Environmental Pollution 190 (2014) 19–26

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

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

Huizhen Li [a,b], Yanli Wei [a,b], Michael J. Lydy [c], Jing You [a,*]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] Center for Fisheries, Aquaculture and Aquatic Sciences and Department of Zoology, 171 Life Science II, Southern Illinois University, Carbondale, IL 62901, United States

ARTICLE INFO

Article history:
Received 12 December 2013
Received in revised form
5 March 2014
Accepted 10 March 2014
Available online 3 April 2014

Keywords:
Dynamic fluxes
Air-(soil)-water-sediment
Chlorpyrifos
Pyrethroids
Regional risk assessment

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

* Corresponding author.
E-mail address: youjing@gig.ac.cn (J. You).

http://dx.doi.org/10.1016/j.envpol.2014.03.013
0269-7491/

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).

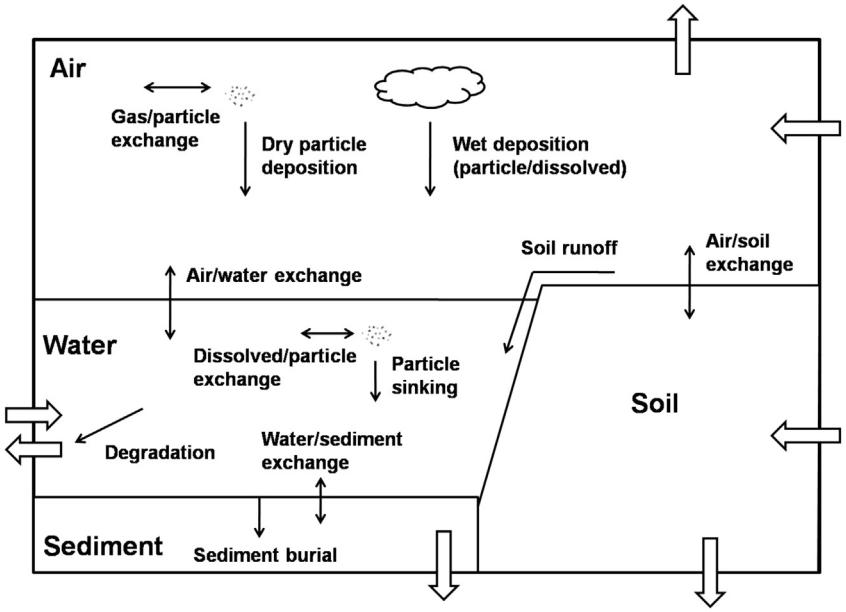

Fig. 1. The key partitioning and transport processes of current-use pesticides in a regional air–water (soil)-sediment system.