# STUDIES ON COPLANAR PCBs IN AGRICULTURE SOILS FROM CHONGMING ISLAND, THE YANGTZE RIVER DELTA (YRD)

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**Introduction**

As one of the twenty-one persistent organic pollutants (POPs) regulated under the Stockholm Convention in 2004, polychlorinated biphenyls (PCBs) possess toxic properties and resist degradation. They can undergo long-range transport through air, water, and migratory species and bioaccumulate. Consequently, they pose health risks in the environment and to human beings. PCB exposure has been associated with adverse effects on human health, especially dioxin-like PCBs (DL-PCBs), those PCB congeners that exhibit toxic actions similar to dioxins[1]. The DL-PCBs (DL-PCBs, PCB-81, 77, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189, IUPAC number) mainly come from the commercial products which are used in an industrial capacity, transformers and oil painting and which are sometimes deposited in the environment. They are generally monitored in agricultural fields, environmental soil and sediment [2-6]. Therefore, it is very important to evaluate the environmental quality of soil concerning with the distribution and contamination of PCBs.In this study, we selected Chongming Island as rural area to investigate systematically PCBs in surface soils. Chongming Island, belonging to the Yangtze River Delta (YRD) geographicallyThe YRD is one of the most industrialized and urbanized regions, contributing about 20% gross domestic product (GDP) in China. In our research, based on the profile of DL-PCBs, we perform the PCA analysis to identify the possible contamination sources.

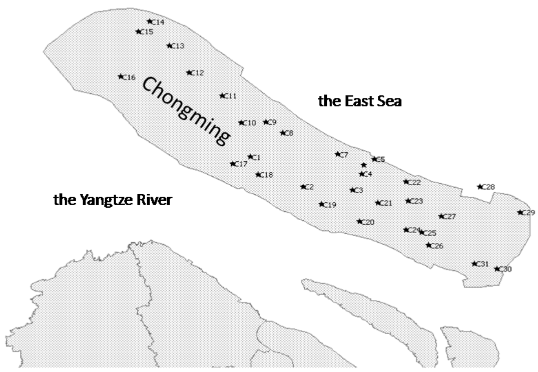


Fig.1 Distribution of sampling sites in chongming island, shanghai

**Materials and methods**

**Materials**

n-Hexane(pesticide) and acetone(pesticide) were obtained from Fluca, USA and dichloromethane (DCM, pesticide) were from J.T.Baker, USA. Silica gel(0.063–0.200mm) and Florisil(0.150～0.250mm)was supplied by Merck, Germany. Anhydrous sodium sulphate (GR) from Shanghai Pharmaceutical Group was baked at 450℃ before use and stored in sealed containers. Nonane (p.a.) was purcursed from Fluka, USA. The standards of PCB were supplied by Wellington Laboratories, USA.

**Sampling and sample preparation**

Thirty-one samples of agricultural soils at a depth of 0-20cm depth were collected within a 5–10 m radius of each sampling site(Fig. 1)shows the location of the sample sites located using the global positioning system (GPS). In May 2007, three types of top soils from 31sites in Chongming Island were taken using a pre-cleaned steel spoon, which include farmland soils(A), vegetable & cotton soil(B) and watermelon & citrus soils(C)(Table 1). In each site, three samples of top soil were taken and then mixed in a glass bottle and transported to the laboratory. The samples were dried at room temperature for 10–14 days. Dried soils were crushed by a ceramic cutting mill and then passed through a stainless steel sieve of 60 mesh. The samples were then labeled and stored in glass flasks at a temperature of -20℃ until analysis.

**Analytical methods**

DL-PCBs were extracted from the soil samples using ASE 200 system (Dionex, USA). The samples were extracted using 1:1 mixture of hexane and dichlomethane followed by clean-up with multilayer silica gel column and florisil column according to USEPA Method 1618a. High resolution gas chromatography-high resolution mass spectrometry(HRG-HRMS) was undertaken on an Agilent 6890 gas chromatograph coupled with an Autospect Premier mass spectrometer (Waters) running with an EI source in SIM mode. The recoveries generally varied between 55.6% and 100.7%, which satisfied the requirements of USEPA Method 1618a. Co-PCBs TEQ calculation was done using I- TEFs.

**Data analysis**

Principal component analysis (PCA) was performed using the Multi-Variate statistical package (MVSP) version 3.13n. Concentrations that were below the MDL were assigned a value half of LOD before conducting PCA and HCA. HCA was performed using Squared Euclidean Distance.

## Results and discussion

**Levels and congeners distribution**

Co-PCBs congeners detected in all agricultural soil samples are summarized in Table 2 and Figure 2. The mean concentrations of the soil samples ranged from 19.42 to 814.5pg $g^{-1}$ dry weight (dw) with a mean of 92.65 pg $g^{-1}$ dw. Among all soil samples, mono-ortho PCB118 was the predominant congener, accounting for around 41.87%(29.12% to 52.85%) of the total concentration of 12 congeners, followed by PCB105, PCB77 and PCB167 which account for 21.45%(15.57% to 28.09%), 10.66%(4.53% to 19.06%) and. and 9.17%(3.63% to 16.18%) respectively. Generally, these four congeners accounted for approximately 86.46 % (62.52 to 92.55%) of the sum of PCB congeners measured. No apparent differences in PCB profiles were observable between soils from different locations and an example of the typical PCB.

Compared with domestic and foreign soil co-PCBs (Table 3), TEQ levels of Chongming region far less than that of Taizhou in China, China Taiwan, Hangzhou China, Italy, India and Spain, slightly higher than Australia, closer to agricultural soils of New Zealand, Poland and the United States[7-16]. above results indicate that the chongming region was not contamined basically in spite of the existence of certain co-PCBs. Various isomers of co-PCBs TEQ contribution was shown in Figure 2, PCB126(67.35 to 96.20%) is the greatest contribution to the total TEQ. However, The highest I-TEQ (0.486 pg·I-TEQ·g-1) was found at site C8(total concentration of 205.17pg g-1) and the second I-TEQ (0.289 pg·I-TEQ·g-1) at site C31(total concentration of 814.5pg g-1). Therefore it is necessary to study their source.

Table 1 Concentrations of Co-PCBs in chongming soil samples

| Num | Soil type | Co-PCBs(pg/g) | | | | | | | | | | | | | ∑I-TEQ (pg/g) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | non-orhto | | | | mono-orhto | | | | | | | | total | |
| | | PCB 77 | PCB 81 | PCB 126 | PCB 169 | PCB 105 | PCB 114 | PCB 118 | PCB 123 | PCB 156 | PCB 157 | PCB 167 | PCB 189 | | |
| C2 | A | 10.06 | 0.36 | 1.40 | 0.23 | 25.39 | 0.84 | 59.35 | 1.64 | 9.89 | 2.22 | 15.90 | 0.81 | 128.08 | 0.158 |
| C4 | A | 1.98 | 0.31 | 0.56 | 0.13 | 6.47 | 0.30 | 13.63 | 0.44 | 2.59 | 0.66 | 3.69 | 0.29 | 31.05 | 0.061 |
| C5 | A | 5.68 | 0.70 | 1.15 | 0.44 | 11.12 | 0.57 | 24.55 | 0.54 | 4.28 | 0.90 | 5.47 | 0.97 | 56.36 | 0.126 |
| C6 | A | 3.44 | 0.55 | 1.02 | 0.21 | 9.85 | 0.47 | 26.56 | 1.01 | 4.72 | 1.18 | 6.41 | 0.40 | 55.81 | 0.111 |
| C7 | A | 12.21 | 1.46 | 1.82 | 0.69 | 16.30 | 0.95 | 38.43 | 1.06 | 4.79 | 1.02 | 6.27 | 0.25 | 85.24 | 0.199 |
| C9 | A | 3.26 | 0.44 | 1.06 | 0.19 | 11.21 | 0.42 | 27.15 | 0.62 | 4.92 | 1.11 | 7.14 | 2.72 | 60.23 | 0.116 |
| C10 | A | 20.14 | 1.99 | 4.61 | 0.42 | 18.00 | 0.93 | 41.06 | 1.27 | 8.35 | 2.04 | 6.37 | 0.49 | 105.67 | 0.479 |
| C11 | A | 2.86 | 0.38 | 0.90 | 0.14 | 9.44 | 0.40 | 22.99 | 0.45 | 3.73 | 0.85 | 5.71 | 0.35 | 48.2 | 0.097 |
| C12 | A | 2.17 | 0.33 | 0.57 | 0.16 | 5.57 | 0.31 | 14.24 | 0.42 | 2.06 | 0.47 | 3.29 | 0.24 | 29.83 | 0.062 |
| C15 | A | 5.67 | 0.51 | 1.09 | 0.20 | 20.56 | 0.66 | 50.40 | 1.29 | 7.82 | 1.53 | 11.16 | 0.59 | 101.45 | 0.124 |
| C16 | A | 7.67 | 1.03 | 1.49 | 0.37 | 20.39 | 1.01 | 53.71 | 1.52 | 6.84 | 1.38 | 9.24 | 0.52 | 105.16 | 0.166 |
| C18 | A | 9.61 | 0.93 | 1.90 | 0.46 | 25.00 | 0.91 | 58.80 | 1.27 | 9.19 | 1.97 | 13.29 | 1.04 | 124.36 | 0.211 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C19 | A | 2.88 | 0.33 | 0.98 | 0.20 | 9.48 | 0.42 | 20.06 | 0.75 | 4.59 | 1.12 | 7.16 | 0.57 | 48.53 | 0.106 |
| C21 | A | 3.79 | 0.96 | 1.23 | 0.19 | 10.63 | 0.85 | 25.97 | 2.55 | 4.70 | 1.55 | 8.20 | 0.51 | 61.12 | 0.133 |
| C23 | A | 3.09 | 0.22 | 0.60 | 0.14 | 6.20 | 0.38 | 11.33 | 0.37 | 2.26 | 0.53 | 3.07 | 0.28 | 28.46 | 0.065 |
| C24 | A | 4.04 | 0.42 | 0.91 | 0.21 | 9.37 | 0.45 | 19.57 | 0.74 | 5.15 | 1.35 | 8.27 | 0.64 | 51.11 | 0.1 |
| C25 | A | 6.67 | 0.88 | 1.68 | 0.37 | 17.51 | 0.78 | 42.70 | 1.15 | 7.61 | 1.76 | 11.82 | 0.91 | 93.83 | 0.184 |
| C26 | A | 2.03 | 0.68 | 0.59 | 0.95 | 5.83 | 0.47 | 10.89 | 4.27 | 1.95 | 4.82 | 4.64 | 0.30 | 37.42 | 0.074 |
| C27 | A | 2.23 | 0.68 | 1.07 | 0.30 | 5.95 | 0.58 | 12.37 | 0.31 | 2.47 | 0.80 | 3.13 | 0.56 | 30.43 | 0.114 |
| C1 | B | 3.12 | 0.43 | 0.99 | 0.20 | 10.56 | 0.54 | 21.54 | 0.76 | 4.71 | 1.07 | 6.45 | 0.50 | 50.88 | 0.108 |
| C3 | B | 2.47 | 0.26 | 0.71 | 0.14 | 6.89 | 0.36 | 16.24 | 0.47 | 2.74 | 0.73 | 4.11 | 0.35 | 35.47 | 0.077 |
| C13 | B | 3.04 | 0.33 | 0.61 | 0.20 | 5.92 | 0.23 | 10.98 | 0.49 | 2.44 | 0.69 | 3.55 | 0.33 | 28.8 | 0.067 |
| C14 | B | 5.57 | 0.53 | 1.28 | 0.32 | 14.69 | 0.65 | 35.13 | 1.21 | 7.95 | 1.75 | 12.68 | 0.94 | 82.68 | 0.143 |
| C17 | B | 9.17 | 1.31 | 1.79 | 0.20 | 33.78 | 1.28 | 92.78 | 1.77 | 12.83 | 2.23 | 17.56 | 0.88 | 175.57 | 0.203 |
| C20 | B | 6.33 | 1.12 | 1.42 | 0.31 | 14.18 | 0.82 | 35.51 | 0.84 | 4.89 | 1.15 | 6.50 | 0.57 | 73.63 | 0.154 |
| C28 | B | 2.24 | 0.22 | 0.48 | 0.13 | 8.05 | 0.37 | 25.77 | 0.67 | 3.98 | 0.91 | 6.38 | 0.27 | 49.45 | 0.055 |
| C30 | B | 1.43 | 0.14 | 0.28 | 0.06 | 5.44 | 0.29 | 12.88 | 0.36 | 0.49 | 1.96 | 3.41 | 0.12 | 26.86 | 0.032 |
| C8 | C | 29.10 | 1.58 | 4.51 | 1.17 | 34.66 | 1.00 | 87.20 | 2.10 | 11.97 | 3.14 | 28.06 | 0.68 | 205.17 | 0.486 |
| C22 | C | 1.42 | 0.48 | 0.52 | 0.05 | 3.91 | 0.40 | 7.26 | 0.79 | 1.63 | 0.46 | 2.36 | 0.15 | 19.42 | 0.055 |
| C29 | C | 3.68 | 0.19 | 0.33 | 0.13 | 4.86 | 0.27 | 12.39 | 0.48 | 1.78 | 0.46 | 2.42 | 0.38 | 27.36 | 0.038 |
| C31 | C | 129.03 | 11.62 | 1.95 | 0.16 | 228.77 | 12.75 | 366.39 | 10.47 | 4.02 | 18.83 | 29.59 | 0.93 | 814.5 | 0.289 |

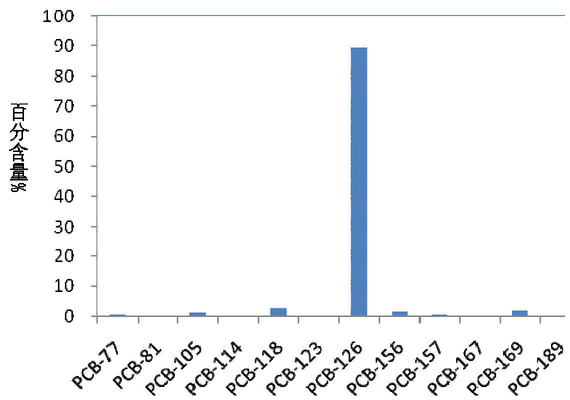


Fig.2 TEQ distribution of co-PCBs congeners in chongming agricultural soils

**Principal component analysis (PCA)**

Principal component analysis (PCA) was conducted to preliminary analysis of the sources of pollution using MVSP (version 3.13n) software. Three principal components was obtained by extracting the factors whose eigenvalues was greater than one. Principal component eigenvalues and percentage was listed in table 2. The cum. percentage of three principal components of PCBs was 46.367%, 29.588% and 11.782%. The cum. percentage of three principal components was 87.737% s, and therefore the other components of percentage can be ignored.

Table 3 Results of eigenvalue and percentage analysis

| principal component | Eigenvalues | Percentage(%) | Cum. Percentage(%) |
|---|---|---|---|
| 1 | 29.069 | 46.367 | 46.367 |
| 2 | 18.55 | 29.588 | 75.955 |
| 3 | 7.387 | 11.782 | 87.737 |

31 Soil samples can be divided into three groups by PCA. Group 1 consists of 29 samples and the Group 2and 3 are respectviely a soil sample C31 and C26, which indicated that there were different pollution sources. Contrast to the distribution characteristics of the isomers，it can be inferred that the group 1 may be subject to the combined effect of Aroclor1232, Aroclor1242 and Aroclor1248. In addition, PCB156 and PCB167 in group 1 relatively increased, which may be affected by Aroclor1254. At the same time, PCB156 and PCB167 were produced in indoor coal combustion and wood combustion[17], PCB105 concentration percentage of Group of 2(C31) was the highest among all soil samples. PCB77 concentration percentage of Group of 2(C31) was second to the group of 3(C10), while total concentration percentage of PCB118, PCB 105, PCB77 had accounted for 88.91%. So Group of 2 is affected by Aroclor1232, Aroclor1242 and Aroclor1248. PCB118, PCB105 and PCB77 concentration percentage of Group 1 were greater than70%, however only 50% in group of 3(C10). And PCB123, PCB156, PCB157 and PCB167 concentration percentage of Group 3 increased apparently. PCB123 concentration percentage of Group 3(C10) was the highest among all soil samples. It is reported in the literature that Municipal solid waste and medical waste incinerators typically release PCB-118 and PCB-123 into the atmosphere[18], so group of Group 3(C10) may be affected by the municipal waste and medical waste burning effect. At the same time, Aroclor1254, Aroclor1260 and indoor burning coal, wood burning may also account for PCB156, PCB 157 and PCB167.
The results suggested that the other pollution sources of PCBs existed such as housecoal, hardwood combustion and municipal solid and medical waste combustion besides PCB Construction as an ecological island of chongming, requires special attention to prevent further increase of the co-PCBs in soil, reducing the integrity of a healthy ecosystem.

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