Fates and ecological effects of current-use pesticides (CUPs) in a typical river-estuarine system of Laizhou Bay, North China[☆]

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ABSTRACT

Current-use pesticides (CUPs) are widely applied in agriculture; however, little is known about their environmental behaviors, especially in the freshwater–seawater transitional zone. Water and sediment samples were collected in an intensively human impacted river (Xiaoqing River) from the headwaters to Laizhou Bay to investigate the distributions and environmental fates of four CUPs: trifluralin, chlorothalonil, chlorpyrifos, and dicofol. These CUPs were frequently detected in water and sediment samples. Σ CUPs in water and sediment samples ranged from 1.20 to 100.2 ng L⁻¹ and 6.6–2972.5 ng g⁻¹ dry weight (dw), respectively. Chlorpyrifos and chlorothalonil were the most abundant CUPs in water and sediment samples, respectively. Spatial distribution of CUPs in the Xiaoqing River aquatic ecosystem was mainly influenced by point sources, agricultural activities, the dilution effect by seawater, and environmental parameters. Field-based sediment water partitioning coefficients, normalized by organic carbon (log K_{oc}), were calculated. Interestingly, temperature and salinity exhibited significant impacts on the distribution of log K_{oc} of the four CUPs. The effect of temperature on the distribution of log K_{oc} of the four CUPs varied between the CUPs. In most water samples, the levels of chlorpyrifos exceed the freshwater screening benchmarks. Hence, urgent control measures need to be devised and implemented.

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1. Introduction

Some historic-use pesticides (HUPs), such as chlordane, -alpha hexachlorocyclohexane (alpha-HCH), beta hexachlorocyclohexane (beta-HCH), and lindane, had been listed as persistent organic pollutants (POPs) by the Stockholm Convention (www.pops.int), and hence have been phased out of use. Demands for alternative and more effective pesticides are increasing from the agricultural sector, and current-use pesticides (CUPs) are thus widely and intensively applied worldwide. Even though most CUPs are considered to be less persistent compared with HUPs (Pucko et al., 2017), they have been widely detected in air, water, and sediment (Carratala et al., 2017; Liu et al., 2018; Moreno-Gonzalez and Leon, 2017; Pascual Aguilar et al., 2017). Additionally, some CUPs were

found in the remote areas (Chernyak et al., 1996; Zhong et al., 2012a). Some CUPs are toxic to humans, including the likely human carcinogens, chlorothalonil (EPA, 2011) and dicofol (EPA, 2006). Dicofol fulfils the criteria set out in Annex D to the Stockholm Convention (UNEP, 2017) and has been listed as a candidate POP. Hence, the CUP contamination of the environment has received considerable attention.

Riverine discharge is a major source of many pollutants and poses a threat to coastal ecosystems (Ma et al., 2016; Pan et al., 2011; Wang et al., 2015; Zhao et al., 2011). Most of the previous studies have focused on the levels and fate of CUPs in marine environments, such as seawater in the Arctic (Zhong et al., 2012a), air-seawater exchange, and sediment distribution of CUPs in the Bohai and Yellow Seas (Zhong et al., 2015; Zhong et al., 2014), ice and fog for the Bering and Chukchi Seas (Chernyak et al., 1996); relatively little attention has been paid to CUPs in the freshwater–seawater transitional aquatic ecosystems (especially for China). Thus, this paper filled the gap of the CUPs distribution in freshwater-seawater transitional zone. Besides, Some studies have investigated the partitioning of POPs between water and sediment for better

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understanding the transport and fate of POPs in aquatic ecosystems (Habibullah-Al-Mamun et al., 2016; Ya et al., 2017). The physico-chemical characteristics of the compounds and some environmental parameters, such as the organic carbon fraction of sediment, water salinity and pH, might influence the partitioning behaviors of these contaminants (Habibullah-Al-Mamun et al., 2016). To our knowledge, the present study is the first to report on the partitioning characteristic of CUPs based on field observations in the world.

Global usage of each of the four CUPs investigated in this paper (trifluralin, chlorothalonil, chlorpyrifos, and dicofol) is over 3600 tonnes year⁻¹ (Hoferkamp et al., 2010) and the market demand for these CUPs in China was also high (Zhong et al., 2014). Shandong Province is the second largest pesticides producer in China (Zhong et al., 2015). In 2015, the consumption of pesticides for agriculture was 0.15 million tonnes in Shandong Province (www.stats.gov.cn). The Xiaoqing River is an important drainage river in the Shandong Peninsula, and it passes through several important mega-cities, including Jinan, Zibo, Binzhou, Weifang, and Dongying, before finally discharging into Laizhou Bay. Besides being an important chemical industrial base, Weifang is also an important agricultural area and is known as the 'Home of Vegetable' in China. This area produces a huge amount of fruit and vegetables for the neighboring Beijing-Tianjin-Hebei metropolitan region. There are also several important pesticide manufacturing plants scattered in the Xiaoqing River Basin. For example, a chemical plant, Shandong Tiancheng Biotechnology Co., Ltd., with an annual production of 15,000 tonnes of chlorpyrifos, is located at Zibo. Our previous studies have shown that the Xiaoqing River is seriously polluted by certain emerging contaminants, such as perfluoroalkyl carboxylic acids and brominated flame retardants (Heydebreck et al., 2015; Zhen et al., 2018b). However, little is known about the situation concerning CUPs in this area, especially in the Xiaoqing River; this is an important issue because CUPs are widely applied in this region.

In this study, trifluralin, chlorothalonil, chlorpyrifos, and dicofol were analyzed in the water and sediment samples of the Xiaoqing River. The aims of this study were to: (1) identify the occurrences and distribution characteristics of the four CUPs in water and sediment samples; (2) provide probably first partition coefficients of CUPs and explore the partitioning behavior and environmental fate of these CUPs between water and sediment; and (3) evaluate the ecological effects of these compounds in coastal environment.

2. Materials and methods

2.1. Sample collection

The Xiaoqing River, with a length of ca. 233 km, is the second longest freshwater river, after the Yellow River, which drains into Laizhou Bay (Zhen et al., 2018a). The Xiaoqing River is a major source of organic pollutants into Laizhou Bay because of the anthropogenic input from nearby cities (He et al., 2018). In 2017, the water quality of the Xiaoqing River was bad (Zhen et al., 2018a). Twenty-two surface sediments (0–5 cm) and 30 water samples (~15 L) were collected in April 2014. Fig. 1 shows each sampling site and Table S1 provides detailed information. Water samples were passed through a glass fiber filter (GF/F, 0.7 µm, Whatman®) to trap water particulates and then through a self-packed Amberlite XAD-2 resin glass column for absorbing the CUPs in the dissolved phase. Sediments were collected using a stainless-steel grab bucket, and then sealed in clean polyethylene (PE) bags. Glass columns were stored at 4 °C. The filters and sediments were stored at –20 °C prior to extraction. Detailed information on the sampling of water and sediments had been reported in previous studies (Jiang et al., 2017; Zhen et al., 2018b).

2.2. Extraction and quantification

Individual trifluralin and chlorpyrifos standards were purchased from AccuStandard (CT, USA). A pesticides-mix 323 containing chlorothalonil and chlorpyrifos were purchased from Dr. Ehrenstorfer GmbH. D₈-Trifluralin was used as a surrogate and was also purchased from Dr. Ehrenstorfer GmbH. PCB 208, used for internal standards, was also purchased from AccuStandard. All samples were spiked with 10 ng of trifluralin-d₁₄ as surrogate standard prior to extraction. An XAD-2 resin glass column was extracted in a modified Soxhlet apparatus for 24 h using dichloromethane (DCM) (Möller et al., 2012; Xie et al., 2011). Filters and sediments were both extracted by DCM in a Soxhlet apparatus for 24 h. All extracts were concentrated to 2–3 mL by a rotary evaporator using hexane (HEX) as a keeper and then cleaned on a 2.5 g silica column (10% water deactivated) topped with 3 g of anhydrous sodium sulfate. The extracts were then eluted with 20 mL of HEX/DCM (1:1) and reduced to a final volume of 50 µL.

Quantification of the four CUPs was measured with a 7890A gas chromatograph equipped with an Agilent 5975C mass spectrometer in the electron capture negative ionization mode with a HP-5MS column (30 m × 0.25 mm i.d. × 0.25 µm film thickness). The oven programs were held at 60 °C for 1 min, ramped to 150 °C at 30 °C min⁻¹, and then to 300 °C at 5 °C min⁻¹, which was held for 5 min (Liu et al., 2018). The front inlet temperature was held at 290 °C, and both the ion source and quadrupole temperature were 150 °C. A splitless injection mode was used.

2.3. QA and QC

All water columns were precleaned with three individual solvents (methanol, acetone, and DCM) each for 24 h prior to use. In addition, filters and glassware were baked at 450 °C for 5 h prior to sampling. Three field blanks for filters and XAD resin columns were collected, respectively. Besides, three lab blanks were done for filters, XAD resin columns, and sediment. The method detection limits (MDLs) for filters and XAD resin columns were calculated based on the mean values of the solvent plus three standard deviations of the field blanks. The MDLs for sediments were calculated based on the mean values of the solvent plus three standard deviations of the lab blanks. MDLs ranged from 0.09 to 2.91 pg L⁻¹ for water samples, and from 3.64 to 288.8 pg g⁻¹ dry weight (dw) for sediment samples, respectively. The mean recoveries of D₈-Trifluralin were 82 ± 36%, 135 ± 24%, and 220 ± 64% for water filters, water columns, and sediments, respectively. None of the CUP concentrations in this study were corrected by recoveries. In addition, if the CUP values were below the MDLs, they were considered not detected (n.d.) as discussed below.

2.4. Calculation of distribution coefficient and statistical analysis

The distribution coefficient (K_d) is a common parameter in the evaluation of partitioning of organic pollutants in water (Liu et al., 2013). The sediment–water partition coefficient K_d of CUPs (L kg⁻¹) and the organic carbon normalized partition coefficient (K_{oc}) of CUPs (L kg⁻¹) were calculated following equation (1) and equation (2), respectively:

$$K_d = 10^3 \times \frac{C_s}{C_w} \quad (1)$$

$$K_{oc} = \frac{K_d}{\overline{TOC}} \quad (2)$$

where C_s and C_w were the concentrations of CUPs in sediment and

Fig. 1. Location of sampling sites from the Xiaoqing River to the Laizhou Bay.

water, with units of $\text{ng g}^{-1} \text{ dw}$ and ng L^{-1} , respectively; total organic carbon (TOC) was the relative content of total organic carbon in the sediments.

Statistical analyses were performed with PASW Statistics 18 software (IBW, USA). Descriptive statistics were calculated using Microsoft Excel 2010. Pearson correlations analysis was used to examine the correlations between log Koc and environmental parameters (salinity, temperature, pH, and TOC). The sampling site map was drawn by ArcMap (ArcGIS, ESRI, USA). The distribution of CUPs and log Koc were analyzed using Origin Pro 8.5 (OriginLab, USA).

3. Results and discussion

3.1. Occurrence of current-use pesticides in water samples

Means and ranges of CUP concentrations in water samples from the Xiaoqing River are listed in Table 1, and more details are presented in Table S2. CUPs were detected in both particulate and dissolved phases of water samples. CUPs were found to be ubiquitous in the dissolved phase of the Xiaoqing River with 100% detection frequencies for individual target compounds (except for chlorothalonil which had a detection frequency of 83%). The detection frequencies of chlorpyrifos, trifluralin, dicofol, and chlorothalonil in the suspended particulate matters (SPM) were 100%, 97%, 87%, and 40%, respectively. The observed data indicated that CUPs are widely used in this region. CUP concentrations were much higher in the dissolved phase than in the SPM. In particular, the most abundant compounds in the dissolved phase were chlorpyrifos and dicofol, with concentrations in the ranges of $0.55\text{--}86.3 \text{ ng L}^{-1}$, and $0.48\text{--}50.9 \text{ ng L}^{-1}$, respectively. The dissolved concentrations were in the ranges of $0.006\text{--}1.40 \text{ ng L}^{-1}$, and n.d. to 0.034 ng L^{-1} for trifluralin and chlorothalonil, respectively. Chlorpyrifos and dicofol were also the predominant CUPs in the SPM, with concentrations ranging from 0.012 to 6.71 ng L^{-1} , and n.d. to

3.03 ng L^{-1} , respectively. Additionally, trifluralin and chlorothalonil in SPM had concentration ranges of n.d. to 0.21 ng L^{-1} , and n.d. to 0.015 ng L^{-1} , respectively. Therefore, chlorpyrifos and dicofol were the most abundant CUPs in both dissolved and SPM phases. A previous study had reported that domestic demand of chlorpyrifos was 18,000 tonnes in 2008, and the recent dicofol consumption in China was 3500 tonnes yr^{-1} (Zhong et al., 2015). Hence, the high levels of chlorpyrifos and dicofol in water indicate their wide application in this study area. In particular, the high concentrations of dicofol and chlorpyrifos in the dissolved phase were probably controlled by their relatively higher solubility (0.8 and 0.001 mg L^{-1} in 25°C in water, respectively) (Zhong et al., 2015).

The mean chlorpyrifos concentration measured in the Xiaoqing River water (sum of SPM and dissolved phase) was higher than those reported in other studies in freshwater ecosystems - e.g., $1.95\text{--}8.68 \text{ ng L}^{-1}$ for the Júcar River of Spain (Pascual Aguilar et al., 2017) and $0.053\text{--}0.165 \text{ ng L}^{-1}$ for the Guanting Reservoir, Beijing (Xue et al., 2005). The mean chlorpyrifos concentration was also approximately three orders of magnitude higher than those previously reported in seawater (Liu et al., 2018; Pucko et al., 2017; Zhong et al., 2014; Zhong et al., 2012b), but lower than that in marine ice (170 ng L^{-1}) from the Bering and Chukchi Seas (Chernyak et al., 1996). More details are provided in Table S3. Dicofol is widely applied in China. To the best of our knowledge, this is the highest dicofol concentration reported in water (Table S3). Trifluralin is commonly used as pre-emergence herbicide and registered to be used in China. Generally, the concentrations of trifluralin in fresh water were higher than those in seawater (Liu et al., 2018; Pucko et al., 2017; Zhong et al., 2014), but lower than that in freshwater from the Guanting Reservoir (Xue et al., 2005). There is very limited data about chlorothalonil in freshwater and previous studies were focused on chlorothalonil in seawater (Table S3). Undoubtedly, the observed chlorothalonil concentration in the Xiaoqing River water was higher than those in open sea

Table 1
Concentrations of CUPs in water and sediment samples from the Xiaoqing River.

Phase	Trifluralin		Chlorothalonil		Chlorpyrifos		Dicofol	
	Range	mean	Range	mean	Range	mean	Range	mean
SPM (ng L ⁻¹)	n.d. - 0.21	0.017	n.d. - 0.015	0.002	0.012–6.71	1.73	n.d. - 3.03	0.32
Dissolved phase (ng L ⁻¹)	0.006–1.40	0.15	n.d. - 0.034	0.008	0.55–86.3	24.6	0.48–50.9	7.80
Sediment (ng/g dw)	0.40–1209	140	2.46–2578	227	0.61–3.94	1.69	n.d. - 9.20	2.39

water (Liu et al., 2018; Zhong et al., 2012a). As previously mentioned, Shandong is a large agricultural province. The huge usage of CUPs around the Xiaoqing River might be responsible for the high levels observed in this study. In summary, the contamination of these four CUPs in the Xiaoqing River water is considered to be relatively serious, and deserving of further study.

3.2. Occurrence of current-use pesticides in sediment samples

The four CUPs were detected in all sediment samples of the Xiaoqing River (except for dicofol, which had a 95% detection frequency). Unlike in water samples, chlorothalonil and trifluralin were the most abundant CUPs in sediment. This result might be ascribed to the relatively high Koc and low solubility of trifluralin (Zhong et al., 2015). The concentrations ranged from 2.46 to 2578 ng g⁻¹ dw, 0.40–1209 ng g⁻¹ dw, n.d. to 9.20 ng g⁻¹ dw, and 0.61–3.94 ng g⁻¹ dw for chlorothalonil, trifluralin, dicofol, and chlorpyrifos, respectively (Table 1). To the best of our knowledge, this is the first report of chlorothalonil in sediment environment (Table S4). In addition, the trifluralin concentration measured in the Xiaoqing River sediment was also the highest compared to those previously reported in sediment - e.g., n.d. to 62.7 ng g⁻¹ dw for the Guanting Reservoir (Xue et al., 2005) and n.d. to 0.0098 ng g⁻¹ dw for the Bohai and Yellow Seas (Zhong et al., 2012b). This indicates that trifluralin and chlorothalonil are widely used in this area. Previous studies have also demonstrated relatively higher chlorpyrifos concentrations in sediment (Hintzen et al., 2009; Li et al., 2011; Moreno-Gonzalez and Leon, 2017). However, the contamination of chlorpyrifos was at a moderate level compared with those in other studies (Table S3). Generally, the dicofol concentrations in the Xiaoqing River sediment were three orders of magnitude lower than that in fresh water from the Guanting Reservoir (Xue et al., 2005), which had dicofol concentrations ranging from 120 to 1010 ng g⁻¹ dw, but higher than that in sediments from the Bohai and Yellow Seas (Zhong et al., 2012b).

3.3. Spatial distributions

High levels of the four CUPs in sediments were observed at the X10 station (Fig. 2 and Fig. 3). In the water samples, dicofol also showed the highest concentration also at X10. Although chlorpyrifos in the water had relatively low concentrations at X10, the highest chlorpyrifos level was detected at site X11. The site X10 was located in the Zhulong River, which is influenced by Huantai County and the city of Zibo. High concentrations of some persistent organic pollutants (POPs), such as HFRs (halogenated flame retardants) and PFASs (perfluoroalkyl substances), have been reported at X10 in the same sample batch (Heydebreck et al., 2015; Zhen et al., 2018b). The similar distribution of CUPs and POPs at this site might result from a substantial point source near the tributary Zhulong River, but the exact sources of the CUPs remain unknown. It also indicates that the Zhulong River contributes to the contamination of CUPs in the Xiaoqing River.

In the present study, the upstream of the Xiaoqing River (X1–17) was divided into two sections: JN (X1–X6) and ZB (X7–X17). JN and

ZB are located in Jinnan City and Zibo City, respectively. Concentrations of dicofol in water samples from JN were generally lower than those from ZB. Furthermore, the mean concentrations of trifluralin and chlorothalonil in the water samples in JN were three and twelve times lower than those in ZB, respectively. For the water samples, the concentrations of chlorpyrifos at sites (X8, X7, X11, and X12) were influenced by tributaries (Fig. 1), flowing from the farmland around Zibo, and were higher than those at other sampling sites. Whereas ZB is influenced by agricultural pollution, JN is more influenced by domestic pollution. In 2016, the pesticides consumption of the Zibo City was up to 5140 tonnes and the total sown area of farm crops was more than 250,000 ha (Shandong Provincial Bureau of Statistics, 2017). Recently, Sun et al. (2016) reported that agricultural activities resulted in the high levels of pesticides in the Yangtze River Delta. Similar distributions for four CUPs were also found in sediment samples in the Xiaoqing River (X1–X17). Apart from the point source, agricultural activities are also a factor influencing the distribution of CUP concentrations.

For water samples, high levels of CUPs (including trifluralin, chlorpyrifos, and dicofol) were observed from the Xiaoqing River estuary (X18–X23) compared to the bay samples (X24–X30) (Fig. 2). There were significant negative correlations between these three CUPs and salinity in water samples from site X18 to site X30 ($p < 0.01$, Table S7). The concentrations of these three CUPs decreased from the estuary to bay and this may be a result of the strong dilution effect of the seawaters. For sediment samples, concentrations of trifluralin and chlorothalonil decreased from site X18 to site X30, which was opposite to distance from the Xiaoqing River (Figs. 1 and 3). The distributions of these two CUPs in the estuary–bay were affected by river input. Hence, the Xiaoqing River was an important source for CUPs in Laizhou Bay. In addition, chlorothalonil concentrations were relatively evenly distributed between estuary and bay for water samples. Zhong et al. (2014) found that high levels of chlorothalonil for water in the southern Yellow Sea were influenced by the East China Sea and depended on ocean currents. Chlorothalonil was also used as an antifouling paint biocide for ships (Feng et al., 2018). Chlorothalonil emission from shipping activities might be another important factor for distribution of chlorothalonil in the estuary–bay system.

In terms of sediment, Fig. 3 showed that chlorpyrifos and dicofol were quite uniformly distributed from site X18 to site X30. Besides, the levels of chlorpyrifos and dicofol from estuary to bay were both higher than that of trifluralin, which was the most contaminated pollutant in sediment in the Xiaoqing River. The log Koc of chlorpyrifos and dicofol were increased from site X18 to site X30 with increasing salinity, indicating that capacity adsorption of these two CUPs on sediment was increased from site X18 to site X30 (discussed in section 3.4). Hence, the salinity might be related to distribution of these two CUPs. There was a significant correlation between TOC (total organic carbon) and chlorpyrifos or dicofol (Table S8), and the similar trends had occurred between the TOC and these two CUPs in sediments from site X02 to site X30 (Fig. S2). Both trifluralin and TOC for sediment had the highest levels at site X10. Previous study has shown that TOC has high affinity for CUPs and OCPs (Hu et al., 2009; Zhong et al., 2015). Hence, the

Fig. 2. Spatial distribution of trifluralin (a), chlorothalonil (b), chlorpyrifos (c) and dicofol (d) in the water samples of the Xiaoqing River.

Fig. 3. Spatial distribution of trifluralin (a), chlorothalonil (b), chlorpyrifos (c) and dicofol (d) in the sediment samples of the Xiaoqing River.

distribution of these two CUPs in sediments might be to some extent affected by the TOC.

3.4. Partitioning behavior of CUPs between water and sediment

Log K_{oc} values can be used to estimate the sorption of hydrophobic pollutants on sediments and the results are shown in Table S5. In the present study, the average log K_{oc} ranged from 3.89 (chlorpyrifos) to 8.29 (chlorothalonil) (Table S5). Compared to the log K_{oc} of chlorpyrifos and dicofol, the log K_{oc} of chlorothalonil and trifluralin was relatively high, suggesting its strong partitioning in sediment; this is consistent with the relatively high levels of chlorothalonil and trifluralin observed in sediments. Furthermore, chlorpyrifos and dicofol with low log K_{oc} had relatively low concentrations in sediments. Table S5 also shows that the log K_{oc} of trifluralin in this study was much higher than log K_{oc} values in the

database of the EPI (Estimation Programs Interface) suite™ developed by US Environmental Protection Agency. However, chlorpyrifos and dicofol had comparable log K_{oc} compared to those from the database of the EPI suite™. The log K_{oc} values could be estimated using the Sabljic molecular connectivity method with improved correction factors or the traditional method based on measured log K_{ow} values (Agency, 2019). In the present study, no significant relationship was observed between log K_{ow} values of model estimation and the log K_{oc} calculated based on the measured data in this study. The fundamental reason is that the absorption behavior of CUPs might have differences in the n-octanol phase and in the organic matters of sediments. Besides, the field-based measured log K_{oc} might be affected by environmental parameters (discussed in section 3.4).

Previous studies had demonstrated that some environmental parameters, such as organic carbon of sediments and salinity,

Fig. 4. The distribution of log Koc for four CUPs and temperature in the Xiaoqing River Basin.

temperature, and pH of water samples, might affect the partitioning of POPs between water and sediment (Habibullah-Al-Mamun et al., 2016; Lamichhane et al., 2016). Temperature could affect both the sorption equilibrium and the sorption kinetics of hydrophobic organic contaminants (HOCs) (Enell et al., 2005). Fig. 4 shows the distribution of log Koc for individual CUPs in the Xiaoqing River Basin. There was an obvious increase of log Koc for chlorpyrifos and dicofo from site X22 to site X30; there was a decrease in temperature of water samples from site X22 to site X30. A similar distribution of salinity and log Koc for two of these CUPs occurred from the estuary to the bay (Fig. S3). The most remarkable characteristic was that there were significant correlations between all target compounds and temperature (Table S6 and Fig. S1). Among the correlations, both chlorpyrifos and dicofo had obviously negative correlations with temperature. The log Koc for chlorpyrifos and dicofo increased from site X18 to site X30, which was to some extent responsible for the similar concentrations between the river and bay with the dilution effect of seawater. Previous studies have shown that the adsorptions of HOCs on the soil or sediment decreased when temperature increased (Jiang et al., 2018; Lamichhane et al., 2016). On the other hand, the trend of HOCs transferring to the sorbent surface was less than that of the tendency to escape from sorbent surface to the solution with the increasing temperature in the exothermic process (Lamichhane et al., 2016). In addition, both chlorpyrifos and dicofo had positive correlations with salinity ($p < 0.05$, Table S6). Lamichhane et al. (2016) had suggested that the water solubility of polycyclic aromatic hydrocarbons (PAHs) decreased with increasing the salinity, which ultimately increased the PAHs adsorption capacity on sediment. Thus, it can be inferred that the temperature and salinity are two key factors influencing the distributions of log Koc for chlorpyrifos and dicofo.

In contrast, log Koc for trifluralin and chlorothalonil decreased from site X22 to site X30 and the distributions of log Koc for these two CUPs were similar to that of temperature for water samples. Table S6 showed that both trifluralin and chlorothalonil had a positive correlation with temperature. Ren et al. (2019) had demonstrated that the effect of temperature on the sorption of HOCs was dependent on the type of HOC. Unlike previous studies, in the present study, the absorption capacity of HOCs to the soil or humic acid (an important composition of sediment) increased with increasing temperature from 5 °C to 35 °C (Jia et al., 2010;

Lamichhane et al., 2016). In addition, desorption hysteresis of HOCs to humic acid occurred at all studied temperatures (5 °C, 25 °C, and 35 °C) (Jia et al., 2010). The adsorption of HOCs on graphene nanomaterials was reduced as the temperature increased when HOCs were at a low level in water (Ren et al., 2019); this was consistent with the relatively low levels of trifluralin and chlorothalonil in water samples. Thus, temperature had a significant impact on the sediment adsorption capacity of these two CUPs and ultimately affected log Koc of the CUPs.

3.5. Evaluation of ecological effects

The ecological effects of CUPs in freshwater can be evaluated by comparing CUP concentrations in this paper with freshwater screening benchmarks. Sediment screening benchmarks for these four CUPs are not available. Hence, only the ecological effects of CUPs in freshwater are considered here. Freshwater screening benchmarks for trifluralin, chlorothalonil, and chlorpyrifos are 0.2, 0.18, and 0.002 $\mu\text{g L}^{-1}$, respectively (Canadian Environmental Quality Guidelines, www.ccme.ca). The freshwater screening benchmark for dicofo is 19.8 $\mu\text{g L}^{-1}$ (Zhong et al., 2015). Table S1 shows the concentrations of individual CUPs in current study. The concentrations of CUPs reported in this paper are much lower than the freshwater screening benchmarks for trifluralin, chlorothalonil, and dicofo. It should be noted that the chlorpyrifos concentrations for the sites from X1 to X23 were all higher than the freshwater screening benchmarks. Hence, more attention should be paid to control the use and emission of chlorpyrifos.

4. Conclusion

Trifluralin, chlorothalonil, chlorpyrifos, and dicofo were ubiquitous in the Xiaoqing River Basin. For the water samples, CUP concentrations mainly occurred in the dissolved phase, and chlorpyrifos and dicofo were the most prevalent CUPs. For sediments, trifluralin and chlorothalonil were the most prevalent. The high levels of CUPs in this study area can be explained by the widespread recent application of these pesticides in the Xiaoqing River Basin. The factors affecting the distribution of CUPs in the Xiaoqing River Basin included point sources, agricultural activities, dilution of seawater, salinity, and TOC. This study provided the distribution coefficients for the four CUPs. The distribution coefficients of

chlorpyrifos and dicofol from estuary to bay were mainly controlled by the combination of temperature and salinity. For trifluralin and chlorothalonil, temperature was the main factor affecting their log K_{oc} distribution. More research is needed to understand the fate and behavior of CUPs in aquatic environments. The ecological effects of CUPs in freshwater indicated that chlorpyrifos exceeds the freshwater screening benchmarks. Hence, immediate control measures are recommended.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2019.05.141>.

Declarations of interest

None.

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