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# Influence of dissolved organic carbon on multimedia distribution and toxicity of fipronil and its transformation products in lotic waterways

Weizong Li, Hao Hu, Fen Liu, Huizhen Li\*, Jing You

School of Environment and Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou 511443, China

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## ABSTRACT

Environmental fate and ecological impacts of fipronil and its transformation products (FIPs) in aquatic environment have caused worldwide attention, however, the influence of dissolved organic carbon (DOC) on multimedia distribution, bioavailability, and toxicity of FIPs in field waterways was largely unknown. Here, we collected 11 companion water and sediment samples along a lotic stream in Guangzhou, South China. FIPs were ubiquitous with total water concentrations ranging from 1.22 to 43.2 ng/L ( $14.8 \pm 12.9$  ng/L) and fipronil sulfone was predominant in both water and sediment. More than 70% of FIPs in aqueous phase were bound to DOC and the  $K_{DOC}$  values of FIPs were approximately 1–2 orders of magnitude higher than  $K_{d,s}/K_{OC}$ , emphasizing the significance of DOC in phase partitioning and transport of FIPs in aquatic environment. Water and sediment samples were more toxic to *Chironomus dilutus* than *Hyallela azteca*, and FIPs (especially fipronil sulfone) pronouncedly contributed toxicity to *C. dilutus*. Toxic units (TU) based on freely dissolved concentrations in water determined by solid phase microextraction significantly improved toxicity estimation of FIPs to the invertebrates compared to TUs based on aqueous concentrations. The present study highlights the significance of DOC association on fate and ecological risk of hydrophobic insecticides in lotic ecosystem.

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## Introduction

Insecticides have drawn worldwide attention due to their threat on aquatic ecosystem (Stehle and Schulz, 2015). Once entering aquatic environment, hydrophobic insecticides tend to bind to suspended particulate matters (SPM) and colloids such as dissolved organic carbon (DOC). More than 70% of aqueous pyrethroids are bound to DOC in a laboratory spiking water-sediment system (Delgado-Moreno et al.,

2010), suggesting DOC serves as a critical phase in controlling phase distribution of hydrophobic contaminants in aquatic system (Liu et al., 2021). DOC binding greatly influences the bioavailability of aqueous contaminants depending on many factors including the types of DOC, contaminants, and biota (Haftka et al., 2013; Li et al., 2018; Rizzuto et al., 2021; Yang et al., 2006a, 2006b). In field waterways, the DOC-contaminant complexes are relatively stable and subjected to long-distance transport, which subsequently change the spatiotemporal distribution and ecological risk of the contaminants (Bai et al., 2019; Lin et al., 2018; Nybom et al., 2021; Ripszam et al., 2015).

\* Corresponding author.

E-mail: [lihuizhen@jnu.edu.cn](mailto:lihuizhen@jnu.edu.cn) (H. Li).

To date, most of studies quantified organic contaminants in aqueous and SPM phases through filtration, which ignored the role of DOC in phase distribution and partitioning assessment in field waterways (Li et al., 2022). The amount and source characteristics of DOC are influencing the phase distribution of contaminants in field waterways (Liu et al., 2021; Nybom et al., 2021), yet it is difficult to calculate the concentrations of DOC-bound contaminants using laboratory-derived partitioning coefficients. Passive sampling has been developed to determine the freely dissolved concentrations of organic contaminants in aqueous phase, providing an effective approach in improving the measurements of phase partitioning coefficients (Delgado-Moreno et al., 2010; You et al., 2011). Furthermore, the freely dissolved concentrations significantly improved sediment toxicity estimation of cypermethrin to the amphipod *Hyalalella azteca* (Li et al., 2013a).

Insecticides are easily transformed via photolysis, hydrolysis, and biotic degradation in waterways (Gunasekara et al., 2007; Singh et al., 2021). Changes in structure and functional groups of the transformation products (TPs) may pronouncedly alter their physiochemical properties, phase partitioning behaviors, and intrinsic toxicity (Lao, 2021; Schlenk et al., 2001; Weston and Lydy, 2014). Sinclair and Boxall (2003) compared toxicity of 37 parent compounds and their 89 TPs to aquatic organisms, and found that 70% of TPs were similarly or less toxic but 30% were more toxic than the respective parent compounds (Sinclair and Boxall, 2003). Fipronil, a systemic and broad-spectrum phenylpyrazole insecticide, has been widely used in agricultural and residential pest control (Tingle et al., 2003) and is easily degraded in aquatic environment (Connelly, 2001). Extensive use of fipronil worldwide has caused its residues in waterways high up to that can cause hazardous effects to aquatic species, including rivers and streams (e.g., > 2.1 µg/L) (Ensminger et al., 2013), residential runoff (e.g., 0.13–12.6 µg/L) (Gan et al., 2012) and agricultural runoff (e.g., > 19 µg/L) (Schlenk et al., 2001). A statewide investigation in the U.S. found that fipronil residues in 70% and 20% of the urban and agricultural waterways, respectively, exceeded its aquatic life benchmark (Stone et al., 2014), calling for concerns on the toxicity and risk of this insecticide to aquatic species. FIPs are highly toxic to nontarget aquatic organisms, e.g., the 50% lethal concentrations (LC50) were 0.076 µg/L for *Chironomus dilutus* (Weston and Lydy, 2014). Furthermore, its TPs show comparable or even more toxic than the parent compound (Gibbons et al., 2015; Gunasekara et al., 2007; Pisa et al., 2015). Sediment-associated FIPs in the Pearl River, China have been identified as major toxicity contributors to benthic invertebrate *C. dilutus* (Li et al., 2013b; Li et al., 2019). The influence of phase partitioning on environmental fate and toxicity of FIPs in aquatic ecosystems is still limitedly studied, which is important for understanding aquatic ecological risk of FIPs.

The main objectives of the present study were to (1) assess the occurrence and distribution of FIPs in water-sediment system of an urban stream in South China; (2) investigate the multimedia partitioning of FIPs in the water-sediment system with a consideration of DOC-binding; (3) evaluate the toxicity of FIPs to two aquatic invertebrates (*C. dilutus* and *H. azteca*) and examine if freely dissolved concentrations can improve

the accuracy of toxicity assessment compared to total concentrations.

## 1. Materials and methods

### 1.1. Sample collection

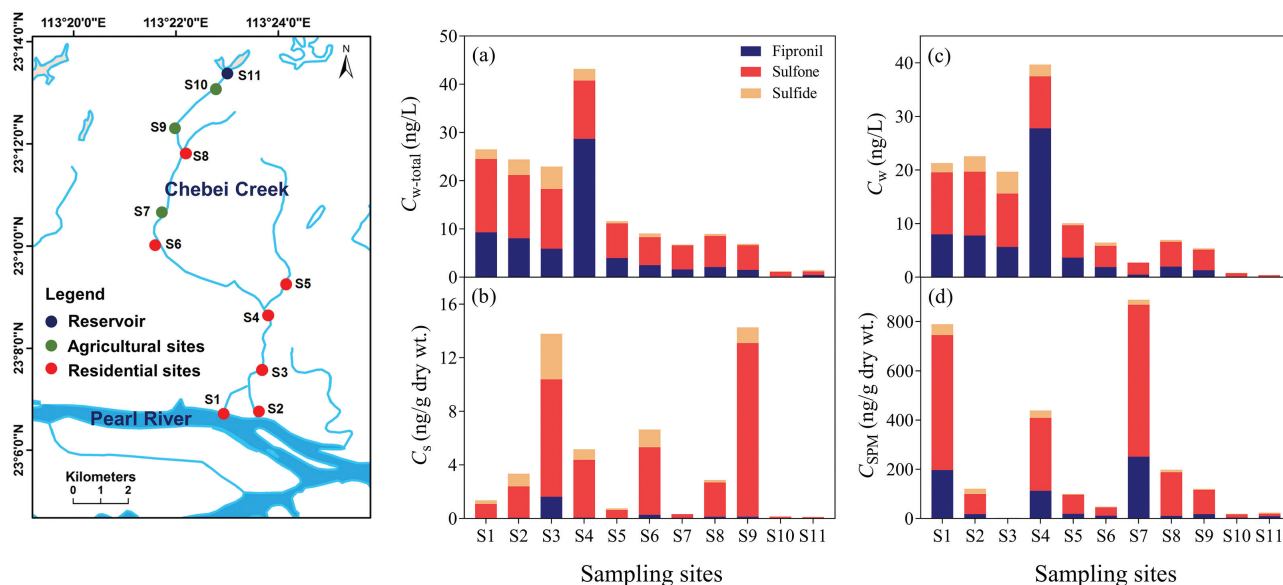
Sediment and water samples were collected from an urban stream (Chebei Creek) in Guangzhou, China (Fig. 1) which has an overall length and drainage area of 25.4 km and 80 km<sup>2</sup>, respectively. Chebei Creek originates from a drinking water reservoir, flows through residential, industrial, and agricultural areas, and finally empties into the Pearl River, which is the largest river in South China. In total, 11 pair of surface water and sediment samples were collected using active sampling method along Chebei Creek in September, 2015 and the sites were scattered in different functional areas. Water samples were collected using a stainless bucket and filled up two pre-cleaned 4-L brown glass jars. One jar of water that was used for chemical analysis was added with 1 mL of 1 mol/L HCl and 1 mL of 1 mg/mL NaN<sub>3</sub> to reduce microbial degradation of contaminants. The other jar of water without HCl and NaN<sub>3</sub> was used for the bioassays. Surface sediment (5 cm) was collected using a stainless-steel spade shovel and stored in pre-cleaned glass jars after sieving through a 2-mm sieve on site to remove large debris and rocks. The water and sediment samples were immediately transported to the laboratory and stored at 4°C prior to biological and chemical analyses within one week except that the sediment samples for chemical analysis were stored at -20 °C. Brief descriptions on the sampling sites and characteristics of water and sediment samples are presented in Appendix A Table S1.

### 1.2. Sample extraction and cleanup

Water sample was filtered using a 0.7-µm glass fiber filter (GFF, Whatman) to obtain aqueous phase and SPM. Waterborne FIPs were extracted using liquid-liquid extraction (LLE) with 50 mL of dichloromethane after adding 50 ng of surrogates and 2 g of NaCl to aqueous samples. The FIPs in SPM and sediment samples were extracted using a CW-2000 ultrasound-assisted microwave extractor (Xintuo Company) according to a previous method (Li et al., 2010). The extract was cleaned using solid phase extraction (SPE) cartridges packed with 600 mg of primary secondary amine (PSA) and 300 mg of granular carbon black (Supelco). The cleaned extract was concentrated, solvent exchanged to 0.5 mL of hexane, and analyzed on GC/MS after adding the internal standard. Detailed procedures on sample preparation are presented in Appendix A.

### 1.3. Solid phase microextraction

In the laboratory, passive sampling, namely solid phase microextraction (SPME) was applied to measure the freely dissolved concentrations of FIPs in surface water and sediment porewater. An envelope contained SPME fibers coated with 30 µm of polydimethylsiloxane (PDMS) were used to obtain



**Fig. 1** – Map of the sampling sites in Chebei Creek, Guangzhou, China and concentrations of fipronil and its two transformation products (fipronil sulfone and fipronil sulfide) in (a) water (total concentration including aqueous and suspended particulate (SPM) phases); (b) sediment; (c) aqueous phase (including freely dissolved and dissolved organic carbon (DOC)-bound concentrations) and (d) SPM from Chebei Creek.

bioavailable concentrations of FIPs in water and sediment after 14- and 28-days testing, respectively. At the end of tests, SPME fibers were retrieved from the water or sediment samples, washed using distilled water, dried using paper towel, and sonicated using 5 mL of acetone for three times after adding 10 ng of the surrogates. The extracts were cleaned using PSA, solvent exchanged to hexane, and finally concentrated to 50  $\mu$ L for analyzing FIPs on GC/MS after adding the internal standard. More details on SPME are presented in Appendix A.

#### 1.4. Toxicity tests

Ten-d sediment and 2-d water bioassays using the midge *C. dilutus* and amphipod *H. azteca* were conducted in the present study. For sediment bioassays, 80 g of wet sediment and 250 mL of reconstituted moderately hard water were added to a 400-mL beaker. After settling overnight, 10 individuals of the midges (3<sup>rd</sup> instar) or amphipod were added to each beaker. The bioassay was conducted at  $23 \pm 1$  °C under a 16-hr light: 8-hr dark photoperiod in an automated water delivery system. Overlying water (~150 mL) was changed twice daily. Organisms were fed 1 mL of ground fish food per day, and water quality (dissolved oxygen, conductivity, temperature, pH) was monitored daily. At the end of the exposure, mortality of the organisms was recorded by sieving sediment with a 500-mm sieve. For water bioassays, 300 mL of field water, 10 g of clean sand (for the midges), and 10 individuals of organisms were added to a 400-mL beaker. No water changes nor feeding were performed during the 2-d bioassay. Negative controls were performed simultaneously with the field collected samples and all tests were conducted in five replicates. Sediment from a drinking water reservoir in Conghua, Guangzhou was used as control sediment. The control sediment showed no

acute lethality to the two species and no target analytes were detected.

#### 1.5. Instrumental analysis

The FIPs were analyzed on GC/MS (Shimadzu QP-2010-plus series) in negative chemical ionization (NCI) mode and detailed information is presented in the Appendix A. The amounts of SPM in the water samples were determined by weighing dry suspended particles in the GFF membrane. The content of dissolved organic carbon ([DOC]) in dissolved aqueous phase was analyzed using an elemental analyzer (ElementarVario EL III) after adding phosphoric acid. Total organic carbon (OC) and black carbon (BC) contents in the sediments were analyzed using the elemental analyzer. After removing inorganic carbon using 1 mol/L HCl, the sediments were heated at 60 °C for 24 hr or at 450 °C for 4 hr, and used to analyze the OC and BC contents, respectively.

#### 1.6. Quality assurance and quality control

During sampling, field blanks were conducted by transporting clean water, GFF membrane, and sediment to the field and back to the laboratory. These field blanks were treated and analyzed along with the field samples. At each sampling site, three replicates of water or sediment were collected and combined as one sample. The instrument was calibrated by analyzing calibration standards every 10 samples and the variations of each analyte in the calibration check standards were within 20%. A batch of quality control samples, including solvent blanks, matrix (water, GFF membrane, and sediment) blanks, and matrix spikes were analyzed simultaneously with field samples. No target compounds were detected in the blanks and the recoveries of FIPs

in matrix spikes were from 79.3% to 152%. Two surrogates, 4,4'-dibromooctafluorobiphenyl and decachlorobiphenyl were added to each sample to evaluate the performance of sample preparation processes, and recoveries were  $69.6\% \pm 19.0\%$  and  $94.9\% \pm 25.0\%$ , respectively.

### 1.7. Data analysis

SPME was applied to determine the freely dissolved concentrations of FIPs in water ( $C_{w-free}$ ) and sediment porewater ( $C_{pw}$ ) from Chebei Creek based on equilibrium partitioning theory using the following equation:

$$C_{w-free} \text{ or } C_{pw} = \frac{C_{PDMS}}{K_{PDMS-w}} \quad (1)$$

where,  $C_{PDMS}$  was chemical concentration in PDMS membrane at equilibrium and  $K_{PDMS-w}$  was the partitioning coefficient between PDMS and water.

Phase distribution of FIPs in water-sediment system was evaluated using the following partitioning coefficients:

$$K_{DOC} = \frac{C_w - C_{w-free}}{C_{w-free} \times [DOC]} \quad (2)$$

$$K_{d-SPM} = \frac{C_{SPM}}{C_{w-free}} \quad (3)$$

$$K_{d-s} = \frac{C_s}{C_{pw}} \quad (4)$$

$$K_{OC} = \frac{C_{s-OC}}{C_{pw}} = \frac{C_s/f_{OC}}{C_{pw}} \quad (5)$$

where,  $K_{DOC}$  was the partitioning coefficient between DOC and water,  $C_w$  was the concentration in filtered water determined by LLE,  $[DOC]$  was the DOC content in filtered water;  $K_{d-SPM}$  was the partitioning coefficient between SPM and water,  $C_{SPM}$  was the concentration in SPM on dry weight basis;  $K_{d-s}$  was the partitioning coefficient between sediment and porewater,  $C_s$  was the sediment concentration on dry weight basis;  $K_{OC}$  was the partitioning coefficient between sediment OC and porewater,  $C_{s-OC}$  was the OC normalized sediment concentration, and  $f_{OC}$  was the content of organic carbon in sediment.

Observed toxicity of water and sediment to the testing organisms based on the bioassays was calculated using Eq. (6). Toxic units of individual FIPs in water ( $TU_w$ ) and sediment ( $TU_s$ ) to the testing organisms based on chemical analysis were calculated using Eqs. (7)–(10).

$$\text{Observed toxicity} = \frac{\text{Mortality}}{50} \quad (6)$$

$$TU_w = \frac{C_w}{4 - d \text{ water LC50}} \quad (7)$$

$$TU_{w-free} = \frac{C_{w-free}}{4 - d \text{ water LC50}} \quad (8)$$

$$TU_s = \frac{C_{s-OC}}{10 - d \text{ sediment LC50 (OC normalized)}} \quad (9)$$

$$TU_{s-pw} = \frac{C_{pw-OC}}{10 - d \text{ sediment LC50 (OC normalized)}} \quad (10)$$

$$C_{pw-OC} = C_{pw} \times K_{OC} \quad (11)$$

Due to the lack of 2-d water thresholds of FIPs, 4-d median lethal concentration (LC50) to *H. azteca* and 4-d EC50 to *C. dilutus* (Weston and Lydy, 2014) were used for calculating the respective  $TU_w$  values. The 10-d sediment OC normalized LC50 values (Hintzen et al., 2009; Maul et al., 2008) were used for calculating  $TU_s$  to the organisms. The  $C_{pw-OC}$  is OC-converted freely dissolved concentration in porewater (Eq. (11)).

## 2. Results and discussion

### 2.1. Occurrence of FIPs in water and sediment of Chebei Creek

Fipronil and its two TPs were frequently detected in the water and sediment samples collected from Guangzhou Chebei Creek, South China, with total water concentrations (including aqueous and SPM phases) and sediment concentrations of FIPs ranging from 1.22 to 43.2 ( $14.8 \pm 12.9$ ) ng/L and from 0.12 to 14.3 ( $4.44 \pm 5.20$ ) ng/g dry wt., respectively (Fig. 1 and Appendix A Fig. S1, Table S2). Geographically, residues of FIPs in water steadily increased from the source (reservoir, S11) to the end (S1) of the stream where Chebei Creek empties to the Pearl River, except for one residential site (S4) with extraordinarily high residue of fipronil (Fig. 1a). Accidentally fresh input of residential discharge containing high residues of fipronil and the confluence of two stream branches may be the reasons. Residues of FIPs in water from the tree nursery (S10) and agricultural area (S9) were much lower than those in water from residential areas (Appendix A Table S1), suggesting that fipronil was mainly used for pest control, e.g., fire ant control in residential area (Li et al., 2013b). More crowded residents in downstream than upstream residential areas induced higher usage and inputs of fipronil to the stream. In addition, transport of waterborne chemicals from upstream may drive the accumulation of FIPs in downstream, especially the contaminants in more mobile aqueous phase and fine SPMs (Delgado-Moreno et al., 2011). Spatial distribution of FIPs in Chebei Creek sediments was different from that in water (Fig. 1). The highest concentration of FIPs was observed in sediment from S9, and long-term use of fipronil in agriculture may be the reason. Concentration of FIPs in sediment from S3 located in the downstream was the second highest among the 11 sites, indicating a possible transport of FIPs from the upstream and/or high residential input around the sampling site. The different spatial distribution of FIPs in water and sediment was reasonable because the grab water samples reflected the instantaneous pollution status in lotic water, while sediment recorded pollution within a longer time period.

Residues of FIPs in Guangzhou Chebei Creek, South China were compared to that from other regions (Table 1). Total water concentrations of FIPs in Chebei Creek were comparable to that from urban areas in California, the U.S. (Weston and Lydy, 2014) and Singapore (Xu et al., 2011), agricultural areas in California (Delgado-Moreno et al., 2011) and Japan (Iwafune et al., 2011), and embayment habitats in California (Du et al., 2022). Alternatively, lower concentrations of FIPs

Table 1 – Concentrations of fipronil and its transformation products in water and sediment from different regions

Location	Land use	Sampling time	Fipronil		Fipronil sulfone		Fipronil sulfide		Water sample preparation	Reference
			Water (ng/L)	Sediment (ng/g dry wt.)	Water (ng/L)	Sediment (ng/g dry wt.)	Water (ng/L)	Sediment (ng/g dry wt.)		
California, USA	Urban stream water after rain events	2012	C <sub>total</sub> : <RL <sup>a</sup> -49.1		C <sub>total</sub> : <RL-36.0		C <sub>total</sub> : <RL-14.8		LLE without filtration	(Weston and Lydy, 2014)
California, USA	Urban residential runoff	2006-2008	C <sub>total</sub> : <RL-10004		C <sub>total</sub> : <RL-1961		C <sub>total</sub> : <RL-330		LLE without filtration	(Gan et al., 2012)
California, USA	Agriculture (coastal watersheds)	2009	C <sub>total</sub> : ND <sup>b</sup> -34.8	ND-0.4	C <sub>total</sub> : ND-17.9	ND-3.6	C <sub>total</sub> : ND-6.4	ND-0.9	LLE without filtration	(Delgado-Moreno et al., 2011)
Florida, USA	Urban (residential water)	2009-2010	C <sub>total</sub> : ND-207		C <sub>total</sub> : ND-57.8		C <sub>total</sub> : ND-26.9		LLE without filtration	(Wu et al., 2015)
Louisiana, USA	Agriculture (rice cultivation)	2001	C <sub>total</sub> : ND-6410 (medium: 230.5)		C <sub>total</sub> : ND-282 (medium: 23.5)		C <sub>total</sub> : ND-507 (medium: 22.5)		LLE without filtration	(Mize et al., 2008)
Texas, USA	Urban (residential water)	2006		<RL-3.92 (0.85±1.00)		<RL-6.72 (1.24±1.32)		<RL-1.74 (0.48±0.52)		(Hintzen et al., 2009)
Ibaraki, Japan	Agriculture (drainage)	2008-2009	C <sub>total</sub> : <RL-5.2		C <sub>total</sub> : <RL-1.3		C <sub>total</sub> : <RL-0.9		SPE after filtration	(Iwafune et al., 2011)
Singapore	Urban	2008-2009	C <sub>total</sub> : 1-72						SPE without filtration	(Xu et al., 2011)
Guangzhou, China	Urban (drainage)	2009	C <sub>total</sub> : ND-466	ND-35						(Yang et al., 2010)
Guangzhou, China	Urban (stream water)	2011		<RL-9.14 (1.89±2.84)		<RL-40 (7.84±9.85)		<RL-10.5 (3.15±3.26)	LLE after filtration	(Li et al., 2013b)
Los Angeles, USA	Urban (effluent-dominated)	2011-2013	C <sub>total</sub> : <RL-13.6 (3.72±4.07)		C <sub>total</sub> : <RL-10.6 (2.80±2.60)		C <sub>total</sub> : <RL-2.03 (0.95±0.70)		LLE without filtration	(Lao, 2021)

(continued on next page)

**Table 1 (continued)**

Location	Land use	Sampling time	Fipronil		Fipronil sulfone		Fipronil sulfide		Water sample preparation	Reference
			Water (ng/L)	Sediment (ng/g dry wt.)	Water (ng/L)	Sediment (ng/g dry wt.)	Water (ng/L)	Sediment (ng/g dry wt.)		
Bohai region, China	Residential, industrial (River water)	2018	$C_{total}$ : <RL-4.0 in summer (me-dian:0.38)	$C_{total}$ : <RL-8.9 in summer (me-dian:0.92)	$C_{total}$ : <RL-3.2 in summer (me-dian:0.39)	<RL-4.7 in fall (me-dian:0.18)	<RL-5.24	SPE without filtration	(Naumann et al., 2022)	
			<RL-8.6 in fall (me-dian:0.12)	<RL-3.09	<RL-9.3					
Southern California Bight, USA	Embayment habitats	2018	ND-0.62	<RL-3.09	ND-0.84	<RL-9.3	<RL-5.24		(Du et al., 2022)	
Yangtze river estuary, China	Offshore	2017	ND-0.62	<RL-3.09	ND-0.84	<RL-9.3	<RL-5.24	SPE after filtration	(Pan et al., 2020)	
Guangzhou, China	Urban (stream water)	2015	$C_{total}$ : 0.12-28.7 (5.83±8.16)	$C_s$ : <RL-1.62 (0.22±0.47)	$C_{total}$ : 0.75-15.2 (7.65±4.89)	$C_s$ : 0.08-12.9 (3.46±4.12)	$C_s$ : <RL-3.4 (0.75±1.01)	$C_w$ : LLE after filtration	The present study	
			$C_{SPM}$ : 0.07-1.3 (0.51±0.42)	$C_{pw}$ : 0.32-1.26 (0.88±0.27)	$C_{SPM}$ : 0.29-3.62 (1.75±1.0)	$C_{pw}$ : 0.17-1.37 (0.61±0.28)	$C_{pw}$ : 0.08-0.43 (0.18±0.09)	$C_{w-free}$ : SPME before filtration		

<sup>a</sup> Reporting limit.

<sup>b</sup> Not detected.

were detected in Bohai (Naumann et al., 2022) and Yangtze River in China (Pan et al., 2020). On the contrary, extremely high FIP concentrations in water were observed in residential areas in California (Gan et al., 2012) and agricultural areas from Louisiana, the U.S. (Mize et al., 2008), with peak concentrations being orders of magnitude higher than the concentrations in Chebei Creek. Residues of FIPs in sediment from Chebei Creek were comparable to that in the U.S. (Delgado-Moreno et al., 2011; Hintzen et al., 2009). It is worth mentioning that sediment concentrations of FIPs in the present study were 2–8 folds lower than those in sediments collected in 2011 from the corresponding sampling sites (Li et al., 2013b), indicating that the usage of fipronil may decrease during these years.

## 2.2. Compositions of FIPs in the lotic Chebei Creek

Compositions of fipronil and its oxidation TP (sulfone) and reduction TP (sulfide) in water and sediment of Chebei Creek were distinct among phases (Appendix A Fig. S2). In the aqueous and SPM phases of water, sulfone was the predominant component, accounting for  $62\% \pm 17\%$  and  $71\% \pm 12\%$  of FIPs, respectively, followed by fipronil ( $30\% \pm 17\%$  and  $20\% \pm 9\%$ , respectively), and sulfide was the least with percentages less than 10% on average. The results suggested fipronil was extensively and selectively transformed to the oxidation product and partially to the reduction product in Chebei Creek. The pattern was different from that in urban streams in the U.S., e.g., water concentrations of fipronil were higher than (Weston and Lydy, 2014) or comparable to sulfone (Lao, 2021). Usage frequency, environmental parameters that influence transformation process, and physicochemical properties of chemicals (e.g., hydrophobicity) are critical to occurrence and distribution of FIPs in field waterways (Gunasekara et al., 2007). Fipronil is degraded in waterways via multiple routes including microbial degradation, hydrolysis, and photolysis, which is extensively influenced by environmental factors like temperature, pH, and microbial species (Bonmatin et al., 2015). Different environmental conditions may cause different degradation rates and pathways for fipronil, resulting in different compositions of FIPs in Chebei Creek and waterways in the U.S. (Singh et al., 2021). In addition, more fresh input of fipronil to the waterways during the sampling time period may be another reason for the higher percentage of fipronil in the waterways in the U.S. than that in Chebei Creek (Weston and Lydy, 2014). To date, most studies analyzed FIPs in water by considering aqueous and/or SPM phases as a whole phase, but little is known about the compositions of freely dissolved and DOC-bound FIPs. Different from FIP composition in whole water, fipronil predominated FIPs ( $68\% \pm 8\%$ ) in the freely dissolved phase instead of sulfone ( $22\% \pm 8\%$ ). Freely dissolved contaminants in water are considered as the bioavailable and toxic fraction to organisms (Li et al., 2013a; Reichenberg and Mayer, 2006). Therefore, bioaccumulation and toxicity potential of fipronil should be appreciated in toxicity assessment although fipronil was extensively transformed and the oxidation TP was dominant in whole water. In DOC phase, sulfone became the predominant component ( $59\% \pm 16\%$ ), followed by fipronil ( $33\% \pm 16\%$ ). Relatively lower hydrophobicity of fipronil ( $\log K_{ow}$ : 4.0) than sulfone and sulfide ( $\log K_{ow}$ : 4.42 and 4.82, respectively) may be

a reason for its predominance in the freely dissolved phase, while sulfone dominated DOC phase.

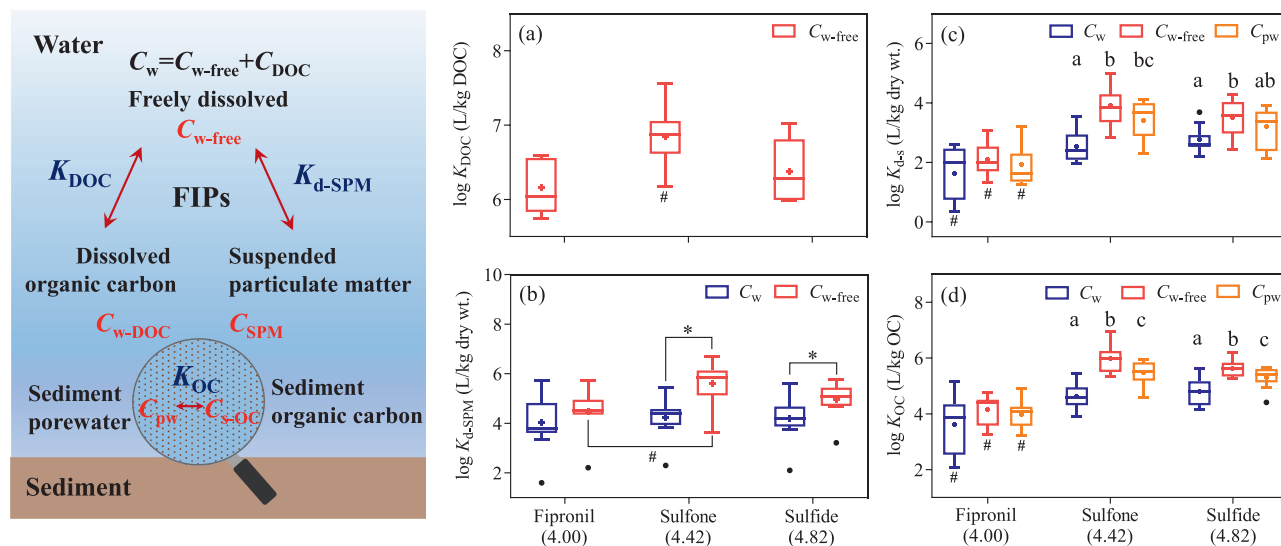
The composition of FIPs in sediment was different from that in water. Sulfone was still predominant in sediment ( $77\% \pm 9\%$ ), but sulfide became the second abundant component ( $16\% \pm 7\%$ ), and fipronil only accounted for 7% of FIPs on average. The higher percentage of TPs than the parent compound suggested additional transformation occurred in sediment and/or higher adsorption of TPs than fipronil in sediment particles due to higher hydrophobicity of TPs. Fipronil is transformed to sulfone under both aerobic and anaerobic conditions, and sulfide is formed only under anaerobic condition (Lin et al., 2008). Both TPs were detected in Chebei Creek sediment, suggesting both aerobic and anaerobic condition were presented in this stream. The predominant occurrence of sulfone in Chebei Creek sediment was consistent with those in California and Texas, the U.S. (Delgado-Moreno et al., 2011; Hintzen et al., 2009).

Different compositions of FIPs in water and sediment demonstrated that field occurrence in water-sediment system was not only related to its usage pattern, but also influenced by the transport, phase distribution, and transformation process. Quantitative partitioning behavior of FIPs in water (freely dissolved, DOC, and SPM phases) and sediment would help to better understand their fate in lotic waterways.

## 2.3. Multimedia partitioning of FIPs in water-sediment system

To date, most of the studies examined total concentrations of FIPs in field water by accounting both aqueous (including freely dissolved and DOC-bound fractions) and SPM phases (Table 1), which may cause large uncertainty in risk assessment due to overestimation of bioavailable concentrations and underestimation of the DOC-bound fractions (Li et al., 2013a; Mayer et al., 2014; Yang et al., 2006b). In the present study, the percentages of FIPs in freely dissolved, DOC, and SPM phases in Chebei Creek water were separately quantified (Appendix A Table S3). The contents of DOC in Chebei Creek ranged from 1.17 to 5.75 mg/L, which were comparable to that in the Pearl River Basin reported in previous studies (e.g., 0.99–8.05 mg/L) (Gong et al., 2019). Waterborne FIPs in Chebei Creek were mainly bound to DOC, accounting for  $74\% \pm 13\%$ ,  $74\% \pm 11\%$ , and  $76\% \pm 7\%$  for fipronil, sulfide, and sulfone, respectively, which were comparable to pyrethroids with 65%–94% in aqueous phase being bound to various types of DOC (Delgado-Moreno et al., 2010). The distribution of FIPs in the freely dissolved and SPM phases varied across compounds (Appendix A Table S3). Fipronil had higher percentage in freely dissolved phase ( $16\% \pm 8\%$ ) than SPM ( $10\% \pm 8\%$ ), while the two TPs were preferable in SPM phase, especially for sulfone, with only 2% in freely dissolved phase. FIPs in freely dissolved and DOC phases were highly dynamic and easily migrated to the downstream of Chebei Creek after entering the lotic waterways, highlighting the necessity to take DOC as a separate phase in fate and risk assessment of these contaminants in field waterways.

As shown in Fig. 2, multimedia distribution scenarios of FIPs in water-sediment system included the partitioning between surface water and DOC ( $K_{DOC}$ ), surface water and SPM



**Fig. 2 – The observed (a)  $K_{DOC}$ , (b)  $K_{d-SPM}$ , (c)  $K_{d-s}$ , and (d)  $K_{OC}$  of fipronil, fipronil sulfide, and fipronil sulfone in water-sediment of Chebei Creek in Guangzhou, China. The  $K_{d-s}$  and  $K_{OC}$  values were calculated from water concentrations measured by liquid-liquid extraction ( $C_w$ ) or passive sampler ( $C_{w-free}$  and  $C_{pw}$ ), respectively. The values in the brackets below the compound names are the  $\log K_{OW}$  values of the individual compounds. The three solid lines in the box represent 25%, 50%, and 75% of the coefficients. Error bars represent standard deviations. The “\*” or different letters on the top of the box imply significant differences ( $p < 0.05$ ) between the measurements of the same compound. The “#” on the bottom of the box represent significant differences ( $p < 0.05$ ) among various compounds of the same measurement.**

( $K_{d-SPM}$ ), surface water/porewater and sediment ( $K_{d-s}$ ), as well as surface water/porewater and sediment OC ( $K_{OC}$ ) (Appendix A Tables S4 and S5). Field-based  $\log K_{DOC}$  values of fipronil, sulfone, and sulfide in Chebei Creek were  $6.15 \pm 0.36$ ,  $6.85 \pm 0.35$ , and  $6.38 \pm 0.41$  L/kg DOC, respectively, indicating that sulfone exhibited the greatest affinity to DOC (Fig. 2). To our knowledge, laboratory- or field-based  $K_{DOC}$  values of FIPs were not previously reported. For organic halogen compounds including polybrominated diphenyl ethers (PBDEs) and organochlorine pesticides (OCPs),  $K_{DOC}$  values were positively correlated with  $K_{OW}$  (i.e.,  $\log K_{DOC} = 0.35 \times \log K_{OW} + 2.84$ ,  $r^2 = 0.90$ ) (Li et al., 2015). Based on this regression,  $\log K_{DOC}$  values of fipronil, sulfone, and sulfide were calculated to be 4.24, 4.39, and 4.53, respectively, which were about 2 orders of magnitude lower than the values derived in the present study. Binding mechanism of FIPs with DOC may be different from that of these organic halogen compounds due to different electron withdrawing ability of the binding atoms to DOC (Nuerla et al., 2013) and/or different steric configurations (Cho et al., 2002). In addition, environmental parameters (e.g., temperature, pH, and salinity) and different types of DOC in lotic waterways may substantially influence binding capacity of DOC to FIPs (Rizzuto et al., 2021), which would cause high variations between field- and laboratory-based partitioning coefficients (Li et al., 2022). Temperature is an important factor controlling the sorption kinetics of organic contaminants in DOC, so different temperature between field and laboratory water would cause variations between field- and laboratory-based partitioning coefficients (Pan et al., 2008). Haftka et al. (2013) found that sorption of acidic and basic organic contaminants to DOC was pH-dependent, i.e., generally increased with increasing pH due to the gradual deprotonated of carboxylic and phe-

nolic acid groups on DOC. For inland river connecting estuary, sorption capacity variation along gradient salinity is of significance in fate assessment of organic contaminants (Li et al., 2022). Kuivikko et al. (2010) observed a decreased sorption of PBDEs and PAHs to DOC with increasing salinity from 0 to 0.5‰. It was possibly explained by the formation of rigid spheres which hindered the binding of organic contaminants to hydrophobic regions at high ionic concentrations. Organic carbon origin has been demonstrated to significantly influence the fate of hydrophobic organic contaminants due to the variable sorption capacity, e.g., the  $K_{OC}$  values of PCBs based on terrestrial derived OC were 0.2–1.0 log units lower than those based on the marine derived OC (Nyblom et al., 2021). The relative contributions of riverine DOC origin in the study area, i.e., the Pear River, were 46%–55%, 27%–33%, and 17%–21% for soil, sewage, and newly produced freshwater plankton, respectively, based on the isotopic mixing model (Ye et al., 2018). Diverse DOC origins supported the site-specific sorption of DOC to hydrophobic organic contaminants, e.g., FIPs in the study area although the specific OC origins were not analyzed in our study.

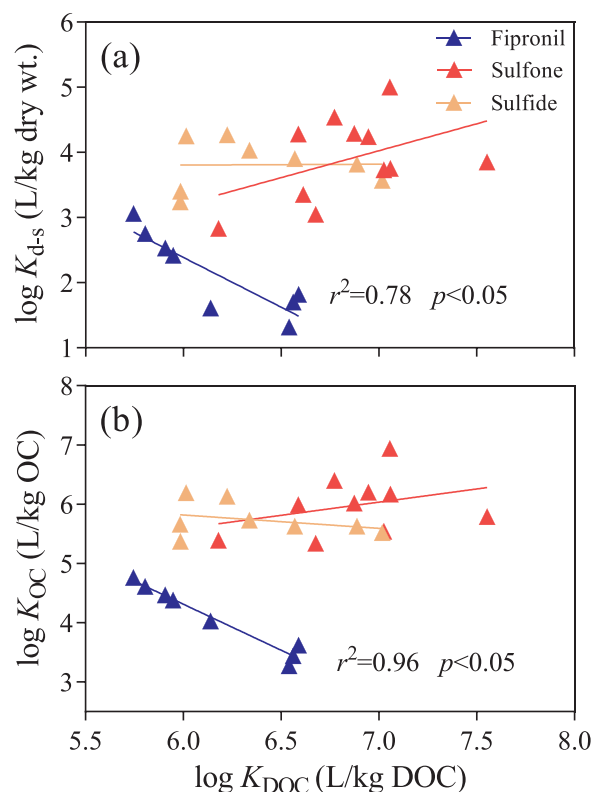
Aqueous concentrations accounting for freely dissolved and DOC-bound fractions were conventionally applied to calculate  $K_d$  (partitioning between water and SPM or sediment) and  $K_{OC}$  (partitioning between water and sediment OC), which may significantly underestimate the partitioning coefficients by constraining on the contaminants bound to DOC (Lee et al., 2003). To evaluate the role of DOC in phase partitioning, the coefficients of FIPs in Chebei Creek were calculated based on aqueous concentrations determined by LLE ( $C_w$ ) and freely dissolved concentrations determined by SPME ( $C_{w-free}/C_{pw}$ ). Consistent with  $K_{DOC}$ ,  $K_{d-SPM}/K_{d-s}$ , and  $K_{OC}$  of the two TPs were



significantly higher than their respective coefficients of the parent compound, as reported in previous studies (Lao et al., 2016; Lin et al., 2009; Ying and Kookana, 2001). The  $\log K_{OC}$  values of FIPs based on  $C_{pw}$  and  $C_{w-free}$  were comparable, indicating similar partitioning of FIPs in porewater-sediment OC and surface water-sediment OC. The results implied the appropriateness of using surface water concentrations in calculating  $K_{OC}$  when porewater concentrations were not available, but freely dissolved concentrations instead of aqueous concentrations are required to reduce uncertainty due to significant binding of hydrophobic contaminants in DOC.

The field  $C_{w-free}$ -based  $\log K_{OC}$  values of fipronil, fipronil sulfone, and fipronil sulfide in Chebei Creek were  $4.14 \pm 0.52$ ,  $5.98 \pm 0.49$ ,  $5.64 \pm 0.32$  L/kg OC, respectively, which were close to the laboratory derived  $C_{pw}$ -based  $\log K_{OC}$  values of 4.51, 5.80, and 5.60 L/kg OC, respectively (Brennan et al., 2009). In addition, the  $C_{pw}$ -based  $\log K_{OC}$  of fipronil ( $3.98 \pm 0.50$ ) was in well agreement with the laboratory  $C_{pw}$ -based  $\log K_{OC}$  ( $3.77 \pm 0.33$ ) determined by Wang et al. (2020). However, these field- and laboratory-based  $K_{OC}$  values determined in the present study, Brennan et al. (2009), and Wang et al. (2020) were one to two orders of magnitude higher than the laboratory-based  $K_{OC}$  values determined by Lin et al. (2009) who used aqueous concentrations in the calculations. The results demonstrated that freely dissolved concentrations effectively reduced uncertainty in phase partitioning assessment in filed lotic waterways even under fluctuating conditions, while aqueous concentration may significantly underestimate partitioning coefficients like  $K_{OC}$ . Moreover, the relative standard deviation (RSD) of  $\log K_{OC}$  based on  $C_{pw}$  (7.2%–12.4%) and  $C_{w-free}$  (5.7%–12.6%) of FIPs in the 10 field samples were lower than those based on  $C_w$  (9.8%–28.9%), supporting that passive sampling serves as an effective approach in measuring partitioning coefficients across water-sediment systems under both laboratory and field conditions.

In comparison, field-based  $K_{DOC}$  values of FIPs in Chebei Creek were one to two orders of magnitude higher than their respective  $K_{OC}$  values, indicating binding capacity of FIPs to DOC in surface water was greater than OC in sediment of Chebei Creek. Previous studies showed that different characteristics of OC sources may show large difference in affinity to organic contaminants (Tang et al., 2016; Ying and Kookana, 2001). The sorption process of natural OC and organic contaminant is complex (Pignatello et al., 2020). Natural OC with a high contribution of aliphatic carbon chains showed high affinity toward organic contaminants, which implied that OC origin from terrestrial and aquatic environments had different sorption capacity against organic contaminants (Nybom et al., 2021). In addition, the hydrophobicity of OC has strong influence on sorption toward organic contaminants for OC with low hydrophobicity, and the significance of OC properties on sorption decreases with increasing hydrophobicity (Liu et al., 2021). Adding DOC significantly enhanced the desorption of sediment-associated pyrethroids, implying that DOC may show stronger sorption affinity to pyrethroids than sediment OC (Delgado-Moreno et al., 2010). Significantly negative correlations were observed between field-based  $K_{DOC}$  and  $K_{d-s}/K_{OC}$  for fipronil in Chebei Creek water-sediment system (Fig. 3), implying that more fipronil would be bound to the DOC phase as  $K_{DOC}$  increases and consequently less with the sed-

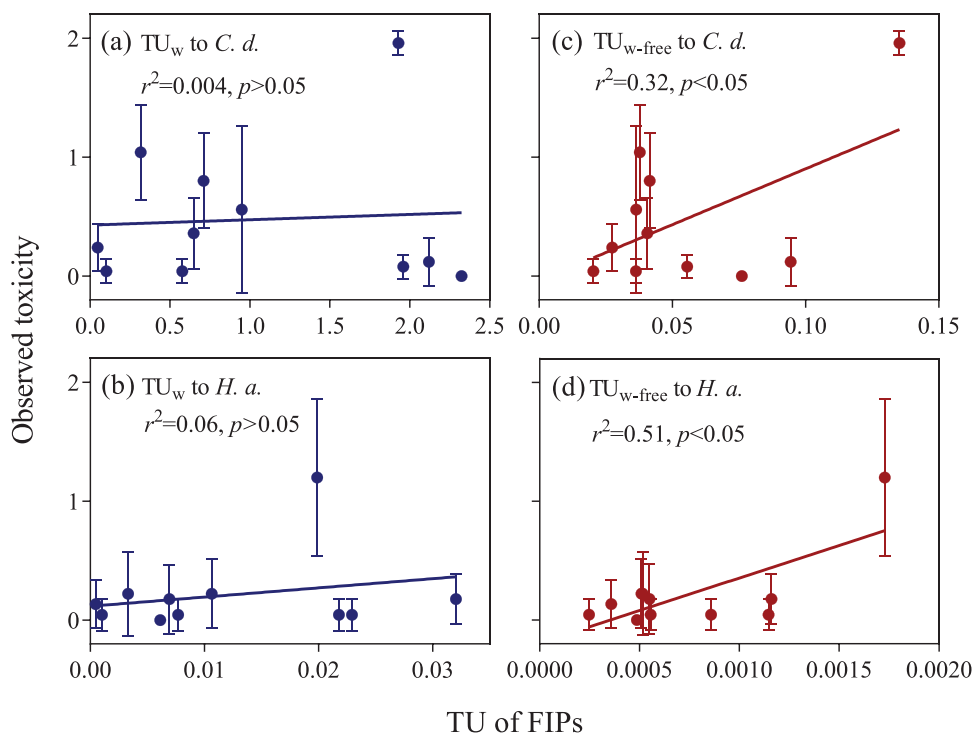


**Fig. 3 – Significantly negative correlations ( $p < 0.05$ ) between  $\log K_{DOC}$  and  $\log K_{d-s}/\log K_{OC}$  of fipronil in Chebei Creek in Guangzhou, China. No significant correlations were observed for fipronil sulfide and fipronil sulfone. The  $K_{d-s}$  and  $K_{OC}$  values were calculated using the freely dissolved concentrations.**

iment phase. Similar result that  $K_d$  of pyrethroids decreased with increasing  $K_{DOC}$  was observed based on laboratory spiking tests (Delgado-Moreno et al., 2010). Water-sediment partitioning coefficients ( $K_d/K_{OC}$ ) are one of the most significant parameters governing the distribution and transport of contaminants in aquatic ecosystem (Li et al., 2022). Given that the formed DOC-FIP complexes are relatively stable in aqueous phase yet not ready to be sorbed by SPM and/or sediment, the complexes are subjected to long-distance transport in lotic waterways. As such, aqueous concentration in downstream may be elevated. Therefore, it is critical to understand the impact of DOC on the occurrence, distribution, and toxicity contribution of FIPs in lotic waterways.

#### 2.4. Bioavailable TU significantly improved toxicity estimation of FIPs to aquatic invertebrates

Mortality of the midges and amphipods were  $<9\%$  in the controls, indicating the effectiveness of bioassay results. Overall, five of 11 water samples (45%) from Chebei Creek exhibited significant ( $p < 0.05$ ) toxicity to *C. dilutus* after 2-d exposure with mortality ranging from 0% to  $98\% \pm 4\%$ , while only one water sample (S3) exhibited significant toxicity to *H. azteca* with mortality ranging from 0% to  $60\% \pm 33\%$ . All



**Fig. 4 – The correlation between observed toxicity in 2-d water bioassays to *Chironomus dilutus* and *Hyalella azteca* and the toxic units derived from fipronil, fipronil sulfide, and fipronil sulfone (FIPs) in surface water from Chebei Creek measured by (a/b) liquid-liquid extraction (TU<sub>w</sub>) and (c/d) passive sampling (TU<sub>w-free</sub>).**

the 11 sediments except for S11 locating in the origin of the creek (Longdong reservoir) exhibited significant toxicity to the midges, and six of them (55%) caused 100% mortality during the 10-d exposure. Comparatively, only two sediments (S3 and S5) collected in residential areas showed significant toxicity to the amphipods with mortality of  $88\% \pm 18\%$  and  $82\% \pm 20\%$ , respectively. The results suggested that Chebei Creek water and sediment exhibited higher toxicity to the midges than the amphipods, which was consistent with previous studies (Li et al., 2013a; Li et al., 2013b). Current-use pesticides including FIPs and pyrethroids have been identified as major toxicity contributors to the invertebrates (Li et al., 2013b; Li et al., 2019). It is imperative to further examine the influence of DOC on toxicity contributions of FIPs in the lotic waterways.

The TU values of FIPs based on total concentrations ( $C_w$  or  $C_{s-OC}$ ) and freely dissolved concentrations ( $C_{w-free}$  or  $C_{pw}$ ) were calculated to evaluate the contributions of FIPs to the observed toxicity (Appendix A Tables S7, S8 and S9). The TU<sub>w</sub> and TU<sub>s</sub> values of FIPs in Chebei Creek water and sediment to *C. dilutus* were  $1.06 \pm 0.86$  and  $2.84 \pm 2.99$ , respectively, with fipronil sulfone being dominated toxicity contribution (80% on average), suggesting that FIPs may cause considerable toxicity to the midges. However, observed toxicity of water and sediment to *C. dilutus* was not significantly ( $p > 0.05$ ) correlated to the respective TU<sub>w</sub> (Fig. 4a) and TU<sub>s</sub> of FIPs, implying total concentrations may cause uncertainty in toxicity assessment due to ignoring bioavailability (Li et al., 2013a). Comparatively, as shown in Fig. 4c, TU based on freely dissolved concentrations in water (TU<sub>w-free</sub>) significantly improved the lin-

ear correlation with observed lethality to *C. dilutus* ( $p < 0.05$ ,  $r^2 = 0.32$ ), confirming toxic potency of FIPs in Chebei Creek water to the midges. The results highlighted the important role of DOC in toxicity estimation of hydrophobic organic contaminants (e.g., FIPs) in field waterways. The TU<sub>s-pw</sub> of FIPs in sediment porewater did not significantly improve the linear correlation with observed sediment toxicity to *C. dilutus*. For *H. azteca*, FIPs in Chebei Creek water and sediment contributed limited toxicity with TU<sub>w</sub> and TU<sub>s</sub> values being  $0.01 \pm 0.01$  and  $0.04 \pm 0.04$ , respectively. As presented in Fig. 4b and d, the correlation between TU<sub>w-free</sub> of FIPs in Chebei Creek water and the observed water toxicity to *H. azteca* ( $p < 0.05$ ,  $r^2 = 0.51$ ) was highly improved compared to that based on TU<sub>w</sub> ( $p > 0.05$ ), again highlighting the necessity to use freely dissolved concentrations in toxicity assessment of hydrophobic organic contaminants in field waterways. Previous studies have shown that aquatic toxicity of FIPs would be significantly altered by DOC, e.g., DOC reduced toxicity of permethrin to *Daphnia magna* (Yang et al., 2006a), while enhanced acute toxicity of fipronil to the copepods *Amphiascus tenuiremis* (Bejarano et al., 2005). In general, DOC reduces bioavailability (i.e., freely dissolved concentration) of contaminants and subsequently reduces toxicity, and the percent reduction is dependent on source characteristics of DOC (Yang et al., 2006a), while the reason for toxicity enhancement by DOC requires further studies. Under the complex scenario of DOC associations in field waterways, the freely dissolved concentrations determined by passive sampling serve as a better metric than aqueous concentration in toxicity assessment of hydrophobic organic contaminants.

### 3. Conclusions

Fipronil and its two TPs were frequently detected in urban stream in Guangzhou, China. The two TPs (sulfone and sulfide) were tended to bind to the DOC and particles (*i.e.*, SPM and sediment), while fipronil was more abundant in freely dissolved phase. Approximate 70% of FIPs were bound to DOC in aqueous phase, emphasizing the significant role of DOC in the environmental fate and toxicity of contaminants. The  $TU_{w-free}$  based on freely dissolved concentrations in water significantly improved toxicity estimation of FIPs in water to aquatic invertebrates. It is essential to consider the associations between organic contaminants and DOC when assessing the distribution, transport, and aquatic risk of the contaminants.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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### Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2022.10.015.

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