Chemosphere 95 (2014) 363–369

Contents lists available at ScienceDirect

Chemosphere

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

Occurrence, seasonal variation and inhalation exposure of atmospheric organophosphate and pyrethroid pesticides in an urban community in South China

Huizhen Li [a,b,c], Hongzhu Ma [d], 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
[d] Institute of Energy Chemistry, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, China

HIGHLIGHTS

- Chlorpyrifos and cypermethrin were frequently detected in the air in South China.
- Peak atmospheric pesticide concentrations occurred in summer and fall.
- Chlorpyrifos was mainly in the gas phase, while most pyrethroids were attached to particles.
- Inhalation exposure risk to atmospheric current-use pesticides was negligible.
- Infants, toddlers and children were more susceptible than adults to atmospheric CUPs.

ARTICLE INFO

Article history:
Received 28 May 2013
Received in revised form 1 September 2013
Accepted 6 September 2013
Available online 11 October 2013

Keywords:
Chlorpyrifos
Pyrethroid pesticides
Seasonal variation
Gas–particle partitioning
Inhalation exposure risk

ABSTRACT

The shift in pesticide usage patterns demands a better understanding of the occurrence, fate and exposure risk of atmospheric current-use pesticides (CUPs). Air samples collected in different seasons from an urban community in Guangzhou, China were analyzed to investigate seasonal variation, gas–particle partitioning and inhalation exposure of atmospheric organophosphate and pyrethroid pesticides. Chlorpyrifos and eight pyrethroids were detected in the air samples and the total concentrations of the nine CUPs ranged from 150 to 3816 pg m^{-3}. Chlorpyrifos and cypermethrin were the most dominant CUPs detected in the atmosphere, accounting for 68% and 15% of the total CUPs, respectively. Seasonal variation in concentration was observed for most CUPs, with peak concentrations occurring in summer and fall, which was consistent with their application patterns. Partitioning of chlorpyrifos between gas and particle phases was also seasonally-dependent, with more chlorpyrifos found in the gas phase in summer and fall. Additionally, gas–particle partitioning analysis suggested that chlorpyrifos might experience long-range transport. Evaluation of potential exposure from inhalation of atmospheric CUPs suggested that children, toddlers and infants had the highest exposure, but the risk quotients were low for all age groups when annual average concentrations were used as exposure metrics. Exposure risk was higher in summer and fall than the annual average level due to higher atmospheric pesticide concentrations, longer exposure times and more pesticides being in the gaseous form.

1. Introduction

Organochlorine pesticides were banned for use in China in 1983 followed by the highly toxic organophosphate pesticides (OPPs) in 2007, and this promoted the extensive use of pesticides with lower mammalian toxicity, like chlorpyrifos and pyrethroid pesticides (http://www.chinapesticide.gov.cn/doc09/09112306.html). The shift in pesticide usage patterns has been followed by a corresponding increase in their occurrence in the environment (Li et al., 2013). Current-use pesticides (CUPs), including OPPs and pyrethroids, have been frequently detected in sediment at high concentration at some sites in China (Li et al., 2011), and some pyrethroids have been identified as major contributors to toxicity in aquatic organisms in this area (Li et al., 2013). The emission of pesticides into air during the time when applications were made accounted for 20–30% of the applied doses (van den Berg et al., 1999) and post-application emissions also occurred via volatilization (Voutsas et al., 2005). Although little information is available concerning atmospheric CUPs in China, the extensive use of CUPs

* Corresponding author. Tel.: +86 20 8529 1497; fax: +86 20 8529 0706.
E-mail address: youjing@gig.ac.cn (J. You).

0045-6535/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2013.09.046

and their widespread presence in aquatic systems suggested possible atmospheric CUP occurrence. Studies have suggested that exposure to atmospheric CUPs might cause adverse effects in humans, especially children (Kawahara et al., 2005). Therefore, it is important to understand the impacts of pesticide applications on local occurrence of atmospheric CUPs and related human exposure risk through evaluating gas–particle partitioning processes (Eisenreich et al., 1981; Bidleman et al., 1986; Sanusi et al., 1999).

Organophosphate pesticides are acetylcholinesterase inhibitors and exposure to low doses of chlorpyrifos caused developmental toxicity to the fetal nervous system (Chanda and Pope, 1996; Landrigan et al., 1999). Bouchard et al. (2011) noted that prenatal exposure to low levels of OPPs caused poorer intellectual development in 7-year old children. Other studies have reported correlations between OPP exposure and adverse health effects, with special concern on the neurodevelopmental toxicity in infants and children (Eskenazi et al., 1999; Kawahara et al., 2005; Wang et al., 2012). Pyrethroids are also suspected developmental neurotoxicants acting by modifying gated sodium channels. Specific toxicity of pyrethroids includes endocrine disruption, immune system suppression, carcinogenesis, and lymph node and spleen damage (Lu et al., 2006; Morgan et al., 2007). Compared to OPPs, fewer studies have been conducted to evaluate adverse health effects of pyrethroids and residential use was considered the most important exposure route for pyrethroids to children (Lu et al., 2006). To date, available data assessing the exposure risk of atmospheric CUPs are limited and no CUP monitoring data are available for ambient air in China.

To fill the knowledge gap on the occurrence of atmospheric CUPs in China and provide a better understanding of CUP exposure, the current study was conducted to: (1) monitor the atmospheric concentrations and seasonal variation of CUPs in an urban community in South China; (2) analyze the gas–particle partitioning processes of CUPs in ambient air; and, (3) assess the age-related inhalation exposure risk to humans of atmospheric CUPs.

2. Materials and methods

2.1. Air sampling

Air samples were collected using a high-volume active sampler (Laoshan Electronic Instrument, Qingdao, China) on the rooftop of a building in Tianhe, Guangzhou, China. The sampling site was located in a residential area with general landscaping and vegetable gardens where pesticides have been extensively applied. Sampling was conducted at night with a consecutive period of 12-h in October and December of 2011 and March, May and July of 2012. In total, 22 sets of particle and gas samples were collected. Air was processed through a glass fiber filter (GFF, Whatman, Maidstone, England) and then a polyurethane foam plug (PUF). The sampling site description and sampling process are detailed in Supplementary material and the meteorological conditions throughout the sampling period are presented in Table S1.

2.2. Sample preparation and analysis

The samples were extracted using 48-h Soxhlet extraction, cleaned with a wet-packed alumina-silica gel column, and then analyzed for five OPPs and 12 pyrethroid pesticides on GC/MS (Shimadzu, Japan). More details on the sample preparation (extraction and cleanup) and instrumental and data analyses are provided in Supplemental material. Field blanks (GFF and PUF) and laboratory controls, including a solvent blank, a matrix blank, a matrix spike and a matrix spike duplicate, were performed as quality assurance/quality control. No target analytes were detected in any of the solvent and matrix blanks. Concentrations of the CUPs in the field blanks were lower than the lowest calibration standard, except for chlorpyrifos in the PUF plugs, which had a mean amount of 80.2 ng per plug. Recoveries of the target pesticides in the matrix spikes were from 53.9% to 101%. Additionally, mean recoveries of the surrogates, 4,4′-dibromooctaflurobiphenyl and decachlorobiphenyl were 66.6 ± 14.3% and 73.9 ± 15.0%, respectively.

2.3. Data analysis

Concentrations of airborne CUPs among seasons were compared using a *t*-test with a p value < 0.05 indicating significant differences. The regression analysis was performed in Sigma Plot version 10.0 (Systat, San Jose, CA, USA).

Concentration of total suspended particles (TSP, μg m^{-3}) in the atmosphere was one of the key parameters influencing the partitioning of chemicals between gas and particle phases (Pankow, 1994), and the partition coefficient between particle and gas phases (K_p) was conventionally applied to describe the partitioning process (Eq. (1)):

$$K_p = \frac{F}{TSP \times A} \tag{1}$$

where F and A are concentrations (pg m^{-3}) of target analytes in the particle and gas phases, respectively.

The relationship between K_p and sub-cooled liquid–vapor pressure (P_L^0, Pa) has been established to assess the influence of vapor pressure on the partitioning as described in the following equation:

$$\log K_p = m_r \log P_L^0 + b_r \tag{2}$$

where m_r and b_r are fitting constants. Since no temperature correction parameters were available for the target analytes, P_L^0 values at 25 °C were used for all seasons in the current study.

Potential exposure from inhalation of atmospheric CUPs was calculated using the following equation:

$$PE = \frac{C \times RR \times D}{BW} \tag{3}$$

where PE is the potential exposure from inhalation (mg kg^{-1} d^{-1}), C is the total air concentration (pg m^{-3}), RR is the respiratory rate (m^3 h^{-1}), D is the duration of exposure, or the cumulative time spent outdoors each day (h d^{-1}) and BW is body weight (kg).

A Monte-Carlo simulation was conducted to evaluate the sensitivity of the estimations from errors for individual parameters during the inhalation exposure. Simulations were performed using 20000 randomizations for the target CUPs (Schleier et al., 2009).

3. Results and discussion

3.1. Annual atmospheric concentration of CUPs

As shown in Table 1, total concentrations (target analytes in particle and gas phases) of the sum of CUPs (ΣCUP) ranged from 150 to 3816 pg m^{-3} throughout the year with an annual mean ± standard deviation of 1465 ± 1012 pg m^{-3}. Chlorpyrifos (1051 ± 861 pg m^{-3}) was the only OPP detected with concentrations greater than the reporting limit (RL), and it was the most dominant CUP detected in the samples, accounting for 68 ± 20% of ΣCUP. Chlorpyrifos was preferentially distributed in the gas phase with gas phase concentrations being 1019 ± 850 pg m^{-3}. Moreover, the detection of chlorpyrifos in PUFs in the field blanks also suggested its high atmospheric concentration.

Eight pyrethroids, including allethrin, bifenthrin, cyfluthrin, *lambda*-cyhalothrin, cypermethrin, dimefluthrin, permethrin and tetramethrin were detected in atmospheric samples in Guangzhou