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Organochlorine pesticides in seawater and the surrounding atmosphere of the marginal seas of China: Spatial distribution, sources and air–water exchange

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HIGHLIGHTS

- ► OCPs were analyzed in air and water samples collected over marginal seas of China.
- ► α-HCH concentrations in the atmosphere were quite uniform.
- ► Atmospheric γ-HCH, TC, CC and DDT concentrations were highest in South China Sea.
- ► Dissolved OCP concentrations in water varied over a narrow range.
- ► Oceans exhibit net volatilization of some OCPs after a long period of prohibition.

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ABSTRACT

Shipboard air and surface seawater samples collected over the Yellow Sea, East China Sea and South China Sea were analyzed for organochlorine pesticides (OCPs). In air, γ-hexachlorocyclohexane (HCH), trans-chlordane (TC) and cis-chlordane (CC) had significantly ($p<0.001$) higher concentrations than α-HCH, *o,p*′-Dichlorodiphenyltrichloroethane (DDT), *p,p*′-DDE, *p,p*′-DDT and α-endosulfan. Generally, α-HCH concentrations in the atmosphere were quite uniform over the Chinese marginal seas. However, the highest concentrations of γ-HCH, TC, CC and DDT compounds were found in the southern parts of the marginal seas, and higher concentrations of α-endosulfan were observed in the northern part of the marginal seas. In water, the OCP concentrations varied over a narrow range, with hundreds picogram per liter levels. Air–water exchange gradients suggested net deposition or equilibrium for γ-HCH and *o,p*′-DDT and net volatilization for α-HCH, CC, TC, *p,p*′-DDE and *p,p*′-DDT. Due to the potential source of those compounds from coastal water runoff, the ocean water played an important role of OCP sources for the atmosphere after a long period of OCP prohibition.

1. Introduction

Organochlorine pesticides (OCPs) are a group of semi-volatile persistent organic pollutants (POPs), which are of worldwide concern because of their persistence, bioaccumulation, and negative effects on human, animal and plant life (Aigner et al., 1998; Jones and de Voogt, 1999). Due to their volatility and persistence, OCPs are subject to global distribution throughout the environment (Wania and Mackay, 1996).

The monitoring of marine POPs is of great importance. Oceans are believed to be the largest sink of POPs (Dachs et al., 2002; Iwata et al., 1993), which may be converted into a secondary source of particular POPs, such as dichlorodiphenyltrichloroethane (DDT) (Stemmler and Lammel, 2009) and alpha-Hexachlorocyclohexane (HCH) (Li and Bidleman, 2003), long after these compounds were banned. In addition, oceans act as remote monitoring sites of regional/global distribution and temporal trend of POPs, as the outflow of these pollutants from adjacent land sources, carried by monsoon/air masses, can travel long distances. This phenomenon has been confirmed by the observation of some oceanic regions (Ding et al., 2009; Lohmann et al., 2009; Wurl et al., 2006; Zhang et al., 2007).

The Yellow Sea, East China Sea and South China Sea are the important marginal seas in Southeast Asia that are surrounded by developing countries, which were considered as potential important sources of OCPs (Iwata et al., 1994; Loganathan and Kannan, 1994; Tanabe, 1991). Due to their efficiency, OCPs were widely used in the Asian countries before the 1980s. In recent years, the production of OCPs was either eliminated or their release into the environment reduced under the Stockholm Convention on OCPs, which was adopted by many countries. However, in Southeast Asian countries, the late production ban as well as the current legal and illegal application for agricultural practices and for the control

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of certain diseases, such as malaria, typhus and cholera, have contributed to higher concentrations of OCPs in the environment (i.e., the atmosphere, water and sediment) (Hung and Thiemann, 2002; Iwata et al., 1994; Zhang et al., 2002), aquatic wildlife (e.g., mussels)(Ueno et al., 2003) and the human population (e.g., human breast milk) (UNEP, 2002; Wong et al., 2002). Oceanic waters are a receptor of land based pollutant sources, and coastal waters are particularly affected by inputs of OCPs via discharges of sewage, industrial effluents and significant rivers that drain into the marginal seas of China. Significant rivers include the Yangtze River, Qiantang River, Ou River and Min River in East China, the Pearl River in South China, the Red in North Vietnam and the Mekong in South Vietnam, which are associated with the significant cities of Shanghai, Guangzhou, Hong Kong, Hanoi and Ho Chi Min (Saigon), respectively. The coastal current (such as the Yellow Sea Coastal Current, the Zhejiang–Fujian Coastal Current and the South China Coastal Current) has a great deal impact on the transport of and discharge from the rivers. Many smaller rivers pass through East Malaysia and the Philippines, despite the presence of large population centers, e.g., Manila (greater than 10 million people). Located in the Asian monsoon controlled areas, the marginal seas experience a monsoonal climate created by the influences of the southwest monsoon in summer and the northeast monsoon in winter. The strong monsoon pushes surface water to flow in a circulative pattern. Anthropogenic pollutants in the marginal seas, inputted from atmospheric deposition and fluviatile transport, could be quickly dissipated by the surface current. Available data for OCP concentrations in the atmosphere and surface seawater over the marginal seas of China are sparse (Ding et al., 2007, 2009; Iwata et al., 1993; Wu et al., 2010; Zhang et al., 2007).

The aims of this study were to determine the concentration levels of OCPs in the air and in the surface seawater collected from the marginal seas of China and to identify potential sources of these contaminants in the air and water. Based on the dataset, the air–water exchange of selected OCPs was also evaluated to determine if atmospheric (gas) deposition of these chemicals was still occurring or if the marginal sea waters were currently a source of selected OCPs to the atmosphere.

2. Material and methods

2.1. Sample collection

A total of 37 day and night air samples (8:00–18:00 for daytime and 20:00–6:00 the following day for nighttime) were taken from September to October, 2006 during a SCIENCE III cruise, which circumnavigated the Yellow Sea, East China Sea and South China Sea from Qingdao to Sanya, Hainan island, and back to Qingdao, which is a distance of approximately 9000 km. The sampling route is showed in Fig. 1. A high volume air sampler was placed windward on the upper-most deck of the ship, approximately 20 m above sea level. Air volumes of approximately 140 m^3 were drawn through a Glass fiber filter (GFF) (Grade GF/A, 20.3 × 25.4 cm, Whatman, UK) and subsequently through two polyurethane foam (PUF) plugs (6.5 cm in diameter, 7.5 cm in thickness, a density of 0.030 g/cm^3). Prior to sampling, the GFFs were baked at 450 °C for 12 h to remove any organic contaminant, and the PUF plugs were Soxhlet-extracted for 48 h with methanol (MeOH) and then acetone for 24 h, followed by two overnight extractions using dichloromethane (DCM). The PUF plugs were dried overnight in a vacuum desiccator and stored in solvent-rinsed glass jars with Teflon-lined lids before use. During sample collection, gloves were worn, and the GFFs and PUF plugs were handled using acetone-rinsed stainless steel tongs. After sampling, loaded GFFs were wrapped with pre-baked aluminum foil and sealed with 2 layers of polyethylene bags, the PUF plugs were placed in solvent rinsed glass jars with Teflon-lined lids and then transported to the laboratory and stored at −20 °C until extraction. Meteorological data, such as temperature, relative humidity, wind speed/direction, and precipitation were recorded at each sampling station.

A total of 12 surface seawater samples, each approximately 50 L, were collected using a metal bucket at 12 sites when the ship was stop for field work (Fig. 1). The collected water was immediately filtered through pre-combusted (4 h at 450 °C), 150 mm diameter GFFs (Gelman Type A/E, nominal pore size 1 μm, Pall Gelman, USA). Dissolved phase pesticides were then collected by passing the filtrate over a mixture resin (Amberlite XAD-2 and XAD-4 1:1 mixtures, Sigma-Aldrich, USA) glass column (25 mm in diameter; 400 mm in length).

2.2. Sample treatment, analytical procedure and quality control

The PUF plugs were spiked with 20 ng of 2,4,5,6-tetrachloro-m-xylene (TCmX) and decachlorobiphenyl (PCB209) as surrogates, and Soxhlet-extracted with DCM (both DCM and hexane obtained from Merck & Co., Inc.) for 48 h. Activated copper granules were added to the collection flask to remove elemental sulfur. The extract was concentrated and solvent-exchanged to n-hexane and purified on an 8 mm diameter alumina/silica column, packed, from the bottom to top, with neutral alumina (6 cm, 3% deactivated), neutral silica gel (10 cm, 3% deactivated), 50% (by mass) sulfuric acid silica (10 cm), and anhydrous sodium sulfate (1 cm). Before use, the neutral alumina, neutral silica gel, and anhydrous sodium sulfate were each Soxhlet-extracted for 48 h with DCM, and then baked for 12 h in 250, 180, and 450 °C, respectively. The column was eluted with 50 mL of DCM/hexane (1:1) to yield the OCPs fraction. The fraction was reduced to a final volume of 25 μL under a gentle stream of nitrogen and solvent exchanged to 25 μL of dodecane containing a known quantity of pentachloronitrobenzene and PCB 54 as internal standards.

The procedures for eluting dissolved organics from XAD resins have been described extensively by Zeng et al. (1999); thus, only a brief description is given here. Each XAD resin column was spiked with surrogate standards, and eluted with 50 mL of methanol, followed by 50 mL of DCM at a flow rate of 5 mL/min. The XAD resin was transferred into a flask and extracted with (2:1) DCM:MeOH in an ultrasonic bath (3 × 100 mL). The combined extracts were back-extracted for three times using an equivalent amount (by volume of MeOH) of saturated NaCl solution and 50 mL of DCM. Then, the DCM fraction was extracted with clean water, to remove the residual MeOH, and drained through a glass column containing 15 g of pre-combusted anhydrous Na_2SO_4 to remove any residual water. The extract for each sample was concentrated and solvent-exchanged to hexane, and further reduced to approximately 1 mL under a gentle nitrogen flow. Concentrated extracts were fractionated with an alumina/silica gel glass column, as was the procedure for the air samples.

GC–MS analysis was carried out on an Agilent-5975 GC–MSD system with a CP-Sil 8 CB capillary column (50 m length × 0.25 mm diameter., 0.25 μm film thickness), operating under the selected ion monitoring (SIM) mode. The oven temperature began at 60 °C for 1 min and increased to 290 °C, with a 10 min hold time, at a rate of 4 °C/min. Split/splitless injection of a 1 μL sample was performed with a 12 min solvent delay time. Injector temperature was at 250 °C. The inlet degradation of DDT was checked daily and controlled within 15%.

Recovery standards were added to the samples, laboratory blanks and field blanks prior to extraction and to monitor the extraction and cleanup procedures. The average recoveries of TCmX and PCB209 were 79.4 ± 8.6% and 89.2 ± 11.7%, respectively, in air samples and were 61.9 ± 11.0% and 78.6 ± 9.6%, respectively, in water samples. The instrumental detection limits (IDLs) values were calculated from the lowest standards, extrapolating to the corresponding amount of analyte that would generate a signal-to-noise ratio of 3:1. The compounds under IDLs were considered as not detected (ND). The method detection limits (MDLs) were assigned as average values of blanks, with 3 standard deviations of blank values. When the compounds were not detected in the blanks, a standard of 3 times the IDLs was used for calculating the MDLs. The target compounds were under the IDLs in the field and lab blanks.

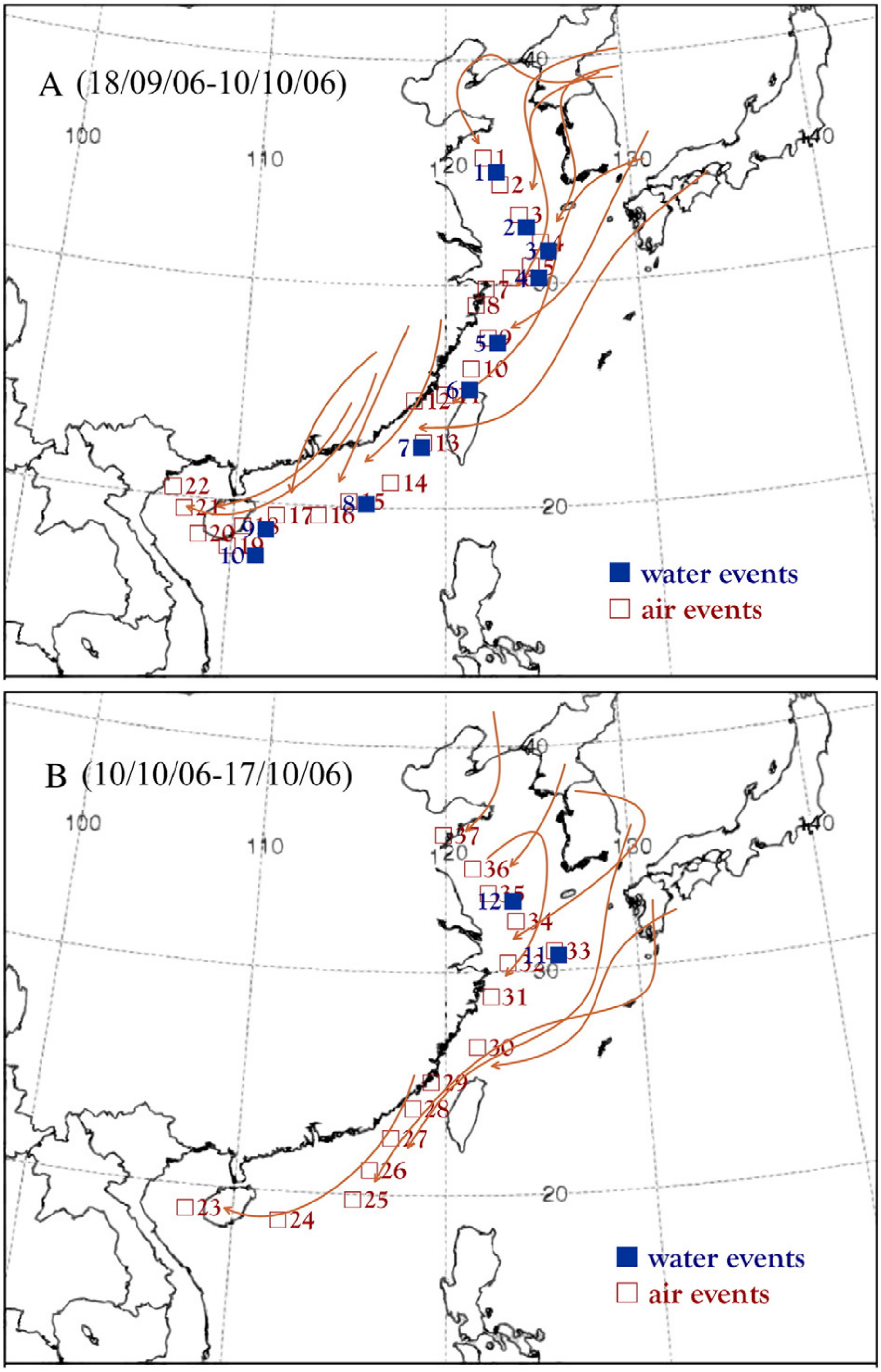

Fig. 1. Sampling locations and origins of the air masses backward trajectories.

Instrumental performance was checked by quality control standards every eight samples. The reported data on OCPs in this study were corrected for the surrogate recoveries.

The breakthrough of PUF samples was tested by two consecutive PUF plugs. The results indicated that the target compounds were under the method detection limit from the subjacent PUF plug.

2.3. Back trajectories

In order to assess the possible sources of OCPs in the active air samples, the HYSPLIT model (HYbrid Single-Particle Lagrangian Integrated Trajectory, Version 4.7), a comprehensive modeling system developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory was used. 5-day back trajectories on the times at the beginning and end for each sampling episode were calculated for each of the sampling sites arriving at 10 m above sea level.

3. Results and discussion

3.1. Concentrations and spatial distribution in air

The OCPs that occurred most frequently in the air samples were HCHs, DDTs, chlordane and endosulfan. Table 1 presents a summary of the data of selected gaseous OCPs. 7 compounds were detected at all sites, that is, α-HCH, γ-HCH, trans-chlordane (TC), cis-chlordane (CC), *p*,*p*′-DDE, *o*,*p*′-DDT, and *p*,*p*′-DDT. Generally, the concentrations of the individual compounds were slightly lower than that monitored in the northern part of the South China Sea in September, 2005 (Zhang et al., 2007).

The atmospheric concentrations of α-HCH and γ-HCH ranged from 4.1 to 39 (13 ± 8.1) pg/m^3 and from 12 to 440 (110 ± 76) pg/m^3, respectively. Compared with that monitored over the open seas recently, α-HCH levels were comparable to that in the North Pacific Ocean and the adjacent Arctic region in 2003 (9.9 ± 8.3 pg/m^3) and in 2008 (33 ± 16 pg/m^3), and higher than that in the Atlantic Ocean in 2001 (<0.1–11 pg/m^3), the Indian Ocean in 2004–2005 (<0.2–19.2 pg/m^3 for α-HCH) and the North Atlantic and Arctic Ocean in 2004 (<1–7 pg/m^3 for α-HCH). However, γ-HCH concentrations were higher than that in the North Pacific Ocean and the adjacent Arctic region in 2003 (0.2–49.4 pg/m^3) and in 2008 (13 ± 7.5 pg/m^3), the Atlantic Ocean in 2001 (<3.6–100 pg/m^3), the Indian Ocean in 2004–2005 (2.3–80.0 pg/m^3) and North Atlantic and Arctic Ocean in 2004 (<1–10 pg/m^3) (Ding et al., 2009; Jaward et al., 2004; Lohmann et al., 2009; Wu et al., 2010; Wurl et al., 2006). Compared with previously reported data from a study conducted in 1989 (Iwata et al., 1993), the α-HCH concentrations in 2006 declined approximately 50 times during about two decades. This downward trend should be greater if taken into account that the sampling sites were far from continent and dominated by ocean-derived air mass in 1989. The decrease of atmospheric α-HCH was likely to be related to the restricted usage of technical HCH in this area and its relative quick degradation processes in the environment. Unlike α-HCH, the high γ-HCH concentrations did not show any significant decline compared to values from 1989 (Iwata et al., 1993). The use of lindane as an insecticide in most Southeast Asian countries may be responsible for the high γ-HCH concentrations.

DDT and its metabolites were detected in all air samples with the exception of *p*,*p*′-DDD, which was consistently lower the limits of detection. The concentrations of *p*,*p*′-DDE and *p*,*p*′-DDT were 1.4–17 pg/m^3 and 1.0–17 pg/m^3, respectively. These values were slightly lower that observed in the North Pacific Ocean and the adjacent Arctic region in 2003 (0.18–42.8 pg/m^3 for *p*,*p*′-DDE and 0.20–112 pg/m^3 for *p*,*p*′-DDT) and in 2008 (ND-16 pg/m^3 for *p*,*p*′-DDE and ND-54 pg/m^3 for *p*,*p*′-DDT) and were comparable to the open Indian Ocean (<0.2–6.3 pg/m^3 for *p*,*p*′-DDE and <0.2–26.7 pg/m^3 for *p*,*p*′-DDT) (Wurl et al., 2006), the open Atlantic Ocean (<1.5–47 pg/m^3 for *p*,*p*′-DDE and <2.2–5.4 pg/m^3 *p*,*p*′-DDT) (Jaward et al., 2004) and the North Atlantic and Arctic Ocean in 2004 (0.1–16 pg/m^3 for *p*,*p*′-DDE) (Lohmann et al., 2009). The concentration of *o*,*p*′-DDT was 4–67 pg/m^3 in this study, which was comparable to that observed in the North Pacific Ocean and the adjacent Arctic region in 2003 (0.19–73.2 pg/m^3) and in 2008 (ND-30 pg/m^3) but was significantly higher than the concentration of *o*,*p*′-DDT found in open seas around the world, where *o*,*p*′-DDT was under the detectable limit in most cases (Jaward et al., 2004; Lohmann et al., 2009; Wurl et al., 2006). The DDT concentrations did not show any significant decline compared to values from 1989 in the marginal seas of China (Iwata et al., 1993), especially for *o*,*p*′-DDT. The high concentration levels of DDTs may be due to the dicofol and DDT-containing antifouling paints that are still widely used in several countries of Southeast Asia and China (Jaward et al., 2005; Lin et al., 2009; Qiu et al., 2004; Taylor et al., 2003).

Table 1
Summary of gaseous OCP concentrations (pg/m^3) in air and dissolved OCP concentrations (pg/L) in water over the marginal seas of China.

	Air (n = 37)			Water (n = 11)		
	Mean	Range	H/L	Mean	Range	H/L
α-HCH	13 ± 8.1	4.1–39	9.6	500 ± 97	330–640	1.9
γ-HCH	110 ± 76	12–440	37.5	790 ± 295	350–1400	4.1
TC	180 ± 150	16–790	4.6	200 ± 77	140–380	2.7
CC	220 ± 170	25–860	35.1	170 ± 36	110–240	2.2
p,*p*′-DDE	5.6 ± 3.5	1.4–17	12	470 ± 210	200–920	4.6
o,*p*′-DDT	19 ± 15	3.7–67	18.2	410 ± 260	120–850	7.1
p,*p*′-DDT	5.1 ± 5.1	1.0–17	17.4	390 ± 160	200–800	4
α-Endosulfan	3.9 ± 3.7	1.0–16	15.9			

H/L: highest concentration/lowest concentration.

High concentrations of TC and CC were observed over the marginal seas with concentrations ranges from 16 to 790 pg/m^3 and from 25 to 860 pg/m^3, respectively. Chlordane used as a termiticide for wooded regions in many parts of the world, was detected in high levels where the technical chlordane was sprayed. As a region with severe termite problems, chlordane has been widely used in Southeast Asia (Iwata et al., 1994), so it is reasonable for the highest levels of chlordane to be observed in close proximity of the coastline. Those high levels of chlordane were significantly higher than the previous in situ study (Iwata et al., 1993) and the other studies, such as in the open Indian Ocean in 2004–2005 (0.3 to 2.7 pg/m^3 for TC and <0.1 to 2.4 pg/m^3 for CC) (Wurl et al., 2006) and the North Atlantic and Arctic Ocean in 2004 (0.01 to 1.9 pg/m^3 for TC and 0.1 to 2.2 pg/m^3 for CC) (Lohmann et al., 2009).

Endosulfan has been widespread used in many parts of the world, especially in Asia, and was applied to a wide number of crop types including cotton, cereals, fruit trees and plantation crops such as tea and coffee (Weber et al., 2010). The concentrations of α-endosulfan were 1.0–15 pg/m^3 with a mean of 3.9 pg/m^3, which were slightly higher than those in the Arctic atmosphere (Weber et al., 2010), but significantly lower than those reported in the northern part of the South China Sea in September 2005 (Zhang et al., 2007).

The α-HCH concentrations in the atmosphere over the Chinese marginal seas were quite uniform with a H/L (highest/lowest) value of 9.6 (Fig. 2), combining with the relatively low α-HCH levels. It should be more representative of regional background levels after technical HCH was restricted for two decades. For DDTs, it was also observed that there was no significant difference in the spatial distribution with a H/L value of 13 (Fig. 2). This result can be interpreted as evidence of high level background of DDT and the DDTs were still widely used regional. However, γ-HCH, TC and CC values varied by a factor of more than 35. This indicates some continuing significant regional emissions of these compounds. The highest concentrations of γ-HCH, TC, CC and DDT compounds were found in the southern parts of the marginal seas, whereas, higher concentrations of α-endosulfan were observed in northern parts of the marginal seas (Fig. 2). As argued in most studies, the changed trends in concentration levels on the cruise appears to be controlled by emission sources and air mass origins (Zhang et al., 2007). The results of the back trajectory indicated that the higher concentrations of γ-HCH, TC, CC and DDT compounds observed at some sampling sites were associated with air masses passing through Southeast China (Fig. 1), whereas, higher concentrations of α-endosulfan were likely to be influenced by the northern cotton producing regions, which were still using endosulfan as a pesticide.

3.2. Concentrations in water

The summary of selected dissolved OCPs in the coastal water is also listed in Table 1. DDTs, HCHs and chlordane were detected in all samples. The OCP concentrations varied over a narrow range at the given locations (Fig. 3). Such even distribution of OCPs in the coastal water of China suggested that the strong source associated with runoff has been fully mixed, after the long distance, with water mass. Generally, α-HCH, γ-HCH, *p*,*p*′-DDE, *p*,*p*′-DDT and *o*,*p*′-DDT had significantly ($p<0.001$) higher concentrations, with an average values of 500, 790, 470, 390 and 410 pg/L, respectively, than the TC, CC and *p*,*p*′-DDD, which showed similar concentrations of 200, 170 and 210 pg/L, respectively. The OCP concentrations were comparable to those during the period of September 16th–September 22th, 2005, previously reported by another study in the South China Sea (Zhang et al., 2007). Compared with other studies, the concentration of HCHs in this study was lower than that previously reported in studies on bulk

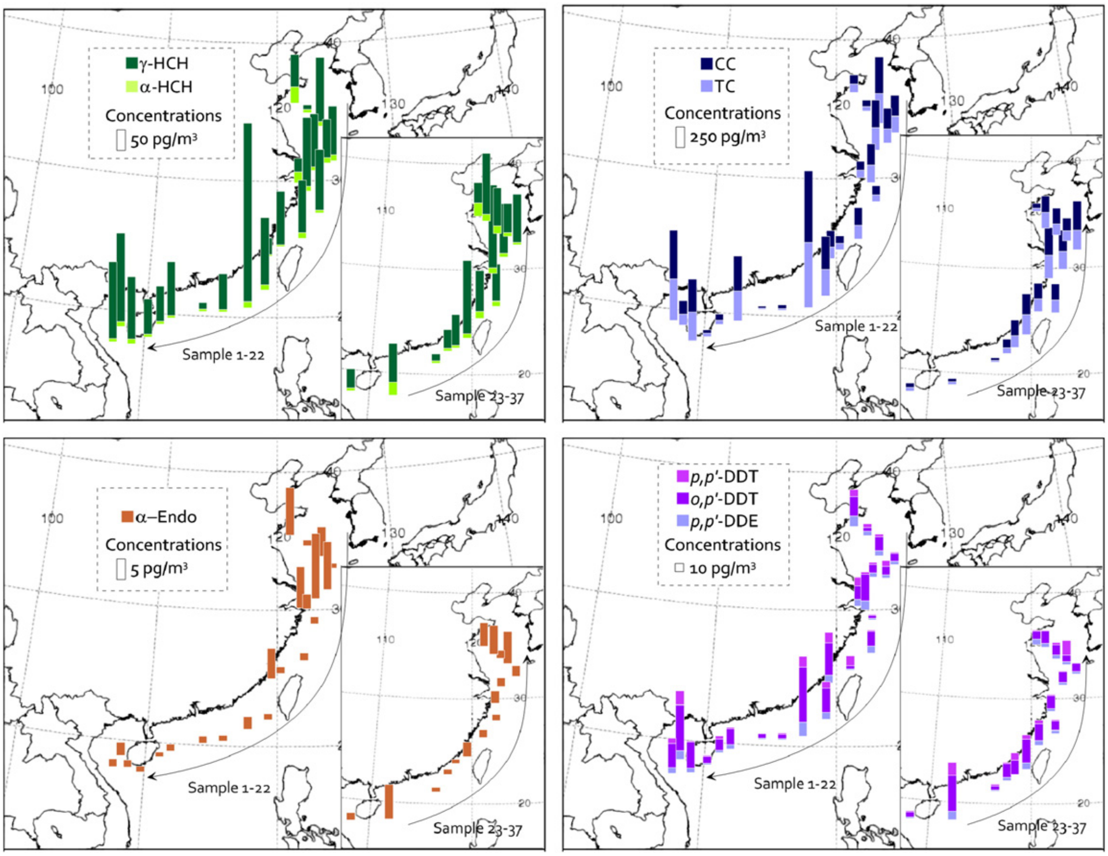

Fig. 2. Spatial distributions of gaseous OCPs in air of the marginal seas of China.

seawater close to land conducted elsewhere in Southeast Asia (ranges from 430 to 42200 pg/L) (UNEP, 2002; Wurl and Obbard, 2005), and slightly higher than that previously reported in studies performed on Bering Sea and Chukchi Sea (144 to 683 pg/L for α-HCH, 30 to 196 pg/L for γ-HCH) (Yao et al., 2002), the Arctic Ocean (γ-HCH ranged from <0.70 to 894 pg/L) (Weber et al., 2006). In addition, HCH concentration was much higher than that previously reported in studies conducted in the open seas, such as the Indian Ocean or the Atlantic Ocean and open sea along the Western Antarctic Peninsula (Dickhut et al., 2005; Jaward et al., 2004). Similar to HCHs, the levels of DDTs in this study were at the upper limits of the reported figure worldwide (Yao et al., 2002). Chlordane was one type of the OCPs that occurred most frequently in the environment all over the world, however, only limited literatures reported the concentration levels of chlordane in the open ocean water (Iwata et al., 1993). Recently, some researchers suggested that skipjack tuna is a suitable bioindicator for monitoring the global distribution of organochlorines in offshore waters and the open ocean (Ueno et al., 2003). Chlordane levels were found to be the second highest OCPs in skipjack tuna liver, which may imply that significant amounts of chlordane exist in seawater. In this study, the concentrations of TC and CC ranged from 140 to 380 pg/L and from 110 to 240 pg/L, respectively. These levels were higher than those in the North Atlantic and Arctic Ocean (Lohmann et al., 2009).

Compared with the OCP concentrations monitored in the same area in 1989 (Iwata et al., 1993), the level of α-HCH concentration was unchanged over the past two decades. γ-HCH and DDT compounds increased; in particular, DDT compounds were significantly increased by 60–220 times. The increase of TC and CC was within the expected range, and the rates of increase were greater than those in air.

3.3. Sources of OCPs

γ-HCH was contained mainly in two forms in China, technical HCH product containing 55–70% α-HCH and 10–18% γ-HCH, and lindane (γ-HCH>99%). Technical HCH was replaced by lindane in the application after 1991 in China and lindane was still in use as an insecticide in China (Zhang et al., 2002). The ratio of two isomers (α-HCH and γ-HCH) is commonly used to identify HCH sources. The ratios of α-HCH to γ-HCH isomer (α/γ-HCH ratios) range from 0.05 to 0.76 and from 0.31 to 0.91 in air and water, respectively, in this study, which were well below those in the technical HCH (4–7). The low α/γ-HCH ratio in the air/water samples implies that lindane is still being used (Li et al., 2003).

The ratios of DDT isomer have been used to identify the possible sources of DDT. A small DDT/(DDE+DDD) ratio is indicative of aged (microbially degraded) DDT, and a value much greater than one indicates fresh application. In this study, the ratio can be simplified as *p,p′*-DDT/*p,p′*-DDE, taking into account that *p,p′*-DDD was not detected in air, and only minor amounts of *p,p′*-DDD were found in water. More *o,p′*-DDT than *p,p′*-DDT in the environment demonstrates the dicofol-type DDT usage (Qiu et al., 2004). The *o,p′*-DDT/*p,p′*-DDT ratio was reported to be 0.20–0.26 in technical DDT and approximately 7.5 in dicofol products (Qiu et al., 2004). However, environmental processes such as evaporation and air–surface exchange can lead to fractionation of the isomers and hence change the ratios. After calibration, these product ratios would result in a calculated ratio of 0.74–0.96 for technical DDT and approximately 28 for dicofol-type DDT in the air (Liu et al., 2009). In this study, the ratios of *o,p′*-DDT/*p,p′*-DDT ranged from 0.33 to 27 in air and from 0.21 to 1.9 in water, which indicated the mixing

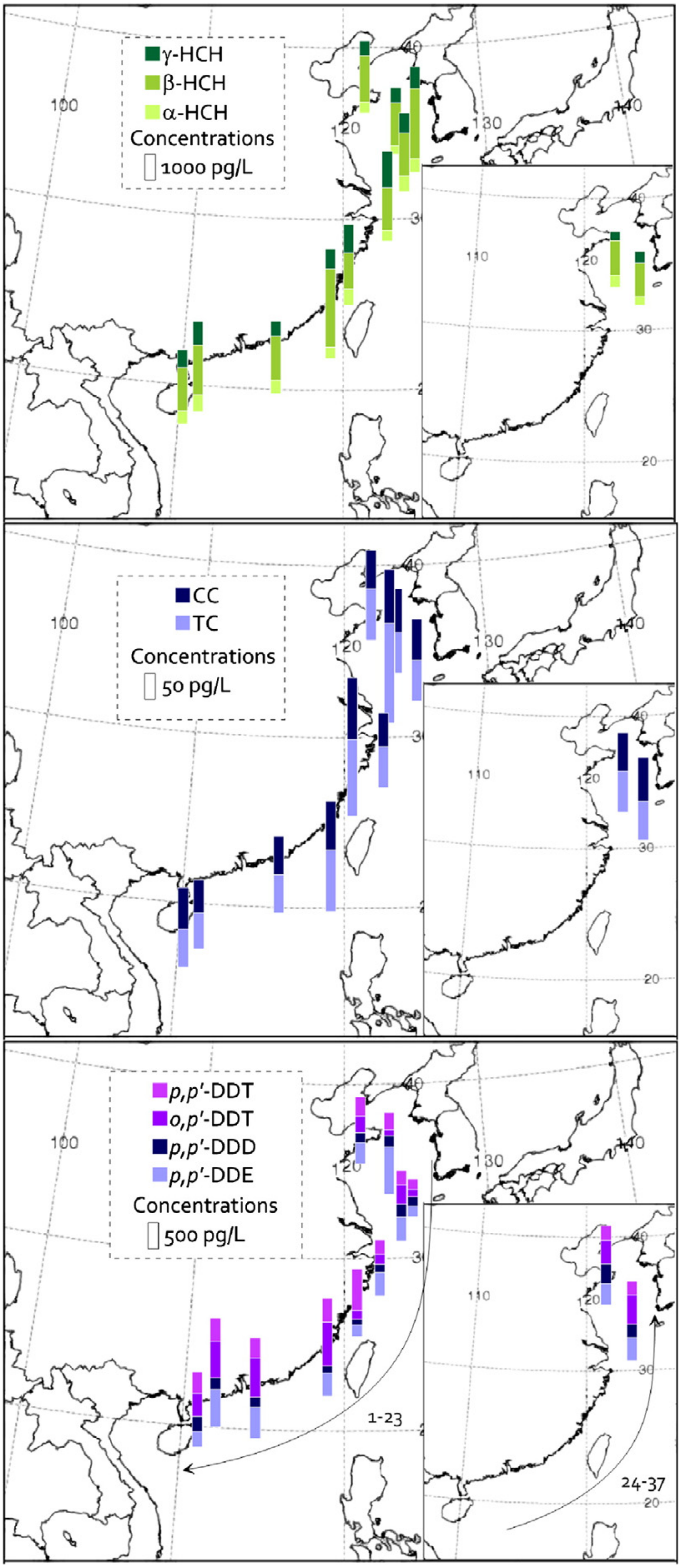

Fig. 3. Spatial distributions of dissolved OCPs in water of the marginal seas of China.

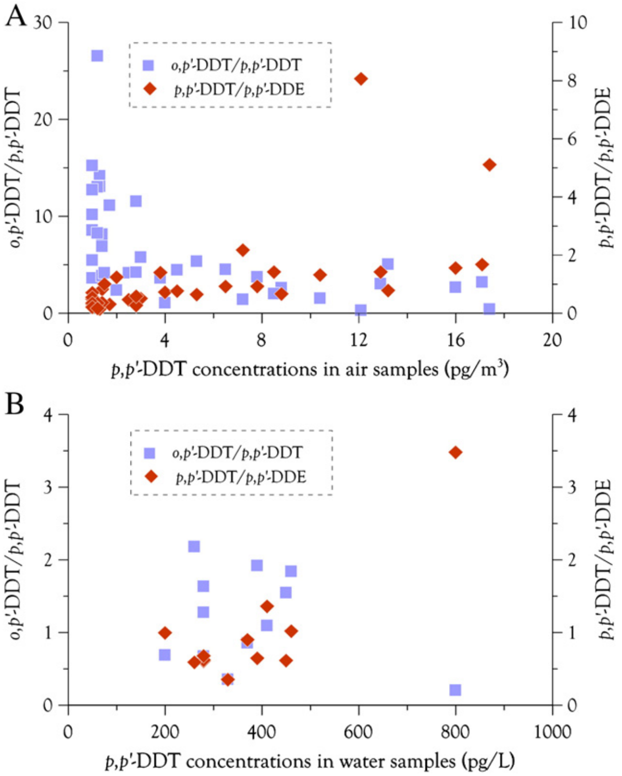

Fig. 4. p,p'-DDT concentrations with the ratios of p,p'-DDT/p,p'-DDE and the ratios of o,p'-DDT/p,p'-DDT in air samples (A) and in water samples (B).

source of technical DDT and dicofol-type DDT in the marginal seas. The p,p'-DDT concentrations and ratios of o,p'-DDT/p,p'-DDT and p,p'-DDT/p,p'-DDE in air and water samples are plotted in Fig. 4A and B. It is interesting that the samples with higher p,p'-DDT concentrations displayed the lower o,p'-DDT/p,p'-DDT ratios and the higher p,p'-DDT/p,p'-DDE values in both air and water. This result may be indicative of a new input from the illegal use of technical DDT in the study area. After technical DDT was banned for almost two decades, the technical DDT released from DDT-activated antifouling paint may help to explain the observed high DDT levels related to the technical DDTs in the marginal sea (Lin et al., 2009).

Technical chlordane is composed of a mixture of abundant components TC (8–15%) and CC (8–13%). China still holds exemptions for its use as a termiticide. Elevated concentrations of TC and CC were observed in the air of the South China (Li et al., 2007) and in the water from the Taihu Lake (Qiu et al., 2008). In addition, a recent air sampling campaign in Japan showed elevated concentrations of TC and CC compared with other countries in Asia (Jaward et al., 2005). TC is more susceptible to photo-degradation than CC in the environment (Hung et al., 2005). In general, the technical mixture TC/CC ratio has been reported to be approximately 1.1, and a ratio less than 1.1 indicates a more aged source (Bidleman et al., 2002; Hung et al., 2005). The ratios of TC/CC ranged from 0.6 to 1.0 (0.80 ± 0.15) in the air and indicated that a great change had occurred in the composition with respect to the technical chlordane after long-range atmospheric transport.

3.4. Air–water gas exchange of selected OCPs

The dynamics of air–water exchange for semi-volatile compounds can be explored by ratioing the fugacity of the chemical in the respective water and air phases, with knowledge of the temperature-dependent Henry's Law constant (H) and ambient air and surface water temperatures (Falconer et al., 1995). Air–water fugacity ratios were calculated from relationships given in equation:

$$f_a/f_w = (C_aRT)/(C_wH)$$

where C_a is the gaseous concentration (mol/m^3), C_w is the dissolved aqueous concentration (mol/m^3), R is the gas constant ($8.314\ \mathrm{Pa \cdot m^3/mol \cdot K}$), T is the ambient air temperature (K) and H is the Henry's law constant ($\mathrm{Pa \cdot m^3/mol}$). For each compound, measurement errors in C_a and C_w, H values were taken into account. The uncertainties of C_a and C_w measurement were taken as 15% (Mai et al., 2002). Most experimental H values for pesticides have been reported at only a single certain temperature, 20 or 30 °C, which are unsuitable for this study without adjustment by water temperature. There is a strong correlation between the H values of OCPs and temperature. The variation in H with temperature was expressed using the Hoff equation [$\ln H = A + B/T(K)$], where slopes (B) and the intercepts (A) for the equation are present in literature (Cetin et al., 2006), and the r^2 values for the plots of ($\ln H$) vs. ($1/T$) ranged between 0.91 and 0.99 for both deionized water and saline water (Cetin et al., 2006). For salinity correction in saline water, the H value was calculated using [$\log(H'/H) = K_sC_s$] where C_s is the molar concentration of salt solution. Salting-out constants (K_s, L/mol) for OCPs were calculated with the method by (Xie et al., 1997). The calculated H values were comparable with results (<12%) measured by (Cetin et al., 2006). The literature sources of the H values in salt water and the corresponding temperature values are listed in Table S4 (Cetin et al., 2006; Kucklick et al., 1991; Qiu et al., 2008; Sahsuvar et al., 2003; Shen and Wania, 2005) .

Theoretically, where $f_a/f_w = 1$ at air–water equilibrium, $f_a/f_w > 1$ indicates net deposition from air to water, and $f_a/f_w < 1$ indicates net volatilization from the water. Although H values have been done for salinity and temperature corrections, the overall uncertainty of H value still existed (Bruhn et al., 2003; Odabasi et al., 2008). While it is not possible to obtain an objective measure of this uncertainty, recommended value of 30% for uncertainty might be appropriate, based on the results of previous evaluations, different laboratory artifacts and the uncertainties in the air and water-side mass transfer coefficients (Bruhn et al., 2003; Odabasi et al., 2008).

In addition, it should be pointed out that the error associate with the volatilization depends on the error associated with C_w while the error associated with the deposition only depends on C_a and H. This is very important for establishing whether the direction of transport is statistically significant at the confidence interval chosen. Thus, a propagation of the errors that is associated with the calculation indicated that the equilibrium is represented by a f_a/f_w ratio of 1.0 ± 0.2. In this study, the fugacity ratios (f_a/f_w) for o,p'-DDT and γ-HCH were generally more than or within 1.0 ± 0.2, which demonstrated a potential of air to water exchange or near equilibrium in the coastal waters (Fig. 5). In fact, after the recent field investigation, lindane is used in the wheat production region of China and o,p'-DDT is the main DDT impurity in commercial dicofol which has been used on many crops, such as fruit trees and cotton. Generally, pesticides sprayed on fields make local air and soil become the direct receptors for contamination. Additionally, pesticides in the atmosphere or re-emission from soil will migrate into the broader environment in a short time after their release.

The fugacity ratios (f_a/f_w) for α-HCH, CC, TC, p,p'-DDE and p,p'-DDT in the coastal water demonstrated that air–water flux was net volatilization at all sampling sites. Compared with the results from two decades ago in the same study area, the flux direction of α-HCH has changed from net deposition to net volatilization (Iwata et al., 1993). The change of sea–air gas exchange direction for α-HCH in past decades was also confirmed in the Arctic (Ding et al., 2007). Because the phase-out of technical HCHs in the 1980s, atmospheric concentrations of α-HCH have declined gradually. Because of the longer lifetimes of

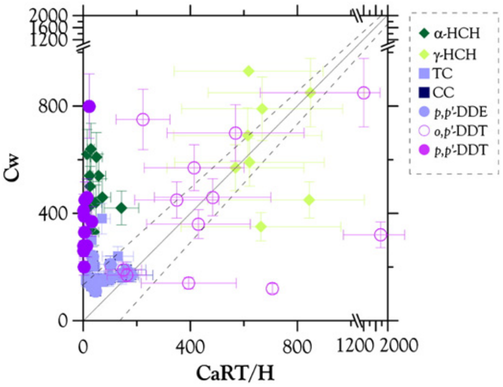

Fig. 5. Water/air fugacity ratios (f_a/f_w) for selected OCPs in the marginal seas of China; $f_a/f_w > 1$ indicates transfer from air to water; and $f_a/f_w < 1$ indicates transfer from water to air. See Fig. 1 for site locations.

α-HCH in oceans than in the atmosphere and continuous input of α-HCH from coastal environment, it is possible that α-HCH accumulated in the oceans can be re-released into the atmosphere by the sea–air exchange (Ding et al., 2007). CC, TC and *p,p′*-DDT had net volatilization fluxes out of the water although the sources of these chemicals were still existed in China. The technical chlordane was mainly used for termite control in residential and commercial buildings, as well as in forest with surface soil burial method, so it would be more inclined to enter into the coastal water by way of runoff. For *p,p′*-DDT, oceans have turned the net volatilization were consistent with that predicted by model (Stemmler and Lammel, 2009). Furthermore, to our knowledge, a large proportion of *p,p′*-DDT annual used as additive in antifouling paint for fishing boats, *p,p′*-DDT release from the boats to coastal waters may be another possible reason. Due to the potential source of those compounds from coastal water runoff, the oceans have been an important source of OCPs in the atmosphere after a long time prohibition of OCPs.

4. Conclusion

In this study, the OCP concentrations and sources were assessed in shipboard air and surface seawater samples collected over the Yellow Sea, East China Sea and South China Sea. Concentrations of γ-HCH, TC and CC both in air and water were significantly higher in the marginal seas of China compared with those found in recent studies from the open ocean around the world. These results indicated that there should have been significant input of these chemicals from the neighborhood of Southeast Asia, especially China. In addition, a comparison of spatial OCP concentrations in air indicated that highest concentrations of γ-HCH, TC, CC and DDT compounds were found in the southern parts of marginal seas, while higher concentrations of α-endosulfan were observed in northern part of marginal seas. The change trends appeared to be associated with regional emissions. Air–water exchange gradients suggested net deposition for γ-HCH and *o,p′*-DDT and net volatilization for α-HCH, CC, TC, *p,p′*-DDE and *p,p′*-DDT. The results confirmed the oceans exhibit net volatilization after a long period of OCP prohibition.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2012.07.028.

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