ISSN 1001-0742
CN 11-2629/X

2012
Volume 24
Number 10

# JOURNAL OF ENVIRONMENTAL SCIENCES

Science Press

Sponsored by
Research Center for Eco-Environmental Sciences
Chinese Academy of Sciences

# JOURNAL OF ENVIRONMENTAL SCIENCES

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ISSN 1001–0742 **Journal of Environmental Sciences** Vol. 24 No. 10 2012

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Serial parameter: CN 11-2629/X*1989*m*162*en*P*20*2012-10

Available online at www.sciencedirect.com
ScienceDirect
Journal of Environmental Sciences 2012, 24(10) 1854–1860
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

# Pollution level and human health risk assessment of some pesticides and polychlorinated biphenyls in Nantong of Southeast China

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Received 03 December 2011; revised 11 January 2012; accepted 10 February 2012

**Abstract**

Food consumption is one of the key exposure routes of humans to contaminants. This article evaluated the residue levels of 51 pesticides and 16 polychlorinated biphenyls (PCBs) in selected fish and food items which were commonly consumed in the Nantong area of Jiangsu Province, Southeast China. The 51 pesticides and 16 PCBs were analyzed by highly sensitive gas chromatography-tandem mass spectrometry (GC-MS/MS). The results showed that organochlorine pesticides such as dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB) and mirex and other pesticides including chlorpyrifos, pyrethroid pesticides, metolachlor, pyridaben and trifluralin were frequently detected in the samples, which was consistent with the accumulation level and characteristics of these toxic chemicals in human adipose tissue of people living in Nantong. Meanwhile, correlation of the residue level of toxic chemicals with their physical chemical properties and historic use pattern in Nantong area was observed. Combined with dietary survey results at the same sampling locations, human health risk assessment of ingestion through the dietary route was performed. The results suggested that the non-cancer risks of the chemicals investigated can be considered negligible in the Nantong area, however, the cancer risks from lifetime dietary exposure to DDTs and HCB have exceeded the acceptable levels.

**Key words**: pesticides; PCBs; human health risk assessment; dietary intake; Nantong

**DOI**: 10.1016/S1001-0742(11)61004-8

## Introduction

While we enjoy enormous benefits brought by pesticides and other chemical substances, we also often suffer from their adverse effects to our health. In order to assure food security in China during the last 40 years, use of pesticides has been a key means to protect food production from pest impact. Even today, pesticides are still heavily used in certain areas in China to control the breakout of pests. Polychlorinated biphenyls (PCB) is another group of chemicals which has also received great attention in China. They are widely used in heat exchangers and dielectric fluids, as stabilizers in paints, polymers, and adhesives, and as lubricants in various industrial processes (Safe, 1994). As a consequence, PCB-containing products are present extensively in our daily life. Consequently, PCBs could potentially get into our food chain through contaminated water and inappropriate waste disposal. Due to the bioaccumulation and toxicity of some organochlorine pesticides (OCPs) and PCBs, they were recognized as persistent organic pollutants (POPs) defined by the Stockholm Convention in 2001 (UNEP, 2001).

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Humans can expose themselves to pesticides and PCBs through skin absorption, respiration and ingestion of contaminated food. Some researches have demonstrated that consumer consumption is the main exposure route accounting for more than 90% of the intake of pollutants by the public (Li et al., 2008). Due to the high lipophilicity of organochlorine substances, such as dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs) and PCBs, they can be accumulated and magnified in food items, especially in those with high contents of lipid such as some fish. Consequently, frequent consumption of such food will bring a potential risk to the consumers and assessment of the risk has therefore become important and necessary.

Some studies have been published in recent years which assessed the dietary exposure and the risk to human health of organochlorine chemicals at the population level in many countries (Jiang et al., 2005; Darnerud et al., 2006; Perugini et al., 2007; Fattore et al., 2008). The present study focused on the Nantong area in Jiangsu Province, which represents the agricultural region of Southeast China where population density is high, and fish are consumed significantly more than in the inland provinces (Jiang et al., 2005). The objective of the presented study was to assess consumer exposure of as many as 67 toxic chemicals by determining the concentrations of these chemicals in selected food species collected in Nantong of Jiangsu Province. Human health risk assessment of these chemicals was also performed using local diet consumption survey data.

# 1 Materials and methods

## 1.1 Sample collection

Fish and mussel (mullet, carassius auratus, mussel), vegetables (carrot, cabbage) and other foodstuffs (bean, rice, wheat) were collected from Nantong of Jiangsu Province in September, 2009. Collected samples were stored in a cooler box with ice and immediately transported to the laboratory. The fish internal organ samples were isolated from the edible portion of fish samples, and then both internal organ and edible portions of fish samples were homogenized and frozen at –20°C. The vegetable and foodstuff samples were stored at 0°C.

## 1.2 Sample preparation and extraction

### 1.2.1 Sample preparation

Fish and mussel samples: an aliquot of sample (10 ± 0.01 g) was homogenized at 15,000 r/min two times with 40 mL acetonitrile (chromatographic grade, Merck, Germany) (plus 20 g anhydrous sodium sulfate; analytical grade; Nanjing Chemical Reagent Co., Ltd., China). Vegetable samples: an aliquot of sample (20 ± 0.01 g) was homogenized at 15,000 r/min two times with 40 mL acetonitrile (plus 20 g anhydrous sodium sulfate). Foodstuff samples: an aliquot of homogenized sample (20 ± 0.01 g) was extracted two times with acetonitrile employing accelerated solvent extraction (Dionex 300, USA) at 80°C and 1500 psi. The preheating time was 1 min and heating time was 5 min. The sample was eluted rapidly with acetonitrile.

### 1.2.2 Sample purification

The supernatant, concentrated by the rotary evaporator (Buchi R-215, Switzerland) and mixed with the internal standard solution (exo-heptachlor epoxide; certified chemical standards; Dr. Ehrenstorfer, Germany), was diluted to 10 mL with ethyl acetate-cyclohexane (1:1, $V/V$) (chromatographic grade, Merck, Germany). After membrane filtration (0.45 μm), the sample solution was cleaned by gel-permeation chromatography (GPC) (J2 Scientific AcCuPrep MPS, J2, USA) to remove the lipid of the adipose sample. The eluent was concentrated to about 1 mL before GC-MS/MS (Quattromicro, Waters, USA) determination.

## 1.3 Instrumental analysis

A total of 67 chemicals including pesticides and PCBs were analyzed simultaneously by GC-MS/MS using an Agilent 7890 gas chromatograph coupled with Waters Quattro micro triple quadrupole MS/MS, operating in EI mode. The final sample extract (1 μL) was injected in the splitless mode into a DB-1701 capillary column (30 m × 0.25 mm × 0.25 μm; Agilent, USA) with helium as carrier gas at a constant flow rate of 1.2 mL/min. The injector temperature was 290°C and the interface temperature was 250°C. The oven was programmed to warm up from 40°C (1 min) to 130°C at a rate of 30°C/min, then to 250°C at a rate of 5°C/min, and then to 300°C (5 min) at a rate of 10°C/min. Ionization energy was 70 eV. The mode of acquiring signal was Multiple Reaction Monitoring, with which 2 parent-product ion transitions were monitored for quantification and qualification (Table 1).

## 1.4 Quality control and assurance

The analytical method was validated and showed no interference in the retention time ($t_R$) region of the test substances. The levels of quantification (LOQ) of all chemicals in the Fish and mussel, vegetable and foodstuff matrix were between 0.010–25.3 ng/g, 0.043–12.7 ng/g and 0.038–11.5 ng/g with recoveries between 72.2%–106%, 72.4%–119.8% and 69.7%–112.9%, respectively. The laboratory reagents, blank samples, and spiked samples were treated and analyzed using the same method as the actual samples (1 reagent blank, 1 matrix blank, and 1 control sample for every 10 samples). The relative standard deviation (RSD) of all the controls was between 7.08%–14.1%, which indicated that the sample processing was stable.

## 1.5 Dietary survey

A questionnaire-based dietary survey was conducted at Nantong of Jiangsu Province in 2009, by randomly selecting and surveying 150 healthy adults from the general population. All the volunteers had lived in the area for at least 10 years at the time of sampling. The questionnaire included 6 food categories: fish and mussels, foodstuffs, vegetables, eggs, meat, and others. Each group comprised about 3–10 food items. Data collected for each food item included frequency of consumption and the quantity consumed on each occasion. Daily intake (in g/(person·day)) was calculated for each individual.

# 2 Results and discussion

## 2.1 Detected frequency and concentration of pesticides in fish and mussels and agricultural products

The detected frequency and concentration of the investigated pesticides in the fish samples are summarized in Table 2. Organochlorine pesticides were generally detected in the fish samples. A relatively high residue level of total DDTs was found in all the selected fish species, which reflected the fact that a large amount of DDT was used in past decades in China including the Nantong area (Yang et al., 2006). The average concentrations of total DDT in the edible portion of mullet, *Carassius auratus* and mussel were 369, 118 and 79.1 ng/g, respectively, which were much higher than the levels in other areas of China and other countries (Li et al., 2008; Hyo-Bang et al., 2009; Jiang et al., 2005; Guo et al., 2010). This might imply

**Table 1** Multiple reaction monitoring transitions of target contaminants in the GC-MS/MS method

| Species | Name | Retention time (min) | Quantification ion | Qualitative ions | Collision energy (V) |
|---|---|---|---|---|---|
| Organochlorine pesticides | *o,p′*-DDD | 25.0 | 235/165 | 235/165; 235/199 | 15; 15 |
| | *o,p′*-DDE | 22.7 | 246/176 | 246/176; 246/211 | 25; 25 |
| | *o,p′*-DDT | 25.5 | 235/165 | 235/165; 235/199 | 25; 25 |
| | *p,p′*-DDD | 26.7 | 235/165 | 235/165; 235/199 | 15; 15 |
| | *p,p′*-DDE | 23.9 | 246/176 | 246/176; 246/211 | 25; 25 |
| | *p,p′*-DDT | 27.2 | 235/199 | 235/199; 235/165 | 25; 25 |
| | α-HCH | 16.1 | 219/183 | 219/183; 219/147 | 5; 15 |
| | β-HCH | 20.7 | 219/183 | 219/183; 219/147 | 10; 20 |
| | γ-HCH | 17.7 | 219/183 | 219/183; 219/147 | 5; 15 |
| | δ-HCH | 21.5 | 219/183 | 219/183; 219/147 | 10; 20 |
| | Aldrin | 19.4 | 263/193 | 263/193; 263/191 | 25; 35 |
| | cis-Chlordane | 23.2 | 373/266 | 373/266; 373/301 | 12; 12 |
| | trans-Chlordane | 23.5 | 373/266 | 373/266; 373/301 | 12; 12 |
| | Dieldrin | 24.5 | 277/241 | 277/241; 277/207 | 12; 12 |
| | Heptachlor | 18.4 | 272/237 | 272/237; 272/235 | 25; 25 |
| | Hexachlorobenzene | 14.4 | 284/249 | 284/249; 284/214 | 18; 25 |
| | Mirex | 28.7 | 272/237 | 272/237; 272/235 | 15; 15 |
| | Dicofol | 21.3 | 250/139 | 250/139; 250/215 | 15; 10 |
| Organophosphorus pesticides | Dimethoate | 19.3 | 125/79 | 125/79; 143/111 | 8; 12 |
| | Omethoate | 16.8 | 156/110 | 156/110; 156/80 | 5; 10 |
| | Chlorpyrifos | 20.9 | 314/286 | 314/286; 314/258 | 5; 5 |
| | Parathlion-methyl | 21.1 | 263/109 | 263/109; 263/246 | 12; 5 |
| | Ethoprophos | 14.4 | 158/97 | 158/97; 158/114 | 12; 7 |
| | Diazinon | 17.1 | 304/179 | 304/179; 304/162 | 8; 8 |
| | Dichlorvos | 7.88 | 185/93 | 185/93; 185/109 | 15; 10 |
| | Phenthpate | 23.4 | 274/246 | 274/246; 274/121 | 5; 25 |
| | Methamidophos | 9.35 | 141/95 | 141/95; 141/80 | 10; 15 |
| Pyrethroid pesticides | Cyfluthrin | 33.3 | 206/151 | 206/151; 206/177 | 15; 20 |
| | Cypermethrin | 33.5 | 163/127 | 163/127; 163/91 | 5; 10 |
| | Deltamethrin | 36.0 | 181/152 | 181/152; 181/127 | 25; 25 |
| | Fenvalerate-1 | 34.6 | 419/225 | 419/225; 419/167 | 5; 5 |
| | Fenvalerate-2 | 35.0 | 419/225 | 419/225; 419/167 | 5; 5 |
| | Lamba cyhalothrin | 31.4 | 197/141 | 197/141; 197/161 | 15; 5 |
| Organic nitrogen pesticides | Chlordimeform | 14.9 | 196/181 | 196/181; 196/152 | 5; 25 |
| | Amitraz | 30.4 | 293/162 | 293/162; 293/132 | 5; 15 |
| | Buprofezin | 25.1 | 105/77 | 105/77; 172/116 | 18; 7 |
| Amide pesticides | Alachlor | 20.2 | 237/160 | 237/160; 237/146 | 8; 20 |
| | Butachlor | 24.0 | 176/150 | 176/150; 176/126 | 25; 25 |
| | Metolachlor | 21.4 | 238/162 | 238/162; 238/133 | 15; 25 |
| Carbamate pesticides | Carbofuran | 8.36 | 164/149 | 164/149; 164/103 | 15; 25 |
| | Pirimicarb | 19.0 | 238/166 | 238/166; 238/96 | 15; 25 |
| Other pesticides | Atrazine | 18.0 | 215/173 | 215/173; 215/200 | 5; 5 |
| | Clomazone | 17.0 | 204/107 | 204/107; 204/78 | 25; 25 |
| | Endosulfan-2 | 26.8 | 241/206 | 241/206; 241/170 | 25; 25 |
| | Isoproturon | 6.58 | 146/128 | 146/128; 146/91 | 15; 15 |
| | Nithophen | 26.3 | 283/162 | 283/162; 283/202 | 25; 25 |
| | Oxyfluorfen | 26.5 | 300/223 | 300/223; 188/144 | 18; 17 |
| | Prometryne | 20.2 | 241/199 | 241/199; 241/184 | 5; 5 |
| | Pyridaben | 32.1 | 147/117 | 147/117; 147/132 | 25; 15 |
| | Simazine | 18.0 | 201/173 | 201/173; 201/138 | 5; 15 |
| | Trifluralin | 15.4 | 306/264 | 306/264; 306/206 | 12; 15 |
| PCBs | PCB 001 | 11.0 | 188/152 | 188/152; 188/153 | 20; 10 |
| | PCB 005 | 15.0 | 222/152 | 222/152; 152/151 | 10; 20 |
| | PCB 028 | 18.2 | 256/151 | 256/151; 256/150 | 50; 50 |
| | PCB 052 | 19.6 | 220/150 | 220/150; 220/185 | 30; 20 |
| | PCB 077 | 24.8 | 290/220 | 290/220; 290/150 | 30; 50 |
| | PCB 081 | 24.2 | 290/220 | 290/220; 290/150 | 30; 50 |
| | PCB 101 | 22.7 | 328/256 | 328/256; 328/293 | 30; 10 |
| | PCB 118 | 25.1 | 326/256 | 326/256; 326/254 | 30; 30 |
| | PCB 126 | 27.7 | 254/184 | 254/184; 254/220 | 30; 20 |
| | PCB 138 | 26.9 | 360/290 | 360/290; 360/288 | 30; 30 |
| | PCB 153 | 25.7 | 290/218 | 290/218; 290/220 | 20; 20 |
| | PCB 169 | 30.5 | 358/288 | 358/288; 362/290 | 20; 20 |
| | PCB 180 | 29.2 | 396/324 | 396/324; 396/326 | 30; 30 |
| | PCB 195 | 31.2 | 428/358 | 428/358; 428/356 | 30; 30 |
| | PCB 206 | 32.4 | 466/394 | 466/394; 466/396 | 40; 40 |
| | PCB 209 | 32.8 | 500/429 | 500/429; 500/428 | 30; 30 |

**Table 2** Results of detected pesticides and PCBs in aquatic products sample from Nantong of Jiangsu Province in Southeast China

| Chemicals | | Edible portion of snakehead fish (*n* = 15) | | Edible portion of *Carassius auratus* (*n* = 24) | | Edible portion of of mussel (*n* = 13) | | Internal organs of snakehead fish (*n* = 12) | | Internal organs of *Carassius auratus* (*n* = 7) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Frequency (%) | Mean (ng/g) | Frequency (%) | Mean (ng/g) | Frequency (%) | Mean (ng/g) | Frequency (%) | Mean (ng/g) | Frequency (%) | Mean (ng/g) |
| Organochlorine pesticides | *o,p′*-DDD | 13.3 | 1.00 | 91.7 | 0.990 | 100 | 1.24 | 100 | 7.84 | 100 | 2.67 |
| | *o,p′*-DDE | 6.67 | 0.690 | 95.8 | 2.59 | 100 | 2.32 | 100 | 6.59 | 100 | 6.09 |
| | *o,p′*-DDT | 6.67 | 0.260 | 79.2 | 1.09 | 38.5 | 0.09 | 100 | 4.27 | 100 | 1.73 |
| | *p,p′*-DDD | 73.3 | 17.9 | 100 | 6.64 | 100 | 6.56 | 100 | 160 | 100 | 23.6 |
| | *p,p′*-DDE | 100 | 346 | 79.2 | 105 | 100 | 67.2 | 100 | 2603 | 100 | 422 |
| | *p,p′*-DDT | 26.7 | 2.39 | 83.3 | 1.84 | 100 | 1.71 | 100 | 39.9 | 100 | 3.07 |
| | Total DDT | 100 | 369 | 100 | 118 | 100 | 79.1 | 100 | 2822 | 100 | 459 |
| | α-HCH | 6.67 | 0.200 | – | – | – | – | 66.7 | 3.90 | 42.9 | 1.81 |
| | β-HCH | – | – | – | – | – | – | 41.7 | 8.84 | 14.3 | 2.97 |
| | γ-HCH | – | – | 4.17 | 0.250 | – | – | 41.7 | 2.45 | – | – |
| | Total HCH | 6.67 | 0.200 | 4.17 | 0.250 | – | – | 66.7 | 15.2 | 42.9 | 4.79 |
| | HCB | 86.7 | 3.75 | 75.0 | 9.79 | – | – | 100 | 34.4 | 85.7 | 19.2 |
| | Heptachlor | – | – | - | – | – | – | 8.33 | 0.630 | – | – |
| | Mirex | – | – | 4.17 | 0.070 | – | – | 66.7 | 1.33 | – | – |
| | Dicofol | 33.3 | 7.28 | 25.0 | 3.64 | 7.69 | 0.230 | 100 | 47.6 | 28.6 | 3.85 |
| Organophosphorus pesticides | Chlorpyrifos | 26.7 | 21.4 | – | – | – | – | – | – | – | – |
| | Dichlorvos | 26.7 | 3.89 | – | – | – | – | – | – | – | – |
| Pyrethroid pesticides | Cyfluthrin | – | – | 16.7 | 2.94 | – | – | – | – | – | – |
| | Cypermethrin | – | – | 16.7 | 0.570 | – | – | – | – | – | – |
| | Deltamethrin | – | – | 4.17 | 4.68 | – | – | – | – | – | – |
| Carbamate pesticides | Carbofuran | – | – | – | – | 7.69 | 0.0700 | – | – | – | – |
| Amide pesticides | Metolachlor | – | – | 4.17 | 0.0049 | 30.8 | 0.340 | 50.0 | 57.1 | 42.9 | 75230 |
| Other pesticides | Pyridaben | – | – | 29.2 | 0.340 | 7.69 | 0.0600 | 66.7 | 0.710 | 85.7 | 0.860 |
| | Trifluralin | 6.67 | 0.870 | 12.5 | 4.47 | 30.8 | 2.10 | 75.0 | 31.3 | 28.6 | 8.11 |
| PCBs | PCB 001 | 33.3 | 0.700 | – | – | – | – | – | – | – | – |
| | PCB 028 | 20.0 | 0.440 | – | – | – | – | 13.3 | 0.220 | – | – |
| | PCB 052 | 40.0 | 83.5 | – | – | – | – | 20.0 | 2.89 | – | – |
| | PCB 101 | – | – | – | – | – | – | 13.3 | 0.700 | – | – |
| | PCB 118 | – | – | – | – | – | – | 40.0 | 1.03 | – | – |
| | PCB 153 | – | – | – | – | – | – | 33.3 | 1.67 | – | – |
| | PCB 138 | 6.67 | 0.090 | – | – | – | – | 66.7 | 2.87 | 14.3 | 0.140 |
| | PCB 180 | – | – | – | – | – | – | 6.67 | 0.080 | – | – |
| | PCB 209 | – | – | – | – | – | – | 6.67 | 0.090 | – | – |

"–": under the limit of quantity.

that DDT was heavily used in the Nantong area. The high concentrations found in the fish samples could also have resulted from the high affinity of organochlorine pesticides for the lipid fraction of fish and mussels and their long persistence in the environment.

PCB analogues were detected only in the edible portion of mullet and the internal organs of mullet and *C. auratus*. The low concentration of PCBs observed in the study agreed with the previous publications (Li et al., 2008; Yang et al., 2006; Nakata et al., 2002), which detected a lower background levels of PCBs in the Chinese environment than in other developed countries (Wang et al., 2010).

The other pesticides detected in fish and mussels were metolachlor, pyridaben and trifluralin, which were commonly used in the local region according to the investigation. The residue concentrations of metolachlor, pyridaben and trifluralin were not as high as those of organochlorine pesticides due to their weaker lipophilicity compared to DDT and HCH.

Figures 1 and 2 show the comparative results of OCPs concentration in different fish and mussel species. It is clear that the residue levels in the internal organ samples of mullet and carassius auratus were much higher than in the edible portions, due to the high lipid content of the internal organs. Meanwhile, it was found that the detected number of OCPs in mussels was much fewer than in the other fish and mussel species, attributed to the fact that the mussels were not high in the food chain, so the concentrations of bioaccumulated OCPs such as DDT and HCH, would be expected to be higher in fish than in mussels. The sum of OCPs concentrations was higher in mullet than in *C. auratus*, and PCBs could be found only in mullet. The results also showed that chlorpyrifos and dichlorvos were found only in mullet and cyfluthrin, cypermethrin and deltamethrin were detected only in *C. auratus*. The above observations indicated that the bioaccumulation of OCPs, PCBs and the other pesticides investigated were species-specific. This could have resulted from their different ecological characteristics, such as feeding habits, habitat and the physical and chemical properties of the chemicals.

The detected frequency and concentration of various kinds of pesticides in crop product samples analyzed in this study are summarized in Table 3. From the results, it can be seen that DDT and its metabolites were generally found

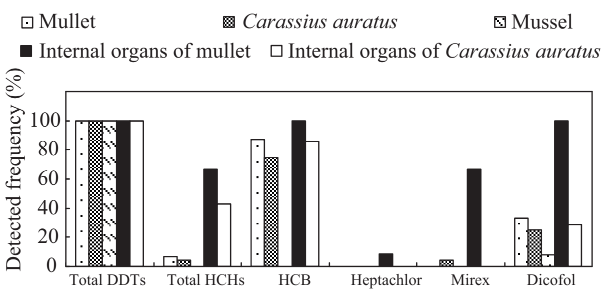


**Fig. 1** Comparative detected frequency of OCPs in different aquatic product species.

**Table 3** Results of detected pesticides in agricultural products sample from Nantong of Jiangsu Province in Southeast China

| Chemicals | | Carrot ($n$ = 5) | | Cabbage ($n$ = 4) | | Bean ($n$ = 12) | | Rice ($n$ = 9) | | Wheat ($n$ = 9) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Frequency (%) | Mean (ng/g) | Frequency (%) | Mean (ng/g) | Frequency (%) | Mean (ng/g) | Frequency (%) | Mean (ng/g) | Frequency (%) | Mean (ng/g) |
| Organochlorine pesticides | *o,p′*-DDD | 40.0 | 0.140 | – | – | – | – | – | – | – | – |
| | *o,p′*-DDE | 40.0 | 0.290 | – | – | – | – | – | – | – | – |
| | *o,p′*-DDT | 40.0 | 1.14 | – | – | – | – | – | – | – | – |
| | *p,p′*-DDD | 40.0 | 2.24 | – | – | – | – | – | – | – | – |
| | *p,p′*-DDE | 60.0 | 36.9 | 25.0 | 0.800 | 8.33 | 0.380 | – | – | 11.1 | 0.570 |
| | *p,p′*-DDT | 60.0 | 3.32 | 25.0 | 0.160 | – | – | – | – | – | – |
| | Total DDT | 80.0 | 44.0 | 25.0 | 0.970 | 8.33 | 0.380 | – | – | 11.1 | 0.570 |
| Organophosphorus pesticides | Chlorpyrifos | – | – | – | – | – | – | 33.3 | 174 | – | – |
| Pyrethroid pesticides | Cyfluthrin | – | – | – | – | 8.33 | 18.2 | 11.1 | 10.2 | – | – |
| | Cypermethrin | – | – | – | – | 16.7 | 1.84 | 11.1 | 0.970 | – | – |
| organic nitrogen pesticides | Buprofezin | – | – | – | – | – | – | 22.2 | 2.04 | 11.1 | 0.040 |
| Other pesticides | Pyridaben | – | – | 25.0 | 9.98 | 16.7 | 0.910 | 33.3 | 8.47 | – | – |

"–": under the limit of quantity.

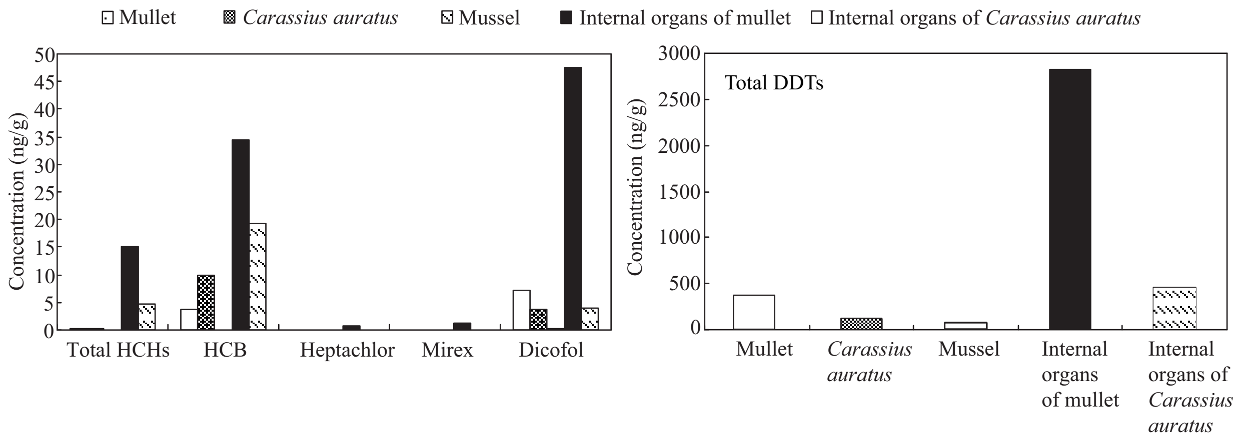


**Fig. 2** Comparative concentration of OCPs in different aquatic product species.

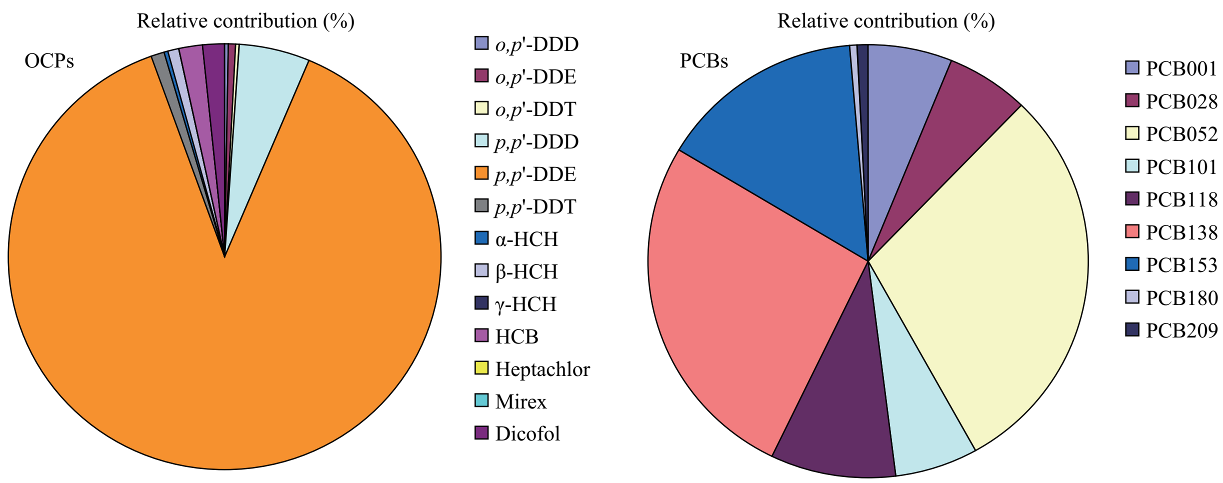


**Fig. 3** Averaged profiles of OCPs and PCBs in aquatic product samples from Nantong. Each OCP and PCB compound was normalized by the total concentrations of OCPs and PCBs, respectively.

in carrots, while smaller amounts of *p,p′*-DDT and *p,p′*-DDE were detected in other crop products; chlorpyrifos, as an orgnaophosphorus pesticide, was found in rice at a relatively high residue concentration, which was 174 ng/g. Pyrethroid pesticides were found in beans and rice, but the detected frequency and residue concentrations were not high as those of fish and mussels. Buprofezin and pyridaben partly existed in the crop products except for carrots.

To sum up, the results of all these detected chemicals in fish, mussel and agricultural product samples were consistent with the accumulation level and characteristics of these toxic chemicals in human adipose tissue of people living in Nantong, which was reported in the previous studies (Wang et al., 2010, 2011). According to our survey, although DDT and HCH were banned for use in agriculture the 1980s, a large amount of pesticides including dicofol, chlorpyrifos, metolachlor, pyridaben, trifluralin, are still used in the region nowadays. Meanwhile, dicofol is one of the OCPs which is not forbidden in China; however, the proportion of DDT impurities was 3.54%–10.8% in the product dicofol due to the fact that DDT was the raw material for producing dicofol in the traditional technology (Ding et al., 2011). Therefore, DDT accumulation caused by the application of dicofol should be paid more attention. The exposure levels and detected frequencies of the chemicals reported in this article can be used as an indication of the pollution situation of the Nantong area.

### 2.2 Profiles of OCPs and PCBs in fish and mussels

Considering the relatively low detected frequency and concentration of pesticides in agricultural product samples, we focused on the profiles of OCPs and PCBs in fish and mussels. The profiles of OCPs and PCBs in fish and mussels from Nantong are presented in Fig. 3.

It is known that DDT usually contains 75% of *p,p′*-DDT, 15% of *o,p′*-DDT, 5% of *p,p′*-DDE and less than 5% of other species (Kim et al., 2002). In the present study, *p,p′*-DDE was the dominant compound, which accounted for 88.04% of the total OCPs concentration, because *p,p′*-DDE was the metabolite of *p,p′*-DDT and generally was detected as a main DDT isomer in fish. Other major OCPs in fish and mussel samples were *p,p′*-DDD, HCB, and dicofol. Different from other reports (Li et al., 2008; Yang et al., 2009), the residue concentrations of HCH isomers were very low, which led to its low relative contribution to the total concentrations of OCPs, indicating that the degradation rate of HCH in the environment and organisms was much faster.

For PCBs, PCB 52, PCB 138 and PCB 153 were mainly found in mullet samples, which was consistent with the results of other studies (Li et al., 2008; Hyo-Bang et al., 2009). Although the higher chlorinated PCB congeners have much stronger abilities of accumulation in fish samples, leading to higher percentages of PCB 153 and PCB 138, the lower chlorinated PCB 52 also accounted for a relatively higher percentage, perhaps attributable to the fact that the lower chlorinated PCBs were used more in China than the higher ones (Wang et al., 2010).

### 2.3 Risk assessment to humans

The output of a risk assessment, Hazard Quotient (HQ), is typically a quantitative statement about the estimated exposure relative to the benchmark concentration (BMC) for each compound. For chemicals that are thought to possess non-cancer effects only, HQ is frequently characterized as the ratio of the estimated daily intake (EDI) to the guideline value, generally oral reference dose (RfD). A HQ less than one indicates that the exposure is less than the benchmark and therefore the chemical exposure is unlikely to result in an adverse effect. Conversely, a HQ greater than one indicates that the exposure is greater than the benchmark, so then the sources, pathways, and routes of chemical exposure need to be evaluated further.

For chemicals that may exert a carcinogenic effect, the HQ is calculated as the product of EDI and the cancer slope factor (CSF). The general acceptable health risk value was one in one million ($10^{-6}$). Therefore, the comparison of the HQ and $10^{-6}$ should reflect the risk.

For each contaminant, EDI was calculated by food consumption multiplied by contaminant concentration. The RfD and CSF for each compounds were obtained from the US EPA Integrated Risk Information System (IRIS) (http://www.epa.gov/iris/). The detailed methods for deriving the HQ are described elsewhere (Jiang et al., 2005; Yang et al., 2009).

The pesticides and PCBs investigated in the present study have carcinogenic or non-carcinogenic chronic effects. Therefore, an evaluation of the non-cancer and cancer risks to human health associated with the consumption of fish and mussels and agriculture food products containing various kinds of pesticides and PCBs was undertaken and the results are summarized in Fig. 4.

The results showed that the non-cancer HQs of the detected pesticides were all less than one, which was consistent with the risk evaluation results of many other reports (Jiang et al., 2005; Yang et al., 2009; Hyo-Bang et al., 2009). From Fig. 4, it can be found that the cancer risks of DDTs and HCB were greater than one in one million, indicating that daily exposure to these chemicals through the oral route had a significant lifetime cancer risk. Therefore, DDTs and HCB may be of particular concern among the detected contaminants having carcinogenic effects. As for different food groups, the cancer HQs of fish and mussels and agricultural products were calculated respectively, and the results are presented in Fig. 5. It is shown that the cancer HQs of DDTs both in fish and mussels and agricultural products were all above one in one million, but mostly attributed to fish and mussels; however, the cancer HQ of HCB was all attributed to the

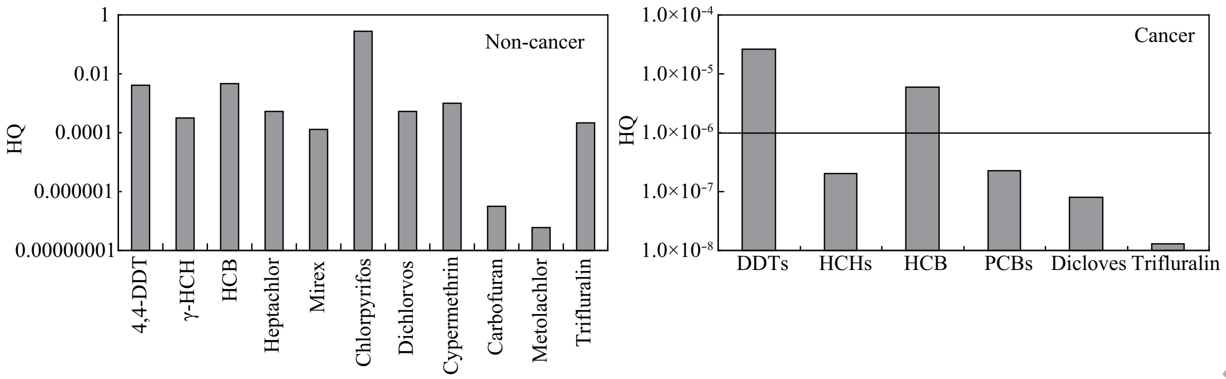


**Fig. 4** Non-cancer and cancer HQs for daily aquatic products and agricultural food product consumption by people in Nantong.

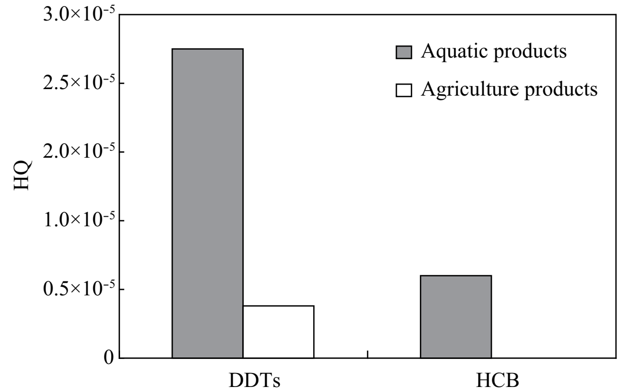


**Fig. 5** Cancer HQs of DDTs and HCB derived from consumption of aquatic and agriculture products.

fish and mussel consumption.

## 3 Conclusions

This article presents a comprehensive study on the residue levels of 51 pesticides and 16 polychlorinated biphenyls in fish, mussels and agricultural products sampled in Nantong of Jiangsu Province, Southeast China. Some of the pesticides and PCBs investigated were detected in the samples. Species and levels of these contaminants varied significantly among different food items. Among the detected chemicals, organochlorine pesticides including DDTs, HCB and dicofol were the dominant contaminants. The results of the study presented the characteristics of dietary exposure of OCPs and PCBs in Nantong area. Based on the residue data, dietary risk assessment was performed using a dietary survey database and published toxicity data of the chemicals. The results suggested that non-cancer risks of OCPs and PCBs through the dietary route can be considered negligible in Nantong, however, the cancer risks from lifetime dietary exposure to DDTs and HCB are not acceptable.

**Acknowledgments**

This work was supported by the 2008 Commonweal and Environmental protection Project of the Ministry of Environmental Protection of the People's Republic of China (MEP) (No. 200809102) and "333 High-level Talent Cultivation Project" research funding of Jiangsu Province-"Research on human health risk assessment of pesticides". We thank Tongzhou Plant Protection Station of Nantong in Jiangsu Province for the sample collection.

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**Journal of Environmental Sciences (Established in 1989)**
**Vol. 24 No. 10 2012**

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| **Supervised by** | Chinese Academy of Sciences | **Published by** | Science Press, Beijing, China |
| **Sponsored by** | Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences | | Elsevier Limited, The Netherlands |
| | | **Distributed by** | |
| **Edited by** | Editorial Office of Journal of Environmental Sciences (JES)<br>P. O. Box 2871, Beijing 100085, China<br>Tel: 86-10-62920553; http://www.jesc.ac.cn<br>E-mail: jesc@263.net, jesc@rcees.ac.cn | Domestic | Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China<br>Local Post Offices through China |
| | | Foreign | Elsevier Limited<br>http://www.elsevier.com/locate/jes |
| **Editor-in-chief** | Hongxiao Tang | **Printed by** | Beijing Beilin Printing House, 100083, China |

**CN 11-2629/X**    **Domestic postcode: 2-580**    **Domestic price per issue RMB ¥ 110.00**

ISSN 1001-0742