

## RESEARCH ARTICLE

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## Key Points:

- The Yangtze River input and continental outflow have limited influence on the fate of HCH in the YRE
- The enhanced riverine runoff was responsible for sustaining high DDT volatilization in summer
- Most OCPs transported by the river runoff are volatilized into air in the coastal ECS rather than in the YRE

## Supporting Information:

- Supporting Information S1
- Data Set S1

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## Atmospheric deposition and air-sea gas exchange fluxes of DDT and HCH in the Yangtze River Estuary, East China Sea

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**Abstract** The Yangtze River Estuary (YRE) is strongly influenced by the Yangtze River and lies on the pathway of the East Asian Monsoon. This study examined atmospheric deposition and air-sea gas exchange fluxes of dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH) to determine whether the YRE is a sink or source of selected pesticides at the air-water interface under the influences of river input and atmospheric transport. The air-sea gas exchange of DDT was characterized by net volatilization with a marked difference in its fluxes between summer (140 ng/m<sup>2</sup>/d) and the other three seasons (12 ng/m<sup>2</sup>/d), possibly due to the high surface seawater temperatures and larger riverine input in summer. However, there was no obvious seasonal variation in the atmospheric HCH deposition, and the air-sea gas exchange reached equilibrium because of low HCH levels in the air and seawater after the long-term banning of HCH and the degradation. The gas exchange flux of HCH was comparable to the dry and wet deposition fluxes at the air-water interface. This suggests that the influences from the Yangtze River input and East Asian continental outflow on the fate of HCH in the YRE were limited. The gas exchange flux of DDT was about fivefold higher than the total dry and wet deposition fluxes. DDT residues in agricultural soil transported by enhanced riverine runoff were responsible for sustaining such a high net volatilization in summer. Moreover, our results indicated that there were fresh sources of DDT from the local environment to sustain net volatilization throughout the year.

### 1. Introduction

Dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH) are typical compounds of organochlorine pesticides (OCPs), which are among the most important persistent organic pollutants (POPs). DDT was listed as one of the 12 POPs in the Stockholm Convention in 2004, and  $\alpha$ -HCH,  $\beta$ -HCH, and  $\gamma$ -HCH were added to the list in 2009. OCPs have significantly attracted scientific and regulatory interests due to their toxicity, bioaccumulation, and potential negative effects on nontarget organisms [Aigner *et al.*, 1998; Jones and De Voogt, 1999; Kallenborn *et al.*, 1998]. Furthermore, OCPs can also undergo long-range transport from their original pollution sources owing to their environmental persistence, leading them to global-scale distribution and contamination [Wania and Mackay, 1995; Wania *et al.*, 1999; Bailey *et al.*, 2000; Xiao *et al.*, 2010].

China was one of the world's largest producers and users of DDT and HCH from the 1950s to 1980s [Wei *et al.*, 2007]. The estimated total production of technical HCH and technical DDT was  $5 \times 10^6$  and  $2.7 \times 10^5$  t, respectively, over this period [Li *et al.*, 2001; Zhang *et al.*, 2009]. Agricultural use and production of HCH and DDT were officially banned in the early 1980s. However, 3200 t of  $\gamma$ -HCH (lindane) were used from 1991 to 2000 [Li *et al.*, 2000; Tao *et al.*, 2005]. In addition, China is still producing DDT for use in dicofol [Qiu *et al.*, 2005; Xin *et al.*, 2011], and the product continued to be used in China after the prohibition of technical DDT, with an estimated production of dicofol-type DDT of 8770 t from 1988 to 2002 [Qiu *et al.*, 2005]. Despite the continued production and use of DDT and HCH, the nationwide prohibition since 1983 has been effective. Studies in China have revealed a decreasing trend in DDT and HCH levels in the atmosphere [Iwata *et al.*, 1993; Lin *et al.*, 2012; Zhang *et al.*, 2002].

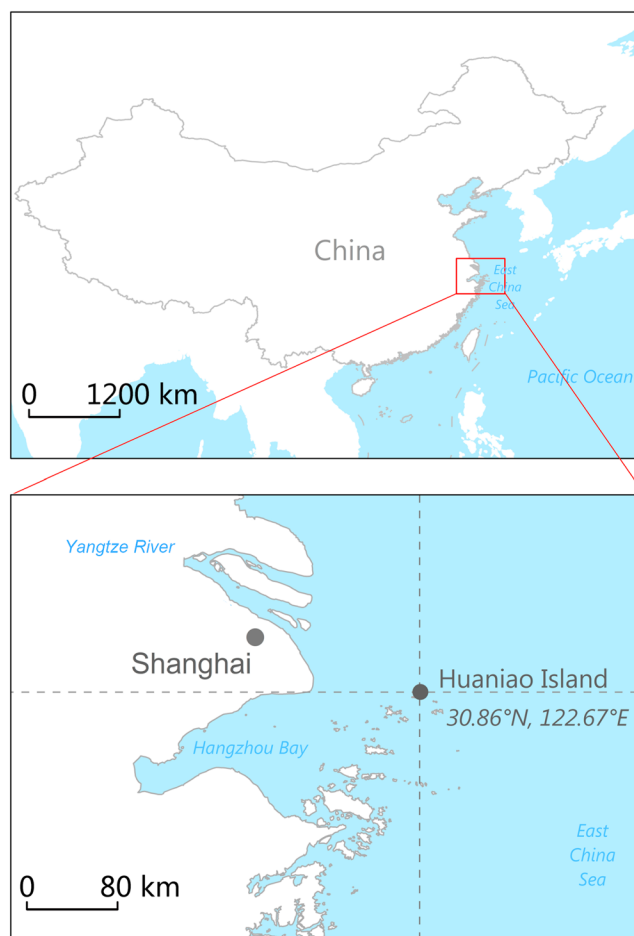
Owing to the decreasing primary sources, OCPs released from secondary sources are becoming increasingly influential. This has resulted in a series of changes on the transport and fate of these chemicals globally. Many studies have focused on the effect of declining air concentrations on the reemission of OCPs from soils directly to the atmosphere [Kurt-Karakus *et al.*, 2006]. The lateral remobilization from contaminated soils

through superficial and diffuse runoff and riverine transport toward marine coastal environments has also received a lot of attention recently. Overall, soil reemission followed by long-range atmospheric transport and riverine transport of contaminated soil might represent two important pathways of OCP remobilization on local or possibly regional scales. Thus, a large river estuarine environment is the ideal place to investigate these changes and compare the relative importance of the two different pathways for OCPs. The Yangtze River Estuary (YRE) is located on the coast of the East China Sea (ECS), adjacent to the Yangtze River Delta, the most urbanized and industrialized region in China. Eastern China has the highest levels of pesticide application in the country [Li *et al.*, 2001; Zhang *et al.*, 2009], and Zhejiang and Jiangsu Provinces ranked top in pesticide consumption per unit area from 1985 to 1991 [Wang *et al.*, 2005]. Recent surveys relating to DDT and HCH levels in coastal eastern China, such as those in air [Ji *et al.*, 2015; Wu *et al.*, 2011], water [Li *et al.*, 2012], sediments [Hu *et al.*, 2011; Liu *et al.*, 2004; Tang *et al.*, 2007], and suspended particulate matter [Li *et al.*, 2012; Liu *et al.*, 2008], indicated that the YRE and adjacent ECS are seriously polluted compared to other coastal areas off China. Results from source analyses indicated that input from the Yangtze River is an important source of HCH and DDT in water and sediments, and the continental outflow driven by the East Asian Monsoon brings large quantities of particulate HCH and DDT to the YRE, especially in winter. Regarding gaseous HCH and DDT in the atmosphere, Ji *et al.* [2015] suggested that the long-range atmospheric transport (continental outflow) might be an important source of DDT and HCH in the YRE and that net volatilization from surface seawater could also provide a significant contribution. However, the relative roles of the two sources remain poorly understood. The most recent study indicated that the major source of HCH and DDT was volatilization from seawater and the large contaminated Yangtze River served as a continuous significant regional secondary source to the upper atmosphere [Lin *et al.*, 2015]; however, that study focused only on one season (summer) rather than all four seasons, and only the air-sea gas exchange flux was estimated. Therefore, further studies are necessary to more fully elucidate the seasonal source-sink relationship according to fluxes of HCH and DDT in the region for the whole year. To this end, we analyzed the data of HCH and DDT in a total of 94 pairs of total suspended particulate (TSP) and polyurethane foam (PUF) samples, 20 surface seawater samples, and nine rainwater samples that we collected at Huaniao Island (HNI) (30.86°N, 122.67°E) during four seasons to determine seasonal variations in the concentrations and composition of HCH and DDT and to estimate the air-sea gas exchange and dry and wet deposition fluxes of these compounds. The objectives of this study were (1) to elucidate the characteristics of air-sea gas exchange and the dry and wet deposition fluxes of DDT and HCH, along with the main factors that influence them, and (2) to assess the source-to-sink processes of DDT and HCH at the air-water interface in estuarine/coastal areas, taking both air-sea gas exchange and atmospheric deposition (including dry and wet deposition) into account.

## 2. Materials and Methods

### 2.1. Sampling

Atmospheric (aerosol and gaseous phases), surface seawater, and rainwater samples were collected at HNI (30.86°N, 122.67°E) in the YRE (Figure 1). HNI is located approximately 66 km from the mainland coast and has a small population (less than 1000), whose livelihoods are based mainly on fishing. Because no pesticides are used in the fishery industry, we can assume local pesticide emissions at HNI to be zero. TSP and gaseous samples were collected simultaneously using a high-volume air sampler (Guangzhou Mingye Technology Company, China) deployed on the roof of a three-story building at HNI, at an elevation of about 50 m above sea level. The high-volume sampler was operated at a flow rate of 300 L/min. TSPs were captured using a precombusted quartz filter (20 × 25 cm, 0.7 mm, 2600QAT; Pall, Port Washington, NY), while compounds in the gaseous phase were collected in a solvent-cleaned PUF plug (length, 8.0 cm; diameter, 6.25 cm; and density, 0.035 g/cm<sup>3</sup>). On average, each paired sample (TSP + PUF) was collected for approximately 23.5 h; two parallel blank samples were also run for each season to measure the background contamination levels. A total of 94 paired aerosol and gaseous samples were collected at HNI during the sampling periods in the four seasons: 20 October to 12 November 2013 (autumn,  $n = 24$ ), 22 December 2013 to 14 January 2014 (winter,  $n = 23$ ), 27 March to 18 April 2014 (spring,  $n = 23$ ), and 29 July to 26 August 2014 (summer,  $n = 24$ ). A total of 20 surface seawater samples (one sample every 5 days, for a total of five each season) were collected during the entire sampling period. The volume of each seawater sample was approximately 25 L, and the samples were collected using a metal bucket. The seawater was immediately filtered through



**Figure 1.** The sampling site at HNI in the East China Sea.

quartz filters were wrapped in aluminum foil and combusted at 450°C for 12 h in a muffle furnace. The PUFs were Soxhlet extracted for 48 h with acetone and dichloromethane (DCM). Vacuum desiccators were used to dry the PUFs, which then were wrapped in aluminum foil and stored in an aluminum box. After sampling, the quartz filters were wrapped in baked aluminum foil and packaged in polyethylene bags. The PUFs were packed in baked aluminum foil, covered with polyethylene bags, and sealed in an aluminum box. The samples were taken to the laboratory and stored at  $-20^{\circ}\text{C}$  until analysis.

## 2.2. Sample Analysis

The samples were Soxhlet extracted for 48 h using DCM. Then, 2,4,5,6-Tetrachloro-m-xylene (TCmX) and decachlorobiphenyl (PCB209) were spiked into the extracts as surrogate recovery. After extraction, the reagent was concentrated by rotary evaporation to 5 mL. Hexane was added to the extracts, and they were further concentrated to 2 mL using a vacuum rotary evaporator to convert the solvent into hexane. The concentrated extracts were purified in an alumina/silica column (diameter, 8 mm). The column was packed, from the bottom to the top, with 3 cm of deactivated neutral alumina, 3 cm of deactivated neutral silica gel, and 1 cm of anhydrous sodium sulfate. The deactivated neutral alumina, deactivated neutral silica gel, and anhydrous sodium sulfate were Soxhlet extracted with DCM for 48 h and baked in a muffle furnace at temperatures of 250, 180, and 450°C before use. The column was subsequently eluted with 20 mL 1:1 DCM and hexane by volume. The effluent was concentrated to 0.5 mL under a gentle steam of nitrogen gas, and then spiked with 1 ng of pentachloronitrobenzene as an internal standard.

The OCPs were analyzed using a gas chromatography/mass selective detector (Agilent 5975; Agilent Technologies, Santa Clara, CA). The parameters of the capillary column were as follows: CP-Sil 8 CB model; length, 50 m; diameter, 0.25 mm; and film thickness, 0.25  $\mu\text{m}$ . The oven operating conditions were initial temperature, 60°C, and heating rate, 4°C/min; final temperature, 290°C; hold time, 10 min. Samples (1  $\mu\text{L}$ ) were

quartz filter with a diameter of 150 mm (Gelman Type A/E, nominal pore size 1  $\mu\text{m}$ , Pall Gelman), and the dissolved phase pesticides were extracted on a solid-phase Amberlite XAD-2 and XAD-4 mixture (1:1, Sigma – Aldrich) in a glass column (25 mm i.d., 200 mm long, and the amount of XAD in a glass column was 30 g). The XADs were ultrasonic extracted three times with acetone and dichloromethane (DCM). Nine rainwater samples were collected using a metal bucket placed on the roof of the three-story building and were then extracted on the solid phase using the same procedure except that they were filtered through QFFs so that the particulate and dissolved phases of the rainwater were collected and measured at the same time. Meteorological data were also simultaneously recorded.

Before collecting the samples, the quartz filters were wrapped in aluminum foil and combusted at 450°C for 12 h in a muffle furnace. The PUFs were Soxhlet extracted for 48 h with acetone and dichloromethane (DCM). Vacuum desiccators

injected into the device at an injector temperature of 250°C. A standard solution of OCPs, including  $\alpha$ -HCH;  $\beta$ -HCH;  $\gamma$ -HCH;  $\delta$ -HCH; p,p'-DDD; p,p'-DDE; o,p'-DDT; and p,p'-DDT, was purchased from AccuStandard, Inc. (New Haven, CT).

### 2.3. Quality Assurance and Quality Control

Strict procedures were implemented during the experiment to reduce operating errors. Three laboratory blanks and all parallel operational sample blanks were analyzed in the same manner as the samples. Compounds that concentrations were below the method detection limit (MDL, 0.06 pg/m<sup>3</sup> for the individual targeted compound) were considered as not detected. Values for the targeted compounds were lower than the MDL in the blanks. The breakthrough of the PUF samples was tested using two consecutive PUF plugs. The results indicated that the target compound values from the subjacent PUF plug were below the MDL. For the air samples, the average recoveries of TCmX and PCB209 were 74 ± 30% and 73 ± 28%, respectively. For the water samples, the average recoveries of TCmX and PCB209 were 89 ± 34% and 78 ± 27%, respectively. The data were not corrected based on the surrogate recoveries.

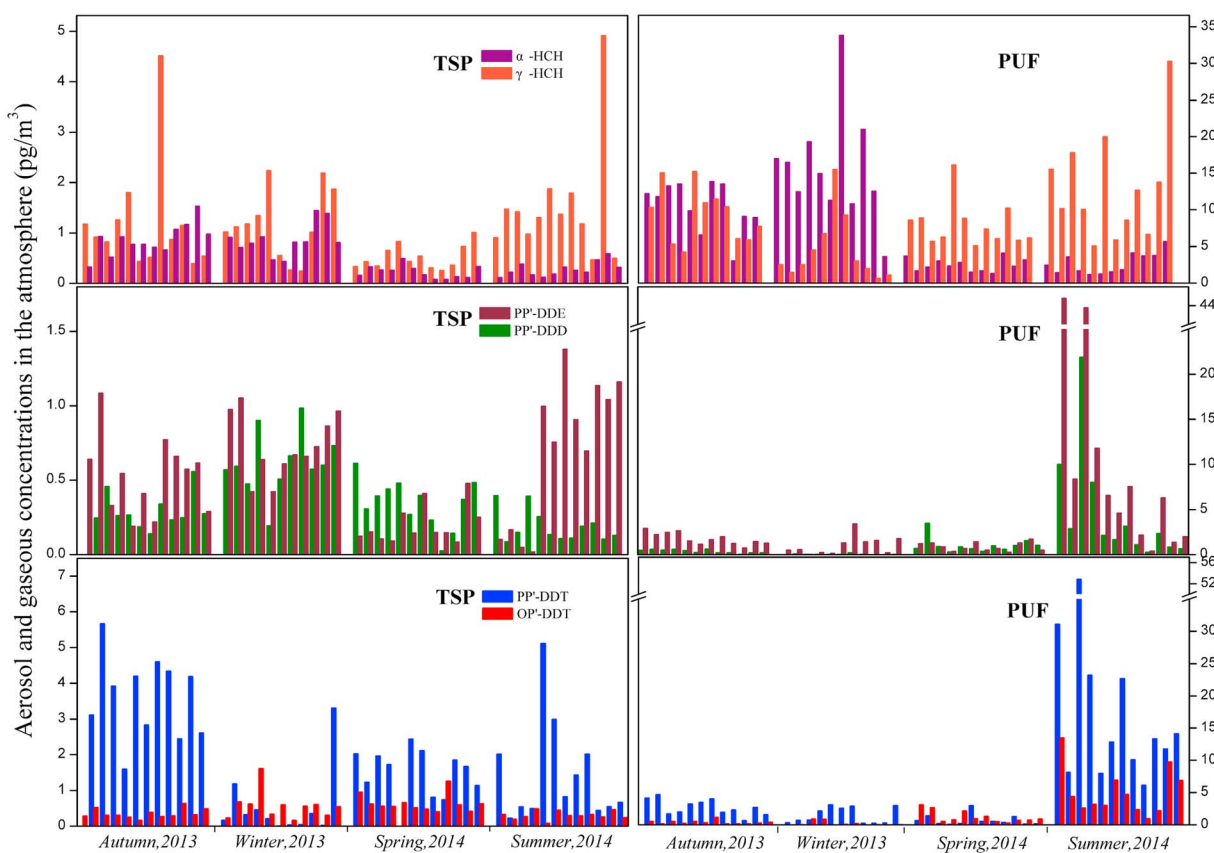
### 2.4. Framework for Deposition and Air-Sea Gas Exchange Calculations

In this study, the state of phase equilibrium for semivolatile compounds at the air-water interface, including the gaseous absorption/deposition and dissolved volatilization, can be addressed by fugacity calculation based on the Whitman two-film theory [Dachs *et al.*, 1999; Odabasi *et al.*, 2008]. Details of the air-sea gas exchange flux calculation and the dry and wet deposition flux calculations in this study are presented in Text S2.4 in the supporting information.

## 3. Results and Discussion

### 3.1. Dry and Wet Depositions

$\beta$ -HCH and  $\gamma$ -HCH were detected in all particle samples. The  $\alpha$ -HCH; p,p'-DDE; p,p'-DDD; o,p'-DDT; and p,p'-DDT were detected in 83–98% of the samples. Near nondetectable or low levels were detected for  $\delta$ -HCH. The particulate phase concentrations of DDT (p,p'-DDT; o,p'-DDT; p,p'-DDD; and p,p'-DDE) and HCH ( $\alpha$ -HCH,  $\beta$ -HCH, and  $\gamma$ -HCH) during the sampling period ranged from 4.8 to 31 pg/m<sup>3</sup> (mean 19 ± 4.5 pg/m<sup>3</sup>). The annual mean concentration of DDT in the particulate phase was 2.9 ± 1.8 pg/m<sup>3</sup>. The highest concentration occurred in autumn (4.7 ± 2.0 pg/m<sup>3</sup>), and the concentrations were 2.9 ± 1.4 pg/m<sup>3</sup> in spring, 2.8 ± 1.7 pg/m<sup>3</sup> in summer, and 2.8 ± 2.7 pg/m<sup>3</sup> in winter, respectively. The annual mean concentration of HCH in the particulate phase was 16 ± 3.9 pg/m<sup>3</sup>.  $\beta$ -HCH had the highest concentration with a mean annual value of 14 ± 3.6 pg/m<sup>3</sup> (the seasonal variation of  $\beta$ -HCH in the aerosol phase is presented in Figure S1 in the supporting information). The higher concentrations of  $\beta$ -HCH were consistent with observations in soils, in which  $\beta$ -HCH is the degradation product of the isomers  $\alpha$  and  $\gamma$ -HCH, and  $\beta$ -HCH has the highest refractory nature among the HCH isomers. The  $\alpha$ -HCH and  $\gamma$ -HCH are major active components of technical HCH and lindane, respectively. The particulate phase concentrations of the sum of  $\alpha$ -HCH and  $\gamma$ -HCH were 2.1 ± 1.7 pg/m<sup>3</sup> in autumn, 2.1 ± 1.0 pg/m<sup>3</sup> in winter, followed by 1.8 ± 1.7 pg/m<sup>3</sup> in summer and 0.7 ± 0.3 pg/m<sup>3</sup> in spring, respectively (Figure 2). The highest concentrations were not observed in winter, and no obvious seasonal change was found in these chemicals during the sampling period. The concentrations of particulate HCH and DDT remained at low levels during all four seasons. In general, HCH and DDT in aerosols were derived mainly from weathered agriculture soils. The residual levels of these chemicals in soils have been decreasing since the prohibition of HCH and DDT in China in the 1980s [Bai *et al.*, 2015]. Hence, any increase in dust from soils should have no significant effect on the concentrations of DDT and HCH in winter. In addition, Ji *et al.* [2015] showed that increased particulate HCH produced a partial shift to gaseous HCH controlled by gas-particle partitioning in winter. This was also confirmed in the present study by the fact that concentrations of DDT and HCH in the gaseous phase were higher than those in the particulate phase. The DDT in the gaseous phase accounted for over 60% of the total atmospheric concentration (gaseous and particulate phases), and for the sum of ( $\alpha$ -HCH +  $\gamma$ -HCH) and  $\beta$ -HCH, the proportions in the gaseous phase in the atmosphere were over 90% and 60%, respectively. This indicates that the majority of DDT and HCH in the atmosphere existed in the gaseous phase. Reemission of DDT and HCH from water may play an important role in contributing to the gaseous contaminants in the sampling area. The particulate-phase concentrations



**Figure 2.** Seasonal variation of isomer concentrations of HCH and DDT in TSP and PUF samples at HNI.

of DDT and HCH were comparable to those reported in recent studies [Ji *et al.*, 2015; Lin *et al.*, 2015] and were significantly lower than those observed in a 2007 study in South China [Zhang *et al.*, 2007].

The dry deposition flux estimation in detail is presented in Text S2.4. Using deposition velocities of 0.5 cm/s in this work, the estimated dry deposition fluxes of HCH and DDT were  $5.8 \pm 2.5$  ng/m<sup>2</sup>/d and  $1.4 \pm 0.40$  ng/m<sup>2</sup>/d, respectively. They are similar to values observed in a study in the U.S. Mid-Atlantic region [Gioia *et al.*, 2005] but lower than those recorded in other areas, such as in Turkey ( $0.6$  ng/m<sup>2</sup>/d for  $\gamma$ -HCH in this study compared to  $3$  ng/m<sup>2</sup>/d) [Odabasi *et al.*, 2008]. The dry deposition flux is directly related to the aerosol concentration; hence, the low fluxes of DDT and HCH observed in this study could be explained by the area's distance from the contaminated Chinese mainland and atmospheric removal processes during their long-range transport.

A total of nine rainwater samples were collected during the sampling period. The rainwater samples contained particulate and dissolved phase compounds together for analysis considering the low volume of rainwater collection (The volume of every rainwater sample is listed in Table S5 in the supporting information). HCH ( $\alpha$ -HCH,  $\beta$ -HCH, and  $\gamma$ -HCH) and DDT (*p,p'*-DDT; *o,p'*-DDT; *p,p'*-DDD; and *p,p'*-DDE) were detectable in all samples. The concentrations of sum DDT and HCH in the rainwater samples ranged from 620 to 4400 pg/L, with a mean value of  $2200 \pm 1400$  pg/L. HCH concentrations ranged from 300 to 1500 pg/L, and DDT concentrations ranged from 330 to 3200 pg/L. The average annual precipitation flux of 1 m/yr presented by the Shengsi Meteorological Bureau close HNI (<15 km) was used in this study. According to the concentrations of DDT and HCH in rainwater and the annual precipitation amount, the estimated wet deposition flux was 0.60–21 ng/m<sup>2</sup>/d (mean  $8.9 \pm 7.4$  ng/m<sup>2</sup>/d). For HCH, it was  $2.1 \pm 1.3$  ng/m<sup>2</sup>/d, and for DDT it was  $6.8 \pm 6.2$  ng/m<sup>2</sup>/d. The wet deposition flux of DDT was therefore higher than that of HCH; this trend differed from that observed in the dry deposition flux. Given that OCPs in the rainwater samples contained the dissolved phase as well as the particulate phase and the higher ratios of DDT/HCH in the wet deposition flux (>3) than that in the dry deposition flux (<0.3), the abundance of DDT in the dissolved phase in the

rainwater was likely greater than that of HCH. Thus, although DDT is less soluble in water than HCH is, the higher abundance of DDT in the dissolved phase could be due to significant sources of DDT in the surrounding environment, e.g., volatilization from seawater. The values of the wet deposition fluxes of DDT and HCH were comparable to those reported in the U.S. Mid-Atlantic region [Gioia *et al.*, 2005] and much lower than those observed at industrialized sites, such as Guangzhou, China [Huang *et al.*, 2010] and Bursa, Turkey [Cindoruk and Tasdemir, 2014]. This is because the wet deposition flux is usually influenced by the annual precipitation at the sampling sites and by the concentrations of both the particulate and gaseous phases in the atmosphere.

### 3.2. Air-Sea Gas Exchange

The  $\alpha$ -HCH was detected in all gaseous and dissolved samples, and  $\gamma$ -HCH; *p,p'*-DDE; *p,p'*-DDD; *o,p'*-DDT; and *p,p'*-DDT were detected in 77–98% of the samples. The  $\beta$ -HCH and  $\delta$ -HCH were barely detectable in the gaseous phase or in the dissolved phase, which was in agreement with previous studies [Ji *et al.*, 2015; Lin *et al.*, 2015]. The total gaseous concentrations of HCH ( $\alpha$ -HCH and  $\gamma$ -HCH) and DDT (*p,p'*-DDT; *o,p'*-DDT; *p,p'*-DDD; and *p,p'*-DDE) in the gaseous phase ranged from 5.0 to 230  $\text{pg}/\text{m}^3$  ( $30 \pm 29 \text{ pg}/\text{m}^3$ ). The annual mean HCH concentration was comparable to that of DDT ( $17 \pm 10 \text{ pg}/\text{m}^3$  compared to  $13 \pm 27 \text{ pg}/\text{m}^3$ ). HCH concentrations did not show any clear seasonal variation trend. The average HCH concentrations were  $22 \pm 7.0 \text{ pg}/\text{m}^3$  in autumn,  $20 \pm 12 \text{ pg}/\text{m}^3$  in winter,  $16 \pm 12 \text{ pg}/\text{m}^3$  in summer, and  $11 \pm 5 \text{ pg}/\text{m}^3$  in spring, respectively. The seasonal variation was particularly pronounced for DDT, with the highest concentrations in summer ( $40 \pm 28 \text{ pg}/\text{m}^3$ ) and lower concentrations of  $5 \pm 3 \text{ pg}/\text{m}^3$  in autumn,  $4 \pm 3 \text{ pg}/\text{m}^3$  in spring, and  $3 \pm 2 \text{ pg}/\text{m}^3$  in winter, respectively (Figure 2). These values indicate the possible short-term input of DDT in summer because the concentration levels in summer were 1 order of magnitude higher than those in the other three seasons [Hermanson *et al.*, 2007]. A similar seasonal variation in DDT concentrations was reported by Ji *et al.* [2015] in the same area; they also observed that concentrations in the gaseous phase were positively correlated with atmospheric temperature. Thus, such high concentrations of DDT in summer might be due to evaporation from the seawater column associated with high temperatures, suggesting that the air-sea air-sea gas exchange of DDT plays a significant role in the YRE, as discussed in more detail below.

These gaseous concentrations were similar to those observed by Ji *et al.* [2015] in the same area and in studies of adjacent regions of Singapore ( $7.2 \pm 4.2 \text{ pg}/\text{m}^3$  for DDT in 2006) [He *et al.*, 2009] and South Korea ( $3.5 \text{ pg}/\text{m}^3$  for DDT and  $22.3 \text{ pg}/\text{m}^3$  for HCH in 2008–2009) [Jin *et al.*, 2013]. The concentrations were also comparable to or slightly higher than those observed in background atmospheric concentrations above the open ocean in the North Pacific and the adjacent Arctic region in 2003 ( $6.49 \text{ pg}/\text{m}^3$  for DDT) [Ding *et al.*, 2009] and 2008 ( $3 \text{ pg}/\text{m}^3$  for  $\alpha$ -HCH and  $2.2 \text{ pg}/\text{m}^3$  for *p,p'*-DDT) [Jaward *et al.*, 2004] and the Southern Ocean and Antarctic Peninsula in 2008–2009 ( $1.5$ – $7.1 \text{ pg}/\text{m}^3$  for HCHs) [Galban-Malagon *et al.*, 2013].

The total dissolved-phase concentrations of DDT and HCH were 110–950  $\text{pg}/\text{L}$ , with an average of  $470 \pm 270 \text{ pg}/\text{L}$  ( $253 \pm 260 \text{ pg}/\text{L}$  for  $\gamma$ -HCH;  $100 \pm 130 \text{ pg}/\text{L}$  for *o,p'*-DDT;  $50 \pm 50 \text{ pg}/\text{L}$  for *p,p'*-DDD;  $27 \pm 28 \text{ pg}/\text{L}$  for *p,p'*-DDT;  $21 \pm 29 \text{ pg}/\text{L}$  for *p,p'*-DDE; and  $15 \pm 10 \text{ pg}/\text{L}$  for  $\alpha$ -HCH, respectively). The high abundances of  $\gamma$ -HCH and *o,p'*-DDT in this study might be derived from the historical use of lindane and dicofol in China [Gong *et al.*, 2007; Wei *et al.*, 2007]. Significant seasonal variations in dissolved  $\gamma$ -HCH showed higher concentrations in autumn, whereas higher concentrations of *o,p'*-DDT; *p,p'*-DDD; and *p,p'*-DDE were found in summer (Figure 3).

The air-sea gas exchange flux estimation in detail is presented in Text S2.4. We estimated the air-sea gas exchange fluxes of HCH and DDT (positive values indicate net volatilization from water into the atmosphere, and negative values indicate net deposition from the atmosphere). The ranges of the estimated fluxes were as follows: *o,p'*-DDT, 1.0–110  $\text{ng}/\text{m}^2/\text{d}$ ; *p,p'*-DDE,  $-23$ – $88 \text{ ng}/\text{m}^2/\text{d}$ ;  $\gamma$ -HCH,  $-11$ – $20 \text{ ng}/\text{m}^2/\text{d}$ ; *p,p'*-DDD,  $0$ – $19 \text{ ng}/\text{m}^2/\text{d}$ ; *p,p'*-DDT,  $-24$ – $12 \text{ ng}/\text{m}^2/\text{d}$ ; and  $\alpha$ -HCH,  $-13$ – $2.0 \text{ ng}/\text{m}^2/\text{d}$ , respectively. These values were similar to those reported for Izmir Bay, Turkey [Odabasi *et al.*, 2008], and the Great Lakes, USA [Khairy *et al.*, 2014]. The uncertainties in air-sea gas exchange flux estimation largely depend on modeled parameters, especially  $H'$  and  $K_{01}$  values. The  $H'$  values were picked from Cetin *et al.* [2006]. The air-sea gas exchange fluxes varied significantly with the temperature and salinity corrections, comparing with the ones with a constant  $H$  value (not temperature and salinity corrected). For instance, the air-sea gas exchange flux of *p,p'*-DDE in summer is about threefold higher after the temperature and salinity correction, suggesting a

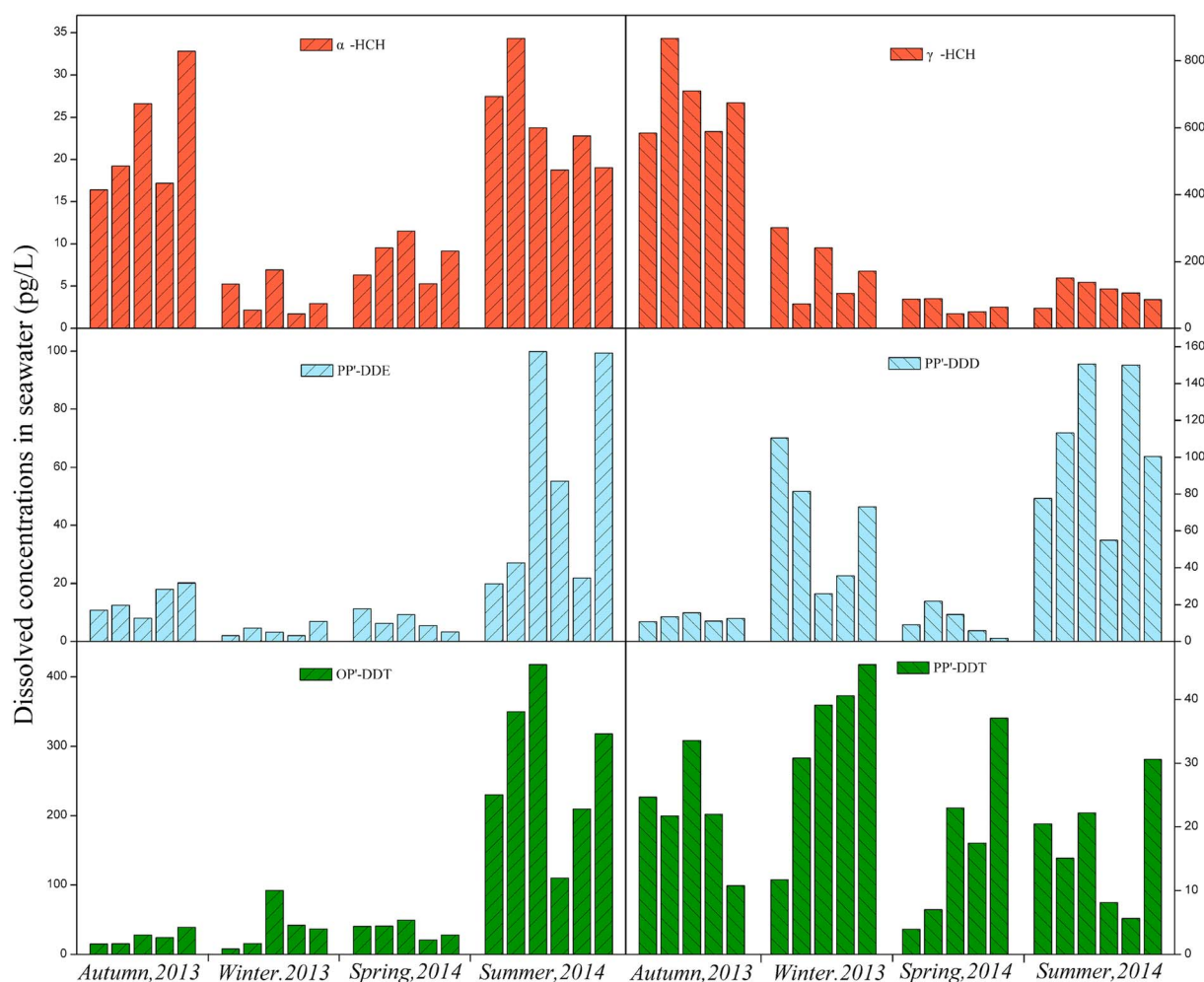
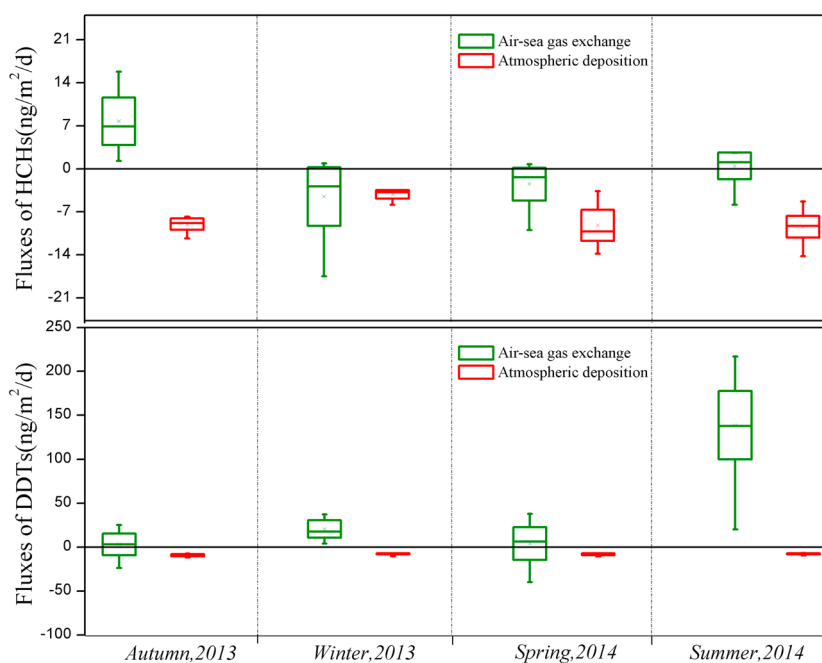


Figure 3. Surface seawater (dissolved phase) concentrations of HCH and DDT at HNI.

major uncertainty of air-sea gas exchange flux that arise from these corrections. According to the correction formula in Cetin et al. [2006], the uncertainties in the  $H'$  values for DDTs and HCHs were estimated from  $\pm 205\%$  (for p,p'-DDE) to  $10\%$  (for  $\alpha$ -HCH).  $K_{oi}$  results were largely influenced by the wind speed. Uncertainty of  $K_{oi}$  is estimated by using data on maximum and minimum wind speed during the sampling period in this work, which we assume to be  $\pm 120\%$ . The standard error for  $C_{g,a}$  and  $C_{d,w}$  is assumed to have relatively a small influence on the flux results ( $< 20\%$ ).

DDT air-sea fluxes exhibited a strong seasonal variation. The air-sea gas exchange flux was extremely high in summer ( $140 \text{ ng/m}^2/\text{d}$ ), whereas in winter, spring, and autumn, DDT fluxes ( $21 \text{ ng/m}^2/\text{d}$ ,  $9.0 \text{ ng/m}^2/\text{d}$ , and  $7.0 \text{ ng/m}^2/\text{d}$ , respectively) were relatively low compared with that in summer (Figure 4). There was significant net volatilization of DDT in summer. In the other three seasons, DDT concentrations almost reached equilibrium, taking into consideration on the results of the uncertainty evaluations. Surface seawater temperature possibly played an important role in determining the air-sea gas exchange of DDT. The diffusive fluxes of o,p'-DDT; p,p'-DDD; and p,p'-DDE showed significant positive correlations with surface seawater temperature ( $R^2 = 0.70$  and  $0.74$ ,  $p < 0.01$ ) (Figure 5). There was no dependence of p,p'-DDT gas exchange flux on surface seawater temperature. Present study found that there was a fresh input for p,p'-DDT in summer and autumn (more details in section 3.3). The fresh input of p,p'-DDT in the atmosphere led to a close fugacity state for p,p'-DDT in both dissolved phase and gaseous phase, which constrained the effect of the surface seawater temperature on the air-sea gas exchange of p,p'-DDT. The DDT volatilization fluxes are also a function of the dissolved-phase concentration in seawater. We observed correlations between the air-sea gas exchange

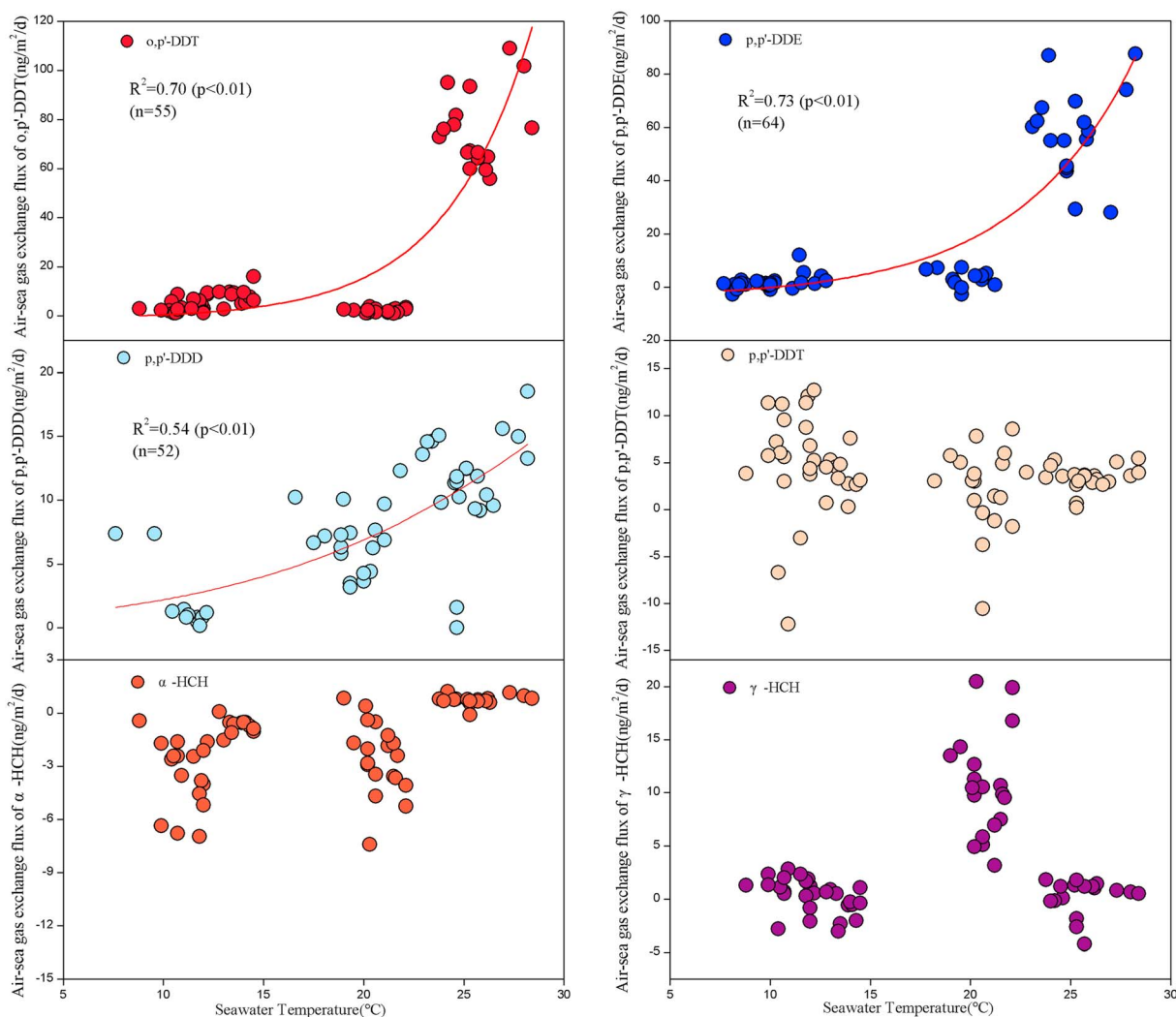


**Figure 4.** Seasonal variation of air-sea gas exchange fluxes and atmospheric deposition fluxes of HCH and DDT. The boxes indicate the STDEV of fluxes. The whiskers extend from the edge of the box to the minimum and maximum data values. The horizontal line and the cross indicate the median value and the mean value, respectively.

fluxes of DDT and the dissolved-phase concentrations ( $R^2 = 0.28\text{--}0.73$ ,  $p < 0.01$ ) (Figure 6). Good correlations were found for *p,p'*-DDE; *p,p'*-DDD; and *o,p'*-DDT ( $R^2 = 0.67$ ,  $0.69$ , and  $0.73$  respectively). Due to recent historical use of DDT, the concentrations of these compounds have remained at high levels in seawater. The tendency toward significant volatilization was the result of higher fugacity values in seawater. The dissolved-phase concentrations of *o,p'*-DDT and two DDT metabolites (*p,p'*-DDE and *p,p'*-DDD) in seawater were related to riverine input, suggesting that the input from the Yangtze River has a strong influence on the air-sea gas exchange fluxes of OCPs in summer [Hu *et al.*, 2011]. The Yangtze River discharges approximately 87% of its annual water and sediments in the flood season from June to October [Lin *et al.*, 2013]. The strong erosion process can transport the residual DDT from soils to the water column. The *p,p'*-DDE and *p,p'*-DDD, degeneration products of technical DDT, were abundant in soils and could be easily transported to the water column by erosion. This explains why the (*p,p'*-DDE + *p,p'*-DDD)/*p,p'*-DDT and *o,p'*-DDT/*p,p'*-DDT ratios in the dissolved phase in seawater were higher in summer (12 and 19, respectively) than in the other three seasons (1.4–3.0 and 1.4–4.0, respectively) (see Table 1). Since the sampling area was surrounded by seawater, the contaminated river was considered to carry large amounts of pollutants into the YRE. These contaminants have high values of water fugacity, which might lead to substantial net volatilization during the flood season. A similar tendency was found in a previous study of Qiantang River, another major river in the YRE area, and the largest river in Zhejiang Province [Zhou *et al.*, 2006].

Compared to DDT, the air-sea gas exchange fluxes of HCH were relatively low, and there was no clear seasonal variation. HCH evaporated from seawater to the atmosphere in autumn ( $8\text{ ng/m}^2/\text{d}$ ) and moved in the opposite direction in winter ( $-5\text{ ng/m}^2/\text{d}$ ), while it almost achieved equilibrium at the air-water interface in spring and summer (Figure 4; the seasonal variation in the air-sea gas exchange fluxes of HCH and DDT is presented in detail in Figure S2). A good correlation was observed for  $\gamma$ -HCH between the air-sea gas exchange flux and the dissolved phase concentration ( $R^2 = 0.57$ ,  $p < 0.01$ ) (Figure 5). In autumn,  $\gamma$ -HCH dominated the evaporated HCH due to its approximately threefold higher dissolved-phase concentrations than in the other three seasons, which led to more volatilization of  $\gamma$ -HCH. High dissolved-phase concentration of  $\gamma$ -HCH in seawater was derived from the recent historical use of lindane (consisting of  $>95\%$   $\gamma$ -HCH) and transported by river runoff, suggesting that the riverine runoff was responsible for the air-sea gas exchange flux of  $\gamma$ -HCH. However, there was no correlation between surface seawater temperature and





**Figure 5.** Correlation between the air-sea gas exchange fluxes and dissolved phase concentrations of HCH and DDT in surface seawater during sampling period at HNI.

fluxes of  $\gamma$ -HCH (Figure 6). More volatilization of  $\gamma$ -HCH in autumn showed that the surface seawater temperature had a smaller influence on air-sea gas exchange flux of  $\gamma$ -HCH compared with the dissolved-phase concentration.  $\gamma$ -HCH has a lower  $H$  value compared with  $\alpha$ -HCH and DDTs, making it hard to evaporate from seawater even with high temperature. The air-sea gas exchange fluxes of  $\alpha$ -HCH showed poor correlations with the dissolved-phase concentrations in seawater as well as surface seawater temperature. Due to the long history of prohibition of technical HCH, the amount of  $\alpha$ -HCH remaining in the aqueous environment was low, and concentration levels remained stable during the four seasons, with concentrations of  $\alpha$ -HCH close to the background level, leading to no dependence of air-sea gas exchange flux on both surface seawater temperature and dissolved phase concentrations. However,  $\alpha$ -HCH showed a slight deposition trend in winter, possibly due to the higher concentrations of  $\alpha$ -HCH in the gaseous phase. The values of the  $\alpha$ -HCH/ $\gamma$ -HCH ratio in the gaseous phase in air were higher in winter (5.8) than those in the other three seasons (0.27–1.3) (Table 1). Technical HCH has been prohibited in China for about 30 years, and there has been no new technical HCH source. Therefore, the high  $\alpha$ -HCH/ $\gamma$ -HCH ratio ( $>3$ ) in winter can be explained by continental outflow rather than fresh input of technical HCH. A backward trajectory (Figure S3) showed that the East Asian monsoon brings air masses from the continent to the sampling area in autumn and winter after long-range transport. The  $\gamma$ -HCH can undergo phototransformation to  $\alpha$ -HCH during long-range transport [Cai *et al.*, 2012]. The  $\gamma$ -HCH has also a lower Henry's law constant than that of  $\alpha$ -HCH, indicating that  $\gamma$ -HCH has a shorter lifetime in the atmosphere and is more susceptible to

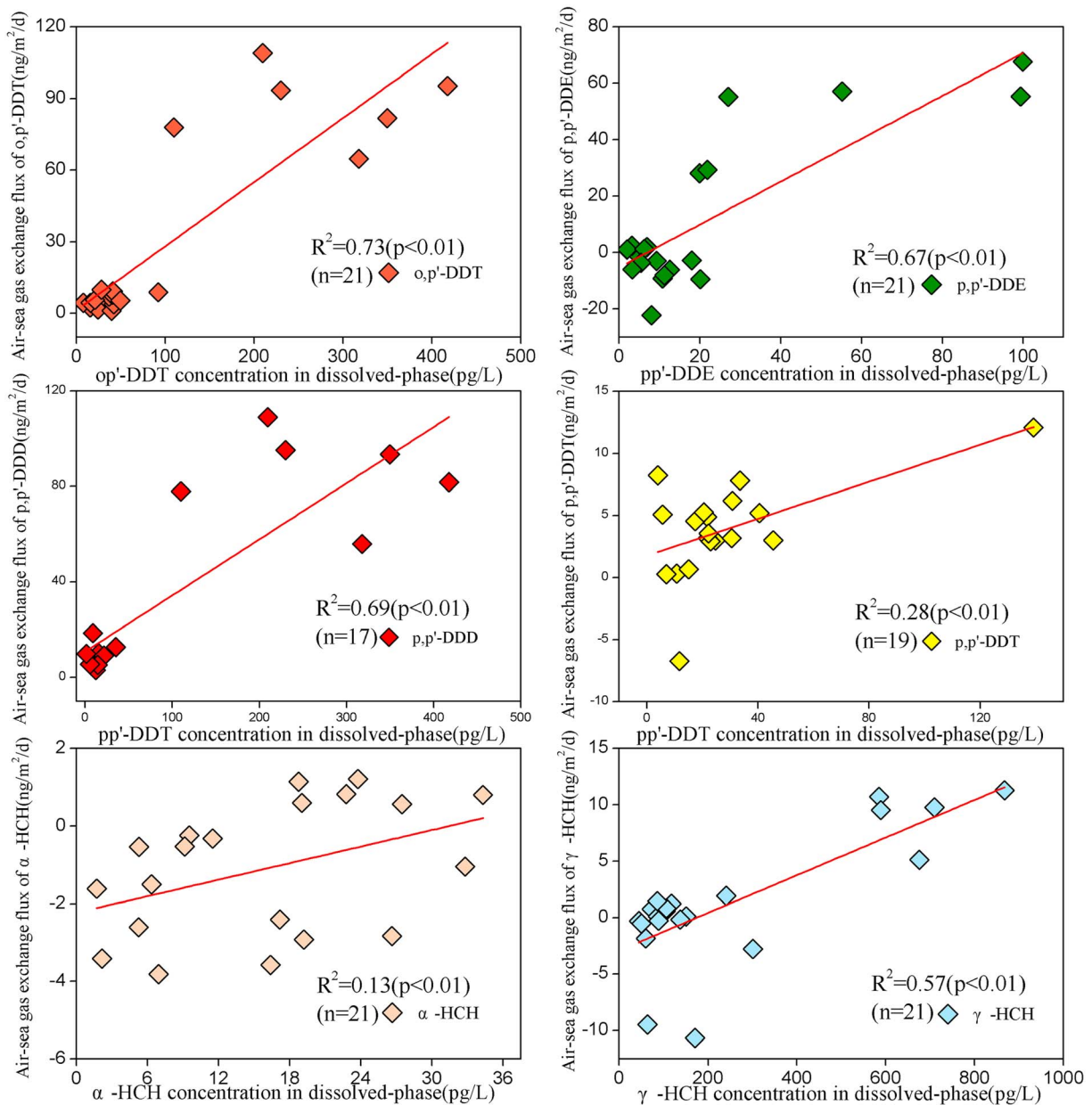


Figure 6. Correlation between air-sea exchange fluxes of HCH and DDT and the surface seawater temperature during sampling period at HNI.

Table 1. Ratios of  $\alpha$ -HCH/ $\gamma$ -HCH; (DDE + DDD)/p,p'-DDT; and o,p'-DDT/p,p'-DDT in Air (Gaseous and Particulate Phases) and Seawater (Dissolved Phase) During Sampling Period at HNI

	Ratio of $\alpha$ -HCH/ $\gamma$ -HCH			Ratio of (DDE + DDD)/p,p'-DDT			Ratio of o,p'-DDT/p,p'-DDT		
	Air		Seawater	Air		Seawater	Air		Seawater
	Particulate Phase	Gaseous Phase	Dissolved Phase	Particulate Phase	Gaseous Phase	Dissolved Phase	Particulate Phase	Gaseous Phase	Dissolved Phase
Spring	0.54 ± 0.32	0.36 ± 0.16	0.14 ± 0.07	0.45 ± 0.29	4.82 ± 4.55	2.19 ± 2.22	0.63 ± 0.85	3.35 ± 4.73	4.04 ± 4.01
Summer	0.33 ± 0.33	0.27 ± 0.17	0.24 ± 0.11	1.49 ± 1.90	0.68 ± 0.58	12.61 ± 2.1	0.61 ± 0.76	0.42 ± 0.41	19.0 ± 10.4
Autumn	1.45 ± 1.18	1.33 ± 0.84	0.03 ± 0.01	0.28 ± 0.19	1.10 ± 0.97	1.42 ± 3.87	0.13 ± 0.10	0.19 ± 0.23	1.39 ± 1.28
Winter	1.27 ± 1.20	5.76 ± 4.64	0.02 ± 0.01	7.07 ± 8.47	2.08 ± 2.96	3.02 ± 5.00	2.43 ± 2.22	1.39 ± 2.09	2.66 ± 4.25

removal through direct partitioning into or through washout by precipitation during long-range transport [Oehme, 1991; Ding *et al.*, 2009]. This increased the  $\alpha$ -HCH concentration and  $\alpha$ -HCH/ $\gamma$ -HCH ratio in winter in the sampling area; thus,  $\alpha$ -HCH dominated the depositional HCH in winter.

### 3.3. Implications for the Fresh Input of p,p'-DDT

The YRE is adjacent to Jiangsu and Zhejiang Provinces, where technical DDT was used in significant quantities from the 1950s to 1980s, and is still permitted in small quantities. The air-sea gas exchange fluxes showed that the residual DDT entered the YRE via surface runoff, increasing the dissolved-phase concentrations of DDT in seawater (Figure 3), which sustained significant net volatilization during the flood season. However, close correlations between the air-sea gas exchange fluxes and the dissolved-phase concentrations or seawater temperature values were found for p,p'-DDE; p,p'-DDD; and o,p'-DDT but not in p,p'-DDT ( $R^2 = 0.28$ ). In addition, the net volatilization fluxes of p,p'-DDE; p,p'-DDD; and o,p'-DDT were all higher than that of p,p'-DDT in summer. Under the scenario of no other input sources of DDT, the (p,p'-DDE + p,p'-DDD)/p,p'-DDT and o,p'-DDT/p,p'-DDT ratios should be higher in the atmosphere than in seawater. However, they were significantly lower in the gaseous phase (0.68 and 0.42, respectively) than in the dissolved phase in seawater (12 and 19, respectively) in summer (Table 1). Most importantly, the (p,p'-DDE + p,p'-DDD)/p,p'-DDT and o,p'-DDT/p,p'-DDT ratios in the atmosphere were significantly lower in summer and autumn compared to those in spring and winter. Values of the (p,p'-DDE + p,p'-DDD)/p,p'-DDT ratio  $> 2$  in spring and winter (4.8 and 2.1, respectively) suggested a long residence time of DDT in the environment, whereas the lower values in summer and autumn (0.68 and 1.1, respectively) suggested a new input of p,p'-DDT (Table 1) [Hitch and Day, 1992; Li *et al.*, 2006]. These results indicated a possible new source of p,p'-DDT input in the surrounding atmospheric environment, especially in summer and autumn, which was consistent with the seasonal variation in higher particulate p,p'-DDT in summer and autumn (Figure 2). The Chinese government enforces a strict "no fishing policy" during summer, when all fishing activities are banned, and fishing boats are harbored at port, where many of them undergo maintenance, including repainting with antifouling paints. These paints contain small amounts of technical DDT to prevent biofouling [Lin *et al.*, 2009]. Thus, the stripping and repainting of antifouling paints during frequent boat maintenance activities might provide a new source of p,p'-DDT.

### 3.4. Implications for a Source or Sink at the Air-Water Interface

Combining the results of gas exchange and dry and wet deposition across the air-water interface, we can assess whether seawater in the YRE is a source or sink for contaminants during the sampling period [Mandalakis *et al.*, 2005]. The dry and wet deposition fluxes are combined as the total atmospheric deposition flux in Figure 4 for comparison with the air-sea gas exchange flux. For HCH, the annual mean fluxes of air-sea gas exchange and dry and wet deposition were  $-2$ ,  $-6$ , and  $-2$  ng/m<sup>2</sup>/d, respectively (deposition from the atmosphere to seawater is indicated by negative values). HCHs are less hydrophobic (i.e.,  $\log(K_{ow}) \leq 5$ ) and hence tend not to associate with particulate matter in the seawater column to a great extent (i.e., are predominantly in the dissolved phase). The air-sea gas exchange fluxes of HCH were relatively low, and the gas exchange flux and dry and wet deposition at air-water interface were similar during the study period. Based on the relatively low concentrations of  $\alpha$ -HCH and  $\gamma$ -HCH observed in the atmosphere and seawater column, the HCH concentrations in this study represented the background levels in the surrounding environment. In summer, the increase in river runoff transported more HCHs to the region, which can change the direction of the air-sea gas exchange of HCH (e.g.,  $\gamma$ -HCH) shortly. Long-range transport brought a moderate amount of particulate HCHs to the YRE and deposited it into the seawater, mainly because of significant HCH metabolism ( $\beta$ -HCH) in particles. Overall, the transport and fate of HCH during the sampling period showed almost no significant influences from the river input and atmospheric transport.

For DDT, the annual mean fluxes of air-sea gas exchange and dry and wet deposition were 42,  $-1$ , and  $-7$  ng/m<sup>2</sup>/d, respectively. Air-sea gas exchange was the dominant process for DDT in the study area. The DDT gas exchange flux was almost fivefold higher than that of atmospheric deposition at air-water interface. The volatilization of DDT occurred mostly in summer, while the gas exchange at the air-water interface in the other three seasons essentially reached equilibrium. The net flux of DDT was 34 ng/m<sup>2</sup>/d, and the seawater column remained a source of DDT for the atmospheric environment. DDT residues in agricultural soil were transported by enhanced riverine runoff to sustain net volatilization in summer. Lin *et al.* [2015] concluded that the river plume including the Yangtze and Qiantang Rivers was unable to sustain the volatilization flux of DDT over a full year based on samples that had been collected only in summer. They assumed that DDT

can show a deposition trend at other times to maintain the annual balance between riverine input and volatilization. However, in the present study, DDT demonstrated net volatilization during all four seasons, and the expected shift between volatilization and deposition was not observed. This indicated that there is existence of fresh sources of DDT in coastal areas to maintain the balance between volatilization and deposition. As discussed above, we identified the track of fresh p,p'-DDT sources, especially in summer and autumn. Thus, the use of technical DDT in coastal provinces in the study area might help to sustain the volatilization trend, in addition to the annual input from the Yangtze River.

The YRE has a surface area of approximately 20,000 km<sup>2</sup>. Based on the values of the dry and wet deposition fluxes in this study, the atmospheric deposition fluxes of HCH and DDT were about 0.05 and 0.06 t/yr, respectively. The atmospheric deposition fluxes of HCH and DDT were slightly higher than the results of Lin *et al.* [2015] in the coastal ECS, who estimated atmospheric deposition fluxes of 0.03 t/yr for HCH and 0.15 t/yr for DDT using a surface area of 100,000 km<sup>2</sup>. This suggests that atmospheric deposition acted as a relatively effective removal mechanism and deposition fluxes decreased with continental outflow. Based on the air-sea gas exchange fluxes of HCH and DDT during the sampling period, the net deposition of HCH into the study area was estimated to be 0.02 t/yr, and the net volatilization of DDT from the study area was estimated to be 0.31 t/yr (with an area of 20,000 km<sup>2</sup>). The air-sea gas exchange fluxes of HCH and DDT in this study were significantly lower than those of Lin *et al.* [2015] in the coastal ECS. In the latter study, the air-sea gas exchange fluxes of HCH and DDT from the seawater to the atmosphere were approximately 3.5 and 11 t/yr (with an area of 100,000 km<sup>2</sup>), respectively. Higher volatilization from water was observed in the open sea due to higher wind speeds, low gaseous concentrations, and the higher Henry's law constants in saline water. In addition, release from sediment during resuspension was an important contributor to dissolved OCPs in the water column. This indicated that the reemission of OCPs transported by the Yangtze River runoff occurred mainly in the coastal ECS rather than in the YRE. Thus, lateral remobilization from contaminated soils through large volumes of river runoff toward remote marine environments can play an important role in the global transport and recycling of OCPs [Stemmler and Lammel, 2009], under a regime where primary emissions are exhausted and secondary sources dominate.

#### 4. Conclusions

This study presented the estimated air-sea gas exchange and dry and wet deposition fluxes of HCH and DDT in the YRE under the scenario of decreasing primary sources. The air-sea gas exchange flux of DDT was markedly higher in summer than in the other three seasons, whereas the air-sea gas exchange flux of HCH showed no significantly seasonal variation during the study period. The air-sea gas exchange flux of DDT in summer was correlated with the increase in surface seawater temperatures and higher concentrations in the dissolved phase, possibly triggered by the flood season of the Yangtze River. For HCH, the concentration levels observed in this study represented the background levels in the YRE, considering that these substances have now been prohibited for more than 30 years. The influences of riverine input and continental outflow on the fate of HCH were limited.

The air-sea gas exchange flux of DDT was about fivefold higher than the deposition fluxes, while the gas exchange flux of HCH was comparable in magnitude to the combined dry and wet deposition fluxes. In terms of the net flux, the seawater column in the YRE was a source of DDT to the atmosphere due to significant net volatilization in summer. Although Yangtze River runoff was an important source of OCPs to the upper atmosphere in the YRE, most OCPs transported by the Yangtze River runoff are volatilized into air in the coastal ECS rather than in the YRE. It was different that atmospheric particle deposition fluxes of OCPs loaded by continental outflow are high at the coastal sampling sites but decreased sharply as distance to the coast increases. Thus, lateral remobilization from contaminated soils via large volumes of river runoff toward remote marine environments can play an important role as a secondary source in the large-scale transport and recycling of OCPs.

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