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

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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.

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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

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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, $\mu g\ m^{-3}$) 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 20 000 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

Table 1
The reporting limits of individual pesticides (RL, pg m^{-3}) and atmospheric concentrations (pg m^{-3}) of chlorpyrifos, cypermethrin, sum of pyrethroids (ΣPYR) and sum of current-use pesticides (ΣCUP) in Guangzhou, China.

Sampling date	RL	Chlorpyrifos			Cypermethrin			ΣPYR			ΣCUP		
		Particle	Gas	Total[a]	Particle	Gas	Total	Particle	Gas	Total	Particle	Gas	Total
10-11-2011	7.5	36.9	1044	1081	85.9	<RL[b]	89.6	158	50.1	209	195	1094	1289
10-18-2011	7.8	42.0	2207	2249	1306	<RL	1310	1503	63.6	1567	1545	2270	3816
10-19-2011	6.9	80.0	2821	2901	237	<RL	241	459	46.1	505	539	2867	3406
10-20-2011	7.7	103	2110	2214	123	<RL	127	188	35.8	223	291	2146	2437
10-21-2011	6.7	31.4	2492	2523	98.3	<RL	102	148	26.2	174	179	2518	2697
10-22-2011	7.9	49.8	1009	1059	151	<RL	155	269	33.3	302	319	1043	1361
12-22-2011	6.4	18.1	135	153	31.2	9.1	40.2	57.6	129	187	75.6	264	340
12-23-2011	7.3	49.4	59.9	109	17.1	8.3	25.4	47.8	26.8	74.6	97.2	86.7	184
12-25-2011	7.1	–[c]	116	116	–	15.3	15.3	–	33.9	33.9	–	150	150
12-26-2011	7.3	74.6	226	301	146	11.8	158	237	41.7	279	312	268	579
03-27-2012	6.2	21.7	374	395	102	6.3	108	200	22.9	223	222	393	615
03-28-2012	6.7	34.2	38.5	72.7	1380	8.5	1388	1765	31.2	1796	1799	69.7	1869
03-29-2012	7.1	25.4	411	437	95.7	7.3	103	168	72.3	240	193	484	677
03-30-2012	6.3	16.8	484	501	120	7.3	127	209	31.7	241	226	516	742
05-22-2012	7.8	37.9	1064	1102	84.1	10.1	94.2	713	53.0	766	751	1117	1868
05-23-2012	9.2	26.4	1630	1656	133	10.1	143	275	60.6	336	301	1690	1991
05-24-2012	9.1	21.7	1214	1236	141	10.6	151	308	49.6	358	330	1264	1593
05-25-2012	9.4	21.7	2104	2125	109	16.1	125	226	100	326	248	2204	2451
07-11-2012	9.3	12.2	671	683	223	12.0	235	368	259	628	381	930	1311
07-12-2012	11.8	<RL	843	848	37.1	<RL	43.0	110	66.4	176	116	909	1025
07-13-2012	8.3	<RL	731	735	46.3	<RL	50.4	149	38.8	188	153	770	923
07-14-2012	8.1	<RL	626	630	124	<RL	128	187	87.5	275	192	713	905
Annual Mean		37.0	1019	1051	218	10.2	225	352	61.8	414	403	1080	1465
Standard deviation		25.5	850	861	369	3.0	368	443	51.4	444	450	848	1012

[a] Total concentration was the total of pesticide concentrations in particle and gas phases.
[b] Lower than the reporting limit (RL). The RL was the product of the lowest concentration of the calibration standards and the volume of solution used for instrumental analysis divided by the volume of the air sampled. When the concentration of pesticide in a sample was <RL, half of the RL value was used to calculate the total and mean concentrations.
[c] Data were not available due to the loss of the sample.

with concentrations greater than RLs in at least one sample. Total yearly concentrations of the pyrethroids (ΣPYR) ranged from 33.9 to 1796 pg m^{-3}. Cypermethrin, permethrin and allethrin were the three dominant pyrethroids in the air samples, and they accounted for 45%, 18% and 11% of ΣPYR, respectively (Tables 1 and S2).

As shown in Table 2, atmospheric chlorpyrifos concentrations in Guangzhou were similar to concentrations found in Iowa, USA (Peck and Hornbuckle, 2005), Central Region of France (Coscollà et al., 2010) and Tokyo, Japan (Kawahara et al., 2005), but slightly higher than that found in California, USA (Rudel et al., 2010). Similar atmospheric chlorpyrifos concentrations have been found in urban and agricultural areas, which were not surprising, since it has both agricultural and urban applications (http://www.chinapesticide.gov.cn/doc07/07102301-1.html). Furthermore, atmospheric transport of chlorpyrifos may also cause concentrations to be similar in different regions of the world. Interestingly, approximately 20 times less chlorpyrifos was detected in agricultural areas in Ontario, Canada (Hayward et al., 2010) compared to other countries (including the current study). In that study, Hayward et al. (2010) noted that pesticide concentrations in the air had no relationship with their usage in the study area, and suggested that other parameters, like ambient temperature, TSP concentrations and precipitation, might also affect atmospheric pesticide concentrations.

Compared to chlorpyrifos, fewer studies have monitored airborne pyrethroids and most of them were conducted in agricultural areas (Table 2). Sulaiman et al. (2007) reported that atmospheric cypermethrin were at concentrations of 142–3740 pg m^{-3} near vegetable and flower farms in Malaysia, and these results were comparable to the current study (15.3–1388 pg m^{-3}). Malaysia is located near Guangzhou and the similar concentrations of atmospheric cypermethrin may have corresponded to the similar pesticide usage patterns. Owing to its lower price, cypermethrin is the most commonly used pyrethroid in Asia (Whittle, 2010). Conversely, atmospheric bifenthrin and permethrin concentrations were much lower in Guangzhou compared to concentrations found in the US (Bradman et al., 2007; Morgan et al., 2007). The difference in the composition of atmospheric pyrethroid residues in China and the US was consistent with the composition of sediment-associated pyrethroids in the two countries (Li et al., 2011). Cypermethrin dominated pyrethroid residues in sediments in China, reflecting its extensive use in Asia (Li et al., 2011), whereas bifenthrin and permethrin were two of the most commonly used pyrethroids in residential areas in the US and were detected at high frequency and elevated concentrations in sediment (Weston et al., 2005).

3.2. Seasonal variation in atmospheric CUPs

Seasonal variation in CUP detections was observed in ambient air in Guangzhou (Fig. S1). In general, atmospheric concentrations of CUPs increased in spring (March), reached peak concentrations in summer (May and July) or fall (October) and then dropped in winter (December). Peak atmospheric pesticide concentrations have also been reported in summer in previous studies (Peck and Hornbuckle, 2005; Coscollà et al., 2010) and elevated concentrations were expected in summer due to the relatively larger application of pesticides in this season. Chlorpyrifos was recommended as a replacement for the more highly toxic OPPs for pest control in agriculture, vegetable and fruit gardens, and was also used in termite control (http://www.chinapesticide.gov.cn/doc07/07102301-1.html). Pyrethroids were widely used in professional landscaping and residential pest control. Both chlorpyrifos and pyrethroids were heavily used in Guangzhou (http://www.gzstats.gov.cn/gzsq/201112/t20111229_27422.htm). Additionally, Guangzhou is located in a subtropical zone with warm and humid weather during the summer and fall, which pro-

Table 2
Atmospheric concentrations (pg m^{-3}) of chlorpyrifos and pyrethroids in different locations.

Location	Type of land use	Sampling year	Concentration (pg m^{-3})				Reference
			Chlorpyrifos	Cypermethrin	Permethrin	Bifenthrin	
California, USA	Urban & rural	1999–2000	ND[a]-860	–[b]	–	–	Rudel et al. (2010)
Iowa, USA	Urban, rural, &suburban	2001–2002	1000 ± 260	–	–	–	Peck and Hornbuckle (2005)
Ohio, USA	Agricultural community	2001	–	–	*cis*-:ND-180 *trans*-:ND-1300	–	Morgan et al. (2007)
California, USA	Agricultural community	2002	–	–	ND-8000	ND-2800	Bradman et al. (2007)
Tokyo, Japan	Agricultural community	2003	2000 (<RL[c] – 5000)	–	–	–	Kawahara et al. (2005)
Panghang, Malaysia	Farming areas	2004	–	142–3740	–	–	Sulaiman et al. (2007)
Ontario, Canada	Rural area (agricultural)	2006–2007	41.6 ± 14.6	–	–	–	Hayward et al. (2010)
Central Region, France	Urban& rural	2006–2008	2860 ± 10960	–	–	–	Coscollà et al. (2010)
Guangzhou, China	Urban	2011–2012	1051 ± 861	225 ± 369	76.3 ± 90.9	28.7 ± 36.5	The current study

[a] Not detected.
[b] Data were not available.
[c] Less than the reporting limit.

motes the propagation of pests. Therefore, it is reasonable that the peak CUP concentrations lasted until fall. Concentrations of ΣCUP, chlorpyrifos and cypermethrin were slightly, but not significantly higher in fall compared with summer (Fig. S1). Atmospheric pesticides could be dispersed by precipitation (McConnell et al., 1998) and summer is the rainy season in Guangzhou. Consequently, more rain events might explain the slightly lower atmospheric CUP concentrations in summer compared with fall.

Bifenthrin, *lambda*-cyhalothrin and permethrin had similar seasonal variation as cypermethrin with peak concentrations being observed during the application period, e.g. summer and fall, while concentrations of allethrin, dimefluthrin and tetramethrin were not significantly different among seasons (Fig. S2). A survey of local stores showed that allethrin, dimefluthrin and tetramethrin were the most commonly used active ingredients in mosquito-control agents in Guangzhou, whereas the other pyrethroids were used for mosquito as well as professional and agricultural pest control. In general, the peak occurrence of agricultural and professional landscaping pests was from late spring to fall. As a result, CUPs used for those purposes, like chlorpyrifos, cypermethrin, permethrin and *lambda*-cyhalothrin, were mainly applied during this period. Conversely, warm and humid weather promoted mosquito breeding in Guangzhou, thus the use of mosquito-control agents was extended year round, resulting in less seasonal variation in atmospheric concentrations of these pyrethroids, e.g. allethrin, dimefluthrin and tetramethrin. Finally, gas–particle partitioning processes of CUPs may also affect the seasonal variations of their occurrence in air.

3.3. Gas–particle partitioning of atmospheric CUPs

Distribution of pesticides between gas and particle phases was one of the critical factors affecting their atmospheric transport and removal via deposition and degradation (Sanusi et al., 1999). Particle-associated compounds were mainly removed from the air by dry deposition or washout of the particles, with residence time in the range of days (Bidleman et al., 1986). Alternatively, gaseous compounds were predominantly removed by vapor deposition or photo-degradation and had longer residence times in the atmosphere, which promoted their long-range transport worldwide (Eisenreich et al., 1981). The gas–particle partitioning of CUPs during different seasons in Guangzhou was presented in Fig. 1. Generally, pesticides with lower vapor pressures had a greater tendency

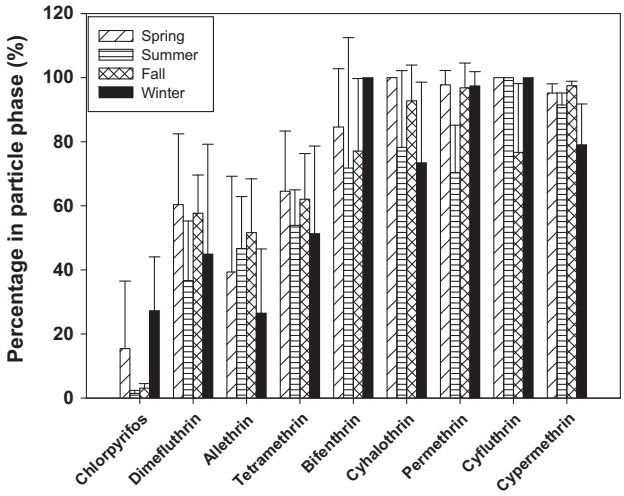

Fig. 1. Percentage of current-use pesticides associated with the particle phase compared to the total atmospheric concentrations (in gas and particle phases) during various seasons in Guangzhou, China. Error bars represent standard deviations of the percentages of pesticides associated with the particle phase of the samples collected throughout the season.

to be associated with the particle phase. The target CUPs were separated into three groups according to their gas–particle partitioning tendency. Chlorpyrifos (group 1) was the most often detected in the gas phase in all seasons with an average of 92% associated with the gas phase and this finding was similar to previous observations in Canada (Sadiki and Poissant, 2008). Group 2 contained dimefluthrin, allethrin and tetramethrin, which were almost equally distributed between the two phases, with 48%, 44% and 58% of the pesticides in the particle phase, respectively. The CUPs in group 3 included bifenthrin, *lambda*-cyhalothrin, permethrin, cyfluthrin and cypermethrin, and were mainly associated with the particle phase, with average percentages attached to particles ranging from 80% to 93%.

Because it was associated mainly with the gas phase, chlorpyrifos could experience long-distance transport throughout the world. This conclusion was supported by the high detection frequencies of chlorpyrifos at elevated concentrations in sea water, marine ice and marine fog in the Bering and Chukchi marine ecosystems (Chernyak et al., 1996). As shown in Table 2, chlorpyrifos

concentrations in ambient air were comparable in different countries and the long-range transport capability of this chemical might be one of the reasons why this is found. Conversely, pyrethroids, especially cypermethrin, were mainly sorbed to particles. Therefore, pyrethroids tended to stay close to the emission sources. Furthermore, differences in gas–particle partitioning also existed among the pyrethroids. The percentage of dimefluthrin, allethrin and tetramethrin (group 2) that was associated with the particle phase was significantly lower than that of cyfluthrin and cypermethrin, and lower than bifenthrin, *lambda*-cyhalothrin and permethrin although not significantly. The higher percentage of a chemical in the gas phase, the longer its residence time in the air. Thus, the difference in gas–particle partitioning may be one of the reasons for the observation mentioned early that dimefluthrin, allethrin and tetramethrin exhibited less seasonal variation in atmospheric concentrations compared with the other pyrethroids.

Several environmental parameters, like ambient temperature and atmospheric humidity, can also affect the distribution of a chemical between the gas and particle phases. Therefore, seasonal variations in gas–particle partitioning of CUPs were analyzed (Fig. 1). The percentage of chlorpyrifos associated with particles in winter (27 ± 17%) was significantly higher than in fall (3.1 ± 1.4%) and spring (4.9 ± 1.3%, except for one sample collected on March 28, 2012), and spring data was significantly higher than that in summer (1.4 ± 0.6%). The outlier collected on March 28, 2012 had extremely low CUP concentrations in the gas phase, thus the percentage of chemical associated with the particle phase was about 10 times higher compared to other spring samples. In theory, the vapor pressure of a compound decreases with decreasing temperature, resulting in an increased percentage of the compound associated with the particle phase. This explained the higher percentage of chlorpyrifos associated with the particle phase in winter compared to other seasons. However, no significant differences were noted in the gas–particle partitioning of pyrethroids across seasons in the current study. Therefore, parameters other than temperature, like ambient humidity and TSP, might govern the partitioning process of pyrethroids between the two phases, as suggested by Sanusi et al. (1999).

As shown in Eq. (1), TSP concentrations were one of the key parameters controlling gas/particle partitioning of the semi-volatile organic compounds in the atmosphere (Pankow, 1994). A significant correlation was observed between $\log K_p$ and $\log P_L^0$ among seasons ($\log K_p = -0.96\ \log P_L^0 - 5.11$, $r^2 = 0.52$, $p < 0.0001$). Similarly, regressions of $\log K_p$ and $\log P_L^0$ were significant for individual seasons, with r^2 values ranging from 0.52 to 0.77 (Fig. S3). All of the slopes were near −1, which implied that the partitioning of CUPs between gas and particle phases was near equilibrium in Guangzhou air (Simcik et al., 1998).

3.4. Potential exposure risk of atmospheric CUPs

Atmospheric CUPs may cause adverse health effects through inhalation exposure. To examine age-related differences in exposure to airborne CUPs, six subgroups of the population were included in the assessment: infants (0.5–1.5 years old), toddlers (2–3 years old), children (5–6 years old), youth (10–12 years old), adult males and females (18–65 years old). The annual average total concentration (in particle and gas phases) of each pesticide was used to estimate the PE (Eq. S3). Estimated respiratory rates and body weights for the subgroups were obtained from the literature (Brochuab et al., 2006; Portier et al., 2007) and presented in Table S3. As suggested in the statistical data collected by the U.S. Environmental Protection Agency (USEPA), the cumulative time spent outdoors was not significantly different among various age groups, thus a value of 154 ± 158 min d^{-1} was applied for all subgroups (USEPA, 1997). Meanwhile, risk quotients (RQ) were calculated by dividing PE of each subgroup to a pesticide by its oral ingestion reference dose (RfD), which was estimated based on the no-observed-adverse-effect level (NOAEL) (Schleier et al., 2009). The NOAEL for inhalation exposure and acute and chronic oral ingestion RfD values were shown in Table S4. The RQ level of concern was set as 1.0, thus a RQ > 1.0 indicated estimated exposure was higher than the ingestion RfD and potential risk was present (Schleier et al., 2009).

The estimated inhalation exposure and acute and chronic RQs for the subgroups were reported in Table S5. The inhalation PE values ranged from 33.0 to 64.1 pg kg^{-1} d^{-1} for all CUPs to the subgroups. Infants, toddlers, and children were more susceptible with higher exposures compared to youth and adults, although the PE values were all 7 to 10 orders of magnitude less than the NOAELs (Tables S4 and S5). The ranges of acute and chronic RQs were 5.05×10^{-6} to 9.81×10^{-6} and 7.93×10^{-4} to 15.4×10^{-4}, respectively, and all were significantly smaller than 1.0. Individually, chlorpyrifos had the highest RQ values, followed by allethrin, *lambda*-cyhalothrin, cypermethrin, bifenthrin, and permethrin (Table S5). Sensitivity analysis demonstrated that the duration of exposure and CUP concentration contributed the majority of the variance to the outputs and no significant difference was observed among subgroups (Table S6). The results implied that health risk from inhalation of atmospheric CUPs in Guangzhou was negligible, but the risk might be underestimated in several ways.

First, additional exposure routes, including ingestion of objects covered with CUP-bound particles and uptake through dermal surfaces could increase the exposure to CUPs, especially for the susceptible population groups. Schleier et al. (2009) claimed that inhalation exposure of pesticides from ultra-low-volume aerosol applications accounted for 60% of the total exposure to children, youth and adults, but it was only 8% for infants and toddlers to whom the major exposure route (60%) was consuming contaminated materials.

Second, the estimates used in the current study did not consider seasonal variation, and the exposure risk in summer and fall might be higher than the annual average level. The cumulative time spent outdoors was longer in summer and fall than in winter, although the difference was not statistically significant (USEPA, 1997). Meanwhile, CUP concentrations in the atmosphere were significantly higher in summer and fall than winter (Fig. 1). The combination of greater CUP concentrations and longer exposure times produced higher risk in summer and fall. In addition, gas–particle partitioning analysis showed that more CUPs were present in the gas phase with elevated summer temperatures, especially for chlorpyrifos. The gaseous chemicals were more easily inhaled and had greater bioavailability; therefore, seasonal variation in pesticide occurrence and partitioning might also cause seasonal variation in exposure risk of CUPs in the atmosphere, and higher risk may occur in summer and fall.

Third, RfD or NOAEL values used for the RQ estimation did not take all toxic mechanisms into consideration and thus the health concern may be underestimated (Castorina and Woodruff, 2003). The CUPs generally have multiple modes of action, thus RfDs derived from a single toxic mechanism may have been overestimated due to the exclusion of other potential toxic mechanisms. Moreover, exposure to CUP metabolites was not included in the assessment. Photodegradation of chlorpyrifos can occur in the air (Aston and Seiber, 1997) and the oxon metabolites are more potent acetylcholinesterase inhibitors than the parent compound (Huff et al., 1994; Poet et al., 2003). Thus, excluding the possible air exposure pathways of the more toxic oxon metabolites in chlorpyrifos risk assessment may underestimate its risk. In addition, interactive effects of multiple stressors could not be assessed by using the RfD or NOAEL values for a single pesticide.

Finally, infants, toddlers and children are of special concern due to their greater vulnerability to atmospheric CUPs. These age groups represent a more sensitive life stage and their developmental processes are easily disturbed; therefore, pesticide-induced dysfunction could be permanent and irreversible during this developmental period (Landrigan et al., 1999; Eskenazi et al., 1999). In addition to infants and children, risk of CUP exposures to pregnant women should also be emphasized. A recent study (Wang et al., 2012) assessed the potential impacts of OPP exposure on the duration of gestation and a significant inverse correlation was observed for infant girls for OPP metabolites and duration of gestation. Although low doses of chlorpyrifos and pyrethroids, as indicated by the presence of metabolites in urine, have been correlated with neurodevelopmental and behavioral impairments in newborns, the relationship between the exposure levels (e.g. air concentrations) and adverse effects has been barely studied. Therefore, more studies are needed evaluating the developmental neurotoxicity to infants and children due to the inhalation exposure of atmospheric chlorpyrifos and pyrethroids.

4. Conclusions

The current study investigated the occurrence and seasonal variation of atmospheric CUPs and their potential risk to public health from inhalation exposure in South China. Chlorpyrifos and eight pyrethroids (mainly cypermethrin) were frequently detected in the air with peak concentrations in summer and fall, which was consistent with the usage patterns. Infants, toddlers and children were the most susceptible to CUP exposure although inhalation exposures from airborne OPPs and pyrethroids were less than NOAELs for all age groups. However, risk might be underestimated due to additional exposure routes, other toxic mechanisms of the pesticides, and vulnerability of more sensitive groups (e.g. pregnant women). Therefore, additional studies are required to better understand the transport and risks of atmospheric CUPs, focusing on the developmental toxicity to vulnerable populations, and ultimately to reduce exposure-related diseases.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013 .09.046.

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