 gas chromatograph (Agilent) coupled to an Autospec Ultima mass spectrometer (Waters), at 10,000 resolving power (10% valley definition). Chromatographic separation was achieved with a DB-5 (J&W) fused-silica capillary column (60 m \times 0.32 mm \times 0.25 μm).

Quality Assurance

The method blanks were run with every set of five samples to check for solvents, reagents, and glassware. Analysis of the blanks indicated that the levels of PCDD/F and most PCB congeners, except those of PCB 105 (0.08 $\text{pg}/\mu\text{l}$) and PCB 118 (0.13 $\text{pg}/\mu\text{l}$), were below detection limits. The blank levels of PCB 105 and PCB 118 were <2% that of all samples. The results reported were not corrected by subtraction of the blank value. The detection limits and recoveries of the selected PCB and PCDD/F congeners met criteria of USEPA 1668A and USEPA 1613B. CIL standard reference material (EDF-2525 fish) was analyzed for selected PCBs and PCDD/F congeners, and reliable results were obtained by comparing the data from our laboratory with those from material reference values (relative SD <20% on results).

The Principal Component Analysis

Principal component analysis (PCA), based on the concentration of individual PCB congeners, was used to extract principal components (PCs) that accounted for the major part of the data variation in PCB concentration, and these PCs were related to the major PCB sources on the basis of both these factor-loading values. The indicator PCBs and dioxin-like PCBs were treated as variables, and the eight bivalve samples, eight gastropods samples, PCB₃, PCB₅, Aroclor 1242, and Aroclor 1254 were treated as cases. PCBs not detected were removed. The concentration data obtained for each congener in sample analysis was expressed as fractional parts of the total and normalized to the sum equal to 100. This normalization minimized the influence of total concentration and permitted a comparison of compositional similarities among samples. The eigenvectors were normal-varimax rotated to improve the interpretability of the results (Sakuraie *et al.* 1998). Statistical analyses were carried out with SPSS 12.0 for Windows, release 12.0 (SPSS).

Results and Discussion

Data Evaluation

The concentration of PCBs was normally expressed as the mass of total PCBs normalized to sample wet weight or to the weight of the lipids extracted simultaneously with the PCBs. The normalization to lipids is generally considered to be highly important because lipids are the primary depositories for lipophilic PCBs in organisms. Lipid normalization is especially called for in the case of aquatic organisms because an equilibrium partitioning of PCBs between organism lipids and ambient water or sediment is frequently established (Barron 1990). Lipid normalization can thus allow to some extent a comparison of

Table 1. Concentration of PCBs in mollusk samples collected from the Bohai Sea (ng/g)

| Mollusks | Yangk | Tianj | Yant | Weih | Qinghd | Dal | Huld | Yingk |
|---------------|-------|-------|------|------|--------|------|------|-------|
| PCBs/wet wt | 0.78 | 0.47 | 3.4 | 1.6 | 0.60 | 0.92 | 1.8 | 0.71 |
| PCBs/dry wt | 1.9 | 3.1 | 21 | 9.2 | 5.3 | 4.9 | 9.5 | 4.3 |
| PCBs/lipid wt | 171 | 108 | 345 | 246 | 201 | 66 | 183 | 231 |
| Gastropods | | | | | | | | |
| PCBs/wet wt | 1.1 | 4.4 | 4.8 | 0.77 | 1.2 | 2.4 | 0.55 | 2.4 |
| PCBs/dry wt | 4.0 | 15 | 16 | 3.0 | 4.2 | 10 | 1.9 | 9.4 |
| PCBs/lipid wt | 141 | 416 | 187 | 82 | 107 | 199 | 68 | 584 |

PCBs = Polychlorinated biphenyls.

PCB concentrations in various species regardless of their lipid contents (LeBianc 1995). In this study, the concentrations of PCBs and PCDD/Fs were calculated on a hexane-extractable lipid-weight basis (Tables 2, 3, and 4). In order to facilitate comparison, Table 1 shows the concentrations expressed as lipid basis, dry matter, and wet weight for total PCBs.

PCBs

Tables 2 and 3 present a summary of the concentrations (pg/g lipid wt) for indicator PCBs, WHO-PCBs, the PCB homologue groups, and the sum of all quantified PCBs. PCBs were detected in all the samples analyzed, and the highest Σ PCBs concentration was detected in gastropods from the site near Yingkou city (583 ng/g lipid wt), but PCBs 123 and 189 were not detected in all the samples analyzed. PCB 81 was not detected in bivalves from the sites near Yantai and Weihai cities, and PCBs 126 and 169 were detected in a few samples analyzed. PCB 77 was determined in all samples analyzed. The dominant congeners in bivalves and gastropods were PCB 105, 118, 28, 52, 101, 138, and 153 congeners. In general, PCB residues in bivalves from Bohai coastline were low. The results were comparable with those reported in the literature (Monirith *et al.* 2003; Chen *et al.* 2002). Recent information on PCB levels in gastropods was limited and fragmentary. Lower residues of PCBs were reported in surface water and coastal sediments in China (Yuan *et al.* 2001; Sun *et al.* 2002), supporting the hypothesis of less use of PCBs in China (Zhou *et al.* 2000). However, the Bohai coastline showed relatively higher PCB concentrations in bivalves except Xiamen Island (Chen *et al.* 2002) and Qingdao (Monirith *et al.* 2003), whereas the levels were one order lower than those from Japan (3000 ng/g lipid wt) and Russia (3200 ng/g lipid wt) (Monirith *et al.* 2003). The relative toxic potentials of WHO-PCBs in bivalves (Table 2) and gastropods (Table 3) were calculated using WHO TEF. The toxic equivalency quotient (TEQ) values of PCBs were low.

PCDD/Fs

Table 4 shows the concentrations expressed as lipid basis for PCDD/Fs and as lipid basis, dry matter, and wet weight for TEQs in bivalves and gastropods. The PCDD/F congener distributions were dominated by octachlorodibenzo-p-dioxin (OCDD). The levels of OCDD ranged between 20 and 2584 pg/g lipid wt in bivalves but between 13 and 274 pg/g lipid wt in gastropods. All of the calculated TEQs were far lower than the

limits proposed in the draft of the European Commission (EC) Regulation for Food Commercialization in the European countries (EC No. 194/97), i.e., 3 pg WHO-TEQ/g whole product for fish. Corsolini *et al.* (2002) reported that PCDD/F concentrations in lower-trophic Antarctic organisms were less than the limits of detection, and the results for bivalves were also comparable with those reported in the literature (Hashimoto *et al.* 1999; Abarnou *et al.* 2002). The results for gastropods were 0.046 to 44 pg WHO-TEQ/g lipid wt, 0.002 to 1.46 pg WHO-TEQ/g dry wt, and 0.0004 to 0.61 pg WHO-TEQ/g wet weight, respectively.

PCA Results

The loading plot and score plot (Figs. 2 and 3, PC1 vs. PC2) were obtained after normal-varimax rotation. For bivalve samples, PC1 accounted for 44% of the variance of the data set and was positively determined by WHO-PCB 81, 126, 77, 114, and 157 congeners as well as indicator PCB 138, 153, and 180 congeners. PC2 accounted for 24% of the total variance and was characterized by WHO-PCB 105, 156, and 118 congeners as well as indicator PCB 101 and 52 congeners. The score plots obtained from the first two principal components are shown in Figure 2, where it can be seen that the bivalves from the sampling sites near Tianjin and Dalian cities were characterized by higher chlorinated PCBs, and the bivalves from the sampling sites near Qinhuangdao, Yinghou, and Huludao cities were in the neighboring position with PCB₃. For gastropod samples, PC1 accounted for 32% of the variance and was characterized by WHO-PCB 157, 169, and 126 congeners as well as indicator PCB 138, 153, and 180 congeners. PC2 accounted for 24% of the total variance and was characterized by WHO-PCB 105, 118, and 156 congeners as well as indicator PCB 101 congeners. In the score plot (Fig. 3), the gastropod samples from the sampling site near Yantai city were separated from others, whereas the same gastropod species were the neighboring position. Figures 2 and 3 illustrate the samples' similarity on the basis of isomer distribution among PCB₃, bivalve, and gastropod samples from the sampling sites near Qinhuangdao, Yinghou, and Huludao cities.

Probable Emission Sources Estimated by Mollusks

The patterns of individual PCB congeners were different in bivalves and gastropods. The results given in Tables 2 and 3

Table 2. Concentrations of PCBs in bivalves from the Chinese Bohai Sea (pg/g lipid wt)

| PCBs | Yangk <i>S. subcrenata</i> ^a | Tianj <i>Amusium</i> spp. | Yant <i>C. farreri</i> | Weih <i>S. grandis</i> | Qinhd <i>M. meretrix</i> | Dal <i>Amusium</i> spp. | Huld <i>C. californiense</i> | Yingk <i>S. cutacoens tricta</i> |
|--------------------|--|------------------------------|---------------------------|---------------------------|-----------------------------|----------------------------|---------------------------------|-------------------------------------|
| PCB77 | 1921 | 1334 | 2285 | 813 | 1287 | 432 | 420 | 936 |
| PCB81 | 162 | 172 | 209 | 195 | 141 | 111 | 73 | 152 |
| PCB105 | 1683 | 1645 | 2009 | 1898 | 1313 | 799 | 698 | 1440 |
| PCB114 | 129 | 156 | 235 | 220 | 155 | 76 | 117 | 198 |
| PCB118 | 5081 | 3893 | 4125 | 3788 | 2477 | 2323 | 1194 | 19627 |
| PCB123 | <6.7 | <4.6 | <2.4 | <3.3 | <7.1 | <1.6 | <2.2 | <7.1 |
| PCB126 | <7.9 | 61 | 55 | 18 | <8.4 | 36 | 8 | 52 |
| PCB156 | 106 | 184 | 113 | 134 | 143 | 81 | 63 | 228 |
| PCB157 | 26 | 99 | 45 | 32 | 42 | 41 | 34 | 76 |
| PCB167 | 48 | 202 | 85 | 72 | 83 | 93 | 59 | 171 |
| PCB169 | <9.1 | <6.3 | 13 | <4.5 | 18 | 9.7 | <3.0 | <9.7 |
| PCB189 | <4.2 | <2.9 | <1.5 | <2.1 | <4.5 | <1.0 | <1.4 | <4.5 |
| Sum WHO-PCBs | 9157 | 7745 | 9173 | 7168 | 5658 | 4002 | 2665 | 22881 |
| WHO-TEQs | 1.02 | 7.05 | 6.70 | 2.62 | 0.87 | 4.18 | 1.16 | 7.71 |
| PCB28 | 7322 | 4529 | 6069 | 5804 | 5671 | 2354 | 7174 | 8085 |
| PCB52 | 3330 | 3177 | 15975 | 13333 | 11099 | 3349 | 14316 | 6475 |
| PCB101 | 3295 | 3143 | 9670 | 6900 | 5431 | 2206 | 4440 | 7176 |
| PCB138 | 5131 | 6029 | 10916 | 6675 | 6630 | 2423 | 3369 | 4729 |
| PCB153 | 5655 | 7354 | 11235 | 6587 | 6398 | 2692 | 3720 | 5873 |
| PCB180 | 407 | 639 | 1902 | 827 | 2103 | 242 | 963 | 925 |
| PCB209 | 200 | 48 | 128 | 87 | 1489 | 1.0 | 1067 | 24113 |
| Sum indicator PCBs | 25340 | 24919 | 55864 | 40212 | 38822 | 13266 | 20762 | 57376 |
| 1-PCB | 598 | 244 | 344 | 258 | 1499 | 53 | 253 | 563 |
| 2-PCB | 998 | 302 | 466 | 315 | 2175 | 180 | 476 | 1184 |
| 3-PCB | 15877 | 8985 | 20766 | 16746 | 14977 | 180 | 20489 | 15802 |
| 4-PCB | 102441 | 51321 | 182978 | 152888 | 125422 | 38217 | 119675 | 102079 |
| 5-PCB | 26658 | 22044 | 59930 | 44907 | 32519 | 13962 | 24885 | 57926 |
| 6-PCB | 19745 | 19756 | 43844 | 23303 | 14083 | 7969 | 11701 | 17826 |
| 7-PCB | 4118 | 4629 | 35449 | 6983 | 70 | 1634 | 3515 | 5110 |
| 8-PCB | 475 | 281 | 919 | 416 | 1060 | 90 | 1014 | 1512 |
| 9-PCB | 1.8 | 1.3 | 46 | 1.0 | 239 | 1.0 | 160 | 4976 |
| Total PCBs | 171110 | 107609 | 344870 | 245902 | 200522 | 62286 | 183235 | 231092 |

PCB = Polychlorinated biphenyls, WHO = World Health Organization.

^a Site = Species.

Table 3. Concentrations of PCBs in gastropods from the Chinese Bohai Sea (pg/g lipid wt)

| Gastropods | Yangk <i>R. venosa</i> ^a | Tianj <i>N. didyma</i> | Yant <i>N. cumingii</i> | Weih <i>R. venosa</i> | Qinhd <i>R. venosa</i> | Dal <i>N. didyma</i> | Huld <i>N. didyma</i> | Yink <i>R. venosa</i> |
|--------------------|--|---------------------------|----------------------------|--------------------------|---------------------------|-------------------------|--------------------------|--------------------------|
| PCB77 | 212 | 625 | 1086 | 240 | 252 | 2658 | 388 | 1380 |
| PCB81 | 57 | 117 | <1.0 | <1.4 | <1.3 | 420 | 33 | 168 |
| PCB 105 | 662 | 2037 | 3622 | 1208 | 1318 | 5104 | 883 | 1544 |
| PCB114 | 91 | 224 | 362 | 135 | 121 | 492 | <2.7 | 191 |
| PCB118 | 1396 | 5698 | 9011 | 2723 | 2991 | 9253 | 1898 | 2829 |
| PCB123 | <2.9 | <2.0 | <1.0 | <2.2 | <2.0 | <2.8 | <2.7 | <5.5 |
| PCB126 | 10 | 55 | 138 | <2.6 | 15 | 57 | <3.2 | <6.5 |
| PCB156 | 158 | 603 | 1375 | 234 | 242 | 366 | 313 | 126 |
| PCB157 | 40 | 211 | 638 | 153 | 73 | 111 | 104 | 43 |
| PCB 167 | 95 | 397 | <1.0 | 145 | 218 | 203 | 38 | 95 |
| PCB 169 | <3.9 | 21 | 30 | <3.0 | <2.7 | <3.8 | <3.7 | <7.5 |
| PCB189 | <1.8 | <1.3 | <1.0 | <1.4 | <1.3 | <1.8 | <1.7 | <3.5 |
| Sum WHO - PCBs | 2721 | 9989 | 16260 | 4838 | 5230 | 18663 | 3658 | 6376 |
| WHO-TEQs | 1.4 | 7.1 | 16 | 0.68 | 2.2 | 7.9 | 0.53 | 0.78 |
| PCB28 | 4567 | 9115 | 2171 | 2045 | 11345 | 7105 | 3902 | 23286 |
| PCB52 | 8237 | 18766 | 2921 | 3142 | 3335 | 16080 | 2392 | 43768 |
| PCB101 | 3988 | 14844 | 5653 | 3554 | 3418 | 8049 | 2143 | 11465 |
| PCB138 | 5297 | 26183 | 18774 | 6195 | 4740 | 9947 | 3191 | 9349 |
| PCB153 | 6655 | 36713 | 32932 | 8670 | 6354 | 7928 | 1878 | 21861 |
| PCB180 | 1555 | 11188 | 4204 | 1079 | 802 | 1447 | 712 | 1653 |
| PCB209 | 2095 | 1576 | 1912 | 568 | 508 | 1162 | 2260 | 6866 |
| Sum indicator PCBs | 32394 | 118383 | 68566 | 25253 | 30502 | 51719 | 16477 | 118276 |
| 1-PCB | 175 | 140 | 18 | 62 | 283 | 172 | 194 | 564 |
| 2-PCB | 432 | 414 | 274 | 66 | 660 | 54 | 221 | 1459 |
| 3-PCB | 16713 | 25728 | 2788 | 3433 | 25939 | 20659 | 7340 | 80665 |
| 4-PCB | 68300 | 163245 | 49939 | 31215 | 36340 | 73598 | 32069 | 369501 |
| 5-PCB | 21628 | 65461 | 40113 | 18483 | 20000 | 61010 | 13532 | 65677 |
| 6-PCB | 24024 | 110510 | 72644 | 21808 | 17392 | 31674 | 7548 | 48413 |
| 7-PCB | 6790 | 42813 | 16629 | 5619 | 5024 | 9508 | 3210 | 8468 |
| 8-PCB | 579 | 5364 | 1146 | 346 | 339 | 812 | 241 | 1252 |
| 9-PCB | 396 | 495 | 1207 | <1.0 | <1.0 | 272 | 1012 | 756 |
| Total PCBs | 141132 | 415745 | 186671 | 81600 | 106485 | 198922 | 67626 | 583621 |

PCB = Polychlorinated biphenyls, WHO = World Health Organization.

^a Site = Species.

revealed that the lighter congeners in bivalves were higher than those in gastropods, but the heavier congeners in bivalves were lower than those in gastropods. Perhaps this is because the collected bivalves are grass-eating mollusks, whereas the three collected gastropod species (*R. venosa*, *N. didyma*, and *N. arthritica cumingii*) are all predatory flesh-eating mollusks, the main food of which are bivalves. From the view of trophic levels, the gastropods are superior to bivalves and can bioaccumulate higher PCBs. Another phenomenon observed was that the concentrations of PCBs 138 and 153 in bivalves were similar, but for gastropods the levels of PCBs 138 and 153 were quite different. The levels of PCB 153 were higher than those of PCBs 138 except in the gastropods from the sampling sites near Dalian and Huludao cities. This can be explained by the fact that bivalves and gastropods have different feeding habits and that PCB 153 predominated in biota and water, whereas PCB 138 predominated in sediments (Monod *et al.* 1995; Kannan *et al.* 1995). In addition, the PCA results also revealed that the same species maintained the PCB profile independent of the sampling sites. This suggests that different species of mollusks have different bioaccumulation of PCBs depending on feeding habits.

The PCA results showed that the samples near Qinhuangdao, Huludao, and Yingkou cities had a similar PCB pattern with PCB₃. These sampling sites were located near a former

capacitor production factory that used PCB₃ as the impregnant of power capacitor from the 1960s to the 1970s. The PCA results also showed that the samples from the sampling sites near Tianjin and Dalian cities were characterized by higher PCBs and had similar pattern independent of mollusk species. The patterns of PCBs in the two samples were different from those of PCB₃ and PCB₅. The sources analysis pointed to the former Tianjing Paint General Factory and the Dalian Paint Factory, which used PCB₅ as paint additive in the 1960s.

In addition, the higher PCB levels were observed in gastropods from the sampling sites near the former capacitor and paint factories, but this was not the case for the bivalve samples. Perhaps this is so because bivalves live in close contact with bottom sediments, which transfer PCBs and PCDD/Fs from sediments to aquatic food webs, and bivalves serve as a food source for fish, waterfowl (Cope *et al.* 1999), crab (Cai *et al.* 1994), and gastropods.

Conclusion

The levels of PCBs detected in mollusks from Bohai Sea were higher than those in mollusks from other coastal areas of China, but they were lower than those from some developed countries.

Table 4. Concentration of PCDD/Fs in bivalves and gastropods from the Chinese Bohai Sea (pg/g lipid wt)

| Species | Yangk | | Tianj | | Yant | | Weih | | Qinhd | | Dal | | Huld | | Yink | |
|----------------|-----------------------|-------------------|-----------------------|----------------|-----------------------|----------------|-----------------------|----------------|-----------------------|----------------|-----------------------|----------------|-----------------------|----------------------|-----------------------|-------------------|
| | Gastro- pods R. | Bivalves S. | Gastro- pods N. | Bivalves S. | Gastro- pods R. | Bivalves C. | Gastro- pods R. | Bivalves S. | Gastro- pods R. | Bivalves S. | Gastro- pods N. | Bivalves M. | Gastro- pods N. | Bivalves M. | Gastro- pods N. | Bivalves C. |
| PCDD/Fs | <i>venosa</i> | <i>subcrenata</i> | <i>didyma</i> | <i>didyma</i> | <i>venosa</i> | <i>farreri</i> | <i>venosa</i> | <i>grandis</i> | <i>venosa</i> | <i>venosa</i> | <i>metrix</i> | <i>didyma</i> | <i>didyma</i> | <i>californiense</i> | <i>venosa</i> | <i>constricta</i> |
| 2378-TCDF | <4.2 | <9.7 | <2.9 | 10.7 | <3.2 | <3.4 | <4.8 | <4.8 | <2.9 | <10 | <4.0 | <2.3 | <27 | <3 | <8.9 | <10 |
| 12378-PeCDF | <5.3 | <12 | <3.7 | <8.5 | <4.1 | <4.4 | <6.2 | <6.2 | <3.7 | <13 | <5.0 | <2.9 | 6.0 | <4 | <10 | <13 |
| 23478-PeCDF | <5.3 | <12 | <3.7 | <8.5 | <4.1 | <4.4 | <6.2 | <6.2 | <3.7 | <13 | <5.0 | <4.0 | 10.5 | <4 | <10 | <13 |
| 123478-HxCDF | <8.8 | <21 | <6.2 | <14 | <6.8 | <7.3 | <10 | <10 | <6.0 | <22 | <8.5 | <4.9 | 12.6 | <6.8 | <17 | <22 |
| 123678-HxCDF | <4.2 | <9.7 | <2.9 | <6.7 | <3.2 | <3.4 | <4.8 | <4.8 | <2.9 | <10 | <4.0 | <2.3 | 4.8 | <3 | <8.0 | <10 |
| 234678-HxCDF | <8.6 | <20 | <6 | <14 | <6.6 | <7.1 | <10 | <10 | <6.0 | <21 | <8.3 | <4.7 | 6.8 | <6.6 | <17 | 17 |
| 123789-HxCDF | <10 | <24 | <7.1 | <16 | <7.8 | <8.4 | <12 | <12 | <7.0 | <25 | <9.8 | <3 | <9.8 | <7.8 | <20 | <25 |
| 1234678-HpCDF | <5.5 | <13 | <3.8 | <8.8 | <4.2 | <4.5 | <6.4 | <6.4 | <3.8 | <14 | <5.3 | 3.5 | 7.8 | <4.2 | <11 | 55 |
| 1234789-HpCDF | <7.5 | <18 | <5.3 | <12 | <5.8 | <6.2 | <8.8 | <8.8 | <5.3 | <19 | <7.3 | <4 | <7.0 | <5.8 | <15 | <19 |
| OCDF | <6.5 | <15 | <4.5 | <10 | <5.0 | <5.4 | <7.6 | <7.6 | 3.5 | <16 | <6.3 | <3.6 | <11 | <5 | 15317 | <16 |
| 2378-TCDD | 6.1 | <10 | 6 | <7.1 | <3.4 | 5.8 | <5.2 | <5.2 | 3.8 | 18 | 44 | 3.3 | <4.0 | 14 | <12.7 | 8.5 |
| 12378-PeCDD | <5.7 | <13 | <4.0 | <9.2 | <4.4 | <4.7 | <6.7 | <6.7 | <4.0 | <14 | <5.5 | <3 | 5.1 | <4 | <11 | 21 |
| 123478-HxCDD | <7.8 | <18 | <5.5 | <13 | <6.0 | <6.5 | <9.1 | <9.1 | <5.5 | <19 | <7.5 | <4.3 | 4.0 | <6 | <15 | <19 |
| 123678-HxCDD | <7.8 | <18 | <5.5 | <13 | <6.0 | <6.5 | <9.1 | <9.1 | <5.5 | <19 | <7.5 | <4.3 | <7.0 | <6 | <15 | <19 |
| 123789-HpCDD | <8.3 | <19 | <5.8 | <13 | <6.4 | <6.7 | <9.7 | <9.7 | <5.8 | <21 | <8.0 | <4.6 | <7.8 | <6.4 | <16 | 8.5 |
| 1234678-HpCDD | <6.5 | 47 | <4.5 | <10 | 4.2 | <5.4 | <7.6 | <7.6 | 4.5 | <16 | <6.3 | <3.6 | 5.9 | <5 | 8.5 | 97 |
| OCDD | 52 | 583 | 18 | 41 | 35.6 | 143 | 159 | 159 | 26.5 | 140 | 51 | 19.9 | 46 | 71 | 274 | 2584 |
| WHO-TEQ/lipid | 6.1 | 0.53 | 6.0 | 1.073 | 0.05 | 5.79 | 0.016 | 0.016 | 3.86 | 18.3 | 44 | 5.4 | 16.4 | 14 | 1.44 | 27 |
| WHO-TEQ/wet wt | 0.05 | 0.002 | 0.06 | 0.005 | 0.0004 | 0.05 | 0.0001 | 0.0001 | 0.04 | 0.06 | 0.34 | 0.07 | 0.13 | 0.14 | 0.06 | 0.08 |
| WHO-TEQ/dry wt | 0.17 | 0.006 | 0.22 | 0.03 | 0.002 | 0.33 | 0.0006 | 0.0006 | 0.15 | 0.48 | 1.5 | 0.39 | 0.7 | 0.72 | 0.23 | 0.5 |

PCDDs = Polychlorinated dibenzo-p-dioxins, PCDFs = Polychlorinated dibenzofurans, TEQ = Toxic equivalency quotient, WHO = World Health Organization.

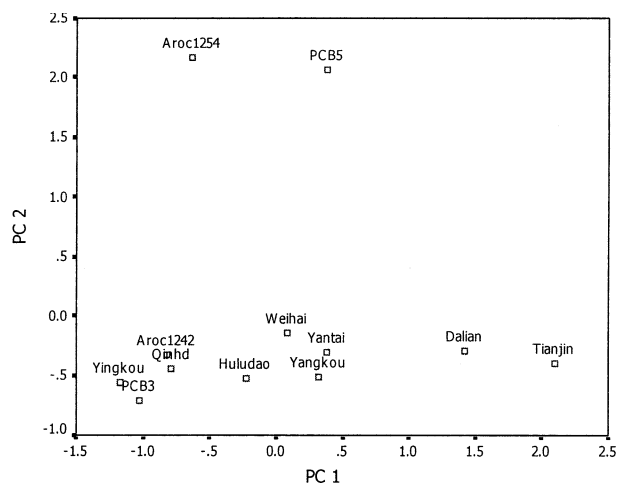


Fig. 2. Two-dimensional principal component score plot obtained from the data correlation matrix of eight bivalve samples along Bohai Sea coastline.

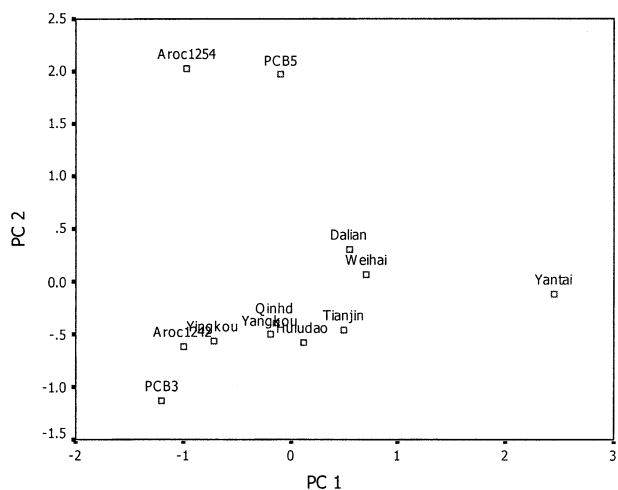


Fig. 3. Two-dimensional principal component score plot obtained from the data correlation matrix of eight gastropod samples along Bohai Sea coastline.

The sources of PCBs were identified using PCA based on the concentration of the individual PCB congeners in mollusks in some coastal areas. The PCB sources analysis implicated a former capacitor and two paint factories located along the Bohai Sea. The patterns of PCBs in bivalves and gastropods are different because of their different feeding habits, whereas identical species had similar patterns independent of the sampling sites. The higher gastropod PCB concentrations were related to the existence of a former capacitor factory and paint factories located near the sampling sites, but this was not the case regarding the level of PCBs in bivalves. This suggests that some gastropod species may be used as bioindicators to monitor PCB pollution in marine environment.

Acknowledgments. This study was supported by National Basic Research Program of China (2003CB415006) and Hi-Tech Research and Development program of China 2002AA641010.

References

- Abad E, Pérez F, Llerena JJ, Caixach J, Rivera J (2003) Evidence for a specific pattern of polychlorinated dibenzo-p-dioxins and dibenzofurans in bivalves. *Environ Sci Technol* 37:5090–5096
- Abarnou A, Fraisse D (2002) Dioxin and dioxin-like PCBs in mussels and fishes from the French coastal waters. *Organohal Comp* 56:469–472
- Barron MG (1990) Bioconcentration. Will water-borne organic chemicals accumulate in aquatic animals? *Environ Sci Technol* 24:1612–1618
- Bi X, Chu S, Meng Q, Xu X (2002) Movement and retention of polychlorinated biphenyls in a paddy field of Wen Tai area in China. *Agric Ecosys Environ* 89:241–252
- Cai Z, Ramanujam VMS, Gross ML, Cristini T, Tucker RK (1994) Levels of polychlorodibenzo-p-dioxins and dibenzofurans in crab tissues from the Newark/Raritan Bay System. *Environ Sci Technol* 28:1528–1534
- Chen W, Zhang L, Xu L, Wang X, Hong L, Hong H (2002) Residue levels of HCHs, DDTs, and PCBs in shellfish from coastal areas of east Xiamen Isand and Minjiang Estuary, China. *Mar Pollut Bull* 45:385–389
- Chu S, Cai M, Xu X (1999) Soil–plant transfer of polychlorinated biphenyls in paddy fields. *Sci Total Environ* 234:119–126
- Cope WG, Bartsch MR, Rada RG, Balogh SJ, Ruppreche JE, Young RD, et al. (1999) Bioassessment of mercury, cadmium, polychlorinated biphenyls, and pesticides in upper Mississippi River with zebra mussels (*Dreissena polymorpha*). *Environ Sci Technol* 33:4385–4390
- Corsolini S, Kannan K, Imagawa T, Focardi S, Giesy GP (2002) Polychloronaphthalenes and other dioxin-like compounds in Arctic and Antarctic marine food webs. *Environ Sci Technol* 36:3490–3495
- EC No. 194/97 (2000) Setting maximum levels for certain contaminants in foodstuffs, amending commission regulation EC No. 194/97 of 31 January 1977; DG ENTR/E/1GS D(99); Brussels, Belgium
- Everaarts JM, Heesters R, Fischer CV, Hillebrand MThJ (1993) Baseline levels of cyclic pesticides and PCBs in benthic invertebrates from the continental slope of the Banc d'Arguin (Mauritania). *Mar Pollut Bull* 26:515–521
- Hashimoto S, Horiguchi T, Shibata Y, Morita M (1999) Polychlorinated dibenzo-p-dioxins and dibenzofurans in invertebrate animals from a rural beach in Japan. *Chemosphere* 39:2661–2669
- Jang K, Li L, Chen Y, Jin J (1997) Determination of PCDD/Fs and dioxin-like PCBs in Chinese commercial PCBs and emission from a testing incinerator. *Chemosphere* 34:941–950
- Kannan N, Reusch TBH, Schulz-bull DE, Petrick G, Duinlcer GC (1995) Chlorobiphenyls: Model compounds for metabolism in food chain organisms and their potential use as ecotoxicological stress indicators by application of the metabolic slope concept. *Environ Sci Technol* 29:1851–1859
- LeBianc GA (1995) Trophic-level differences in the bioconcentration of chemicals: Implications in assessing environmental biomagnification. *Environ Sci Technol* 29:154–160
- Lung SC, Chen C, Hu S, Bau Y (2003) Exposure of Taiwan residents to polychlorinated biphenyl congeners farmed, ocean-caught, and imported fish. *Environ Sci Technol* 37:4579–4585
- Méndez BMP, España MSA, Montelongo FG (1996) Polychlorinated biphenyls in two molluscs species from the coast of Tenerife (Canary Island, Spain). *Chemosphere* 32:2371–2380
- Monirith I, Ueno D, Takahashi S, Nakata H, Sudaryanto A, Subramanian A, et al. (2003) Asia-Pacific mussel watch: Monitoring contamination of persistent organochlorine compounds in coastal waters of Asian countries. *Mar Pollut Bull* 46:281–300

- Monod JL, Arnaud PM, Arnoua A (1995) PCB congeners in the marine biota of Saint Paul and Amsterdam Islands, Southern Indian Ocean. *Mar Pollut Bull* 30:272–274
- Nakata H, Kawazoe M, Arizono K, Abe S, Kitano T, Shimada H, et al. (2002) Organochlorine pesticides and polychlorinated biphenyl residues in foodstuffs and human tissues from China: Status of contamination, historical trend, and human dietary. *Arch Environ Contam Toxicol* 43:473–480
- Qin ZF, Zhou JM, Chu SG, Xu XB (2003) Effects of Chinese domestic polychlorinated biphenyls (PCBs) on gonadal differentiation in *Xenopus laevis*. *Environ Health Perspect* 111:553–556
- Sakurai T, Suzuki N, Masunaga S, Nakanishi J (1998) Origin attribution of polychlorinated dibenzo-p-dioxins and dibenzofurans in sediment and soil from a Japanese freshwater lake area through congener-specific data analysis. *Chemosphere* 37:2211–2224
- Yuan D, Yang D, Wade TL, Qian Y (2001) Status of persistent organic pollutants in the sediment from several estuaries in China. *Environ Pollut* 114:101–111
- Zhou JL, Hong H, Zhang Z, Maskaoui W (2000) Multi-phase distribution of organic micropollutants in Xiamen Harbour, China. *Water Res* 34:2132–2150