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Inter-compartmental transport of organophosphate and pyrethroid pesticides in South China: Implications for a regional risk assessment

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ABSTRACT

The dynamic flux of an organophosphate and four pyrethroid pesticides was determined in an air-(soil)-water-sediment system based on monitoring data from Guangzhou, China. The total air–water flux, including air–water gaseous exchange and atmospheric deposition, showed deposition from air to water for chlorpyrifos, bifenthrin and cypermethrin, but volatilization for *lambda*-cyhalothrin and permethrin. The transport of the pesticides from overlying water to sediment suggested that sediment acted as a sink for the pesticides. Additionally, distinct annual atmospheric depositional fluxes between legacy and current-use pesticides suggested the role of consumer usage in their transport throughout the system. Finally, pesticide toxicity was estimated from annual air–water-sediment flux within an urban stream in Guangzhou. A dynamic flux-based risk assessment indicated that inter-compartmental transport of chlorpyrifos decreased its atmospheric exposure, but had little influence on its aquatic toxicity. Instead, water-to-sediment transport of pyrethroids increased their sediment toxicity, which was supported by previously reported toxicity data.

1. Introduction

Multi-media fate models, e.g. inter-compartmental transport in an air-(soil)-water-sediment system, have seen increasing use for predicting the transport of environmental contaminants (Hursthouse and Kowalczyk, 2009). By identifying the most critical media for a contaminant, the output of fate models provides a means to integrate transport dynamics of the contaminants into regional risk assessments (Cowan et al., 1995; Lammel et al., 2007). To date, attempts to assess inter-compartmental transport have focused on persistent organic pollutants, like polycyclic aromatic hydrocarbons (Palm et al., 2004), polychlorobiphenyls (Meijer et al., 2006; Palm et al., 2004), polybrominated diphenyl ethers (Guan et al., 2009) and organochlorine pesticides (Lammel et al., 2007; Zhang et al., 2011).

Current-use pesticides (CUPs), such as organophosphates and pyrethroids, have recently been detected in various environmental compartments worldwide (Gan et al., 2005; Hintzen et al., 2009; Li et al., 2013a, 2014; Mehler et al., 2011; Weston et al., 2005, 2009), however, little information is available on their transport within ecosystems. While transport of chlorpyrifos, an organophosphate, has been reported in an air–water system (Harman-Fetcho et al., 2000; Luo and Zhang, 2009; Zhong et al., 2012), studies detailing the transport of pyrethroids have been limited to surface runoff (Gan et al., 2005; Jiang and Gan, 2012; Jiang et al., 2012). To our knowledge, no assessment of inter-compartmental transport of pyrethroids has been reported to date.

Chlorpyrifos and pyrethroids have been extensively used in China, with the annual demands for chlorpyrifos and pyrethroids in 2013 being expected to be approximately 20,000 tons (http://www.chinapesticide.gov.cn/doc13/13092520.html) and 3700 tons (http://www.chinapesticide.gov.cn/doc12/12112813.html), respectively. The Pearl River Delta (PRD) is the economic center of South China and Guangzhou is the largest city in the PRD. The warm and humid weather in this area promotes pest proliferation and therefore pesticide use. Both chlorpyrifos and pyrethroids have been detected at high frequency and concentrations in the atmosphere and aquatic systems in Guangzhou (Li et al., 2013a, 2014), which suggested that it was

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an ideal city for studying inter-compartmental transport of these pesticides.

Pesticides travel within the air-(soil)-water-sediment system diagrammed in Fig. 1, upon entering the environment. Pesticides enter the atmosphere mainly by drift and evaporation during or after application (Gil and Sinfort, 2005) and experience dispersion and transport processes in the atmosphere. Pesticides then move to aquatic and terrestrial ecosystems via dry (gas and particle phases) and wet (rain and snow precipitation) deposition (Majewski et al., 1998). Pesticides in aquatic system can volatilize, be sorbed to sediment particles and accumulate within aquatic food chain (Meijer et al., 2006). Similarly, pesticides in soil can volatilize and enter aquatic system through runoff during rain events.

In order to better understand the inter-compartmental transport of CUPs and how it affects their ecological risk, the present study was conducted to: (1) describe the dynamic flux of target CUPs in an air-(soil)-water-sediment system in Guangzhou, China based on monitoring data; (2) estimate the annual flux of CUPs in an urban stream in Guangzhou and in the PRD; and, (3) assess the risk of CUPs in critical compartments within the ecosystem by integrating their dynamic flux information.

2. Methods

2.1. Data collection and flux calculations

Flux calculations were performed for the most frequently detected CUPs in Guangzhou, China, including chlorpyrifos, bifenthrin, *lambda*-cyhalothrin, cypermethrin and permethrin, and their physicochemical properties are presented in Table S1 in Supplemental material. Dynamic fluxes for each inter-compartmental transport system were calculated using annual atmospheric (Li et al., 2014) and soil pesticide concentrations (unpublished data) from Guangzhou, along with water (unpublished data) and sediment (Li et al., 2013a) concentrations taken from Chebei Creek, an urban stream in Guangzhou (Table 1).

After pesticides are released into the environment, a variety of biotic and abiotic processes may occur. In the present study, we limited our evaluation to abiotic inter-compartmental processes, including air–water gaseous exchange and atmospheric deposition, water-sediment diffusion, sinking of suspended particles and sediment burial, air-soil gaseous exchange and soil runoff during rain events (Fig. 1). The total air–water flux is the sum of the air–water gaseous exchange flux (F_{aw}) and the atmospheric depositional flux, which includes dry and wet particle deposition fluxes (F_{dry} and $F_{wet,p}$, respectively) and wet dissolved deposition flux ($F_{wet,d}$). The total water-sediment flux includes the water-sediment diffusion flux (F_{ws}), the flux of sinking suspended particles ($F_{sinking}$) and the sediment burial flux (F_{burial}). The total air-soil flux is the sum of the air-soil gaseous exchange flux (F_{as}) and the atmospheric depositional flux. Finally, the soil runoff flux was also computed during rain events ($F_{soil\ runoff}$). The detailed calculations for all fluxes among environmental compartments are presented in Supplemental material (Eqns. S1–S25).

2.2. Sensitivity and uncertainty analysis

A Monte Carlo simulation was used to evaluate the sensitivity and uncertainty of the estimations in the inter-compartmental fate model analysis. Concentrations of the target CUPs in each compartment were log-normally distributed with mean values and standard deviations (Table 1), and were the major calculable sources of errors in the estimation. The Monte Carlo simulation was performed using 20,000 randomizations with confidence interval being 95% for the target pesticides.

2.3. Annual flux of pesticides and estimated sediment toxicity

From the dynamic flux of pesticides (F, mg/km^2/d) calculated above, the annual flux of the target CUPs (F_{annual}, kg/yr) was estimated using the following equation:

$$F_{annual} = FA \quad (1)$$

where, A was the area of the target region for annual flux estimation. In the present study, two regions were considered, Chebei Creek in Guangzhou and the PRD, with areas being 80 and 53,580 km^2, respectively.

The annual cumulative CUP concentrations (C_{annual}, μg/g organic carbon (OC)) were estimated from the annual water-to-sediment transport flux of CUPs in Chebei Creek (F_{annual}, kg/yr), and the concentrations were then used to estimate sediment toxicity to benthic organisms (flux-based toxic unit (TU)). The calculations were conducted using the following equations:

$$\text{Flux-based TU} = \frac{C_{annual}}{LC50} \quad (2)$$

$$C_{annual} = \frac{F_{annual}}{m \times f} \quad (3)$$

$$m = A \times h \times \rho \times r \quad (4)$$

where, LC50 (μg/g OC) was the medium lethal concentration of the compounds to the organisms and the values are listed in Table S1 in Supplementary material. The m was the weight (kg) of the surface sediment, while f represents the OC content of sediments in Chebei Creek and an average value of 5.54% was used (Li et al., 2013a). In the calculation of the m value, the drainage area of Chebei Creek was used (A = 80 km^2), and the thickness of the surface sediment (h), the density of dry sediment (ρ) and the sediment-water ratio (r) were assumed to be 5 cm, 1.5 kg/m^3 and 50%, respectively (Zou et al., 2007).

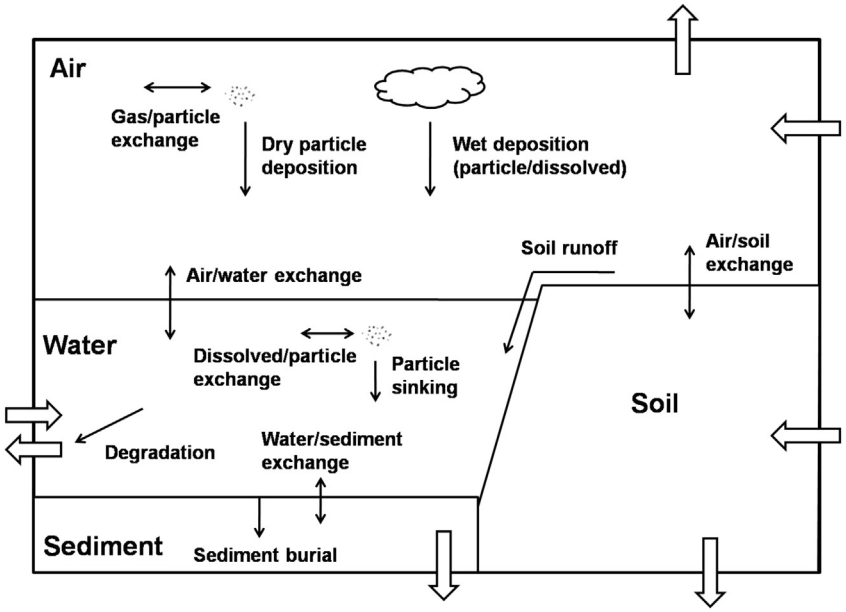

Fig. 1. The key partitioning and transport processes of current-use pesticides in a regional air–water (soil)-sediment system.

Table 1
Concentrations (mean ± standard deviation) of the target current-use pesticides in air (gas (C_a) and particle phases (C_{ap})), water (dissolved (C_w) and suspended particle phases (C_{wp})), sediment and soil on a dry weight (dw) basis in Guangzhou, China.

Concentration	Chlorpyrifos	Bifenthrin	*lambda*-Cyhalothrin	Cypermethrin	Permethrin
C_a (pg/m^3)[a]	1019 ± 850	5.19 ± 11.0	1.67 ± 2.08	7.68 ± 3.87	9.57 ± 13.1
C_{ap} (pg/m^3)[a]	34.2 ± 25.8	24.6 ± 37.7	13.2 ± 13.7	228 ± 375	66.3 ± 85.5
C_w (ng/L)[b]	1.73 ± 1.86	0.28 ± 0.25	0.52 ± 0.59	5.02 ± 3.30	3.67 ± 3.10
C_{wp} (ng/L)[b]	0.95 ± 0.69	0.84 ± 0.58	4.33 ± 4.41	20.0 ± 14.5	9.02 ± 7.18
C_{sed} (ng/g dw)[c]	5.07 ± 4.26	6.11 ± 5.24	11.1 ± 8.23	68.9 ± 67.3	40.0 ± 55.8
C_{soil} (ng/g dw)[d]	0.74 ± 1.50	0.37 ± 1.17	1.32 ± 3.87	22.0 ± 57.9	0.99 ± 3.34

[a] Data from Li et al. (2014).
[b] Unpublished data and brief descriptions of the methods were presented in Supplementary material.
[c] Data from Li et al. (2013a).
[d] Unpublished data and brief descriptions of the methods were presented in Supplementary material.

3. Results and discussion

3.1. Transport processes

3.1.1. Air-water-sediment

The air–water gaseous exchange flux of chlorpyrifos and the target pyrethroids were estimated using annual gaseous concentrations taken from Li et al. (2014) and the dissolved water concentrations in an urban creek in Guangzhou (unpublished data) (Table 1). As presented in Tables 2 and S2 in Supplemental material and Fig. 2, the air–water gaseous exchange of chlorpyrifos exhibited absorption (from air to water) with a flux of 806 mg/km^2/d, while the pyrethroids were all volatilized (from water to air) with fluxes of 6.22, 25.6, 154 and 261 mg/km^2/d for bifenthrin, *lambda*-cyhalothrin, cypermethrin and permethrin, respectively. The high absorption flux for chlorpyrifos in the system was driven by its high gaseous concentration, and relatively low water concentration. Alternatively, the higher fugacity of pyrethroids in water than that in air drove their volatilization from water to air. Chlorpyrifos had a higher gaseous exchange flux compared to the pyrethroids, which was due to not only its higher total atmospheric concentrations, but also its higher vapor pressure and subsequently higher percentage of compound in the gas phase relative to the particles (Li et al., 2014). This result was supported by the research conducted by Palm et al. (2004). Surprisingly, chlorpyrifos had lower water concentrations than cypermethrin and permethrin, which was contradictory to its higher usage amount and air to water flux. One possible reason for this finding was the significant degradation of chlorpyrifos, which had reported half life of 26.5–126 d in natural water and was less hydrophobic than the pyrethroids (Liu et al., 2001). Galbán-Malagón et al. (2013) suggested that a "degradative pump" was one of the important enhancements to the air–water gaseous exchange for less hydrophobic compounds, since degradation induced depletion of chemical concentrations in the water column.

The flux of bulk atmospheric deposition, including dry and wet particles, and wet dissolved deposition, were 63.9, 21.4, 11.3, 195 and 56.8 mg/km^2/d for chlorpyrifos, bifenthrin, *lambda*-cyhalothrin, cypermethrin and permethrin, respectively (Table 2). Chlorpyrifos had comparable fluxes of wet dissolved deposition and the total (wet and dry) particle deposition in Guangzhou, which was consistent with a previous study conducted in Chesapeake Bay in the United States (McConnell et al., 1997). As for the fluxes of dry and wet particle deposition, they were similar for both chlorpyrifos and the pyrethroids. In contrast, the flux of wet dissolved deposition, which accounted for 54.6% of the bulk atmospheric deposition for chlorpyrifos, was much lower for the pyrethroids (average percentage in bulk atmospheric deposition was 1.21%). The variation in vapor pressures among the target pesticides was the reason for these differences, and the low contribution of wet dissolved deposition to bulk atmospheric deposition for the pyrethroids was the consequence of their low distribution in the gas phase (Li et al., 2014).

In total, the air–water fluxes were 870, 15.2 and 40.9 mg/km^2/d from the air to the water for chlorpyrifos, bifenthrin and cypermethrin, respectively, whereas the flux from the water to the air for *lambda*-cyhalothrin and permethrin were 15.2 and 204 mg/km^2/d, respectively (Fig. 2). Thus, air represented a source of chlorpyrifos, bifenthrin and cypermethrin to the water, while water represented a source of *lambda*-cyhalothrin and permethrin to the air. The air–water flux of chlorpyrifos in Guangzhou was comparable to the flux found in Chesapeake Bay in the United States (McConnell et al., 1997). To our knowledge, however, no information was available on the air–water transport of pyrethroids. In the air–water system, the air–water gaseous exchange flux was the main transport process for chlorpyrifos, accounting for 92.7% of the total air–water

Table 2
The calculated flux (mg/km^2/d) of current-use pesticides in air–water (soil)-sediment system in Guangzhou, China. Negative values indicate the transport direction is from the air to the water, the water to the sediment, and the air to the soil. Positive values indicate the opposite direction among these compartments and from the soil to the water for soil runoff.

Types of flux	Chlorpyrifos	Bifenthrin	*lambda*-Cyhalothrin	Cypermethrin	Permethrin
Air–water exchange	−806	6.22	34.1	154	261
Dry particle deposition	−14.8	−10.6	−5.68	−98.5	−28.6
Wet particle deposition	−14.3	−10.3	−5.49	−95.3	−27.7
Wet dissolved deposition	−34.9	−0.52	−0.11	−0.98	−0.52
Water-sediment diffusion	116	2.60	10.7	77.3	11.7
Suspended particle sinking	−756	−652	−3358	−15518	−6998
Sediment burial	−13.2	−16.0	−28.9	−180	−104
Air–soil exchange	−1.76	−0.03	−0.003	0.05	−0.03
soil runoff	13.3	6.60	23.7	394	17.8
Total air–water	−870	−15.2	22.8	−40.9	204
Total water-sediment	−653	−666	−3375	−15621	−7091
Total air-soil	−65.7	−21.5	−11.3	−195	−56.9

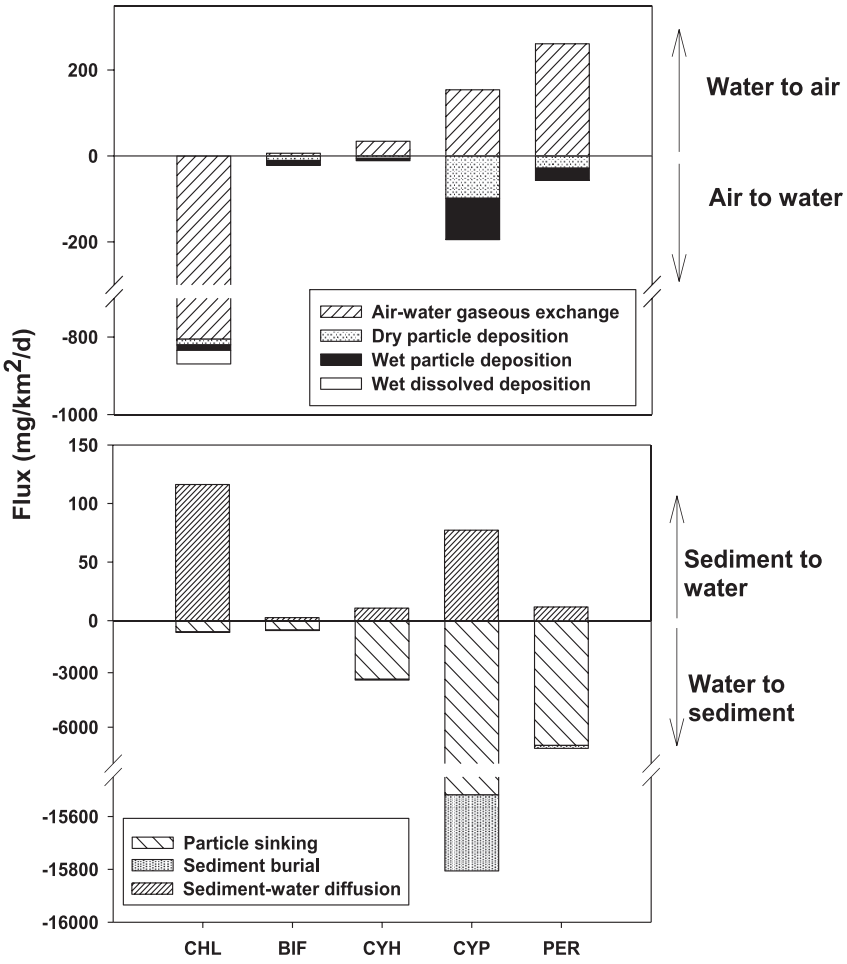

Fig. 2. The calculated dynamic flux (mg/km^2/d) of the individual inter-compartmental process in the air–water-sediment system in Guangzhou, China.

flux. Instead, all air–water gaseous exchange and dry and wet particle deposition fluxes contributed to the transport of pyrethroids, accounting for 56.0%, 22.1% and 21.3% of the total air–water flux, respectively. Different gas-particle distribution patterns were found for chlorpyrifos and pyrethroids and this was one of the reasons for the different transport processes for the two classes of CUPs. It should be noted, however, that the estimation used in the present study was based on annual atmospheric and water concentrations within a limited time scale so the conclusions do not represent the absolute transport directions. The air–water gaseous exchange processes were also controlled by environmental conditions, like temperature and wind speed, and seasonal variation in directions of air–water gaseous exchange has been observed in previous studies (McConnell et al., 1997; Palm et al., 2004).

Contaminants found in the water did not only experience volatilization into the air, but also accumulated into sediments due to the sinking of suspended particles, sediment burial processes and water-sediment diffusion (Meijer et al., 2006). The flux of sinking particles into the sediments for chlorpyrifos, bifenthrin, cyfluthrin, *lambda*-cyhalothrin, cypermethrin and permethrin were 756, 652, 3358, 15518 and 6998 mg/km^2/d, respectively, while the respective fluxes for sediment burial were 13.2, 16.0, 28.9, 180 and 104 mg/km^2/d (Table 2). Conversely, the direction for water-sediment diffusion was from sediment porewater to overlying water for the target CUPs, with fluxes being 116, 2.6, 11.6, 77.3 and 11.7 mg/km^2/d, respectively. Consequently, the total water-sediment fluxes of the five CUPs were 653, 666, 3375, 15621 and 7091 mg/km^2/d, respectively, from the water to the sediment (Fig. 2). Here, sinking of the suspended particles was the dominant transport process, accounting for 85% and 98% of the total water-sediment flux of chlorpyrifos and the pyrethroids, respectively. Compared to the pyrethroids, chlorpyrifos is relatively less hydrophobic and subsequently a smaller portion of chlorpyrifos was associated with suspended particles and sediments, resulting in its smaller water-sediment flux. Conversely, pyrethroids have a high affinity to OC in suspended particles, thus the sinking of the particles caused the pyrethroids to move from the water to the sediment (Table 2). In addition, chemicals can be bioaccumulated by phytoplankton in water column and as the phytoplankton die they subsequently sink to the bottom and can play an important role in the movement of hydrophobic organic compounds to the sediment. This process has been coined the term “biological pump” (Dachs et al., 2002; Galbán-Malagón et al., 2013). However, the role of the biological pump in the air-water-sediment transport of pyrethroids was not quantitatively evaluated due to the lack of information, e.g. concentrations of pyrethroids in phytoplankton and the sinking rate of phytoplankton.

3.1.2. *Air-soil exchange and soil runoff*

Air-soil gaseous exchange and atmospheric deposition, including dry particle, wet particle and wet dissolved deposition, represent the main processes of air-soil exchange examined in the present study. As shown in Tables 2 and S2, the air-soil gaseous exchange fluxes for chlorpyrifos, bifenthrin, *lambda*-cyhalothrin

and permethrin were 1.76, 0.02, 0.003 and 0.03 mg/km^2/d from the air to the soil, respectively, while cypermethrin had a flux of 0.05 mg/km^2/d from the soil to the air. Consequently, the total air-soil fluxes, which were the sum fluxes of air-soil gaseous exchange and atmospheric deposition, were 65.7, 21.5, 11.3, 195 and 56.9 mg/km^2/d for chlorpyrifos, bifenthrin, *lambda*-cyhalothrin, cypermethrin and permethrin, respectively, from the air to the soil (Table 2). These results suggested that atmospheric deposition contributed the most to the air-soil fluxes, and atmospheric chlorpyrifos and pyrethroids were the sources of those CUPs to the soils in Guangzhou.

The opposite result was found for the legacy pesticide *p,p′*-dichlorodiphenyltrichloroethane (DDT) in the PRD where Guangzhou is located (Zhang et al., 2011). In their study, researchers found that *p,p′*-DDT had an air-soil gaseous exchange flux of 3.88 mg/km^2/d via vaporization, suggesting that *p,p′*-DDT in the soil was a significant source of atmospheric *p,p′*-DDT. The likely reason for the different air-soil gaseous exchange directions for chlorpyrifos and *p,p′*-DDT was their different application history and environmental persistence. Chlorpyrifos is currently used in China and has recently been detected at elevated concentrations in air; however, it typically has relatively low soil concentrations due to possible degradation with a half-life of days to months, e.g. 20.3–223 d (Bondarenko and Gan, 2004). In contrast, *p,p′*-DDT was banned for use in China in 1983 and has seen decreasing gaseous concentrations over time. However, due to the elevated concentrations of *p,p′*-DDT in soil from its extensive application in the past and high persistence with long environmental half-life (e.g. $t_{1/2} = 15$ yr), it still represents an issue in soils (Zhang et al., 2011). In addition to the application history of the pesticides, soil properties and meteorological conditions, like wind speed and temperature, might also influence the air-soil gaseous exchange process (Ruzickova et al., 2008). More discussion on atmospheric deposition of chemicals in the PRD was shown in supplementary material.

Remnant levels of pesticides in soils was not only a source of atmospheric contaminants via vaporization, but also an important input to water bodies via soil erosion and runoff during rain events (Dabrowski et al., 2002; Luo et al., 2008). The fluxes of pesticides into water bodies from soil runoff, estimated from soil concentrations and soil erosion rates during rain events, were 13.3, 6.60, 23.7, 394 and 17.8 mg/km^2/d for chlorpyrifos, bifenthrin, *lambda*-cyhalothrin, cypermethrin and permethrin, respectively (Table 2). After entering surface water, the CUPs will re-distribute between the freely dissolved and particle-bound forms (Palm et al., 2004) and experience different transport processes (e.g. remain in the water column or be deposited in the sediment).

3.1.3. Seasonal variation in air related fluxes

Seasonal variation in atmospheric CUP concentrations was observed in Guangzhou with peak concentrations in summer and fall with CUP concentrations dropping during the winter months (Li et al., 2014). The influence of varying atmospheric concentrations on the air–water and air-soil transport fluxes were evaluated using Monte Carlo simulation and the results are presented in Table S3 in Supplementary material. In general, the direction of the air–water gaseous exchange flux for the CUPs remained constant among seasons, with the exception of chlorpyrifos during the winter. The changes in the flux values for air–water gaseous exchange and atmospheric deposition among seasons also caused changes in the direction of the total air–water transport for bifenthrin in winter and for cypermethrin in summer and winter. However, in most cases, the high certainty, which indicated the possibility of seasonal transport data having the same direction as the corresponding mean fluxes, suggested that the variation found in the seasonal and annual atmospheric concentrations did not significantly impact the CUP transport in the air–water system. Although different directions in air-soil gaseous exchange were observed among seasons, the direction of the total air-soil flux for all CUPs remained constant regardless of seasons, since atmospheric deposition was the predominant contributor to the total air-soil flux in this area.

3.1.4. Mass balance

In order to get a clearer picture of the inter-compartmental transport processes in a system a mass balance assessment must be completed. A schematic of the dynamic flux-based mass balance for chlorpyrifos and cypermethrin was presented in Fig. S1 in Supplementary material. Cypermethrin was chosen as a representative pyrethroid, because it was the most abundant pyrethroid detected in different compartments in Guangzhou (Li et al., 2013a, 2014). Compared to cypermethrin, chlorpyrifos generally had higher dynamic fluxes in unbound forms that were not associated with particles, including dissolved wet deposition, air–water gaseous exchange, water-sediment diffusion and air-soil gaseous exchange, whereas cypermethrin had higher dynamic fluxes on particle-bound forms than chlorpyrifos, including particle deposition, sinking of suspended particles, sediment burial and soil runoff (Table 2).

Chlorpyrifos had comparable fluxes for air-to-water (870 mg/km^2/d) and water-to-sediment processes (661 mg/km^2/d), which suggested that atmospheric loading of chlorpyrifos was a major source to the water and sediment budgets (the sum of input and output to a system). Atmospheric deposition of dry and wet particle-bound chlorpyrifos (29.1 mg/km^2/d), however, was 26 times less than the flux of suspended particles being deposited into the sediments (756 mg/km^2/d), suggesting that atmospheric particle-bound chlorpyrifos only accounted for a small portion of the particle-bound chlorpyrifos found in the water column. Since the contaminants can re-distribute between the unbound and particle-bound forms after they are deposited into water (Palm et al., 2004), this complicates the balance of chlorpyrifos within the air–water-sediment system.

The water-sediment fluxes for bifenthrin and cypermethrin were 44 and 382 times greater than those from the air to the water, respectively. Thus, additional sources other than atmospheric loading, e.g. soil runoff, might be contributing pyrethroids to aquatic systems. However, the fluxes of pyrethroids from soil runoff during rain events were unexpectedly 100, 142, 40 and 399 times lower than that from water to sediment for bifenthrin, *lambda*-cyhalothrin, cypermethrin and permethrin, respectively. It is reasonable that the annual flux of cypermethrin in soil runoff during rain events accounted for approximately 7% of its soil inventory in Guangzhou (unpublished data). Together, atmospheric loading and soil runoff during rain events only accounted for a small portion (2.8%) of the water to sediment budgets for cypermethrin, suggesting additional input sources of cypermethrin in the aquatic system.

Weston and Lydy (2009) demonstrated that residential runoff, municipal wastewater treatment plants and agricultural drains are the main sources for pyrethroids in surface waters in the Sacramento-San Joaquin River Delta of the United States. Cypermethrin was detected at concentrations of up to 220 ng/L in agricultural drainage waters in Guangzhou (Yang et al., 2010), which suggested that urban and agricultural drains may also be the sources of pyrethroids for the aquatic budgets in South China. However, estimating the flux of pesticides from the drains was difficult due to the lack of parameters, e.g., the amount of drainage and particle contents in the drainage.

In addition to the sinking of suspended particles, biota uptake and degradation also contributed to the removal of CUPs from the water column. Zhang et al. (2011) demonstrated that

bioaccumulation had little impact on the inter-compartmental transport of contaminants within a short time scale. Moreover, it was difficult to quantitatively determine the amounts and rates of CUP bioaccumulation, because data on the biota masses and bioaccumulation kinetics were scarce. Degradation of the CUPs in the water column was estimated using Eqn. S26 and the results are presented in Table S4 in Supplementary material. The half-lives of CUPs from the literature showed large variations (Table S4), thus it was difficult to evaluate the accuracy in the degraded masses and the subsequent contribution of the degradation process to mass balance of the CUPs in the inter-compartmental transport processes.

3.2. Sensitivity and uncertainty analysis

Sensitivity of the variable parameters, including CUP concentrations in different compartments (gaseous phase in air, freely dissolved in water and sediment), air–water exchange mass transfer coefficients (k_{ol}, 40%) and the Henry's Law constants (H, 30%) (Zhong et al., 2012), used in the estimations of exchange fluxes was performed by Monte Carlo Simulation and the sensitivity contributions in the estimations are presented in Table S5 in Supplementary material. Other potential sources of uncertainties may exist, but those parameters were not included, due to the difficulty in obtaining an estimate of their uncertainty. Because of the negligible contributions (less than 5%) of k_{ol} and H values to sensitivities of the fluxes, only the contributions of CUP concentrations were further discussed. For chlorpyrifos, the uncertainty in the air concentrations contributed 92.2% and 98.0% to the uncertainties in the air–water and air-soil gaseous exchange fluxes, respectively, while the uncertainty in sediment concentrations contributed 97.0% to the uncertainties in the water-sediment diffusion flux. For pyrethroids, the uncertainty in water concentrations contributed to 93.1% of the uncertainty in the flux of the air–water gaseous exchange, and the uncertainty in the sediment concentration contributed to 80.0% of the uncertainty in the flux of the water-sediment diffusion. In addition, the uncertainty in cypermethrin concentration in soil contributed 75.4% to the uncertainties in the air-soil gaseous exchange flux, and uncertainties in the air concentrations of the other three pyrethroids (bifenthrin, *lambda*-cyhalothrin and permethrin) contributed, on average, 75.1% to the air-soil gaseous exchange flux.

Finally, the variation in the spatial and temporal distributions of the CUPs may also contribute to the uncertainties in the transport fluxes, including air–water and air-soil gaseous exchange and atmospheric depositions. These uncertainties were quantified using the mean fluxes along with their standard deviations using Monte Carlo Simulation (Tables S2 and S4 in Supplemental material). On average, the flux for the air-soil gaseous exchange had the largest uncertainty, followed by the water-sediment diffusion and air–water gaseous exchange, with average relative standard deviation among the target CUPs of 475%, 205% and 135%, respectively. In summary, uncertainty in the inter-compartmental estimates was largely due to the uncertainty in the monitoring data including their spatial and temporal variability.

3.3. Implications for a regional risk assessment

Inter-compartmental transport of CUPs affected their final destination and ecological risk. Atmospheric deposition resulted in the movement of compounds from the air to the aquatic and territorial environments where the chemicals experienced further transport processes, e.g. water to sediment. Therefore, the ecological risk of CUPs was further tested based on the dynamic transport information from an urban stream in Guangzhou where 231 streams were scattered throughout the city. Chebei Creek is the longest water body in the Tianhe district, which is the most populous area in Guangzhou. This stream originates at a reservoir and empties into the Pearl River. Chlorpyrifos and pyrethroids were detected in sediment from Chebei Creek and cypermethrin was identified as one of the contributors to toxicity to benthic organisms (Li et al., 2013a).

Annual fluxes of the CUPs moving in and out of Chebei Creek were calculated using transport data from the air-water-sediment system (Table S4). The air–water gaseous exchange showed deposition of 23.5 kg/yr for chlorpyrifos, and volatilization for the pyrethroids, being 0.18, 0.77, 4.5 and 7.6 kg/yr for bifenthrin, *lambda*-cyhalothrin, cypermethrin and permethrin, respectively. The total annual air–water flux in Chebei Creek was defined as the sum of air–water gaseous exchange and atmospheric depositional fluxes, and it showed an annual net deposition for chlorpyrifos, bifenthrin and cypermethrin from air to water of 25.4, 0.44 and 1.20 kg/yr, respectively, and a net volatile loss from water to air of 0.67 and 5.96 kg/yr for *lambda*-cyhalothrin and permethrin, respectively. The gaseous deposition decreased chlorpyrifos concentration in the air, while the gaseous volatilization of pyrethroids increased their atmospheric concentrations, which in turn changed their inhalation exposure risk. A previous study conducted in Guangzhou showed inhalation exposure of CUPs was negligible (Li et al., 2014), therefore the change in inhalation exposure was not further studied.

The water-to-sediment flux data suggested that sediment acted as a sink for chlorpyrifos and the pyrethroids (Tables 2 and S2). To quantitatively evaluate the impact of the transport on sediment toxicity of the target CUPs, their annual cumulative sediment concentrations were predicated from the flux data from Chebei Creek. The annual water-to-sediment fluxes for chlorpyrifos, bifenthrin, *lambda*-cyhalothrin, cypermethrin and permethrin in Chebei Creek were 19.1, 19.4, 98.6, 456 and 207 kg/yr, respectively, and the respective annual cumulative sediment concentrations were 0.12, 0.12, 0.60, 2.76 and 1.26 μg/g OC. From these concentrations, the annual flux-based TUs for two benthic invertebrates *Chironomus dilutus* and *Hyalella azteca* were calculated. Interestingly, the flux-based TUs were similar to the average sediment concentration-based TUs reported in previous studies (Li et al., 2013a, 2013b), which were derived from CUP concentrations in sediments collected from this same creek (Fig. 3). This suggested that the contribution of water-to-sediment transport to sediment budgets for those CUPs was important.

The low annual flux-based TU for chlorpyrifos (<0.1) implied that its accumulation in sediment had little impact on benthic organisms, which was supported by the toxicity evaluation conducted using Chebei Creek sediments (Li et al., 2013a, 2013b). Chlorpyrifos water concentration reached a peak level of 8.36 ng/L assuming no air-to-water gaseous exchange occurred, and this concentration was significantly lower than the 4-d water-only median lethal concentration for *C. dilutus* of 459 ng/L (Harwood et al., 2009). In total, the air to water to sediment transport of chlorpyrifos suggested that its dynamic transport would decrease human inhalation exposure risk, but had little influence on its aquatic toxicity.

Conversely, the transport of pyrethroids from water to sediment might significantly increase their sediment toxicity due to their high toxicity to benthic organisms. The annual flux-based TUs for the pyrethroids were all >0.1 to *H. azteca*, suggesting potential sediment toxicity. Individually, cypermethrin had the highest estimated annual flux-based TUs at 2.06 and 7.27 to *C. dilutus* and *H. azteca*, respectively, followed by *lambda*-cyhalothrin and bifenthrin. The flux-based TUs were consistent with the sediment concentration-based TUs from pyrethroid concentrations analyzed

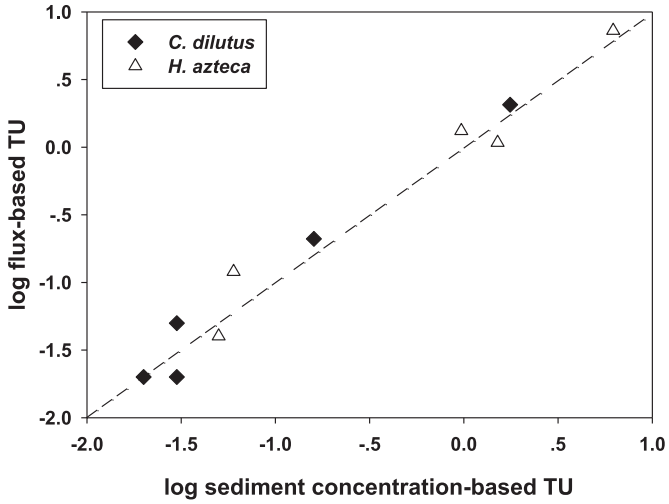

Fig. 3. The relationship between the sediment concentration based-toxic unit (TU) of the current-use pesticides from previous studies (Li et al., 2013a, 2013b) and flux-based TU derived from water to sediment transport flux in current study to *Chironomus dilutus* and *Hyalella azteca* in Chebei Creek of Guangzhou, China. The dashed line stands for $y = x$.

in sediment (Li et al., 2013a, 2013b). Therefore, the transport of pyrethroids might directly increase the risk to benthic invertebrates as well as indirectly influence the aquatic ecosystem balance (Macneale et al., 2010).

It should be noted, however that CUPs may experience degradation in the environment, with half-lives in sediment of 20.3–770 days (Table S1) for chlorpyrifos and the four pyrethroids (Bondarenko and Gan, 2004; Qin et al., 2006; Xu et al., 2008). However, degradation was not included in our calculations, since our target CUPs were considered to be pseudo-persistent organic pollutants, due to their extensive usage and continuous introduction into the environment (Bonansea et al., 2013; Barceló and Hennion, 1997). That is to say, the continuous water-to-sediment transport of the CUPs, especially for the toxicity contributors, e.g. cypermethrin, kept concentrations at toxic levels in the sediment. Overall, the annual dynamic fluxes in the urban area provided a clear picture of the transport of the CUPs in the air-water-sediment system and subsequently assessed the exposure and effects of the transported CUPs in the air, water and sediment.

4. Conclusions

The inter-compartmental fate model analysis used in the present study showed that atmospheric chlorpyrifos in Guangzhou represented an important source of this compound to the aquatic budget and that the air–water gaseous exchange processes dominated this contribution. The total air–water fluxes showed that chlorpyrifos, bifenthrin and cypermethrin moved from the air to the water by deposition, while *lambda*-cyhalothrin and permethrin volatilized from the water into the air. In general, the total air–water fluxes for pyrethroids were lower than chlorpyrifos. Moreover, all pyrethroids had similar fluxes for air–water gaseous exchange and atmospheric deposition.

Sediment acted as a sink for both chlorpyrifos and the pyrethroids. Dynamic transport processes might decrease the inhalation exposure risk of chlorpyrifos, but had little impact on its aquatic toxicity. Conversely, air–water-sediment transport increased the risk of pyrethroids to benthic organisms and the calculated sediment toxicity from the transport flux was consistent with that estimated from sediment concentrations. As mentioned earlier, uncertainties existed in our inter-compartmental fate model, because of the limited monitoring data available and future studies should pair environmental occurrence and toxicity evaluations of the CUPs in each media for systematically integrating the dynamic transport of CUPs into regional risk assessments.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2014.03.013.

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