



## 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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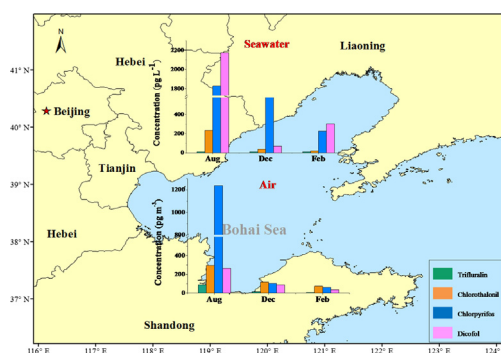
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### HIGHLIGHTS

- 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



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### 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 dicofof) 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  $59.06 \pm 126.94 \text{ pg m}^{-3}$ , and dicofof had the highest concentration dissolved in seawater (mean:  $115.94 \pm 123.16 \text{ pg L}^{-1}$ ). 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](http://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 off-shore 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<sup>2</sup> (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](http://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<sup>3</sup>) 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<sup>3</sup> min<sup>-1</sup>. 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<sup>-1</sup>, and finally to 300 °C at 5 °C min<sup>-1</sup>, 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

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