Organochlorinated Compounds in the Air at NAEO, an Eastern Background Site in China: Long-Range Atmospheric Transport versus Local Sources

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ABSTRACT

Gas and particle samples were collected by a high-volume sampler from July 2009 to March 2010 at an eastern regional background site in Ningbo and analyzed for polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs). The total (gas + particle) air concentrations of 11 OCPs ranged from 5.34 to 417 pg/m^3, of which HCHs, DDTs, chlordane and HCB concentrations ranged from 0.67 to 214 pg/m^3, 2.03 to 198 pg/m^3, 2.25 to 158 pg/m^3, and 0.38 to 77.1 pg/m^3, respectively. The total concentrations of PCBs ranged from 42.4 to 224 pg/m^3, with an average of 102 ± 53.6 pg/m^3. Similar seasonal trends of HCH, DDT, chlordane, HCB concentrations were observed with the winter maximum. Diagnostic ratios indicate that aged technical HCH, DDT and chlordane were the major source of HCHs, DDTs and chlordane, respectively. PSCF analysis identified that northern China, southern China and Japan were major source regions of OCPs at Ningbo background site. As for PCBs, the seasonal trend was characterized with higher concentrations in summer. Those compounds were mainly influenced by the sources nearby and soil volatilization.

Keywords: PCBs; OCPs; Fine aerosol; PSCF; Ningbo.

INTRODUCTION

Organochlorinated compounds, including polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) belonging to persistent organic pollutants (POPs), are ubiquitous organic compounds in the atmosphere and have been of global concern owing to their persistency, bioaccumulative ability and potential mutagenic and/or carcinogenic impact on animals and humans. Due to their volatility and persistence, OCPs and PCBs are subject to long-range atmospheric transport (LRAT) and they were largely used in the low and middle latitude (Li *et al.*, 2000; Breivik *et al.*, 2002). Therefore, OCPs released in the low and middle latitude environments could be dispersed rapidly through air and water movement, and tend to be redistributed on a global scale (Tanabe, 1991; Wania and Mackay, 1996). Many recent studies have shown that the atmospheric

transportation from these regions can even pollute areas far away from sources, such as the North America west coast and Arctic regions (Bailey *et al.*, 2000; Wilkening *et al.*, 2000; Harner *et al.*, 2005).

As a country with the largest agricultural production, China has once been a major producer and consumer of OCPs, such as dichlorodiphenyl-trichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), hexachlorbenzene (HCB), and chlordane (Wong *et al.*, 2005). From the 1950s to 1980s, the productions of HCHs and DDTs in China were 4.9 million t and 0.4 million t, accounting for 33% and 20% of the total world production, respectively (Wang *et al.*, 2009). Major portion has been used in eastern and southern China (Wang *et al.*, 2012). Besides, improper storage and disposal of PCB-containing equipment have resulted in continuing releases there. Until recently, PCBs were still detected in the ambient environment (Chen *et al.*, 2009; Han *et al.*, 2010).

Air monitoring at remote sites is one of the major ways to assess the relative importance of sources on a regional scale and study the environmental fate of pollutants (Wania *et al.*, 1996). The results of modeling indicated that topography and Asian monsoon flow patterns put the

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eastern China regions from 27–40°N as the best sampling location for capturing the outflow plume of air pollutants from China to west Pacific (Zhang *et al.*, 2011). In this paper, a regional background site, Ningbo Atmospheric Environment Observatory (NAEO, 29°40.8′N, 121°37′E, 550 m ASL), in eastern China was selected to monitor organochlorinated compounds. The objectives of this preliminary study are to investigate the concentrations of OCPs and PCBs in the air of NAEO, and to study the influences of air mass origin on the distribution of these compounds, so as to provide important information about potential source regions of these chemicals after phased out of OCPs in China.

METHODS

Site Description and Regional Emission Sources

Ningbo Atmospheric Environment Observatory (NAEO) (29°40.8′N, 121°37′E, 550 m ASL) is located on a rural mountaintop in East China, and is a regional background site (Fig. 1). Details on the site can be found elsewhere (Liu *et al*, 2013).

Sampling Procedure

In total, 36 paired aerosol and gaseous samples were collected once every week from July 2009 to March 2010 on the roof of a building using high volume samplers operated at 0.3 m^3/min. Particulate and gaseous phase samples were captured on pre-combusted (450°C, 12 hr) PALL quartz microfiber filters and pre-cleaned polyurethane foam (PUF, 6.5 cm diameter, 7.5 cm length). Field blanks were obtained by the same sampling method, but were exposed to the atmosphere only for a few seconds. After sampling, all the samples were wrapped with clean aluminum foil, sealed in clean jars, and kept at –18°C until analysis.

Analytical Procedure

Prior to extraction, 10 ng surrogate recovery standards (2,4,5,6-tetrachloro-m-xylene (TCmX), PCB 30 and PCB 198, PCB 209) were added to each of the samples. Activated copper granules were added to the collection flask to remove elemental sulfur. All the collected PUF plugs and QFFs were extracted separately with (1:1, v/v) DCM in hexane for 24 hrs in a soxhlet apparatus. The extracts were concentrated

to a volume of 1mL using a Rotary evaporator. The elute was cleaned up by 7 mm i.d. alumina/silica column including anhydrous sodium sulphate (1 cm), neutral silica gel (3 cm, 3% deactivated) and neutral alumina (3 cm, 3% deactivated). OCPs and PCBs were collected by eluting the column with a mixture of dichloromethane and hexane (1:1, v/v). The samples were reduced to 0.2 mL under a gentle stream of nitrogen and exchanged into 25 µL of dodecane. Then 20 ng of pentachloronitrobenzene (PCNB) and PCB54 were added into each sample as internal standards for analyzing OCPs and PCBs.

33 PCBs and 11 OCP compounds (α-HCH, β-HCH, γ-HCH, δ-HCH, *o,p'*- and *p,p'*-DDE, -DDD and -DDT, trans-chlordane (TC), cis-chlordane (CC), HCB) were determined by Agilent 7890/7000 GC-MS/MS with a capillary column (VARIAN, CP-Sil 8 CB, 50 m, 0.25 mm, 0.25 µm). The mass spectrometer was operated with an EI source (–70 eV) in multiple reaction monitoring (MRM) mode. The temperatures of transfer line, injector interface and ion source were set at 280°C, 250°C and 230°C, respectively. The GC oven temperature program was set at 80°C for 0.5 min, then 20 °C/min to 160°C, 4 °C/min to 240°C, and finally 10 °C/min to 295°C, and hold for 10 min. 1 µL of sample was injected in splitless mode. Helium was used as carrier gas at the flow rate of 1 mL/min. Collision induced dissociation (CID) gas and quench gas in collision cell were nitrogen and helium at the flow rate of 1.5 mL/min and 2.25 mL/min, respectively. Among 33 target PCB compounds, only 10 PCB congeners (PCB 28, PCB 52, PCB 44, PCB101, PCB 118, PCB153, PCB 138, PCB 180, PCB 169, PCB 170) were above detection limits and quantified.

Quality Control

Chemical standards were purchased from Accustandard Co.U.S. Laboratory. Lab blanks were pre-cleaned PUF plugs and filters. Field blanks were obtained by transporting and handling pre-cleaned PUF plugs and filters in the exactly same way as samples. Lab and field blanks were subject to the same storage and analytical procedures as samples, which constituted less than 10% of the total number of samples analyzed. Surrogate standards were added to all the samples to monitor procedural performance and matrix effects. The recoveries for TCmX, PCB 30 and PCB 198, PCB 209 were
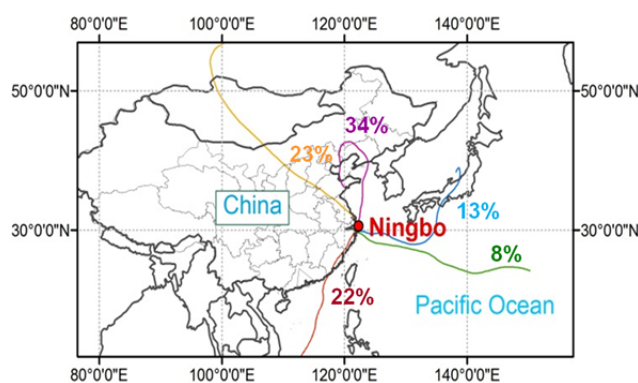
Fig. 1. The Ningbo sampling station and the major directions of air mass back trajectories. The figures expressed in percentage terms are the frequency for representative wind directions.

$73 \pm 5.7\%$, $69 \pm 7.2\%$, $84 \pm 9.7\%$ and $89 \pm 8.6\%$, respectively. All the data were blank corrected using the mean of the field blanks. The method detection limits (MDL) were stemmed from the field blanks and quantified as the mean of the blanks plus 3 times the standard deviations of the blank concentrations. MDLs ranged from 0.02 to 0.5 pg/m^3 for OCP and PCBs. A backup PUF plug was attached to the sampler to check the possible breakthrough of gaseous phase of OCPs and PCBs by analyzing the top and bottom PUF plugs separately and results show that the breakthrough can be ignored.

Air Mass Back Trajectories and Potential Source Contribution Function

For source identification, five-day air parcel back trajectories were calculated every 6 hrs (0, 6, 12, 18 and 24 UTC) at the elevation of 100 m, 500 m, 1000 m above ground level, respectively, using the Hybrid-Single Particle Integrated Trajectories (HYSPLIT 4.8) model. As a result, five major directions were determined, namely, from inland central north China, northwestern China, southeastern China, Japan, Pacific Ocean (Fig. 1).

Potential source contribution function (PSCF) analysis was used to identify source regions of airborne pollutants (Hoh and Hites, 2004). All the hourly endpoints in back trajectories generated by the HYSPLIT 4.8 were classified into 1° latitude by 1° longitude grid cells. The PSCF value for the ijth cell was defined as:

$$PSCF_{(i,\,j)} = m_{(i,\,j)}/n_{(i,\,j)} \tag{1}$$

where $m_{(i,\,j)}$ is the number of endpoints when measured concentrations of a kind of pollutant were higher than its average concentration plus standard deviation; $n_{(i,\,j)}$ is the total number of endpoints falling in the grid cell. All the PSCF values were plotted by ArcGIS 9.2. Only cells including more than 15 total hourly points are displayed here.

RESULTS AND DISCUSSION

Concentration Levels

The average concentrations of PCBs and OCPs found in the gas and particle phases are shown in Table 1. The total OCPs ranged from 5.34 to 417 pg/m^3, with an average of 178 ± 100 pg/m^3. DDTs (35.3% of total OCPs) was the predominant component of OCPs at NAEO, followed by chlordane (27.6%), HCHs (24.9%) and HCB (12.1%). Technical HCHs and Lindane has been phased out in the 1980s and 2003 (Hu *et al.*, 2007; Li *et al.*, 2011), respectively. According to National Implementation Plan for the Stockholm

Table 1. The average concentrations and ranges (pg/m^3) of gas and particulate phase PCBs and OCPs. nd means not detected.

Compounds	Gas	Particulate	Total
PCB-28	25.4 ± 28.2 (0.48–110)	0.01 ± 0.02 (nd–0.14)	25.2 ± 28.6 (0.48–110)
PCB-52	19.3 ± 16.0 (0.69–58.7)	7.29 ± 3.75 (0.60–13.1)	26.8 ± 16.8 (2.91–68.3)
PCB-44	28.7 ± 28.7 (0.04–102)	0.45 ± 1.26 (0.02–5.13)	27.5 ± 27.2 (0.23–102)
PCB-101	4.57 ± 4.13 (0.34–17.2)	0.11 ± 0.38 (nd–1.99)	4.43 ± 3.88 (0.35–17.2)
PCB-118	2.84 ± 1.90 (0.14–8.47)	0.05 ± 0.06 (nd–0.25)	2.82 ± 1.86 (0.16–8.50)
PCB-153	1.88 ± 1.31 (0.02–5.49)	0.06 ± 0.08 (nd–0.37)	1.87 ± 1.25 (0.05–5.54)
PCB-138	2.29 ± 1.61 (0.09–6.65)	0.06 ± 0.08 (nd–0.39)	2.28 ± 1.58 (0.14–6.67)
PCB-180	0.46 ± 0.32 (0.02–1.17)	0.05 ± 0.08 (nd–0.35)	0.51 ± 0.32 (0.02–1.22)
PCB-169	0.51 ± 0.65 (0.02–2.77)	3.77 ± 3.60 (0.02–14.7)	4.26 ± 3.47 (0.16–14.8)
PCB-170	2.02 ± 2.23 (0.05–5.75)	4.32 ± 2.17 (0.14–9.98)	6.38 ± 3.47 (0.27–15.2)
α-HCH	15.6 ± 16.3 (nd–58.6)	1.10 ± 2.14 (nd–20.3)	16.7 ± 16.6 (0.28–15.2)
β-HCH	21.9 ± 37.2 (nd–211)	1.43 ± 3.72 (nd–17.8)	23.3 ± 36.8 (0.50–212)
δ-HCH	2.50 ± 3.46 (nd–12.6)	0.22 ± 1.03 (nd–6.03)	2.73 ± 3.45 (nd–12.5)
γ-HCH	1.42 ± 2.80 (nd–11.3)	0.08 ± 0.41 (nd–2.40)	1.50 ± 3.03 (nd–13.7)
p,p'-DDE	10.7 ± 8.60 (nd–43.7)	2.56 ± 5.91 (nd–25.0)	13.3 ± 11.0 (0.34–48.5)
p,p'-DDD	13.8 ± 10.3 (nd–40.2)	3.72 ± 5.96 (nd–23.8)	17.5 ± 12.2 (0.30–58.8)
o,p'-DDT	8.49 ± 5.81 (nd–29.6)	9.26 ± 17.0 (nd–84.7)	17.7 ± 17.9 (1.18–92.5)
p,p'-DDT	7.15 ± 5.21 (nd–28.8)	7.17 ± 5.60 (nd–164)	14.3 ± 7.35 (0.21–169)
TC	7.84 ± 5.16 (nd–16.2)	2.66 ± 3.91 (nd–20.0)	10.5 ± 6.61 (0.70–29.1)
CC	32.2 ± 30.3 (nd–141)	6.45 ± 11.3 (nd–52.0)	38.7 ± 32.1 (nd–148)
HCB	19.4 ± 18.4 (nd–75.4)	2.21 ± 4.50 (nd–21.4)	21.6 ± 19.1 (0.38–77.1)
$\sum_{10}$PCB	88.1 ± 54.6 (26.0–208)	16.2 ± 4.67 (6.58–28.2)	102 ± 53.6 (42.4–224)
$\sum$HCHs[a]	41.4 ± 42.6 (5.52–213)	2.82 ± 8.52 (nd–46.5)	44.3 ± 43.3 (0.67–214)
$\sum$DDTs[b]	40.2 ± 25.4 (8.64–128)	22.7 ± 31.6 (0.78–171)	62.8 ± 39.9 (2.03–198)
$\sum$Chlordane[c]	40.1 ± 32.6 (11.4–151)	9.11 ± 14.9 (0.22–72.0)	49.2 ± 35.5 (2.25–158)
$\sum_{11}$OCPs[d]	141 ± 85.5 (nd–399)	36.8 ± 53.3 (2.0–247)	178 ± 100 (5.34–417)

[a] $\sum$HCHs = α-HCH + β-HCH + δ-HCH + γ-HCH.
[b] $\sum$DDTs = *p,p'*-DDE + *p,p'*-DDD + *o,p'*-DDT + *p,p'*-DDT.
[c] $\sum$Chlordane = TC + CC.
[d] $\sum_{11}$OCPs = $\sum$HCHs + $\sum$DDTs + $\sum$Chlordane + HCB.

Convention on POPs, China prohibited production and use of HCB by 2008, basically eliminated the production and use of chlordane by 2009 and made an effort to phase out DDT by 2009 (The People's Republic of China National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants, 2007). The relative proportions of pesticides followed the prohibition order, except HCHs, of which historical usage amounts were much higher than other pesticides. The concentration of gaseous HCHs, DDTs, chlordane and HCB were found to be at least two times higher than those in the particulate phase. Some compounds were exclusively detected in the gas phase. It indicates that OCPs were largely distributed in the gaseous phase. 33 PCB congeners were analyzed and 10 (28, 52, 44, 101, 118, 153, 138, 180, 169, 170) were detected in the air samples.

HCHs

The total HCHs concentrations ranged from 0.67 to 214 pg/m^3. The average concentrations of α-HCH, β-HCH, δ-HCH and γ-HCH were 16.7 ± 16.6 pg/m^3, 23.3 ± 36.8 pg/m^3, 2.73 ± 3.45 pg/m^3 and 1.50 ± 3.03 pg/m^3, respectively. As shown in Table 2, the α-HCH and γ-HCH concentrations were lower than the other background site in China, such as Tengchong, Tibetan Plateau, and Mt. Waliguan. Those observations were conducted several years ago. Although a large amount of HCHs were applied in eastern China to improve crop yield in the past, the relatively low levels at NAEO (Table 2) suggests that atmospheric levels of HCHs has decreased since prohibition of technical HCH in 1983 and of lindane in 2003 (Hu *et al.*, 2007; Li *et al.*, 2011).

DDTs

The total concentrations ranged from 2.03 to 198 pg/m^3. The average concentrations of *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT were 13.3 ± 11.0 pg/m^3, 17.5 ± 12.2 pg/m^3, 17.7 ± 17.9 pg/m^3 and 14.3 ± 7.35 pg/m^3, respectively. The level of *p,p'*-DDT was lower than that of Tengchong and higher than those of Tibetan Plateau and Mt. Waliguan (Table 2). The *p,p'*-DDE concentration was higher than these three background sites. Degradation of DDT produces DDE and DDD. The relatively low *p,p'*-DDT and high *p,p'*-DDE concentration indicate historical usage of DDTs. It is interesting to note that the level of *o,p'*-DDT was comparable to those of Tengchong, Tibetan Plateau and Mt. Waliguan, although application of *o,p'*-DDT-containing mixture has been reported in adjacent areas (Qiu *et al.*, 2004). It likely means the decrease of *o,p'*-DDT in eastern China.

Chlordane

The total concentrations of chlordane ranged from 2.25 to 158 pg/m^3. The average concentrations of TC and CC ranged from 0.70–29.1 pg/m^3 (10.5 ± 6.62 pg/m^3) and nd-148 pg/m^3 (38.7 ± 32.1 pg/m^3), respectively. These values were generally lower than the Tengchong background values, and ranges reported at Tibetan Plateau and Arctic (Table 2). The relative high chlordane at NAEO may be attributed to its late prohibition in China (2009) and monsoon movement from source regions, which more or less influenced the air of Ningbo sampling site. Potential sources will be discussed below.

Table 2. Comparison of mean OCP concentrations (pg/m^3) at the Ningbo station with those in other background/rural and suburban sites.

	α-HCH	γ-HCH	o,p'-DDT	p,p'-DDT	p,p'-DDE	TC	CC	HCB	rural/background/urban	sampling period	literature
Ningbo	16.7	1.50	17.7	14.3	13.3	10.5	38.7	21.6	rural/background	2009.07.07–2010.03.17	This study
Tengchong	42	130	11	20	6.1	40	59	270	rural/background	2005.10.22–2006.12.27	(Xu et al., 2011)
Tibetan Plateau	91.0	15.8	13.4	6.13	0.64	0.04	0.03	23.3	rural/background	2007.07–2008.06	(Xiao et al., 2010)
Mt. Waliguan	58.4	139	17.9	4.42	5.12	18.1	22.1	38.4	rural/background	2005.04.22–05.23	(Cheng et al., 2007)
Alert, Arctic	13	1.7	0.22	0.14	0.30	0.25	0.64	52	background	2005	(Hung et al., 2010)
Guangzhou	111	285	598	557	145				urban	2003.12–2004.12	(Li et al., 2007)
Hong Kong	52	51	229	914	195				urban	2003.12–2004.12	(Li et al., 2007)
Tanggu, Tianjin	4497	2082	46	49	46				urban	2006.07–2007.06	(Zheng et al., 2010)
Taihu Lake	89.8	96.1	103.1	137.8	107.3			83.1	urban	2002.07.23–08.11	(Qiu et al., 2004)

HCB

The total HCB concentrations ranged from 0.38 to 77.1 pg/m^3, with an average of 21.6 ± 19.1 pg/m3, which was generally lower than other background site, such as Tengchong, Tibetan Plateau, Mt. Waliguan and Arctic (Table 2). The low HCB concentration at NAEO reflects relatively low background levels in eastern China. Compared to other studies conducted several years ago (Table 2), HCB air concentrations at NAEO have decreased since China prohibited its production and application in 2008 (The People's Republic of China National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants, 2007; http://www.epd.gov.hk/epd/english/intern ational_conventions/pops/files/China_NIP_En.pdf).

PCBs

The total concentrations of PCBs at NAEO ranged from 42.4 pg/m^3 to 224 pg/m^3, with an average of 102 ± 53.6 pg/m^3 which was ~ 9 times higher than 11 background sites in China (average 11.2 pg/m^3) (Wu *et al.*, 2011), indicating that PCB level at NAEO could be largely influenced by adjacent anthropogenic pollutions. The average total gaseous PCBs concentration was 88.1 ± 54.6 pg/m^3 (ranged from 26.0 to 208 pg/m^3), which was three to ten times higher than those of particulate PCBs (6.58–28.2 pg/m^3). The average concentrations of tri-CBs (PCB 28), tetra-CBs (PCB 52, 44), penta-CBs (PCB 101, 118), hexa-CBs (PCB 153, 138, 169), and hepta-CBs (PCB 170, 180) were 25.5 pg/m^3, 54.3 pg/m^3, 7.57 pg/m^3, 8.49 pg/m^3 and 6.87 pg/m^3, respectively. Tri-CBs, tetra-CBs and penta-CBs were more than 90% in the gas phase, while hepta-CBs (PCB 170, 180) presented smaller contributions (37%). Tetra-chlorinated congeners are

the major component of the total PCB in the air. This result was coincident with the conclusion reported at Tibetan Plateau (Wang *et al.*, 2010), but different from other rural and background sites in other parts of China such as Lin'an, Jianfengling and Waliguan, where tri-CBs dominated (Jaward *et al.*, 2005; Zhang *et al.*, 2008).

Seasonal Variations
HCHs

Elevated α-HCH levels were observed in winter (23.7 ± 16.9 pg/m^3) compared with summer (4.59 ± 2.05 pg/m^3), and the same seasonal trend of β-HCH (45.3 ± 57.6 pg/m^3 in winter; 5.69 ± 2.35 pg/m^3 in summer) and γ-HCH (4.21 ± 4.10 pg/m^3 in winter; 0.91 ± 2.00 pg/m^3 in summer) were observed (Fig. 2). Ningbo is located at the middle part of China coastline and enjoys subtropical monsoon climate with temperate and humid weather. In winter, air parcels mainly originated from northern and mainland China, bringing large amounts of pollutants to Ningbo, which resulted in higher levels of α-HCH. While in summer, wind direction partially shifted from continental to marine area along with the precipitations, which lowers the concentration.

The typical technical HCH contains α-, β-, δ- and γ-HCH isomers accounting for 60–70%, 5–12%, 10–15%, and 6–10%, while lindane is almost pure γ-HCH. Thus the ratios of α-HCH/γ-HCH would be between 4 and 7 for the technical mixture, and nearly zero for lindane (Iwata *et al.*, 1995). The average ratio of α-HCH/γ-HCH at NAEO was 5.5, which was different from that of Guangzhou and Hong Kong with abundant lindane usage (Li *et al.*, 2007; Ling *et al.*, 2011). It indicates that technical HCH was the major source of HCHs at NAEO. Although it has been banned
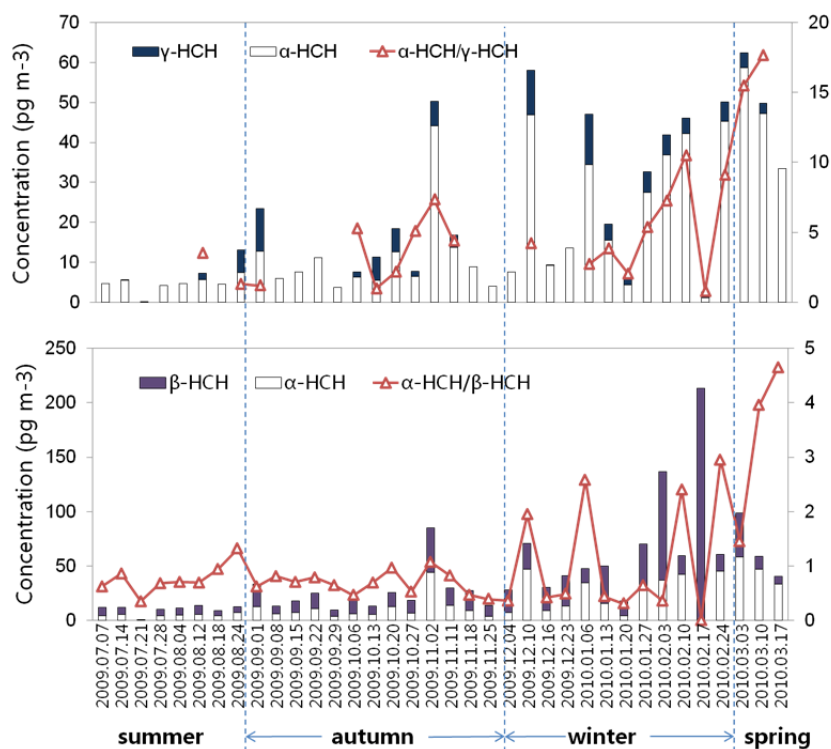

Fig. 2. Seasonal variations of α-HCH, β-HCH and γ-HCH concentrations and isomeric ratios.

since 1983 in China, historical usage of technical HCH has by now been largely contributing to the surrounding atmosphere in eastern China. The relatively low α-HCH/γ-HCH level occurred in several samples, suggesting that the sampling site was not only influenced by technical HCH but also by lindane, but the emission of lindane was of minor importance. For another HCH isomer in technical HCH, β-HCH (23.3 ± 36.8 pg/m^3) was characterized by its low vapor pressure and long half-life. Thus, whether α-HCH/β-HCH ratios are lower than the ratios of technical HCH is a commonly used to identify historical or recent input technical HCH sources. The α-HCH/β-HCH ratio at NAEO was 1.1 that was lower than the ratio in the technical mixture, implying an aged input of technical HCH. It is consistent with technical HCH usage history in eastern China. Also, low α-HCH/β-HCH and high β-HCH concentration was occasionally observed on 3rd and 17th February 2010, indicating that there might be some sources contributing high proportion of β-HCH.

DDTs

Fig. 3 shows seasonal variations of individual DDT concentrations over sampling period. Like HCHs, the seasonal trend of *o,p'*-DDT and *p,p'*-DDT fluctuated with the winter maxima when excluding some episodic event in autumn. A strong peak occurred with *p,p'*-DDT and *o,p'*-DDT on 1st September and 2nd November, respectively. The average concentration ratio of *o,p'*-DDT/*p,p'*-DDT ranged from 0.16 to 1.25 (averaged 0.64 ± 0.28), which was different from the ratio of dicofol-DDT (Qiu *et al.*, 2004) that consists high portion of *o,p'*-DDT than *p,p'*-DDT, but comparable to technical DDT range (0.74–0.96) (Liu *et al.*, 2009). It suggests that technical DDT was the major source of DDT at NAEO

during the sampling period. *p,p'*-DDE is commonly considered as the degradation product of *p,p'*-DDT besides a component of technical DDT. Thus *p,p'*-DDT/*p,p'*-DDE ratio is used to distinguish current or aged input source of DDT. The ratio of *p,p'*-DDT/*p,p'*-DDE was 1.33 ± 1.90 (from 0.52 to 11.4).This result shows that DDT residues at NAEO mainly derived from aged technical DDT. The tremendous historical usage in China lead to relatively high *p,p'*-DDE concentrations at NAEO.

Chlordane

TC and CC displayed seasonal variations with the winter maxima, suggesting that air masses from north China brought chlordane to NAEO. In particular, a distinct peak on 1st September and 11th November (Fig. 4) occurred when air masses coming from Japan and northern China, respectively. The TC/CC ratio in the summertime ranged from 0.64 to 1.09 (average 0.89 ± 0.15), and was from 0.03 to 0.35 (average 0.15 ± 0.10) in the wintertime. The TC/CC ratios were analogue to or less than 1.2, which was the ratio for technical chlordane (Bidleman *et al.*, 2002). A very low TC/CC ratio and high (TC + CC) concentrations were found in the winter samples associated with the annual average ratio of TC/CC (0.03–1.09), inferring that there might be source of chlordane such as aged domestic formulation at NAEO. These results were consistent with the study for chlordane in Hong Kong (Wang *et al.*, 2007).

HCB

As shown in Fig. 5, the average HCB concentration ranged from 6.42 to 77.1 pg/m^3 (33.6 ± 23.4 pg/m^3) in winter and from 0.38 to 12.0 pg/m^3 (5.45 ± 3.18 pg/m^3) in summer,
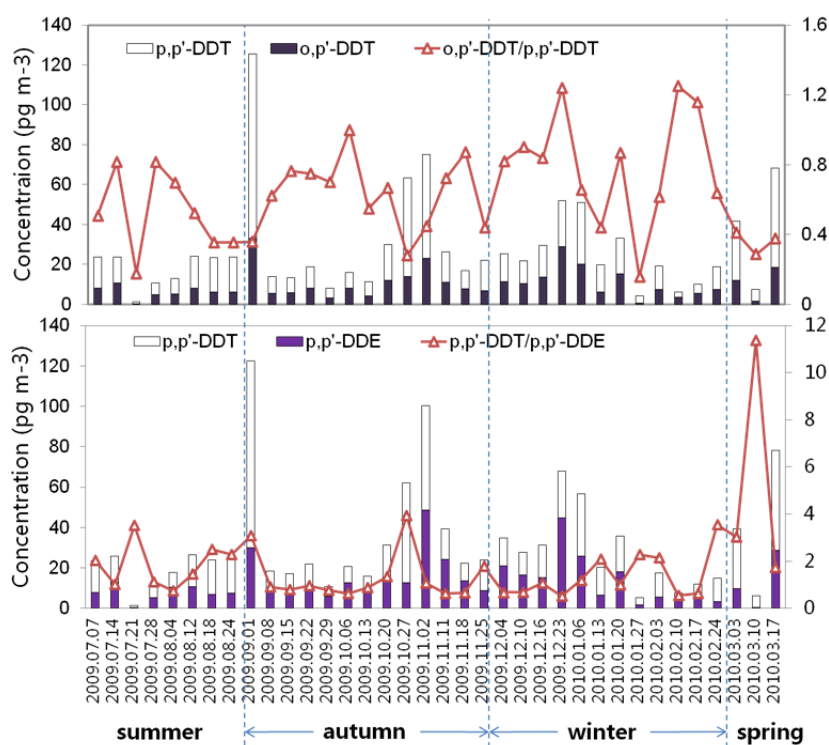

Fig. 3. Seasonal variations of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE concentrations and isomeric ratios.
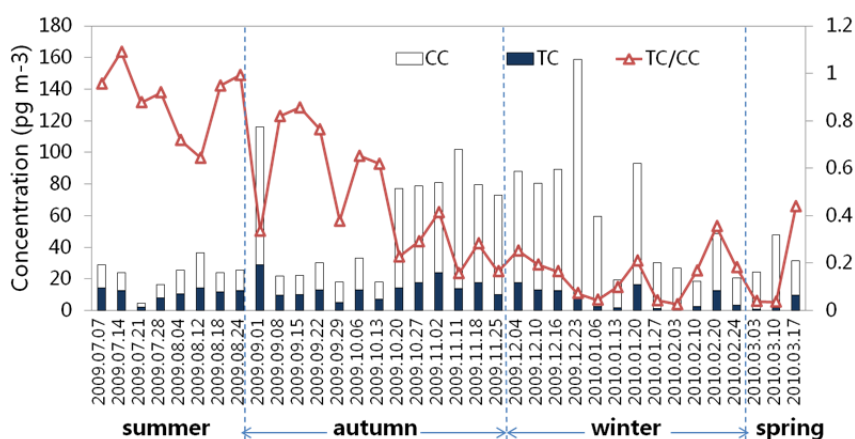
Fig. 4. Seasonal variations of chlordane concentrations and TC/CC ratios.

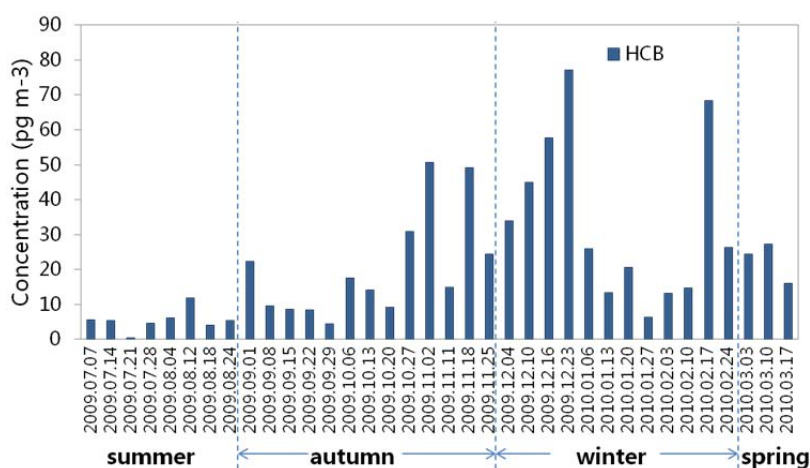**Fig. 5.** Seasonal variations of HCB concentrations.

which was lower than previous report in the Yangtze River Delta (YRD) region (81 pg/m^3 in summer, 257 pg/m^3 in winter) (Wang *et al.*, 2007). Seasonally, elevated HCB was monitored from autumn to winter when continental air masses influenced Ningbo site. During the summertime, relatively clean atmosphere from the oceans could dilute HCB pollutions.
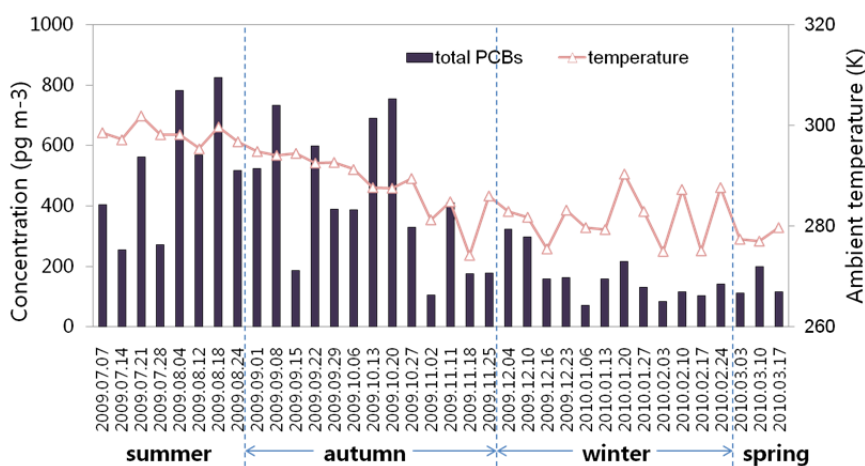
PCBs

As shown in Fig. 6, seasonality of PCBs was different from that of HCHs, DDTs, chlordane and HCB at NAEO. The high average PCBs concentration occurred in the summer months (12.7 pg/m^3), while low concentration in the winter period (7.18 pg/m^3). This might mainly be attributed to increased emission in summer and ambient temperature variations. During the summertime, the air masses from the south generally passed by Taizhou before reaching Ningbo site. Taizhou is a major e-waste recycling site located at the YRD region, and characterized by a high PCBs level in the atmosphere due to improper disposal of electronic waste in which tri-CBs and tetra-CBs dominated (Xing *et al.*, 2011). Since tri-CBs are more degradable than tetra-CBs, chemical composition of PCBs at NAEO could be dominated by high proportion of tetra-CBs.

Controlling Factors

There have many factors influencing the concentrations of OCPs and PCBs, such as temperature, rainfall, wind directions. Elevated PCB concentrations in hot season suggest that PCBs might be influenced by temperature. The opposite temporal variations of OCPs indicate wind directions were the controlling factors for OCPs. The Clausius–Clapeyron equation can be used to investigate temperature dependency of atmospheric OCPs and PCBs. This dependence is described by the equation (Hoff *et al*, 1992):

$$\ln P = m(1/T) + b \qquad (2)$$

where ln$P$ is the natural logarithm of partial pressure in the gas phase, m is the slope, b is the intercept of the line and T is the average temperature (K). Table 3 shows the detailed information of slope m, intercept b, correlation coefficient r^2, number of observations, and the significant level of the linear regression. The steep slopes with high r^2 values indicate that temperature controlled the air surface cycling of pollutants, such as evaporation from polluted sites. For PCB congeners, negative slopes were obtained for all most of PCB congeners with statistically significance. That suggests that PCBs were influenced by air-surface exchange.

Fig. 6. Seasonal variations of PCBs concentrations and ambient temperature during the sampling period. Summer ranged from July to August.

Table 3. Summary of individual OCPs and PCBs regression parameters for Clausius–Clapeyron plots.

Compounds	m	b	N	r^2	level of significance
PCB-28	−1453	−29.25	36	0.013	NS
PCB-52	−7702	−7.797	36	0.377	$p < 0.01$
PCB-44	−5660	−14.76	36	0.115	$p < 0.05$
PCB-101	−6190	−14.46	36	0.434	$p < 0.01$
PCB-118	−5471	−17.35	36	0.362	$p < 0.01$
PCB-153	−6285	−15.08	36	0.356	$p < 0.01$
PCB-138	−6306	−14.81	36	0.399	$p < 0.01$
PCB-180	−5517	−19.28	36	0.248	$p < 0.05$
PCB-169	−9880	−4.347	36	0.480	$p < 0.01$
PCB-170	1853	−44.00	36	0.015	NS
α-HCH	4774	−51.44	35	0.170	$p < 0.05$
β-HCH	6546	−57.26	35	0.548	$p < 0.01$
δ-HCH	−7029	−11.16	35	0.100	NS
γ-HCH	−83.19	−35.36	35	0.000	NS
p,p'-DDE	613.4	−37.07	35	0.007	NS
p,p'-DDD	−885.2	−31.66	35	0.013	NS
o,p'-DDT	−808.6	−32.66	35	0.010	NS
p,p'-DDT	415.0	−36.72	35	0.003	NS
TC	−656.2	−33.03	35	0.007	NS
CC	4660	−50.49	35	0.299	$p < 0.01$
HCB	6679	−57.69	35	0.555	$p < 0.01$

N denotes number of observations. NS: Non-significant correlation.

In contrast, the temperature-dependence cannot be found on OCPs, supporting that those compounds were subject to atmospheric transport.

Potential Sources

As discussed above, PCBs were mainly from the re-evaporation of the surface, while OCPs were likely subjected to long range atmospheric transport, and thus the source regions of OCPs can be identified by PSCF analysis. Potential sources of some OCP congeners are presented in Fig. 7. In the PSCF maps, dark red cells represent high PSCF values. It highlights that inland northern China, southern China and Japan were three major source regions of OCPs at Ningbo background site. The regions extending from North

Mongolia to Inner Mongolia and some southern provinces were identified to be source areas of α-HCH, β-HCH, γ-HCH and HCB. Although the usage of HCB and HCH are different, HCB concentration was statistically correlated with β-HCH during August when air masses come from southern China ($r = 0.957$, $p < 0.01$) and during January–March ($r = 0.740$, $p < 0.01$) when air masses come from northern China, confirming that they may be from similar source regions. Those regions have been considered as areas with a history of heavy pollution. Despite the use of organochlorinated insecticides was banned in China, the historical application of OCPs in these regions appeared to exert an impact on atmospheric level of OCPs at NAEO. The potential source regions of β-HCH were smaller than
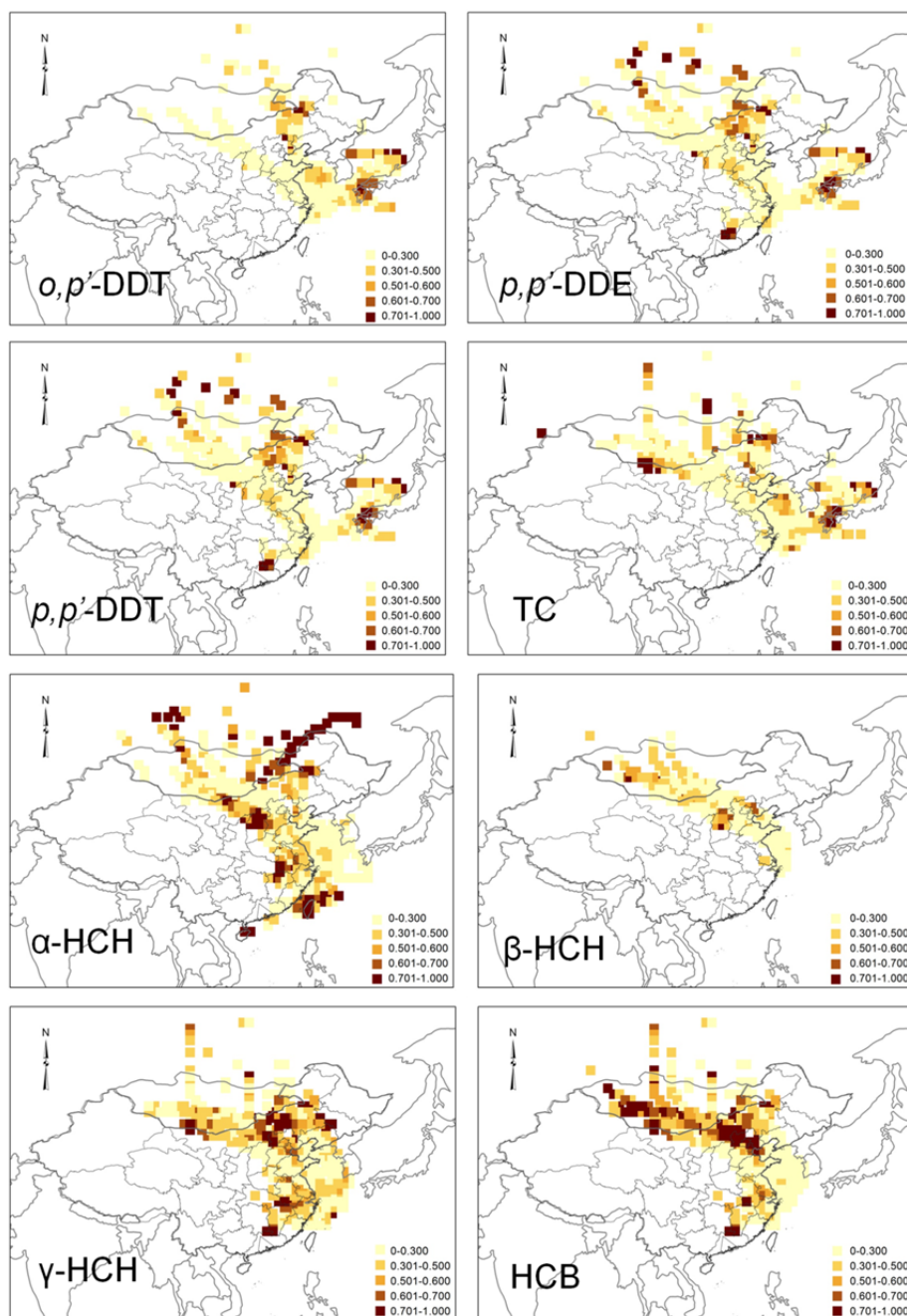
Fig. 7. Maps of potential sources of α-HCH, β-HCH, γ-HCH, HCB, *o,p'*-DDT, *p,p'*-DDE, *p,p'*-DDT and TC.

those of α-HCH, which can be attributed to the fact that α-HCH are prone to undergo LRAT. It also should be noticed that the source region of HCHs was different from that of DDTs and chlordane. Japan, where chlordane has been largely applied for termite control (Murayama *et al.*, 2003) and technical DDT has largely been stockpiled and/or buried (> 10,000 t) (Ueno *et al.*, 2003), was identified as another source region of *o,p'*-DDT, *p,p'*-DDE, *p,p'*-DDT and TC. The similarity of source regions between DDTs and chlordane can be proved by correlation analysis. TC concentration was significantly correlated with DDTs (r: 0.937–0.960, *p* < 0.01) during September and October when air masses come from Japan.

CONCLUSIONS

Gases and particulate OCPs and PCBs samples were collected at the Ningbo background station from July 2009 to March 2010. Concentration levels, seasonal variations and potential sources were investigated in this study. The results show that OCPs concentration levels were relatively low compared to other background sites, while PCBs concentration levels were relatively high. The relatively low levels of OCPs were possibly linked to the implementation of the Stockholm Convention in China during 2004–2009. Similar seasonal trends of HCH, DDT, chlordane and HCB concentrations were observed with the winter maximum.

This could be explained by the meteorological factors such as regional climatic conditions and movements of monsoon. Air masses from northern China carried large portions of pollutants to Ningbo resulted in higher concentrations, while wind direction partially transported from continental to marine area along with the precipitations in the summer period lead to low concentrations. Diagnostic ratios suggest that HCH, DDT and chlordane at NAEO were mainly from historical technical HCH, and technical DDT and chlordane. PCBs concentrations were higher in summer than those in winter. This may be attributed to temperature variation as well as the upwind sources in Taizhou during the summertime. PSCF analysis show that northern China and southern China were identified to be source areas of α-HCH, β-HCH, γ-HCH and HCB, while DDTs and chlordane were largely derived from Japan.

ACKNOWLEDGMENTS

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