Spatial distribution and seasonal variation of four current-use pesticides (CUPs) in air and surface water of the Bohai Sea, China

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HIGHLIGHTS

- Four CUPs were analyzed in air and surface water samples of the Bohai Sea.
- CUPs were presented dominantly in gas phase of atmosphere and in dissolved phase of seawater.
- High seawater CUP levels in August were found around the Yellow River Estuary.
- Volatilization from the surface water was an important source of trifluralin and chlorpyrifos to the air.
- Atmospheric deposition was an important input pathway of chlorothalonil into the Bohai Sea.

GRAPHICAL ABSTRACT
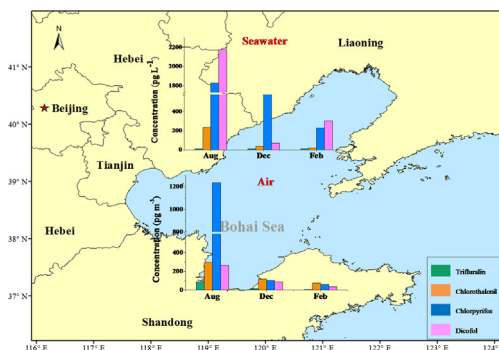
ABSTRACT

Current-use pesticides (CUPs) are widely used in agriculture, and some are listed as persistent organic pollutants (POPs) due to their bioaccumulative and toxic properties. China is one of the largest producers and users of pesticides in the world. However, very limited data are available about the environmental fates of CUPs. Four CUPs (trifluralin, chlorothalonil, chlorpyrifos, and dicofol) in surface seawater and low atmospheric samples taken during research cruises on the Bohai Sea in August and December 2016 and February 2017 were analyzed, we added the spring data sampled in May 2012 to the discussion of seasonal variation. In our study, chlorpyrifos was the most abundant CUPs in the gas phase with a mean abundance of 59.06 ± 126.94 pg m^{-3}, and dicofol had the highest concentration dissolved in seawater (mean: 115.94 ± 123.16 pg L^{-1}). The concentrations of all target compounds were higher during May and August due to intensive use and relatively high temperatures in the spring and summer. Backward trajectories indicated that air masses passing through the eastern coast of the Bohai Sea contained high concentrations of pollutants, while the air masses from the Bohai and Yellow Seas were less polluted. The high concentration of pollutants in seawater was not only influenced by high yields from the source region of production or usage, but also by input from polluted rivers. Volatilization from surface water was found to be an important source of trifluralin and chlorpyrifos in the air. Air-sea gas exchange of chlorothalonil underwent strong net deposition (mean FRs: 51.67), which was driven by higher concentrations in air and indicates that the Bohai Sea acted as a sink for chlorothalonil.

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1. Introduction

Current-use pesticides (CUPs), are designed to be lower environmental persistence and toxic and be more biodegradable in comparison with traditional organochlorine pesticides (Walker and Nidiry, 2002). They are now among the catalog of 'emerging pollutants' (Mai et al., 2013). CUPs are not only identified in the regions where they are applied, such as agricultural and forestry areas (Arinaitwe et al., 2016; Asman et al., 2005; Feng et al., 2016; Yao et al., 2008a), rural and urban areas (Carratala et al., 2017; Coscolla et al., 2017; Estellano et al., 2015), but also in regions far away from their sources, such as the Arctic (Hoferkamp et al., 2010; Morris et al., 2016; Walker and Nidiry, 2002; Zhong et al., 2012a), high mountains (Hageman et al., 2006), the and Indian-Pacific Ocean (Bigot et al., 2016). China produces and consumes the largest amount of CUPs in the world. An estimated 3.74 million tons of technical pesticide products were produced in 2015, and 1.80 million tons were consumed in 2014 (www.stats.gov.cn). However, few data are available about the distribution and fates of CUPs in the marine environment (Zhong et al., 2014).

Seasonal variations of most types of CUPs in the atmosphere are related to their usage, with the highest concentrations measured in the spring or summer (Carratala et al., 2017; Estellano et al., 2015; Yao et al., 2008a; Zhong et al., 2012b). However, little is known about their seasonal distribution in the marine environment, especially in the highly human impacted Bohai Sea. Previous studies have revealed that seawater acts as a major recipient of numerous pesticides through dry or wet atmospheric deposition, riverine discharge, and air-water exchange (Feng et al., 2011; Luek et al., 2017; Mai et al., 2016; Zhong et al., 2011). Riverine inputs could be important sources not only for CUPs with relatively high water solubility, but also for CUPs with low water solubility (Zhong et al., 2014). CUPs can be transported by currents into the offshore and deep ocean regions, and hence threaten coastal and pelagic ecosystems (Carratala et al., 2017; Li et al., 2015; Mai et al., 2013). Air-water exchange is also an important process that transports CUPs. Seawater can act as a secondary source of pesticides, and release pesticides from the sea into the atmosphere. CUPs can then be delivered to remote regions by long-range air transport (LRAT).

The Bohai Sea is a semi-closed interior sea in China with a mean depth of 18 m and area of 70,000 km^2 (Liu et al., 2012), and its water exchange with the Yellow Sea is relatively slow. Hence, pollutants tend to accumulate and become concentrated in this shallow water for a long time (Hu et al., 2010). The Bohai Sea is surrounded by the Liaoning, Hebei, and Shandong Provinces, and the Tianjin Municipality. The Bohai Economic Rim (BER) is one of the largest economic engines as well as the Yangtze and Pearl River Deltas in China. Besides the large population and rapidly growing industries, agriculture also plays a very important role in the BER. A large amount of pesticides is produced and applied in this region. For example, 300,900 tons of pesticides were used in the BER in 2015. Shandong province uses the largest amount of pesticides in China, and a total of 151,000 tons were applied for agricultural activities in 2015 (www.stats.gov.cn). The extensive use of pesticides has caused a series of environmental problems, and has seriously threatened human and ecosystem health.

Spatial distribution and seasonal trends of most pesticides were observed in previous studies in air (Coscollà et al., 2014; Scheyer et al., 2007; Yao et al., 2008b; Yao et al., 2006) and seawater (Bigot et al., 2016; Mai et al., 2013). The same area was studied in May 2012 for trifluralin, chlorothalonil, chlorpyrifos, dicofol and 10 additional contaminants (Zhong et al., 2014). Our work further deepened the previous research and were filled the gap about seasonal variations in the Bohai Sea. In this study, the concentrations of CUPs were measured during the summer (August 2016) and winter (December 2016 and February 2017), and previous study in spring (May 2012) was also added to our discussion of seasonal variations. Air-sea exchange of CUPs was estimated. The aim of this study was to understand the spatial and seasonal patterns of CUPs (trifluralin, chlorothalonil, chlorpyrifos, and dicofol) and identify potential sources in the Bohai Sea.

2. Materials and methods

2.1. Sample collection

Twenty-two air (~300 m^3) and seawater samples (~60 L) were collected onboard a research vessel (*Chuangxin I*) from the Bohai Sea during three sampling campaigns (nine pairs of air and seawater samples in August–September 2016; nine pairs of air and seawater samples in December 2016, and four pairs of air and seawater samples in February 2017). Maps of the tracks for each air and seawater sample are shown in Fig. S1 (A, B, C).

Individual air samples were collected in front of the upper-most deck of the research vessel by a high-volume air sampler for ~24 h at a flow of ~0.21 m^3 min^{-1}. Glass microfiber filters (Whatman™, GF/F, diameter 150 mm) were used to collect particulate samples, followed by a glass column packed with PUF/Amberlite™ XAD-2 for gaseous samples in series (Zhong et al., 2014). Seawater samples were collected from the ship's seawater intake system, which was made of stainless steel and was located in the front of the vessel and 1 m below the waterline. The same glass microfiber filters (Whatman™, GF/F, diameter 150 mm) were used to collect the particulate samples, and a self-packed XAD-2 glass column (30 cm × 2.5 cm i.d., 30 g resin) for the dissolved phase samples. After sampling, the glass columns were stored at 4 °C, and filter samples were stored at −20 °C. The details of air and water sampling information are given in Tables S1 and S2.

2.2. Chemicals

The analytical standards included four CUPs (trifluralin, chlorothalonil, chlorpyrifos, and dicofol). Individual trifluralin and chlorpyrifos standards were purchased from AccuStandard, America. Trifluralin-d14 (surrogate), and a pesticide-mix 323 containing chlorothalonil and dicofol were purchased from Dr. Ehrenstorfer, Germany. PCB-208, used for internal standards, was also purchased from AccuStandard, America.

2.3. Extraction, cleanup, and analysis

Samples were extracted using a modified Soxhlet extractor with dichloromethane (DCM) for 24 h (Xie et al., 2011). Prior to extraction, 10 ng Trifluralin-d14 was added as a surrogate standard. The extracts were evaporated to 1 mL using hexane as a solvent, and then cleaned in an alumina-silica gel column (3% water deactivated) topped with anhydrous sodium sulfate. The extracts were then eluted with 22 mL of hexane/dichloromethane (1:1) and reduced to a final volume of 0.5 mL with nitrogen (purity 99.999%). As an internal standard, 20 ng PCB-208 was added to the solvent.

Analysis was conducted by a gas chromatographer (GC) coupled with a 5975C mass selective detector (MSD) in the electron capture negative ion chemical ionization mode (ECNICI). A HP-5MS (30 m × 0.25 mm i.d., 0.25 mm film thickness) capillary column was used to determine the levels and composition of CUPs. The GC temperature program was set as follows: 60 °C for 1 min, then increased to 150 °C at 30 °C min^{-1}, and finally to 300 °C at 5 °C min^{-1}, which was held for 5 min. The front inlet temperature was 290 °C, and the post-run temperature was 300 °C. The ions 335 and 305 were monitored for trifluralin; ions *m/z* 265.8 and 229.9 for chlorothalonil; ions 312.8 and 168.9 for chlorpyrifos; and ions *m/z* 249.9 and 251.8 for dicofol.

2.4. Quality assurance and quality control

Glass vials, filters, silica gel, neutral alumina, and anhydrous sodium sulfate were baked at 450 °C for 12 h prior to usage, and PUF/XAD-2 and

XAD-2 columns were cleaned using a modified soxhlet extractor with methanol and hexane/acetone (1:1), respectively, for 24 h. After cleaning, all columns were dried under gentle pure nitrogen (purity 99.999%) for sampling, and the air columns were protected against UV-light using aluminum foil to avoid the target compounds degrading in the column during sampling. Field blanks for various samples at different stages were also collected during the campaigns. The mean recoveries of trifluralin-d14 were 123 ± 8, 134 ± 19, 176 ± 29, and $177 \pm 14\%$ for the air and water filters, and air and water columns, respectively. The high recovery could have been due to the evaporation of the keeper of the surrogate. The recovery was assessed by spike tests, the results of which were 75% for trifluralin, 78% for chlorothalonil, 89% forchlorpyrifos, and 95% for dicofol. The method detection limits (MDL) were calculated based on the mean blank values plus three times the standard deviations of the blanks. For this study, if the values were below the MDL, there were considered not detected (n.d.). Atmospheric MDLs ranged from 0.047 to 9.40 pg m^{-3}, and seawater MDLs ranged from 0.24 to 78.26 pg L^{-1}.

2.5. Air mass back trajectories

To identify the source region of CUPs in the air samples, air mass backward trajectories were calculated using NOAA's HYSPLIT model (Draxler and Rolph, 2003). Air mass backward trajectories (BTs) were modeled in 6 h intervals for 120 h, with the sampling height as the arrival height, and the individual backward trajectories are shown in Fig. S2.

3. Results and discussion

3.1. CUPs in air

Concentrations of individual CUPs during different seasons are summarized in Table 1, and details are presented in Tables S5–S7. Generally, chlorpyrifos (63.73 ± 126.12 pg m^{-3}) was the most predominant compound, followed by chlorothalonil (22.32 ± 15.91 pg m^{-3}), dicofol (17.66 ± 22.12 pg m^{-3}), and trifluralin (5 ± 14.53 pg m^{-3}) (Figs. 1 and S3). In order to identify the characteristics of contaminants in particle phase more precisely, the concentration of CUPs in the particulate fraction (air and seawater) also expressed in weight (Tables S7 and S10). In our study, the particle-phase fractions (f_p) of the three target compounds (excluding dicofol due to its low detection rate in particle phase) were noticeably higher in the winter (28–67%) than summer (0–5%) (Fig. 2). This trend is more apparent with the date expressed in weight. Four CUPs in air particle phase increased from summer (82.23 ± 58.02 ng g^{-1}) to winter (444.29 ± 513.79 ng g^{-1}). Previous studies have demonstrated that the partitions between gas and particle phases were probably controlled by physic-chemical properties of the compounds (e.g., vapor pressures (P_L)), or by meteorological

conditions, such as temperature (Mader and Pankow, 2000, 2001a, 2001b; T. Xu et al., 2017).

Chlorpyrifos was one of the most abundant CUPs in gas phase of air samples above the Bohai Sea (135.05 ± 176.53 pg m^{-3} in August 2016; 7.91 ± 11.61 pg m^{-3} in December 2016; 3.20 ± 1.09 pg m^{-3} in February 2017) (Table 1). The concentration in August (135.05 ± 176.53 pg m^{-3}) was comparable with that reported in May 2012 in air (142.08 ± 176.30 pg m^{-3}) (Zhong et al., 2014) (Table S3) in the Bohai Sea. Although the use of chlorpyrifos on vegetables ceased in China on December 31, 2014, this result suggested high consumption and application in the continents adjacent to the Bohai Sea, or continued use in China.

Chlorothalonil is a broad-spectrum organochlorine fungicide that is used to control fungi on vegetables, trees, and other agricultural crops (Estellano et al., 2015). Chlorothalonil was detected in all samples, with concentrations ranging from n.d. to 36.57 pg m^{-3} and 0.59 to 59.48 pg m^{-3} in the particle and gas phases, with averages of 6.53 ± 7.97 pg m^{-3} and 15.79 ± 17.25 pg m^{-3}, respectively. The levels of chlorothalonil calculated in weight (147.03 ± 200.73 ng g^{-1}) have the highest concentration compared with other targets. The concentrations in the gaseous phase in August (31.53 ± 15.64 pg m^{-3}) were comparable to those from the Bohai Seas in May 2012 (31.02 ± 31.31 pg m^{-3}) (Zhong et al., 2014) (Table S3), but the mean values of all samples higher than those from the North Pacific and Arctic Oceans in 2010 (0.64 ± 1.8 pg m^{-3}) (Zhong et al., 2012a), and the western Arctic Ocean in 1993–2013 (0.90 ± 1.8 pg m^{-3}) (Jantunen et al., 2015). This result suggested that chlorothalonil is widely used in China.

Dicofol was only identifiedin4 of 22 samples in the particle phase (18%), so the following discussion will focus on the gas phase. The mean concentration of dicofol was 16.07 ± 22.85 pg m^{-3}, similar to that of chlorothalonil, even though the annual use amount of dicofol in China was 10 times higher than that of chlorothalonil (Zhong et al., 2014). This could be due to the low Henry's law constant (HLC) and high logK_{oa} values of dicofol (Table S4). During the February 2017 sampling campaign, dicofol was only detected in one sample (FA1), which was taken near the Bohai Strait.

Trifluralin is a synthetic dinitroaniline herbicide, which is commonly used as a pre-emergence herbicide (Zhong et al., 2012b). Approximately 3719 and 2540 tons of trifluralin were used for agriculture in the US and China in 2010, respectively (Gong et al., 2016). Although trifluralin has not yet been listed as a persistent organic pollutant (POP), it was a candidate for becoming listed as a POP under the UNECE LRTP conventions (UNECE, 2009). Trifluralin was detected in most air samples (82%). The concentrations of trifluralin were lower than those of other compounds (particle phase: 0.35 ± 0.76 pg m^{-3}, gas phase: 4.65 ± 14.55 pg m^{-3}) (Figs. 1 and S3), which may be due to the rapid degradation of trifluralin under sunlight and its short half-life of a few hours (Aulagnier et al., 2008) in the air and water. Trifluralin concentrations ranged from n.d.

Table 1
Concentrations of current-use pesticides in the air (total of particle and gaseous phases, pg m^{-3}) and aqueous phases (particle and dissolved phases, pg L^{-1})of the Bohai Sea (R = range of concentrations of the target compounds measured during the sampling periods; M ± SD = mean ± standard deviation).

|		Trifluralin		Chlorothalonil		Chlorpyrifos		Dicofol	
		R	M ± SD	R	M ± SD	R	M ± SD	R	M ± SD
Air particle phase (pg m^{-3})	Aug	0.06–0.20	0.11 ± 0.05	0.27–3.31	1.58 ± 1.27	0.74–10.43	2.54 ± 3.06		
	Dec	n.d.–1.53	0.25 ± 0.50	2.33–13.56	6.75 ± 4.17	1.18–8.59	3.44 ± 2.23	n.d.–7.85	0.87 ± 2.62
	Feb	0.24–3.44	1.09 ± 1.57	8.88–36.57	17.17 ± 13.03	3.89–29.65	12.24 ± 11.82	n.d.–11.15	6.80 ± 4.96
Gas phase (pg m^{-3})	Aug	0.16–69.03	9.62 ± 22.46	13.30–59.47	31.53 ± 15.64	15.38–550.04	135.05 ± 176.53	n.d.–87.39	29.45 ± 29.71
	Dec	n.d.–5.85	1.52 ± 1.87	0.59–19.42	6.41 ± 7.46	0.74–34.55	7.91 ± 11.61	n.d.–24.98	8.97 ± 11.14
	Feb	0.11–1.64	0.53 ± 0.74	0.71–3.22	1.47 ± 1.19	1.59–3.98	3.20 ± 1.09	n.d.–7.71	1.93 ± 3.85
Seawater particle phase (pg L^{-1})	Aug	n.d.–0.15	0.02 ± 0.05			1.02–454.14	103.55 ± 157.36		
	Dec	n.d.–1.98	0.40 ± 0.66			n.d.–284.18	37.55 ± 92.93		
	Feb	0.63–1.50	1.08 ± 0.39			1.34–7.06	2.84 ± 2.82		
Seawater dissolved phase (pg L^{-1})	Aug	n.d.–2.27	1.12 ± 0.62	11.53–37.25	25.67 ± 8.68	106.87–219.42	168.63 ± 44.20	339.08–365.48	241.97 ± 83.03
	Dec	n.d.–2.20	0.44 ± 0.72	n.d.–11.39	4.20 ± 3.71	23.13–55.95	32.30 ± 10.21	n.d.–68.99	7.67 ± 22.99
	Feb	0.83–2.71	1.32 ± 0.92	0.99–16.26	4.96 ± 7.53	30.67–102.10	53.53 ± 32.72	47.70–131.71	75.99 ± 37.82
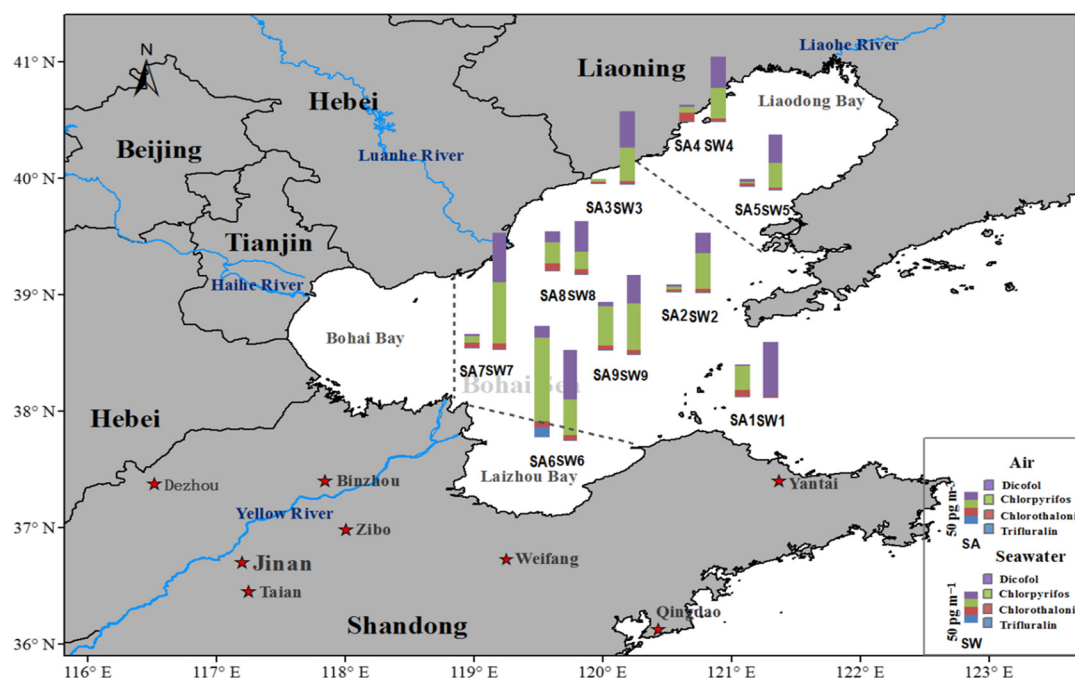
Fig. 1. Spatial distributions of the target compounds in the Bohai Sea in August 2016. (The sampling cruise began at SA1 (SW1) and traveled to SA9 (SW9)).

to 3.44 pg m^{-3} in the particulate phase and n.d. to 8.44 pg m^{-3} in the gas phase (excluding SA6, with concentration of 69.03 pg m^{-3}). This peak coincided with the high values of the other three compounds in the same sample, and was likely associated with the same sources.

3.2. Seasonal variations in the air

CUPs concentrations showed clear seasonal patterns (Tables 1 and S12). Higher concentrations were identified in the gas phase in May 2012 and August 2016 than those in December 2016 and February 2017. In contrast, higher concentrations were observed in the particulate phase in the winter than in summer (see Table S7, Fig. S4).

In this study, the highest concentrations of pollutants in gas phase air samples were all detected in August, as follows: chlorpyrifos (135.05 ± 22.47 pg m^{-3})., chlorothalonil (31.53 ± 15.64 pg m^{-3}), dicofol (29.45 ± 29.71 pg m^{-3}), and trifluralin (9.62 ± 22.47 pg m^{-3}). Compared with previous study in spring (May 2012),
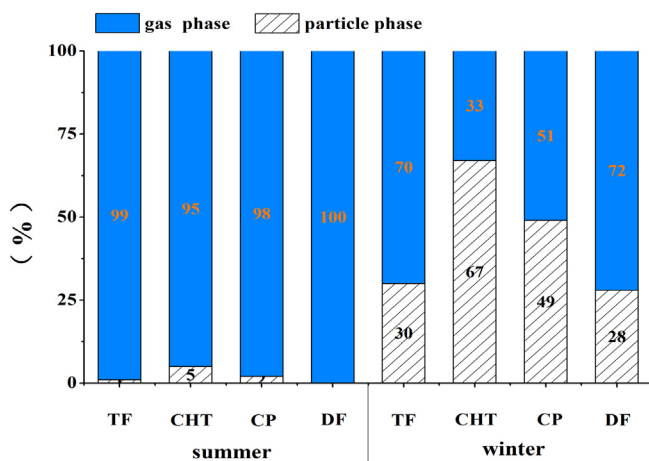

Fig. 2. Gas/particle partitioning of CUPs in the summer (August) and winter (December/February); TF, trifluralin; CHT, chlorothalonil; CP, chlorpyrifos; DF, dicofol.

the concentration of dicofol (3.78 ± 2.17 pg m^{-3}) increased significantly, which attributed to its immunity of many Chinese pesticide enterprises and a large amount of usage although it has been listed as a persistent toxic compound in a series of multilateral agreements. The concentration of other compounds was higher in spring and summer than that in winter. These observations could have been influenced by the agricultural fields that surround the Bohai Sea, which heavily used pesticides during the growing season for crop protection. The average air temperatures in August, December, and February were 23, 3, and 4 °C, respectively. The increased ambient temperatures may accelerate the volatilization of pesticides from the surface to the atmosphere in August. Similar seasonality in the atmosphere has also been observed previously, with higher levels of CUPs during the spring or summer periods (Estellano et al., 2015; Hart et al., 2012; Mai et al., 2013). On the contrary, the concentration of target compounds in particle phase in winter (444.29 ± 513.79 ng g^{-1}) was higher than that in summer (82.23 ± 58.02 ng g^{-1}) (Table S7). One of the influencing factors may be lower temperature in winter, which could lead to high proportions of semi-volatile organic compounds (SVOCs) in the fine particles (Jin et al., 2017). Total suspended particulate (TSP) concentration was also calculated in the sampling air (Table S11). The trend corresponded to their seasonality of f_p, which has the significantly increased concentration from summer (57 μg m^{-3}) to winter (68 μg m^{-3}). This result reflected the concentration of CUPs could increase with increasing concentration of particles. Dicofol was scarcely found in particle phase during the sampling campaign. In contrast, dicofol displayed a widespread distribution in gas phase in samples collected from the Bohai Sea in August 2016 (89%), and was also detected in 44% of the samples in December 2016. The presence of pollutants in the particulate phase depends on the physicochemical properties of each compound (Carratala et al., 2017); the lower detection rate might be attributed to the higher logK$_{oa}$ value of dicofol (Table S4).

To gain a general understanding of the sources of the target compounds in different seasons, backward trajectories (BTs) of air masses were calculated to trace the most likely paths of the air parcel that collected them. In August, air masses in the Bohai Sea were influenced by southerly, south-westerly, and south-easterly winds that passed through East China (Tianjin Municipality, and the Hebei, Shandong,

Jiangsu, and Anhui Provinces) and its adjacent waters, occasionally passing through Liaoning Province and Inner Mongolia. The samples with elevated concentrations were associated with air masses passing through the eastern coastal area of China (see Fig. 4SA6), where agriculturalization and industrialization activities have rapidly developed, discharging large amounts of pesticides to the Bohai Sea (Hu et al., 2009; Pan et al., 2016; Wang et al., 2008). This indicates high levels of pollution from terrestrial sources. It is evident that the samples with relatively low concentrations in August could be associated with cleaner air masses originating from the open sea areas near eastern China (Fig. 4SA3). In December 2016 and February 2017, air masses over the Bohai Sea were influenced by northerly and north-westerly winds that primarily traveled through the Hebei and Liaoning Provinces, the Inner Mongolia Autonomous Region, Mongolia, and Russia. The concentrations in the air of these regions were lower than those in the air masses above the Bohai Rim.

3.3. CUPs in seawater

The concentrations of the four compounds in the dissolved and particle phases are provided in Tables S8–S10. Among the four CUPs, chlorpyrifos was present in both phases, and trifluralin was only detectable in a few filtered seawater samples. The concentrations of all four compounds expressed in volume were primarily higher in the dissolved phase than in the particulate phase. Chlorpyrifos, with the mean value 181.56 ± 163.04 pg g^{-1}, was the predominant contaminant found in particle fraction expressed in weight, followed by trifluralin (25.09 ± 28.12 pg g^{-1}), while chlorothalonil and dicofol were almost not detected. The concentrations of the target compounds in the dissolved phase ranged from n.d. to 365.48 pg L^{-1} (trifluralin: 0.88 ± 0.78 pg L^{-1}, chlorothalonil: 13.12 ± 12.50 pg L^{-1}, chlorpyrifos: 88.28 ± 71.55 pg L^{-1}, and dicofol: 115.94 ± 123.16 pg L^{-1}), excluding chlorpyrifos in SW1 (2150.87 pg L^{-1}), which was one or two orders of magnitude higher than the concentrations in the other samples. The following discussion about chlorpyrifos will not include this outlier.

The concentrations of dicofol in the dissolved phase were higher than those of the other three pesticides. This was consistent with the properties of dicofol, with water solubility (S$_L$) at least an order of 100 times higher and Henry's law constants (HLCs) 100 times lower than those of the other compounds (Table S4). The mean dicofol concentration measured in this study was slightly higher than those observed in the Bohai Sea in 2012 (89.57 ± 72.05 pg L^{-1}) (Zhong et al., 2014) (Table S3), and was markedly higher than those reported in the North Pacific and the Arctic Oceans (9 ± 23 pg L^{-1}) (Zhong et al., 2012a) (Table S3), and the India-Pacific sector of the Southern Ocean (<MDLs) (Marie et al., 2016) (Table S3). Although the pesticide registration of dicofol was banned in China, high levels in the Bohai Sea could have been due to the large use of dicofol, with domestic consumption of 19,500 tons from 2000 to 2012, occupying 69% of the global total (Li et al., 2015).

Higher concentrations of the four compounds were present in SW6 and SW7 in August, which were sampled close to the interface between the Bohai Bay (BB) and Laizhou Bay (LB) (Fig. 1). The spatial distribution found for CUPs in the Bohai Sea was similar to that found in May 2012, which high concentration areas were also present in the BB and LB. BB and LB are in the northern part of Shandong Province, which uses the highest amount of pesticides in China (www.stats.gov.cn). Two of the top ten enterprises that led China's pesticide sales in 2016 were located in Weifang and Binzhou, which are close to the LB and BB, respectively. In addition to these two cities, Tianjin Municipality, and Qingdao, Jinan, Dezhou, Taian, and Yantai have also contributed to the large amounts of CUPs (www.agrichem.cn). From Fig. 1, it can be seen that these places around BB and LB are the most prominent terrestrial sources of CUPs. Studies have shown that pollutants could enter the BB and LB through riverine inputs during the application period (L. Xu et al., 2017; Zhao et al., 2017; Zheng et al., 2011; Zhong et al., 2011). The target

compounds are expected to discharge into the Bohai Sea through the runoff of the Yellow and Haihe Rivers (Fig. 1), which are among the seven largest water systems in China, and receive large volumes of industrial or agricultural wastewater leading to serious pollution levels (Li et al., 2013; Li et al., 2016). For example, the Yellow River flows through Zibo City, which is the largest production base of Chlorpyrifos in Northern China (15,000 t/y), this may explain the high concentration of Chlorpyrifos in SW6 and SW7. The target concentrations in this area are notably lower in winter, which may be ascribed to the decrease of pesticide use (Fig. S3).

The CUPs in particle phase were mostly below the MDLs in seawater, excluding chlorpyrifos (181.56 ± 163.04 pg g^{-1}) (Table S10). Thus, the seasonal trends of particle phase will not be discussed further.

3.4. Seasonal variations in seawater

The seasonal patterns of pesticides in seawater are shown in Fig. 3B.The highest concentrations of the three CUPs (excluding trifluralin) in the dissolved phase were identified in August, and the mean concentrations were as follows: chlorothalonil (25.67 ± 8.68 pg L^{-1}), chlorpyrifos (168.63 ± 44.2 pg L^{-1}), and dicofol (241.97 ± 83.03 pg L^{-1}).The mean concentrations of trifluralin in February slightly exceeded the values measured in August due to usage as pre-emergence herbicides to protect winter grains (Mai et al., 2013). Low temperatures and low solar radiation intensity in winter may severely decrease the hydrolysis and photolysis of these compounds, and therefore increase their environmental half-lives (Chernyak et al., 1996). Compared with this study, the concentration of contaminants (excluding trifluralin) in May 2012 only next to that in August 2016 (Table S13). The most predominant contaminant in the summer was dicofol (August 2016: 241.97 ± 83.03 pg L^{-1}), while chlorpyrifos was the most predominant in the spring and winter (May: 98.29 ± 132.1 pg L^{-1}, December 2016, February 2017: 38.83 ± 21 pg L^{-1}). Dicofol is not susceptible to high temperatures and solar radiation intensity owing to its high water solubility (S$_L$) (Table S4) compared to the other target compounds. Thus, the concentrations of dicofol were high in seawater in summer.

3.5. Air-sea gas exchange

To estimate the direction of gas exchange (state of phase equilibrium) between the two phases, the fugacity ratio (FR, f_a/f_w) was calculated for each paired air-seawater sample for the CUPs with sufficient detection frequency (trifluralin, chlorothalonil, and chlorpyrifos) using the Whitman two-film model (Liss and Slater, 1974; Terry and Bidleman, 1995) (Table S15). The FR was calculated by:

$$FR = f_a/f_w = c_aRT_a/(c_wH_{T,sal.})$$

where c_a is the gas phase concentration (ng m^{-3}), c_w is the dissolved phase concentration (ng L^{-1}), R is the universal gas constant (8.31 Pa m^3 k^{-1} mol^{-1}), and T_a is the air temperature (K), which was measured by the research vessel. Henry's law constant $H_{T, sal}$ (Pa m^3 mol^{-1}) was corrected by water temperature and salinity (Table S14). By considering the uncertainty of the water and air concentrations, Henry's law constants, and air temperature during sampling, an equilibrium window for the CUPs was set up as follows: $0.3 < FR < 3.0$ (Bruhn et al., 2003; Lammel et al., 2015; Zhong et al., 2012a). $FR > 3.0$ indicates net deposition, and $FR < 0.3$ indicates net volatilization. Comparison of FR values in air and seawater (Fig. 5) indicated that net volatilization is driven by the relatively high concentrations in seawater and low concentrations in the atmosphere. For instance, the FRs for trifluralin and chlorpyrifos in most samples were <0.3 due to their lower concentrations in air than seawater.

The FRs of chlorothalonil showed a stronger net deposition than other compounds, especially in December (mean FR: 94.92) (see Fig. 5), and the maximum value was identified in WA3 (WW3). The
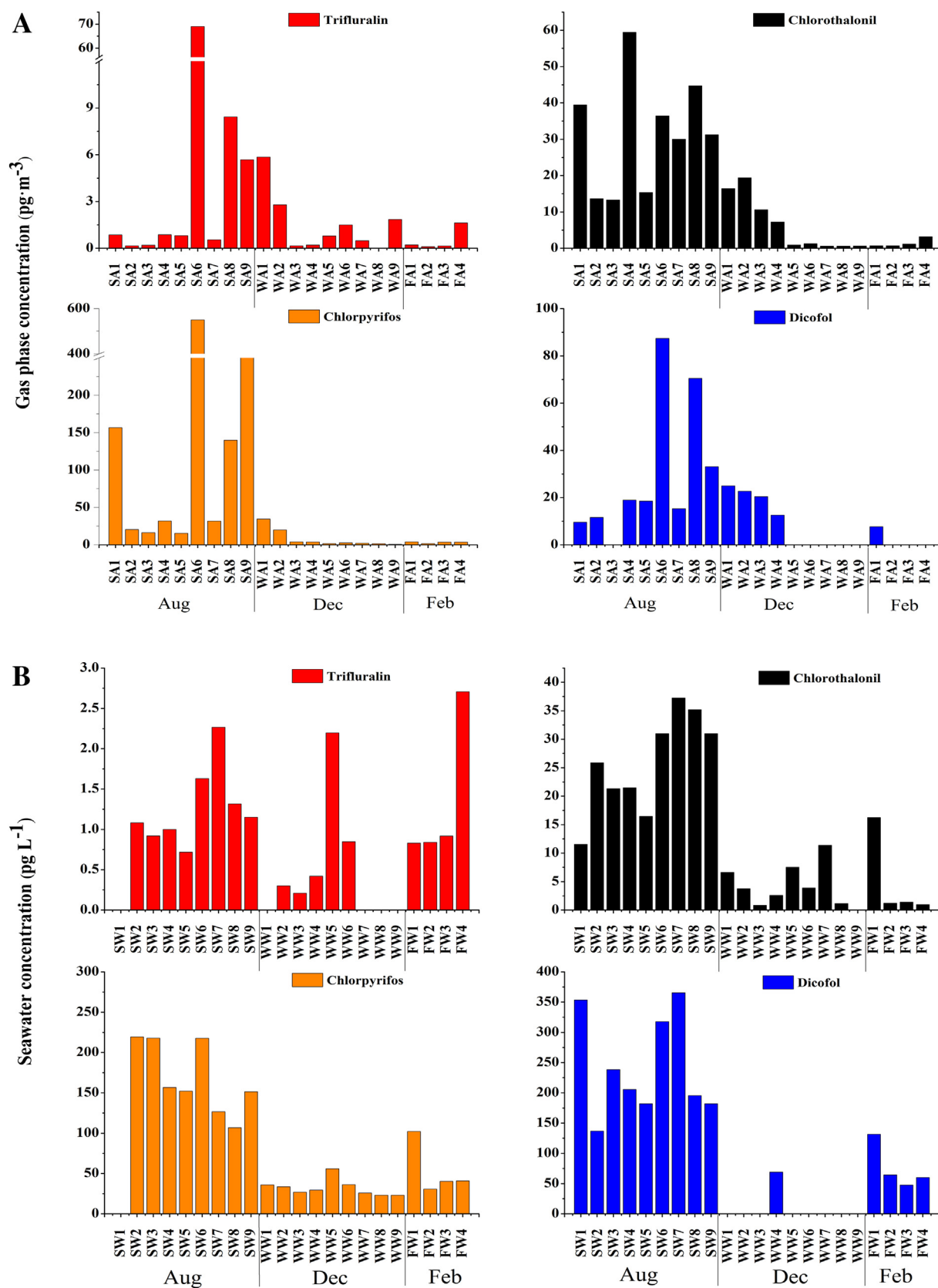
Fig. 3. Concentrations of CUPs in the gas phase (A, unit: pg m^{-3}) and dissolved phase in seawater (B, unit: pg L^{-1}) in August/December 2016 and February 2017.

low concentrations of chlorothalonil in surface seawater samples supported continued deposition from air to water. The calculated FRs indicated that the Bohai Sea continued to act as a sink for chlorothalonil.

Trifluralin showed net volatilization over most of the sampling period. This result was consistent with previous work conducted in the Bohai Sea (Zhong et al., 2014). The direction of air-water gas exchange could
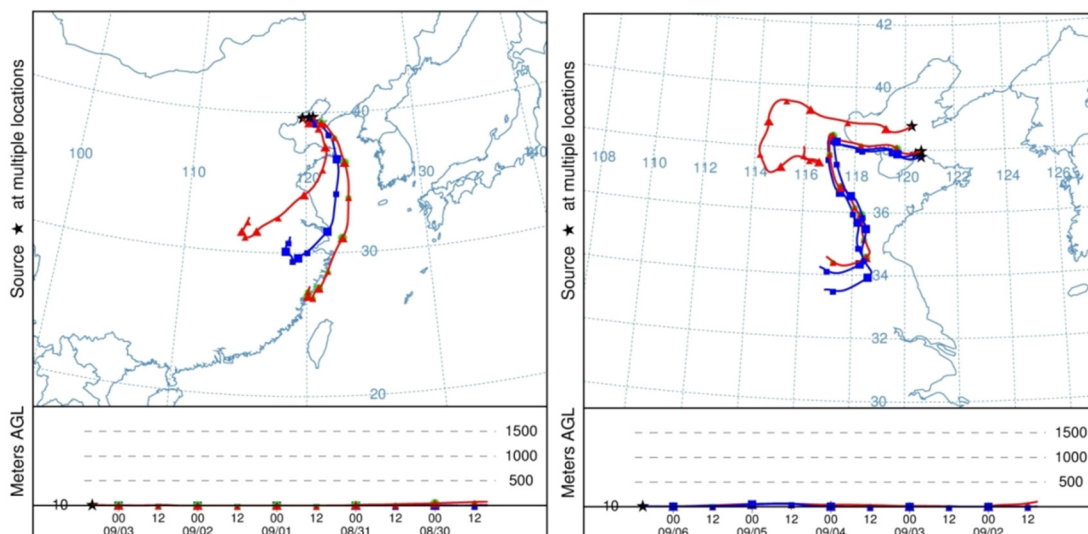
Fig. 4. Two representative air mass back trajectories (BTs) of air samples collected from the Bohai Sea, which reflect those passing through the ocean (left, SA3) and agricultural areas (right, SA6).

be attributed to trifluralin's low water solubility and high volatility. Chlorpyrifos also showed net volatilization in most of the sampling areas, but the mean FR values of the three sampling periods were near the equilibrium (August: 0.38, December: 0.48, February: 0.24). The half-life of chlorpyrifos in air is an order of 100 times lower than that in seawater, <1 day, which could cause relatively higher concentrations in seawater, and have limited potential for LRAT (Muir et al., 2004; Zhong et al., 2014). River discharges is likely to have higher influence for seawater CUPs concentration than air deposition according to our study. In recent years, the distribution of pesticides in rivers around the Bohai Sea in China has been reported by several research groups (Feng et al., 2011; Hu et al., 2010; Tan et al., 2009; Zhong et al., 2011). The highly developed system of agriculture along the river use a large number of pesticides, which applied in the BER may enter Bohai Sea through surface runoff, creating the higher concentration of many contaminants than that in upper atmosphere. Our study confirms that air-seawater exchange is an important pathway for the transport and fate of pollutants. Similarly, the oceans are gradually becoming second sources of POPs to the atmosphere.

Fig. 5. The air-seawater exchange fugacity ratios (fa/fw) of trifluralin, chlorothalonil and chlorpyrifos in the Bohai Sea. The green border highlights an equilibrium window of 0.3 < f_a/f_w < 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusion

This study showed the spatial and seasonal distribution of CUPs in the Bohai Sea, and air mass back trajectories and air-sea exchange were examined to determine the various input sources of CUPs into this area. Trifluralin, chlorothalonil, chlorpyrifos, and dicofol were frequently observed and showed strong seasonal fluctuations in air. Their abundances in air and water were determined by heavy usage during the growing seasons. Back trajectories indicated that samples with elevated concentrations were associated with air masses passing through the eastern coastal area of China (Tianjin Municipality, and the Hebei, Shandong, Jiangsu, and Anhui Provinces), where agricultural production, urbanization, and industrial activities are rapidly growing, leading to the discharge of large amounts of pesticides to the Bohai Sea. The seasonality of target compounds in seawater was not as apparent as that in the air. Higher concentrations of dicofol measured in dissolved phase in the Bohai Sea could be due to the widespread usage of dicofol in China, and the lower HLCs and higher logK_oa values of dicofol also lead to its high abundance in seawater. Volatilization from surface water was proven to be an important source of trifluralin and chlorpyrifos in the air. Atmospheric deposition was found to be a significant input pathway of chlorothalonil into the surface of the Bohai Sea, which has become the second highest source of trifluralin and chlorpyrifos to the atmosphere. As the influence of riverine inputs should be based on samples from rivers and estuaries around the Bohai Sea, further research is still required to identify the multiple factors affecting pesticides.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.11.282.

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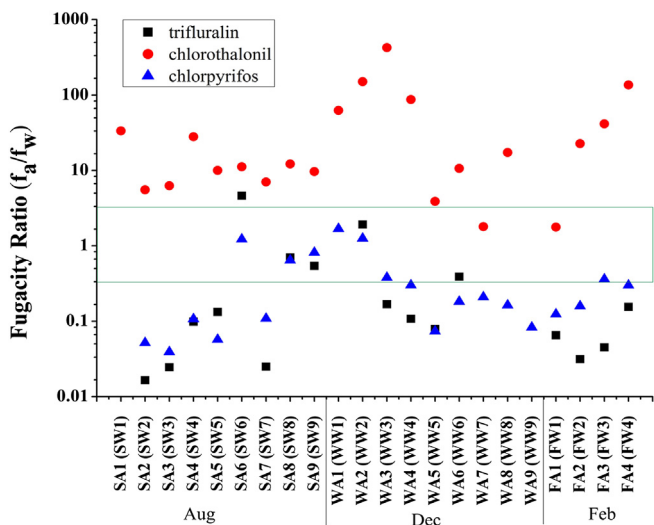
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