

Original

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**Selected current-use and historic-use pesticides in air and
seawater of the Bohai and Yellow Seas, China**

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RESEARCH ARTICLE

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Key Points:

- Chlorpyrifos, chlorothalonil and dicofol were the most abundant CUPs
- Riverine inputs were significant for some CUPs but not for HUPs
- Recent usage amounts strongly affect air-water exchanges of CUPs

Supporting Information:

- Supplemental Figure and Tables

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Selected current-use and historic-use pesticides in air and seawater of the Bohai and Yellow Seas, China

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Abstract Consumption of pesticides in China has increased rapidly in recent years; however, occurrence and fate of current-use pesticides (CUPs) in China coastal waters are poorly understood. Globally banned pesticides, so-called historic-use pesticides (HUPs), are still commonly observed in the environment. In this work, air and surface seawater samples taken from the Bohai and Yellow Seas in May 2012 were analyzed for CUPs including trifluralin, quintozone, chlorothalonil, dicofol, chlorpyrifos, and dacthal, as well as HUPs (hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), and endosulfan). CUP profile in both air and seawater samples generally reflected their consumption patterns in China. HUPs in the air and seawater samples were in comparable levels as those of CUPs with high concentrations. α -Endosulfan, dicofol, and chlorothalonil showed strong net deposition likely resulting from their intensive use in recent years, while CUPs with low consumption amount (quintozone and dacthal) were close to equilibrium at most samplings sites. Another CUP with high usage amount (i.e., chlorpyrifos) underwent volatilization possibly due to its longer half-life in seawater than that in air. α -HCH and γ -HCH were close to equilibrium in the Bohai Sea, but mainly underwent net deposition in the Yellow Sea. The net deposition of α -HCH could be attributed to polluted air pulses from the East China identified by air mass back trajectories. β -HCH showed net volatilization in the Bohai Sea, which was driven by its relative enrichment in seawater. HCB either slightly favored net volatilization or was close to equilibrium in the Bohai and Yellow Seas.

1. Introduction

Since 2001, nine pesticides (aldrin, chlordane, dichlorodiphenyltrichloroethane, dieldrin, endrin, heptachlor, hexachlorobenzene, toxaphene, and mirex) have been initially listed in the Stockholm Convention on Persistent Organic Pollutants (POPs) for their persistence, bioaccumulation, and potential for long-range transport (LRT) (chm.pops.int). Even though these pesticides have been globally restricted for one decade (or even longer in many countries), they are still commonly found in air, water, and fish samples all over the world [*Chang et al.*, 2012; *Guan et al.*, 2009; *Lohmann et al.*, 2012; *Wania et al.*, 2010]. Today more than 900 pesticide active ingredients are used to control pests [*Casida*, 2012]. Although most current-use pesticides (CUPs) are considered to be less persistent and more biodegradable compared with the historic-use pesticides (HUPs, refer to all pesticides globally banned according to Stockholm Convention), they have been frequently observed in air and water of agricultural or urban areas [*Coscollà et al.*, 2010; *Gouin et al.*, 2008; *You et al.*, 2011]. Some CUPs even were found in the remote areas like high mountains, the Pacific Ocean, and the Arctic [*Bradford et al.*, 2010; *Ruggirello et al.*, 2010; *Zhong et al.*, 2012a]. This indicates their LRT potential property. Pesticides are designed to be toxic and they are released into the environment deliberately and in large quantities, so environmental impact of CUPs deserves close attention.

There have been numerous studies on the levels and fate of HUPs in the ocean, but little is known about the occurrence of CUPs in marine environment. Previous studies on HUPs indicate that marine waters act as major recipients of these chemicals [*Goldberg*, 1975; *Strand and Hov*, 1996]. Marine waters receive pesticides through riverine input, atmospheric dry or/and wet deposition, and air-water exchange. HUPs initially

transferred into surface seawater would be removed to deep oceans by absorbing on particles as well as by oceanic deep water formation [Dachs *et al.*, 2002; Lohmann *et al.*, 2006]. Pesticides in deep oceans are believed to hardly re-emit to the atmosphere, making deep oceans an ultimate sink. However, air-water exchange is a reversible process. Marine waters also can release pesticides through air-water exchange, becoming secondary sources. Thus, studies on air-sea gas exchange are of great importance in answering whether marine waters serve as secondary sources or act as recipient (or sink) of pesticides.

In China, production of pesticide technical products was 360 million t in 2012 with an annual increase rate of larger than 10% from 2008 to 2012 (www.stats.gov.cn). Occurrence and fate of CUPs in China coastal waters need to be understood urgently. HUPs in China coastal sediment and biota samples have been extensively monitored [Wang *et al.*, 2008; Yang *et al.*, 2005; Zhang *et al.*, 2009], while studies on air-sea gas exchange are sparse [Lin *et al.*, 2012; Zhang *et al.*, 2007].

The Bohai and Yellow Seas border on China's important agricultural regions (Liaoning, Hebei, Shandong and Jiangsu Provinces, and Tianjin Municipality), which account for 6% of the total land areas but 23.5% of the total pesticide product usages of the country (www.stats.gov.cn). The Yellow River (drainage area: 7.5×10^5 km²) and the Yangtze River (drainage area: 1.8×10^6 km²) are the largest rivers discharging into the Bohai and Yellow Seas, respectively, in terms of annual runoff. In this work, we analyzed air and sea-water samples in the Bohai and Yellow Seas for selected CUPs (trifluralin, quintozene, chlorothalonil, dicofol, chlorpyrifos, and dacthal), HUPs (endosulfan, technical hexachlorocyclohexane (HCH), lindane, and hexachlorobenzene (HCB)), and degradation products (endosulfan sulfate and pentachloroanisole). The selected CUPs first attract our attentions for their high consumption amounts (in China or the rest of the world) and detections in remote oceans (e.g., the Arctic and North Pacific) [Hoferkamp *et al.*, 2010; Zhong *et al.*, 2012a].

The objectives of this study are (1) to provide probably the first information on occurrence of CUPs possessing POP-like properties in China coastal air and waters, (2) to update information of HUP concentrations in China coastal seas, and (3) to investigate spatial distributions, identify possible sources, and explore the behavior of air-water exchanges of both CUPs and HUPs.

2. Usage of the Selected Pesticides in China

Global usage amount of each selected CUPs is at least 200 tonnes/year (t/yr) and most of the CUPs have global usage amount over 1000 t/yr [Hoferkamp *et al.*, 2010]. Chlorpyrifos and dicofol are among the most popular insecticides in China. The domestic market demand of chlorpyrifos was 18,000 t in 2008 (<http://www.ccpia.com.cn/>, China Crop Protection Industry Association) and the domestic consumption of dicofol was 3500 t/yr in recent years [United Nations Development Programme, 2008]. Trifluralin has been used as herbicide in China since the late 1980s [Niu, 1980], but its consumption data are unavailable at present. Recent domestic usage amount is 300 t/yr for chlorothalonil (<http://www.ccpia.com.cn/>) and 32 t/yr for quintozene, estimated from 80 t formulations with common quintozene weight percentage of 40% [Wang *et al.*, 2012]. Dacthal has not been registered as a pesticide in China (<http://www.chinapesticide.gov.cn/>). It has been detected in the North Pacific air and seawater [Zhong *et al.*, 2012a], so it is of interest to learn the status of this chemical in Bohai and Yellow Seas.

The selected HUPs were at one time extensively used in China. The technical grade products of endosulfan contain two isomers: α - and β -endosulfan with α/β -endosulfan ratios from 2.0 to 2.3 [Herrmann, 2002]. Technical endosulfan was used as insecticide in China with a consumption amount of 4100 t in 2010 (chm.pops.int). This insecticide has been listed in Annex A of the Stockholm Convention since May 2011 (chm.pops.int). New registrations of endosulfan-based products have been prohibited in China since July 2011 (<http://www.moa.gov.cn/>), but the usage of endosulfan stockpile may be continued. Technical HCH and lindane are mixtures of HCH isomers. The common composition of technical HCH is α -HCH 71%, β -HCH 6%, γ -HCH 14%, and δ -HCH 9% [Iwata *et al.*, 1993]. Lindane contains more than 99% of γ -HCH. Technical HCH was used in China from 1952 to 1984 with a total consumption of 4 million t [Li *et al.*, 1998]. The historic usage amount of lindane in China was 3200 t from 1991 to 2000 [Li *et al.*, 2001]. HCB was not used as a pesticide in China, but as an intermediate for the production of other pesticides such as pentachlorophenol (PCP) and pentachlorophenol-Na (Na-PCP). From 1988 to 2003, almost 99% of total HCB production (78,000 t) in China was used to produce PCP and Na-PCP [Wang *et al.*, 2010].

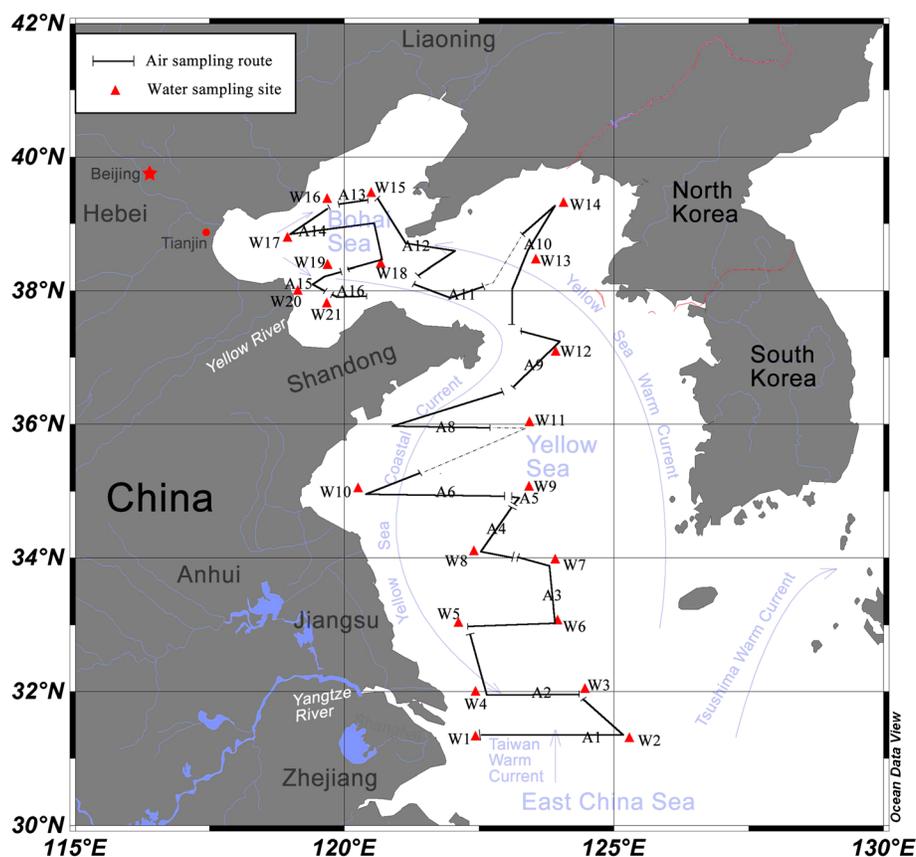


Figure 1. A map showing the moving routes corresponding to each air sample (the line segments) and the location of each seawater sampling site (the red triangles) in the Bohai and Yellow Seas. The sampling cruise started from W1/A1 and ended at W21/A16. The schematic diagram of the circulations was redrawn from *Oceanography of China Seas* [Zhou et al., 1994].

3. Materials and Methods

3.1. Sample Collection

Fifteen air samples ($\sim 420 \text{ m}^3$) and 21 seawater samples ($\sim 70 \text{ L}$) were taken in May 2012. A map of the moving route of each air sample and the location of each seawater sampling site was shown in Figure 1. Air samples were taken in front of the upper-most deck of the China research vessel *Dongfanghong 2* ($\sim 10 \text{ m}$ above sea level) for $\sim 24 \text{ h}$, using a high-volume air sampler equipped with a glass fiber filter ([GFF], GF/F, pore size: $0.7 \mu\text{m}$) to trap airborne particles and a self-packed PUF/Amberlite® XAD-2 glass column for the gas phase. Seawater samples were passed through a GFF (GF/C, pore size: $1.2 \mu\text{m}$) for the particulate phase, followed by a self-packed Serdolit® PAD-2 glass column for the dissolved phase. Glass columns for collecting gaseous and dissolved phases were stored at 4°C and filter samples were stored at -20°C prior to extraction. Detailed information on air and water sampling are given in Tables S1 and S2 in the supporting information.

3.2. Analytical Method

The target analyte list was composed of 14 compounds including CUPs (trifluralin, quitozene, chlorothalonil, dicofol, chlorpyrifos, and dacthal), HUPs (α -endosulfan, β -endosulfan, α -HCH, β -HCH, γ -HCH, and HCB), and degradation products (endosulfan sulfate and pentachloroanisole).

Similar analytical methods and spike test results for examining the method recoveries have been reported elsewhere in detail [Zhong et al., 2012a, 2012b]. In brief, samples were spiked with 500 pg of trifluralin- d_{14} as surrogate prior to 16 h Soxhlet extraction using dichloromethane (DCM). The extracts were reduced to 2 mL using a rotary evaporator and further cleaned on a 2.5 g silica gel column (10% water deactivated) topped on 3 g anhydrous granulated sodium sulfate. Elution started with 20 mL hexane, followed by 30 mL diethylether/DCM (1:3). The eluted samples were evaporated to a final volume of $\sim 30 \mu\text{L}$ and 0.5 ng ^{13}C -PCB141 was added

as internal standard. Samples were analyzed with an Agilent GC/MS-system (6890 GC/5973 MSD) in electron capture negative chemical ionization mode (ECNCI), using methane as ionization gas and equipped with an HP-5MS column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, J&W Scientific).

Three field blanks were run for each sample type (gas phase, air particle phase, seawater dissolved phase, and suspended particle phase). Mean absolute blank values of CUPs ranged from 0.01 to 200 pg (see Table S3 in the supporting information). Method detection limits (MDLs) were derived from mean field blank values plus three times the standard deviation (σ) (for compounds showing no field blanks, the instrumental limits at a signal-to-noise ratio of three were used). Atmospheric MDLs ranged from 0.0005 to 0.3 pg m⁻³ and seawater MDLs ranged from 0.003 to 8 pg L⁻¹ (see Table S4 in the supporting information for details). The mean recoveries of trifluralin-d₁₄ were 48 ± 6%, 61 ± 20%, 54 ± 14%, and 84 ± 22% for gas phase, air particle phase, seawater dissolved phase, and suspended particle phase, respectively. Concentration results in this paper were not corrected with surrogate recoveries, but it does not lead to much difference in the results of gas phase/air particle or seawater dissolved phase/suspended particle partitioning, distribution trends, and air-water exchange fugacity ratios comparing with data corrected with surrogate recoveries.

3.3. Air Mass Back Trajectories

Five-day air mass back trajectories (BTs) were calculated for each air sample in 6 h steps by NOAA's HYSPLIT model [Draxler and Hess, 1997]. The sampling height of air samples (10 m above sea level) was set as the arrival height of the BTs. Air mass BTs of individual air samples are provided in Figure S1 in the supporting information.

3.4. Air-Water Exchange Fugacity Ratio and Flux

A fugacity approach was used to investigate the air-water exchange equilibrium status of a chemical. The calculations of the fugacity ratios (FRs = f_a / f_w) and flux are described in the supporting information in detail. Air-water exchange fluxes were calculated using the Whitman two-film model [Bidleman and McConnell, 1995; Liss and Slater, 1974; Schwarzenbach et al., 2003]. An FR of >1, =1, and <1 indicates net deposition, equilibrium, and net volatilization, respectively. By considering the error of fugacity propagated from the estimated relative standard deviations of the water and air concentrations, air temperature during sampling, and Henry's law constants (HLCs), the uncertainty of FR was ± 36% for α -HCH, γ -HCH, chlorpyrifos, α -endosulfan, and β -endosulfan, ± 42% for HCB, β -HCH, and trifluralin, and ± 300% for other compounds [Zhong et al., 2012a, 2012b]. A positive air-seawater gas exchange flux (F_{aw} , ng m⁻² day⁻¹) value indicates net volatilization from the seawater to the atmosphere and a negative value indicates net deposition. The overall uncertainty of F_{aw} was calculated to be ± 57% for α -HCH, γ -HCH, chlorpyrifos, α -endosulfan, and β -endosulfan, ± 70% for HCB, β -HCH, and trifluralin, and ± 500% for other compounds [Zhong et al., 2012a, 2012b].

4. Results and Discussion

4.1. Partitioning in Particle

Details of pesticides' concentrations in gas phase and air particle phase are given in Tables S5 and S6 in the supporting information. Trifluralin, quinterozone, pentachloroanisole, dacthal, α -endosulfan, HCH isomers, and HCB in air particle phase were below the detection limits (BDL) or accounted for lower than 1% of its air concentrations, so atmospheric dry deposition is not an important transport pathway of these compounds into seawater. Relatively high percentages of chlorothalonil (mean: 10 ± 9%), dicofol (mean: 13 ± 9%), β -endosulfan (19 ± 14%), and endosulfan sulfate (53 ± 20%) partitioned into the particle phase. The high log K_{oa} value can explain this result for dicofol and β -endosulfan but not for chlorothalonil and endosulfan sulfate, which has relatively low log K_{oa} (Table 1).

Pesticides' concentrations in seawater dissolved phase and suspended particle phase are listed in detail in Tables S7 and S8 in the supporting information. Target compounds were generally BDL in seawater particle phase, except for chlorpyrifos, β -endosulfan, and endosulfan sulfate with 2–18%, 5–40%, and 1–38% presented in suspended particle phase, respectively. So sedimentation is an important removal process of chlorpyrifos, β -endosulfan, and endosulfan sulfate in seawater.

Table 1. Physical-Chemical Properties of Target Compounds at 298 K^a

	HLC (Pa · m ³ /mol)	logK _{ow}	logK _{oa}	P _L (Pa)	S _L (mol/m ³)
Chlorpyrifos	3.6 ^b	5.0	8.9	4 × 10 ⁻³	1.0 × 10 ⁻³
Dicofol	0.0025	5.0 ^c	10	1.8 × 10 ⁻⁴	7.8 × 10 ⁻¹
Chlorothalonil	0.20	2.9 ^d	7.1	1.3 × 10 ⁻²	3.0 × 10 ⁻³
Quintozene	4.4	4.6	7.4	3.6 × 10 ⁻³	1.5 × 10 ⁻³
Pentachloroanisole	2.9 ^e	5.7 ^e	8.0	4.6 × 10 ⁻²	1.3 × 10 ⁻³
Trifluralin	11 ^g	4.8 ^h	7.7	1.0 × 10 ⁻²	6.0 × 10 ⁻⁴
Dacthal	0.22	4.4 ^f	8.3	6.4 × 10 ⁻³	1.5 × 10 ⁻³
α-Endosulfan	0.82 ^b	4.9 ⁱ	8.5 ⁱ	4.4 × 10 ⁻³ⁱ	6.3 × 10 ^{-3 i}
β-Endosulfan	0.045 ^j	4.8 ⁱ	9.5 ⁱ	4.0 × 10 ⁻³ⁱ	8.9 × 10 ^{-2 i}
Endosulfan sulfate	0.033	3.7	8.5	3.7 × 10 ⁻⁵	1.1 × 10 ⁻³
α-HCH	0.30 ^b	3.9 ^j	7.5 ^j	2.5 × 10 ^{-1j}	3.3 × 10 ^{-1 j}
β-HCH	0.045 ^j	3.9 ^j	8.7 ^j	5.3 × 10 ^{-2j}	1.4 ⁱ
γ-HCH	0.27 ^b	3.8 ^j	7.7 ^j	7.6 × 10 ^{-2j}	2.5 × 10 ^{-1 j}
HCB	35 ^k	5.6 ⁱ	7.2 ⁱ	9.4 × 10 ⁻²ⁱ	1.4 × 10 ^{-3 i}

^aUnless indicated, all the Henry's law constants (HLCs), K_{ow}, K_{oa}, and vapor pressure (P_L) and water solubility (S_L) values are collected from database *EPI Suite*[™] [United States Environmental Protection Agency, 2010], which is owned by the U.S. Environmental Protection Agency. S_L from *EPI Suite*[™] is for 293 K.

- ^b[Cetin et al., 2006].
- ^c[Saito et al., 1993].
- ^d[Hansch et al., 1995].
- ^e[Nowell et al., 1999].
- ^f[Hansch and Leo, 1987].
- ^g[Staudinger and Roberts, 2001].
- ^h[Tomlin et al., 2009].
- ⁱ[Shen et al., 2005].
- ^j[Xiao et al., 2004].
- ^k[Jantunen and Bidleman, 2006].

4.2. Concentrations of CUPs in Gas and Dissolved Phases

Chlorpyrifos, chlorothalonil, and dicofol were the most abundant CUPs in both gas phase and seawater dissolved phase. CUP profiles in both gas and dissolved phases generally reflected their consumption patterns in China (Figure 2), except that mean gas phase concentrations of dicofol ([dicofol]_{gas}) were lower than the mean [chlorothalonil]_{gas} even though annual usage amount of dicofol in China is 10 times higher than that of chlorothalonil. This result can be explained by the much lower HLC and higher logK_{oa} value of dicofol (Table 1). These properties favor dicofol scavenging from atmosphere, and also dicofol partitioning in seawater and freshwater.

Mean [pentachloroanisole]_{gas} and seawater dissolved phase concentrations of pentachloroanisole ([pentachloroanisole]_{dis}) were 2.2 ± 1.7 pg m⁻³ and 0.76 ± 0.04 pg L⁻¹, respectively. Pentachloroanisole is a

metabolite of quintozene and PCP (or Na-PCP). PCP and Na-PCP production was discontinued in China in 1995 and 2003, respectively [Wang et al., 2010]. However, historical usage amounts of these chemicals (1000–10,000 t/yr from 1983 to 2003) were much higher than those of quintozene [Wang et al., 2010]. In the present work, correlation relationship between [pentachloroanisole]_{gas} and [quintozene]_{gas} was poor (Pearson's correlation *r* = 0.08). Moreover, pentachloroanisole concentrations were found higher than those of quintozene in air (mean: 1.0 ± 1.4 pg m⁻³) and seawater (mean: 0.36 ± 0.41 pg L⁻¹). This result suggested pentachloroanisole emissions originating from past extensive uses of PCP and Na-PCP.

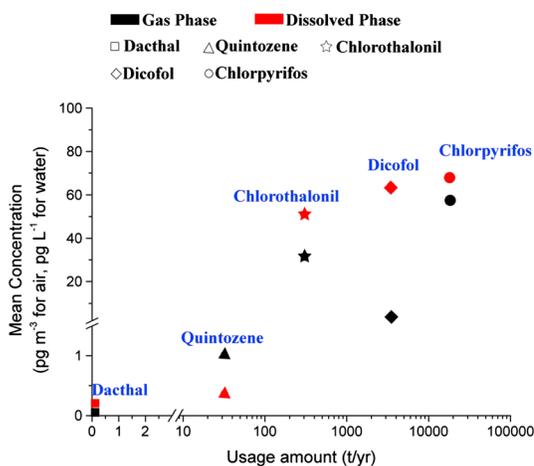


Figure 2. Scatterplot of mean gas phase and dissolved phase concentrations of current-use pesticides (CUPs) at the Bohai and Yellow Seas, with the annual usage amounts of CUPs in China.

Table 2. Comparison of Current-Use Pesticides Concentrations From the Present Study in the Bohai and Yellow Seas and From Our Previous Work in the German Bight (North Sea), and in the North Pacific and the Arctic

	Year	Chlorpyfos	Dicofol	Chlorothalonil	Quintozene	Pentachloroanisole	Trifluralin	Dacthal
				Air (pg m^{-3})				
Bohai and Yellow Seas ^a	2012	57 ± 110	3.8 ± 2.3	31 ± 20	1.0 ± 1.4	2.2 ± 1.7	2.1 ± 3.3	0.041 ± 0.045
German Bight, North Sea ^b	2010	16 ± 19	... ^d	... ^d	0.25 ± 0.29	10 ± 12	1.9 ± 2.5	12 ± 18
North Pacific and the Arctic ^c	2010	13 ± 35	14 ± 29	0.64 ± 0.89	... ^d	... ^d	2.0 ± 2.6	0.14 ± 0.30
				Seawater (pg L^{-1})				
Bohai and Yellow Seas ^a	2012	68 ± 110	63 ± 65	51 ± 50	0.36 ± 0.41	0.76 ± 0.40	1.3 ± 2.3	0.19 ± 0.15
German Bight, North Sea ^b	2010	65 ± 34	... ^d	... ^d	0.060 ± 0.050	1.2 ± 0.8	3.7 ± 5.3	30 ± 13
North Pacific and the Arctic ^c	2010	8 ± 26	9 ± 23	0.049 ± 0.049	... ^d	... ^d	0.023 ± 0.055	1.0 ± 1.2

^aThis study.

^b[Zhong *et al.*, 2012b].

^c[Zhong *et al.*, 2012a].

^dNot available.

The selected CUPs have been analyzed in our previous studies in the German Bight (North Sea) and/or in the North Pacific and the Arctic [Zhong *et al.*, 2012a, 2012b]. CUP concentrations from our present and previous studies are compiled (Table 2). Chlorpyrifos is one of the most abundant CUPs in gas and dissolved phases of all the studied areas especially in the Bohai and Yellow Seas, suggesting that chlorpyrifos is one of the most popular pesticides in the adjacent continents and the relatively higher usage amount in China. For instance, high consumption amounts of chlorpyrifos have been reported in the European Union (1200 t/yr) and the United States (4500 t/yr) [European Commission, 2012; United States Environmental Protection Agency, 2012], but they are at least four times lower than that of China. Dacthal levels were observed to be low in air and seawater of the Bohai and Yellow Seas and were consistent with the fact that dacthal was not registered as pesticide in China. Mean [Trifluralin]_{gas} in Bohai and Yellow Seas was comparable with those in the German Bight, the North Pacific, and the Arctic, while mean [Trifluralin]_{dis} showed greater variability among different areas.

4.3. Concentrations of HUPs in Gas and Dissolved Phase

[α -Endosulfan]_{gas} in the Bohai and Yellow Seas varied from 5.9 to 47 pg m^{-3} (mean: $28 \pm 13 \text{ pg m}^{-3}$), similar with those in the island of Okinawa (~ 10 to 50 pg m^{-3}) situated in the East China Sea [Primbs *et al.*, 2007], but higher than [endosulfan]_{gas} in the Yellow Sea, East China Sea, and South China Sea in 2006 reported by Lin *et al.* [2012] ($3.9 \pm 3.7 \text{ pg m}^{-3}$). Endosulfan sulfate is the predominant metabolite of endosulfan in a variety of environmental media [Weber *et al.*, 2010]. [Endosulfan sulfate]_{gas} accounted for less than 2% of [Σ Endosulfans]_{gas} (Σ Endosulfans: sum of α -, β -endosulfan, and endosulfan sulfate). [α -HCH]_{gas} and [γ -HCH]_{gas} in this work ranged from 2.4 to 21 pg m^{-3} and from 0.67 to 3.9 pg m^{-3} , respectively. Their levels are much lower than those of the northern South China Sea in 2005 reported by Zhang *et al.* [2007] ([α -HCH]_{gas}: 27 to 206 pg m^{-3} ; [γ -HCH]_{gas}: 343 to 1950 pg m^{-3}), and the Yellow Sea, East China Sea, and South China Sea in 2006 reported by Lin *et al.* [2012] ([α -HCH]_{gas}: 4.1 to 39 pg m^{-3} ; [γ -HCH]_{gas}: 12 to 440 pg m^{-3}). [β -HCH]_{gas} accounted for 8 ± 4% of [Σ HCHs]_{gas} (Σ HCHs: sum of α -, β - and γ -HCHs).

Mean [α -endosulfan]_{dis} ($2.2 \pm 1.5 \text{ pg L}^{-1}$) in the Bohai and Yellow Seas were slightly higher than those reported in the North Pacific and the Arctic ($0.6 \pm 1.3 \text{ pg L}^{-1}$) [Zhong *et al.*, 2012a]. [α -HCH]_{dis} and [γ -HCH]_{dis} ranged from 7 to 56 pg L^{-1} and 2 to 22 pg L^{-1} , respectively. Unlike air samples, [endosulfan sulfate]_{dis} and [β -HCH]_{dis} accounted for high percentages of [Σ Endosulfans]_{dis} (mean: 63 ± 15%) and [Σ HCHs]_{dis} (mean: 66 ± 8%), respectively. [HCB]_{dis} in the present work (mean: $20 \pm 9 \text{ pg L}^{-1}$) was not at similar values as other regions of the Northern Hemisphere as we observed for air samples. For instance, mean [HCB]_{dis} reported in the German Bight and the North Pacific were $6.7 \pm 7.3 \text{ pg L}^{-1}$ and $1.0 \pm 0.5 \text{ pg L}^{-1}$, respectively [Zhang and Lohmann, 2010; Zhong *et al.*, 2012b].

4.4. Spatial Distributions and Possible Sources

4.4.1. Air

Air mass BTs were used to track possible source origins of target compounds in the air. All air mass BTs are shown in Figure S1 in the supporting information and three representative ones (A1, A9, and A13) are given in Figure 3.

When the sampling campaign took place at the southern Yellow Sea (A1–A6), the air mass BTs mainly passed through the East China (Zhejiang, Jiangsu, Anhui, and Shandong Provinces) and occasionally passed through

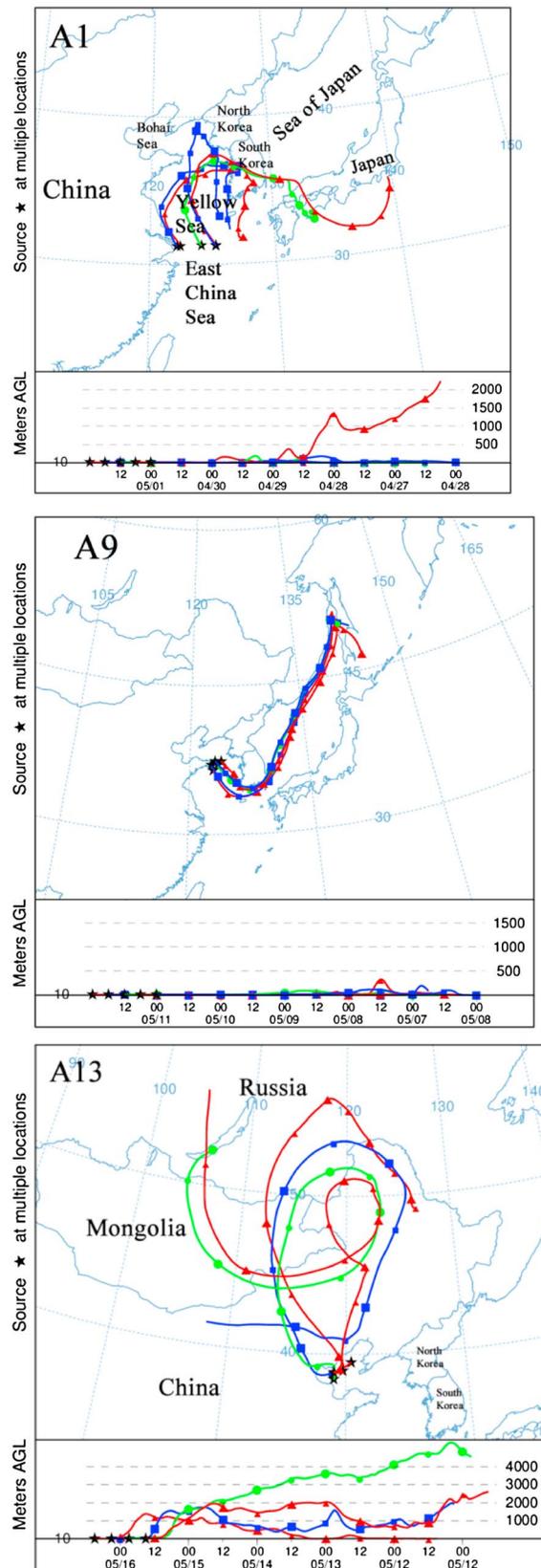


Figure 3. Three representative air mass back trajectories (BTs) of air samples taken in the Bohai and Yellow Seas. Air mass BTs of A1, A9, and A13 represent air mass BTs of A1–A6, A8–A10, and A11–A16, respectively.

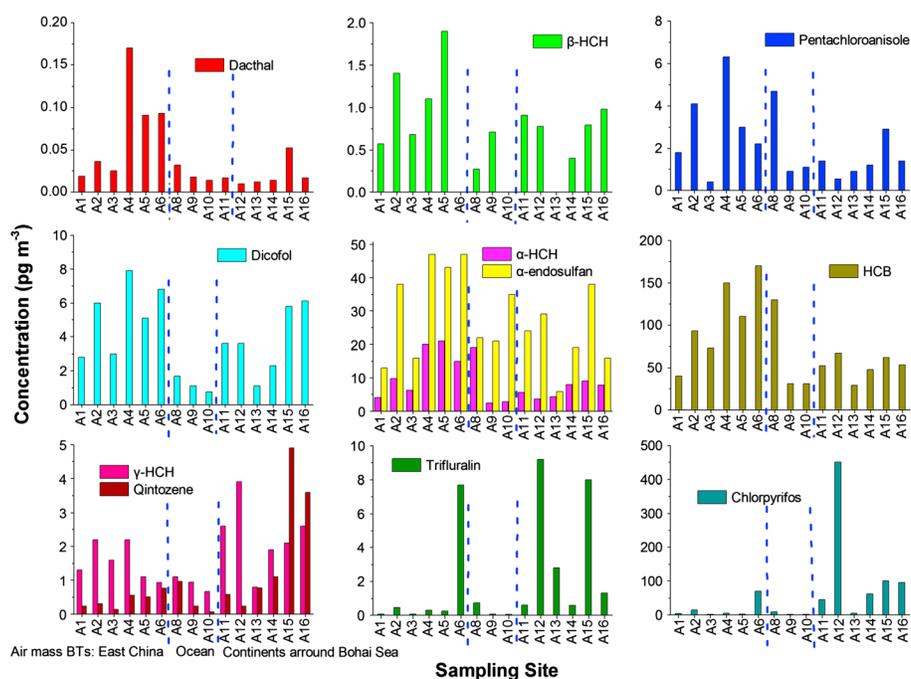


Figure 4. Gas phase concentrations of target compounds in the Bohai and Yellow Seas (pg m^{-3}). Sampling sites A1–A6, A8–A10, and A11–A16 were at the southern Yellow Sea, the middle and northern Yellow Sea, and the Bohai Sea, respectively. The sampling sites are grouped according to similarity of corresponding air mass BTs.

Japan and Korea. Generally, compounds including dacthal, β -HCH, pentachloroanisole, dicofol, α -HCH, α -endosulfan, and HCB showed higher concentrations in the southern Yellow Sea (Figure 4), which most likely was due to sources from the East China. It is unexpected to observed possible sources of dacthal from the East China. Further research need to be carried out to confirm whether there are dacthal emissions from nonagricultural activities. PCP, Na-PCP, and technical HCH are pesticides containing HCB as an impurity [Bailey, 2001]. Co-emission of HCB, pentachloroanisole, and α -HCH from the East China suggests HCB sources from past intensive application of technical HCH, PCP, and Na-PCP.

The air mass BTs show that air sampled in the Bohai Sea (A12–A16) swept through region around the Bohai Sea (Shandong Province, North China, and Northeast China). Higher levels of γ -HCH, trifluralin, quintozene, and chlorpyrifos appeared in the Bohai Sea attributing to sources from these regions. One high concentration of trifluralin also existed outside the Bohai Sea (i.e., A6). α -/ γ -HCH ratios in the Bohai Sea (0.9–5.4) were lower than those of the southern Yellow Sea (9.0–16). This result is caused by different terrestrial sources of HCHs for the two regions. Namely, air sampled at the Bohai Sea passed through the North and Northeast China where lindane was the main HCH product used [Li *et al.*, 2001], whereas air sampled at the southern Yellow Sea passed through the East China where technical HCH was intensively used [Li *et al.*, 2001].

Air masses sampled in the middle and northern Yellow Sea (A8–A10) passed through the ocean (the Yellow Sea and the Sea of Japan). Dicofol, chlorpyrifos, and trifluralin showed significantly lower concentrations at these sampling sites likely owing to atmospheric removal processes. Dicofol is prone to atmospheric deposition (dry deposition, wet deposition, and air-water exchange) as we mentioned above. Chlorpyrifos and trifluralin tend to be oxidized in the air with estimated half-life of 0.12 day and 0.44 day based on the reaction with OH-radicals, respectively [United States Environmental Protection Agency, 2010]. For chlorpyrifos, significant oxidation in the air was evidenced by a field study at the Canadian Prairie agricultural region, where the oxon degradation product can be at similar or higher concentrations as chlorpyrifos [Raina *et al.*, 2010].

4.4.2. Seawater

Concentrations of target compounds at the Yangtze River estuary (W1 and W4, Figure 1) and the Yellow River estuary (W20 and W21) can be indicators of riverine input from the Yangtze River and the Yellow River, respectively. Dissolved phase concentrations of target compounds were shown in Figure 5. Comparing to offshore samples, very high levels were detected in the samples from the estuaries of Yellow River and

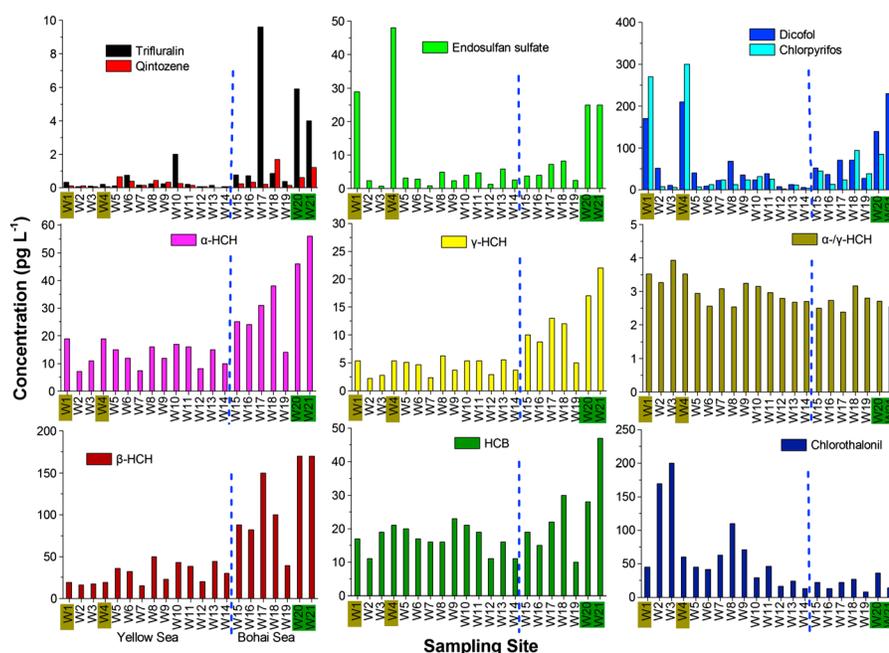


Figure 5. Concentrations of seawater dissolved phase in the Bohai and Yellow Seas (pg L^{-1}). Sampling sites W1–W14 and W15–W21 were at the Yellow Sea and the Bohai Sea, respectively. W1 and W4 were sampling sites near the Yangtze River estuary, and W20 and W21 were sampling sites near the Yellow River estuary.

Yangtze River for CUPs (including quintozene, trifluralin, dicofol, and chlorpyrifos) and endosulfan sulfate, indicating a strong riverine input source; but this was not so notable for HUPs.

Mean concentrations of dicofol and chlorpyrifos near the Yangtze River and Yellow River estuaries (W1, W4, W20, and W21) were seven and twelve times higher than those at other sampling sites, respectively. Relatively high concentrations of trifluralin and quintozene appeared near the Yellow River estuary (W20 and W21), but high values also existed at one or two offshore sampling sites. These results also showed that riverine inputs could be important sources not only for CUPs with relatively high water solubility (e.g., dicofol), but also for CUPs with lower water solubility (e.g., trifluralin). The concentrations of endosulfan sulfate near the Yangtze River estuary (W1 and W4) and the Yellow River estuary (W20 and W21) were at least seven times higher than the mean concentration of other sampling sites, but α -endosulfan and β -endosulfan did not show such high values in the estuarial sites comparing to other sites (Figure 5).

HCH isomers were evenly distributed in the Yellow Sea, probably due to efficient mixing by ocean currents and a lack of fresh input sources. Concentrations of HCH isomers in the Bohai Sea (W15–W21) were generally three times higher than those in the Yellow Sea (W1–W14). α - γ -HCH ratios (mean value: 2.8 ± 0.3) showed that the HCH pollution in seawater was a mixture of technical type and lindane type, as that found in air samples. However, α - γ -HCH ratios were evenly distributed in seawater of the Bohai and Yellow Seas ranging from 2.4 to 3.9, in contrast to the wide range of α - γ -HCH ratios in air samples. Also, contrary to the result observed for air samples, HCB was quite uniformly distributed in seawater of the Bohai and Yellow Seas except that one relatively high concentration occurred at W21. It suggested efficient mixing of HCB by ocean currents and no point sources.

As one of the most abundant pesticides in seawater, chlorothalonil did not show significant input from the Yellow River or Yangtze River, but higher levels were observed in the southern Yellow Sea especially at W2 and W3 reflecting transport of chlorothalonil from the East China Sea by ocean currents (see Figure 1 for ocean currents). Chlorothalonil is used as an antifouling paint biocide [Konstantinou and Albanis, 2004]. Chlorothalonil was detected in Greek coastal sediment samples with higher concentrations captured during the months of high boating activity [Albanis et al., 2002]. Concentrations of chlorothalonil in Korean coastal water have been observed to increase from 2006 to 2009 following the ban of tributyltin, which was extensively used as antifouling paint biocide [Lee et al., 2011]. To our knowledge, emissions of chlorothalonil owing

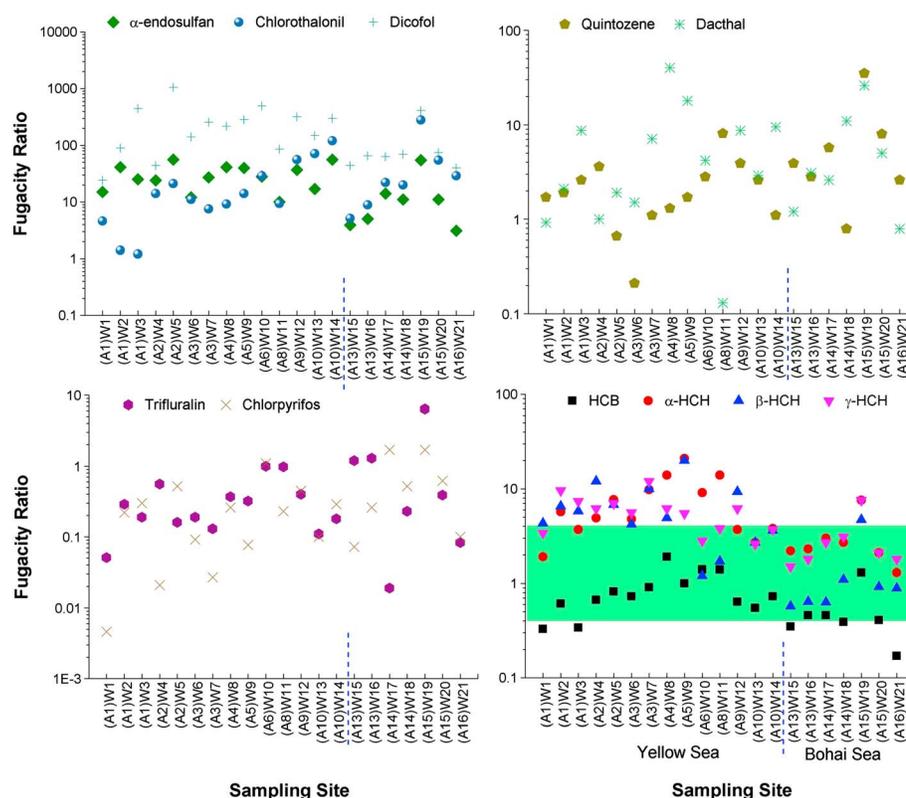


Figure 6. Air-water exchange fugacity ratios (f_a/f_w) of target compounds in the Bohai and Yellow Seas. Numbers in the parentheses are the paired air samples for the calculation of fugacity ratio. The green background of plots of hexachlorobenzenes and hexachlorocyclohexanes highlights an equilibrium window of $0.3 < f_a / f_w < 3$.

to antifouling paint usages have not been reported in Chinese coastal waters yet. Whether there are chlorothalonil emissions from shipping activities at the Bohai and Yellow Seas needs further studies.

4.5. Air-Water Exchange

The air-water exchange of some pesticides which have been intensively used in recent years, such as α -endosulfan, dicofol, and chlorothalonil, were dominated by net deposition with high FR values (Figure 6). Equilibriums of chlorothalonil were only observed at W2 and W3, because the delivery of chlorothalonil from the East China Sea through ocean currents resulted in higher seawater concentrations at these sampling sites. Net deposition fluxes of α -endosulfan in Bohai and Yellow Seas ranged from 0.9 to 20 $\text{ng m}^{-2} \text{day}^{-1}$ (see Table S9 in the supporting information), higher than those observed in the German Bight (North Sea) (0.05–10 $\text{ng m}^{-2} \text{day}^{-1}$) [Zhong *et al.*, 2012b] and Chukchi Sea (0.2–0.8 $\text{ng m}^{-2} \text{day}^{-1}$) [Zhong *et al.*, 2012a]. Net deposition fluxes of chlorothalonil (0.8–70 $\text{ng m}^{-2} \text{day}^{-1}$) and dicofol (0.3–4 $\text{ng m}^{-2} \text{day}^{-1}$) in Bohai and Yellow Seas were also higher than those at Chukchi Sea (chlorothalonil: 0.02–0.7 $\text{ng m}^{-2} \text{day}^{-1}$; dicofol: 0.4–1.5 $\text{ng m}^{-2} \text{day}^{-1}$), respectively.

The FR values of pesticides with low consumption amounts like quintozene and dacthal were relatively lower and air-water exchanges near equilibrium were observed at most sampling sites. Net deposition fluxes of these chemicals were generally $< 0.1 \text{ ng m}^{-2} \text{day}^{-1}$, as a result of their low air and seawater concentrations. For dacthal, deposition fluxes $< 0.1 \text{ ng m}^{-2} \text{day}^{-1}$ were also observed in western North Pacific, but deposition fluxes $> 1 \text{ ng m}^{-2} \text{day}^{-1}$ were found in the high Arctic and the German Bight (North Sea) [Zhong *et al.*, 2012a, 2012b].

Chlorpyrifos also has a high consumption amount; however, this chemical mainly underwent net volatilization at Bohai and Yellow Seas. Net volatilization was also observed for trifluralin. One reason for the net volatilization was that riverine input could result in relative enrichment of these compounds in seawater. Net volatilization of chlorpyrifos was generally observed in marine water close to continents with intensive

agricultural activities, e.g., the German Bight (North Sea) [Zhong *et al.*, 2012b], Izmir Bay (Turkey) [Odabasi *et al.*, 2008], and the Sea of Japan [Zhong *et al.*, 2012a], but net deposition appeared in remote areas like the Sea of Okhotsk, Bering Sea, and Chukchi Sea [Zhong *et al.*, 2012a], which receive less river discharge. Compounds including dicofol, quintozone, and endosulfan sulfate also showed riverine input, but no net volatilization. Explanation for this difference could be the inherent physical-chemical properties of chlorpyrifos and trifluralin. Trifluralin's HLC is 2–3 orders of magnitudes higher than those of dicofol, endosulfan sulfate, and quintozone (Table 1). Chlorpyrifos' half-life in air is a hundred times lower than that in seawater [United States Environmental Protection Agency, 2010], which could lead to relative enrichment of chlorpyrifos in seawater.

In the present study, FR values of legacy pesticides undergoing long-term ban (i.e., HCB and HCHs) were in a narrow range from 0.17 to 21. Generally, an equilibrium window of $0.3 < FR < 3$ was estimated for POPs in previous studies, considering the uncertainty of FR calculation [Bruhn *et al.*, 2003; Lohmann *et al.*, 2009; Zhang and Lohmann, 2010].

α -HCH was close to equilibrium in the Bohai Sea (mean FR: 3.0 ± 2.1), but mainly underwent net deposition in the Yellow Sea (mean FR: 7.6 ± 5.5). Xie *et al.* [2011] summarized that the air-water exchange of α -HCH in the North Atlantic changed from net deposition in 1990 to equilibrium in 1999, and a new equilibrium had established at lower seawater concentrations in 2008. Cai *et al.* [2012] reported that air-water exchange of α -HCH was near equilibrium in the western North Pacific and western Arctic Ocean in 2010 except that net volatilization appeared near the East Asian continents due to higher dissolved concentrations. α -HCH was also close to equilibrium in the German Bight (North Sea) in May (mean FR: 2.5 ± 1.3), but significant riverine inputs and stronger volatilization of α -HCH from local surface combining polluted air masses, respectively, resulted in slightly lower FR values in March and higher FR values in July (mean FR: 0.87 ± 0.97 for March, 3.4 ± 2.1 for July) [Zhong *et al.*, 2012b]. Overall, air-water exchange equilibrium of α -HCH establishes in most oceans of the Northern Hemisphere, but the equilibrium could be broken up and changed to net volatilization by riverine input or switched to net deposition by polluted air masses. In our study, the net deposition of α -HCH in the Yellow Sea was likely a temporary condition due to polluted air pulses from East China (A2–A6) (Figure 3), considering the uniform distributions of α -HCH concentrations and α -/ γ -HCH ratios in seawater of the Yellow Sea aforementioned.

γ -HCH was also close to equilibrium in the Bohai Sea, but mainly underwent net deposition in the Yellow Sea as a result of the lower dissolved concentrations. Air-water exchange direction for γ -HCH has been dominated by net deposition in most studies [Xie *et al.*, 2011], and this is consistent with the fact that lindane has been globally banned for agricultural use just recently. However, atmospheric concentrations of γ -HCH might also show greater seasonality and net volatilization could happen in seasons with much lower gaseous concentrations [Zhong *et al.*, 2012b].

β -HCH was mostly undergoing net volatilization in the Bohai Sea for its high dissolved concentrations, whereas the dissolved concentrations in the Yellow Sea were not high enough to drive the net volatilization (Figure 5). Cai *et al.* [2012] reported net volatilization of β -HCH in the North Pacific and the Arctic Ocean in comparable dissolved concentrations (mean: $38 \pm 23 \text{ pg L}^{-1}$) as those of the Yellow Sea and in two orders of magnitude lower atmospheric concentrations than those of the Yellow Sea. The low HLC of β -HCH, which restrains the atmospheric transport of β -HCH and causes much higher atmospheric concentrations near continental sources, was one of the reasons leading to the different air-water exchange directions of β -HCH in the Yellow Sea and in the North Pacific and the Arctic Ocean. Additionally, β -HCH can be efficiently delivered through ocean currents, which is reported by Li *et al.* [2002] and is supported by the comparable dissolved concentrations of β -HCH in the Yellow Sea, the North Pacific, and the Arctic Ocean mentioned above. This is in favor of supersaturation of β -HCH especially in seawater of remote areas where the atmospheric concentrations are much lower.

The FR values of HCB varied from 0.17 to 1.9, so HCB either slightly favored net volatilization or was close to equilibrium in the Bohai and Yellow Seas. However, net volatilization fluxes of HCB were relatively high (average: $9 \pm 10 \text{ ng m}^{-2} \text{ day}^{-1}$) for its high air and seawater concentrations. HCB was also undergoing net volatilization or was close to equilibrium in Atlantic [Lohmann *et al.*, 2012]. HCB was near equilibrium in the open Pacific [Zhang and Lohmann, 2010] and was net deposition or near equilibrium in the North Pacific, North Atlantic, and Arctic [Cai *et al.*, 2012; Lohmann *et al.*, 2009]. Overall, the FR values obtained by these works varied within a narrow range from 0.2 to 6. In our study, air masses more polluted by HCB (A4–A8, see Figure 4) resulted in a slight increase of FR values (W8–W11, Figure 6). Similarly, a study on HCB in the German

Bight (North Sea) in March, May, and July 2010 also showed that mean FR values of HCB in different seasons were similar (2.0–3.6), even though more polluted air masses and stronger local volatilizations happened in July [Zhong *et al.*, 2012b]. Air-water exchange equilibrium of HCB is readily established for its high HLC (35 Pa · m³/mol, Table 1) making it more transferable across the air-water interface.

5. Conclusion

The selected CUPs (trifluralin, quintozone, chlorothalonil, dicofol, chlorpyrifos, and dacthal) were ubiquitous in air and seawater of the Bohai and Yellow Seas. Chlorpyrifos, chlorothalonil, and dicofol were the most abundant CUPs in both air and seawater samples. Air concentration of dicofol was much lower than those of chlorpyrifos and chlorothalonil, whereas level of dicofol in seawater was comparable with those of chlorpyrifos and chlorothalonil. This result can be explained by dicofol's high water solubility and low HLC. Endosulfan sulfate and β -HCH were at relatively low levels in the air, but they were the most abundant endosulfan-related compounds and HCHs in seawater, respectively. Transport of dicofol, endosulfan sulfate, and β -HCH through ocean currents deserves further research.

Air mass back trajectories were used to track the source origins of pesticides. HCB, α -HCH, β -HCH, α -endosulfan, pentachloroanisole, dicofol, and dacthal showed higher concentrations in the southern Yellow Sea, most likely due to the sources from East China. γ -HCH, trifluralin, quintozone, and chlorpyrifos had higher concentrations in the Bohai Sea attributing to the sources from continents around the Bohai Sea. Riverine inputs from the Yangtze River and/or the Yellow River were significant for some CUPs but not for legacy pesticides. Recent usage amount could strongly affect air-water exchange of pesticides. However, some CUPs (i.e., chlorpyrifos and trifluralin) showed net volatilization likely as a result of riverine input and the inherent physical-chemical properties. Previous numerical and field study showed marine waters have been losing POPs for a decline in primary atmospheric emissions [Stemmler and Lammel, 2009; Nizzetto *et al.*, 2010]. Our result indicates that marine waters would be secondary sources of pesticides, not only when pesticides undergo long-term ban and thereby causing a decline of atmospheric concentrations.

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