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Assessing the effects of urbanization on the environment with soil legacy and current-use insecticides: A case study in the Pearl River Delta, China

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HIGHLIGHTS

- High soil insecticide concentrations occur in the rapidly urbanizing central PRD.
- Anthropogenic impacts play a role in the spatial patterns of soil insecticides.
- High levels of insecticides in the residency land may be due to land-use change.
- Soil was a significant secondary source of HCHs and p,p'-DDT to the atmosphere

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ABSTRACT

To evaluate the impacts of anthropogenic events on the rapid urbanized environment, the levels of legacy organochlorine pesticides (OCPs) and current-use insecticides (CUPs), i.e., dichlorodiphenyltrichloroethane and its metabolites (DDTs), hexachlorocyclohexanes (HCHs), pyrethroids and organophosphates in soil of the Pearl River Delta (PRD) and surrounding areas were examined. Spatial concentration distributions of legacy OCPs and CUPs shared similar patterns, with higher concentrations occurred in the central PRD with more urbanization level than that in the PRD's surrounding areas. Furthermore, relatively higher concentrations of OCPs and CUPs were found in the residency land than in other land-use types, which may be attributed to land-use change under rapid urbanization. Moderate correlations between gross domestic production or population density and insecticide levels in fifteen administrative districts indicated that insecticide spatial distributions may be driven by economic prosperity. The soil–air diffusive exchanges of DDTs and HCHs demonstrated that soil was a sink of atmospheric *o,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD and *o,p′*-DDT, and was a secondary source of HCHs and *p,p′*-DDT to atmosphere. The soil inventories of DDTs and HCHs (100 $\pm$ 134 and 83 $\pm$ 70 tons) were expected to decrease to half of their current values after 18 and 13 years, respectively, whereas the amounts of pyrethroids and organophosphates (39 and 6.2 tons) in soil were estimated to decrease after 4 and 2 years and then increase to 87 and 1.0 tons after 100 years. In this scenario, local residents in the PRD and surrounding areas will expose to the high health risk for pyrethroids by 2109. Strict ban on the use of technical DDTs and HCHs and proper training of famers to use insecticides may be the most effective ways to alleviate the health effect of soil contamination.

1. Introduction

Urbanization and land conversion have increasingly intensified during the last several decades within urban agglomerations and surrounding areas. It is estimated that 41 urban agglomerations worldwide are projected to house at least 10 million inhabitants each by 2030 (United Nations, 2014). At the same time, rapid urbanization has been accompanied with numerous environmental problems (Tao et al., 2008). For example, as the change of land use type from agricultural to residential or commercial, legacy insecticides used in agricultural activities may subject residents to high health risk. Urbanization has obviously reduced crop growing areas; e.g., the sown areas of crops decreased from 5.4×10^5 to 4.5×10^5 km^2 from 1985 to 2010 in Guangdong Province of South China (Agricultural Statistical Yearbook of Guangdong, 2009; Statistical Bureau of Guangdong Province, 1990, 2011), where the Pearl River Delta (PRD; Fig. S1 of the Supplementary data; "S" represents figures and tables of target analytes in the Supplementary data thereafter), one of the largest city clusters in China, is located. However, the amount of insecticides used during the same period increased from 7.3×10^4 to 1.04×10^5 tons for improving crop production, boosting the likelihood of air and water pollution.

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Therefore, understanding the relationship between urbanization and the environmental fate of insecticides is important for implementing efficient measures to mitigate soil pollution by insecticides during the development of large city clusters.

The PRD is an ideal site for examining such a relationship, as its urbanized area increased by 2615 km^2 during the period of 2000–2010 (Statistical Bureau of Guangdong Province, 2001, 2011). To meet the demand for foods with population growth and reduction in crop growing areas, insecticides have been increasingly used to improve agricultural output. For instance, the annual pesticide application (37.2 kg/yr ha) in the PRD from 1980 to 1995 was four times higher than the average national level (Guo et al., 2006). Thus, organochlorine pesticides (OCPs), such as dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs), have been frequently detected in water, soil, sediment, and biota sampled in the PRD (Guan et al., 2009; Guo et al., 2009; Li et al., 2006; Ma et al., 2008; Yu et al., 2011), although they were banned in the 1980s. Because of low toxicity to mammal, organophosphates and pyrethroids have been introduced to replace OCPs (Ma et al., 2008; Yang et al., 2012; Yu et al., 2013; Zhang et al., 2012), and widely used in agricultural and urban settings (Amweg et al., 2005). Under these applications, the occurrence of current-use insecticides may closely correlate with the intensity of urbanization. Soil can be considered as an environmental compartment directly impacted by rapid urbanization, and is also a predominant sink of insecticides upon application (Meijer et al., 2003; Tao et al., 2008). Therefore, soil legacy and current-use insecticides collectively can be used as reliable tracers to assess the impacts of anthropogenic activities on the environment in rapidly urbanized regions.

To accomplish the above-mentioned objectives, we conducted an extensive survey on soil insecticides including OCPs and current-use pesticides (CUPs) in the PRD and surrounding areas. In addition to assessing their residues, spatial patterns and land-use type distributions of insecticides were also examined associated with local economic and farming-related factors. Soil–air exchange fluxes of insecticides were calculated to evaluate their transfer modes. Furthermore, projected soil inventories of legacy and current-use insecticides were profiled with a box model containing the fluxes of inter-compartmental processes.

2. Materials and methods

2.1. Sample collection

Detailed sampling procedures were described previously (Y.-L. Wei et al., 2014). Briefly, 229 soil samples were collected from the PRD and surrounding areas, South China (Fig. S1) from December 2009 to March 2010 and the sampling areas were divided into six land-use types, i.e., residency, industry, landfill, agriculture, forestry, and drinking water source (Fig. S1b). In addition, the administrative districts within the sampling region were divided into four groups to elucidate the spatial patterns of soil insecticide contamination. Specifically, the central PRD includes Shenzhen, Dongguan, Zhuhai, Zhongshan, Guangzhou, and Foshan; the PRD's periphery contains Zhaoqing, Qingyuan, Jiangmen, and Huizhou; and the East or West regions are consisted of Shaoguan, Heyuan, and Shanwei or Yangjiang and Yunfu, respectively (Fig. S1b).

2.2. Sample extraction and instrument analysis

Each freeze-dried soil sample (~20 g) was Soxhlet-extracted after being spiked with surrogate standards (4,4′-dibromooctafluorobiphenyl, PCB-67, PCB-191, PCB-204, and PCB-209). The extract was concentrated and subject to purification/fractionation with column chromatography after solvent exchange to hexane. The fraction containing all insecticides was collected and concentrated. Known amounts of the internal standards (PCB-24, PCB-82, PCB-189, and parathion-d_{10}) were added to the extract before GC/MS analysis. Detailed procedures of sample extraction and purification/fractionation are presented in the Supplementary data.

A total of 23 insecticides and its metabolites (Table S1) were quantified with a Shimadzu GC/MS-QP2010 Plus (Shimadzu, Kyoto, Japan). Legacy OCPs were separated with a DB-5MS column (60 m × 0.25 mm-i.d., 0.25 μm film thickness); their mass spectra were acquired in the electron ionization mode. Pyrethroids and organophosphates were separated with a DB-5HT column (15 m × 0.25 mm-i.d., 0.10 μm film thickness) and their mass spectra were acquired in the negative chemical ionization mode (Li et al., 2013).

2.3. Quality assurance and quality control (QA/QC)

For each batch of 17 field samples, a procedural blank, spiked blank, matrix blank, matrix spiked sample, and three sample replicates were processed. Extracted soil samples were randomly selected as matrix blank and matrix spiked samples. The recoveries (mean ± standard deviation) for all insecticides in spiked samples were in the ranges from 52 ± 12% to 106 ± 23%. In addition, the recoveries of the surrogate standards, i.e., PCB-67 and PCB-191 for OCPs in all samples were 124 ± 20% and 101 ± 16%, respectively. Recoveries of surrogate standards, i.e., 4,4′-dibromooctafluorobiphenyl, PCB-191, PCB-204, and PCB-209, were 57 ± 17%, 68 ± 16%, 70 ± 18%, and 100 ± 32%, respectively. The lowest calibration concentrations dividing individual sample weights were defined as the reporting limits (RLs), which were 0.17–0.36 ng/g for individual OCPs and 0.08–0.17 ng/g for individual pyrethroids and organophosphates.

2.4. Data analysis

The sum of 11 legacy OCP congeners was labeled as $\sum_{11}$OCP, including seven DDT compounds ($\sum_7$DDX; *o,p*′-DDE, *p,p*′-DDE, *o,p*′-DDD, *p,p*′-DDD, *o,p*′-DDT, *p,p*′-DDT, and *p,p*′-DDMU) and four HCH compounds ($\sum_4$HCH; α-HCH, γ-HCH, β-HCH, and δ-HCH). The sum of all DDT and its metabolites except for *p,p*′-DDMU was designated as DDTs. The sum of 12 CUPs was defined as $\sum_{12}$CUP, including nine pyrethroids ($\sum_9$PYRE; bifenthrin, fenpropathrin, tefluthrin, λ-cyhalothrin, permethrin, cyfluthrin, cypermethrin, esfenvalerate, and deltamethrin) and three organophosphates ($\sum_3$OP; parathion-methyl, malathion, and chlorpyrifos). Furthermore, insecticide concentrations were normalized to dry sample weight, but not corrected by surrogate standard recoveries. Concentrations of OCPs were blank corrected because several of them in blank samples were higher than the RLs. Zero and half of RL were used for measured values below the RL in concentration and compositional assessments, respectively.

Spatial patterns of soil insecticide concentrations were analyzed with the Ordinary Kriging interpolation method using ArcGIS Version 10.0 (ESRI, Redlands, USA) (Juang and Lee, 1998). Significant differences in insecticide concentrations were examined with one-way analysis of variance tests with SPSS Version 13.0 (SPSS, Chicago, USA). A Welch's *t*-test was used to determine any significant difference between two sets of samples with unequal variances from the present study and previous studies. In all statistical analyses, the criterion of significance was defined as $p < 0.05$.

In addition, due to the lack of atmospheric CUPs data, soil–air fluxes (F_{sa}) in different geographic regions were estimated for OCPs only by the following equation:

$$F_{sa} = D_{SA}(f_S - f_A) \quad (1)$$

where f_S (Pa) and f_A (Pa) are the fugacity values of an analyte in soil and air, respectively; and D_{SA} (mol Pa^{-1} m^{-2} h^{-1}) is the diffusive coefficient of the target analyte across soil–air interface (Supplementary data text 2). Atmospheric concentrations of individual OCPs were obtained from Ling et al. (2011) (Table S2). Moreover, projected soil inventories (I_t) for OCPs and CUPs were profiled with a box model containing the fluxes of four inter-compartmental processes, i.e., atmospheric deposition (F_a), runoff (F_{runoff}), degradation (F_d), and soil–air gaseous exchange (F_{sa}) (Zhang et al., 2011):

$$I_t = I_0 + \int_0^t (F_a - F_{runoff} - F_d - F_{sa})dt. \tag{2}$$

Considering the use patterns of OCPs and CUPs, Eq. (2) estimating the temporal change in the soil inventory of OCPs can be revised to

$$I_t = I_0 + \int_0^t \left(\left(F_{dry} + F_{wet}\right) \times (1 - k_d)^t - F_{runoff} - F_d - F_{sa}\right)dt. \tag{3}$$

Similarly, the projected soil inventory of CUPs can be estimated by

$$I_t = I_0 + \int_0^t \left(\left(F_{dry} + F_{wet}\right) \times (1 + k_a)^t - F_{runoff} - F_d - F_{sa}\right)dt \tag{4}$$

where I_0 is the initial soil inventory; F_{dry} and F_{wet} are the annual fluxes of dry and wet deposition, respectively; k_d is the annual decay ratio of individual OCPs; and k_a is the annual increasing rate of individual CUPs in the atmosphere. It should be noted that k_d and k_a vary with the amounts of insecticides used. In the present study, k_d and k_a were assumed to be constant in simulation of projected soil inventories of OCPs and CUPs. Detailed procedures for estimating the fluxes of riverine runoff and degradation are presented in the Supplementary data text 2. Monte Carlo simulation was used to estimate the sensitivity and uncertainty of each parameter for multi-parameter calculations (Y.-L. Wei et al., 2014; Zhang et al., 2011).

3. Results and discussion

3.1. Residues of soil insecticides

Concentrations of $\sum_{11}$OCP varied in the range of <RL–1750 ng/g with mean (median) values of 33 (8.1) ng/g (Table S1). Moreover, the mean values of $\sum_7$DDX and $\sum_4$HCH levels were 18.4 and 14.2 ng/g (Table S1). An extremely high concentration of $\sum_7$DDX (1750 ng/g) was found in a soil sample collected from a garden in a community hospital of Huizhou. *p,p′*-DDT was also extremely abundant (1380 ng/g) and accounted for 78% of $\sum_7$DDX in this soil sample, possibly impacted by point-source inputs of technical DDT (Metcalf, 1973). As a result, this soil sample was excluded from significant difference tests and Kriging interpolation for spatial concentration distribution. With this exclusion, the concentrations of $\sum_{11}$OCP were in the range of <RL–1560 ng/g (mean: 25 ± 117 ng/g; median: 7.9 ng/g) (Table S1). A comparison of HCH and DDT data in the present study with those previously acquired in the PRD indicated that HCH levels in soil increased from 1999 to 2010 in the PRD and surrounding areas, whereas concentrations of soil DDXs in the PRD remained relatively unchanged (Table S3).

Compared to the levels of banned pesticide (OCPs), the concentrations of $\sum_{12}$CUP were relatively lower with a range of <RL–380 ng/g. The mean concentrations of $\sum_9$PYRE and $\sum_3$OP were 9.1 and 0.90 ng/g (Table S1). Specifically, cypermethrin was the most detectable CUP compound with a detection frequency of 43% and was predominant with a mean concentration of 4.6 ng/g (Table S1). This compositional profile was consistent with a previous finding in sediment samples collected from the PRD (Li et al., 2011), but was different from the patterns of pyrethroids in sediment collected across California with bifenthrin as the dominant component (Weston et al., 2005). This distinction may attribute to preferential usage of insecticides in these two regions, as cypermethrin is one of the most commonly used pyrethroids in Asia (Whittle, 2010) because of its low price.

3.2. Spatial distribution of soil insecticides

Spatial $\sum_{11}$OCP concentration distribution showed that hot spots were concentrated in the central PRD, i.e., Guangzhou, Dongguan, and Foshan (Fig. 1a), whereas relatively lower contaminated sites were mainly situated in the East and West regions which are less economically developed and populated than those in the central PRD (Fig. 1) (Statistical Bureau of Guangdong Province, 2011). This distribution was consistent with that of OCPs in Haihe Plain of North China (Tao et al., 2008), suggesting that economic prosperity has been a significant contributor to soil contamination by insecticides. For instance, Guangzhou, Dongguan, and Foshan have historically been megalopolises, so that farmers in these regions could afford DDTs and HCHs for pest control before their widespread usage was banned (Qiu et al., 2005; Zhang et al., 2002).

As expected, the spatial distribution of $\sum_{12}$CUP was similar to that of $\sum_{11}$OCP, but the hot spots of $\sum_{12}$CUP were extended from the central PRD to the administrative districts of the PRD's periphery, i.e., Huizhou, Zhaoqing, and Zhongshan (Fig. 1b). This extension of hot spots is apparently resulted from large amounts of pyrethroids used in landscaping and mosquito coil for pest control in urban areas (Li et al., 2011). Although there are no statistical data about the usage amounts of pyrethroids in cities of China, approximately 70% of pyrethroids in California was used in urban settings (Spurlock and Lee, 2008). In addition, the spatial distributions of $\sum_7$DDX, $\sum_4$HCH, and $\sum_9$PYRE were similar to those of $\sum_{11}$OCP and $\sum_{12}$CUP (Figs. S2 and S3a), but higher $\sum_3$OP concentrations mainly occurred in Jiangmen, Zhongshan, Zhuhai, and Huizhou (Fig. S3b), relatively less developed regions. The different spatial patterns of $\sum_9$PYRE and $\sum_3$OP may be due to the difference in the amounts of these chemicals used in agriculture, as well as in the sown areas and gross domestic production (GDP) values for different administrative districts. Organophosphates have been used mainly for pest control in agriculture; thereby, Jiangmen, Zhongshan, Zhuhai, and Huizhou with sown areas of 140–3700 km^2 were expected to use larger amounts of $\sum_3$OP than the central PRD with sown areas of 0.1–1500 km^2. Furthermore, farmers in these regions (Jiangmen, Zhongshan, Zhuhai, and Huizhou) with annual GDP at 120–180 billion RMB could afford more organophosphates than those in the less developed districts (Shanwei, Heyuan, Shaoguan, Qingyuan, Yunfu, Zhaoqing, and Yangjiang) with annual GDP ranging from 39 to 110 billion RMB (Statistical Bureau of Guangdong Province, 2011). In addition, Huang et al. (2005) found that the concentrations of individual organophosphates (including dichlorvos, methamidophos, acephate, omethoate, dimethoate, malathion, quinalphos, phorate, monocrotophos, parathion, parathion-methyl, and isocarbophos) ranged from <RL to 5.7 μg/g in vegetable samples collected from Zhongshan. The concentrations of organophosphates in 30% of the vegetable samples exceeded the maximum permissible thresholds in vegetables, i.e., from 0.01 (phorate) to 8 μg/g (malathion) in China (National Health and Family Planning Commission of the People's Republic of China, Ministry of Agriculture of the People's Republic of China, 2014). Overall, the spatial distribution patterns of insecticides were consistent with the results from our previous studies (G.-L. Wei et al., 2014; Y.-L. Wei et al., 2014), i.e., higher concentrations of soil polycyclic aromatic hydrocarbons (PAHs) and linear alkylbenzenes in the central PRD than those in other three geographic regions.

In addition, the concentrations of $\sum_{11}$OCP and $\sum_{12}$CUP varied considerably among six land-use types (Fig. 2). Specifically, the mean concentrations of $\sum_{11}$OCP in the PRD and surrounding areas decreased in the order of residency > industry > landfill > agriculture > forestry > drinking water source, while the mean concentrations of $\sum_{12}$CUP followed the order of landfill > residency > agriculture > industry > forestry > drinking water source. The similar patterns for levels of OCPs and CUPs may be attributed to land-use change under rapid urbanization in the PRD and surrounding areas. The dynamics of land-use change ranged from 2.1% to 3.9% between 1996 and 2008 in eight administrative districts (Guangzhou, Foshan, Jiangmen, Zhuhai,

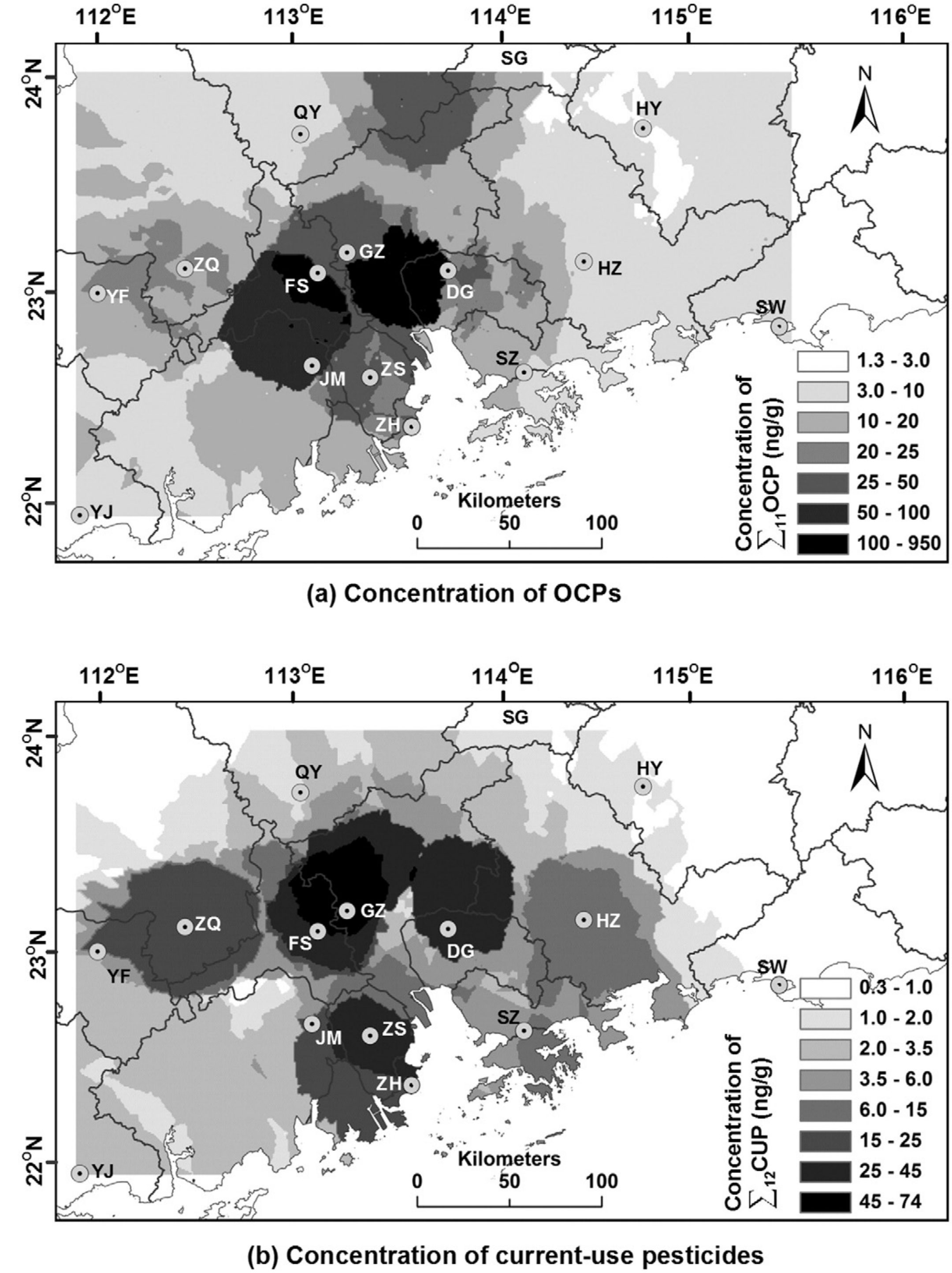

Fig. 1. Maps showing spatial distributions of (a) legacy OCPs ($\sum_{11}$OCP) and (b) current-use pesticide ($\sum_{12}$CUP) concentrations (ng/g dry weight) in soil of the Pearl River Delta and surrounding areas, South China (Fig. S1). YJ, YF, ZQ, QY, JM, HZ, GZ, FS, DG, ZS, ZH, SZ, HY, SW, and SG are the acronyms of district names, i.e., Yangjiang, Yunfu, Zhaoqing, Qingyuan, Jiangmen, Huizhou, Guangzhou, Foshan, Dongguan, Zhongshan, Zhuhai, Shenzhen, Heyuan, Shanwei, and Shaoguan, respectively. A residential soil with an extremely high concentration of $\sum_{11}$OCP (1750 ng/g) in Huizhou was excluded.

Dongguan, Shenzhen, Huizhou, and Heyuan), five out of which were higher than 2.5%, indicating large conversion of land-use (Tang et al., 2010). For example, approximately 35.5 km^2 of agricultural land with frequent use of legacy OCPs had been converted to residency land by 2008 (http://www.mlr.gov.cn/tdsc/tdly/201006/t20100612_151886.htm). As a result, residual OCPs in the residency land may evaporate and subject local residents to high health risk.

3.3. Anthropogenic impacts on the distributions of legacy OCPs and CUPs

Spatial distribution patterns of $\sum_{11}$OCP and $\sum_{12}$CUP were similar to those of GDP and population density (Figs. 1 and S4). Moreover, the log-transformed soil concentrations of $\sum_{11}$OCP or $\sum_{12}$CUP were moderately correlated ($r^2 = 0.30$–0.41 and $p < 0.05$ for all regressions; Fig. 3) with GDP or population density in fifteen administrative districts (Statistical Bureau of Guangdong Province, 2011). On the other hand,

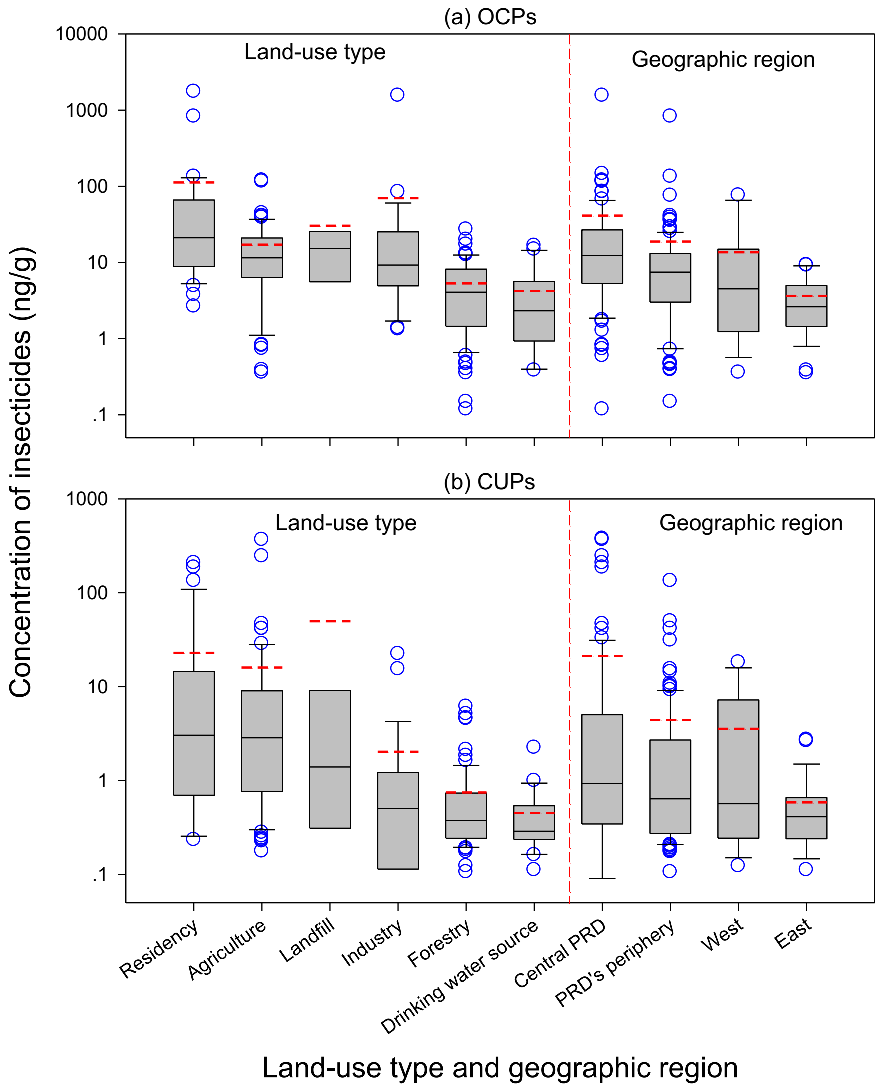

Fig. 2. Concentrations (ng/g dry weight) of (a) OCPs and (b) CUPs in six land-use types and four geographic regions from the Pearl River Delta and surrounding areas (Fig. S1). Error bars adjacent to the bottom and top parts of each box stand for the 10th and 90th percentiles, respectively, and horizontal lines from the bottom to the top of each box stand for the 25th, 50th, and 75th percentiles, respectively. Imaginary lines stand for the mean concentrations of insecticides. Four geographic regions are shown in Fig. S1. A residential soil with an extremely high concentration of $\sum_{11}$OCP (1750 ng/g) in Huizhou was excluded.

sown areas and total output of major farm crops (rice, wheat, corn, potato, and soybean) were also examined for their impacts on the use patterns of insecticides. However, poor correlations were found between the sown areas or total output of major farm crops and soil levels of $\sum_{11}$OCP or $\sum_{12}$CUP ($r^2 = 0.09$–0.18 and $p > 0.05$ for both regressions; Fig. S5). These results implied that socio-economic factors instead of farming protocols may have a moderate role in shaping the spatial distribution patterns of OCPs and CUPs in the PRD and surrounding areas. It is possibly due to geographic variation in pest dynamics and farmer behavior. As known, overuse and misuse of insecticides are prevalent across several Asian countries, e.g., China, Philippines, and Thailand (http://www.worldbank.org/html/cgiar/newsletter/Oct96/6pest.html).

In addition, total organic carbon content in soil has been identified as a significant factor in distributing contaminants in soil environments (Doong et al., 2002). However, the present study obtained only weak correlations between the log-transformed concentrations of $\sum_{11}$OCP or $\sum_{12}$CUP and log-transformed contents of total organic carbon ($r^2 =$ 0.14 and 0.15 and $p < 0.01$ for both regressions), indicating that natural factors in highly urbanization areas may have insignificant impact on the occurrence of soil insecticides. Overall, these results indicate that anthropogenic activities have a significant impact in shaping the distributions of soil insecticides in the PRD and surrounding areas. Moreover, Li et al. (2014) showed that pesticide application amounts in 31 provinces of China were positively correlated with GDP ($r^2 = 0.42$ and $p < 0.001$), further emphasizing the importance of anthropogenic impacts on the spatial distribution of insecticides in highly urbanization regions.

3.4. Regional implications for insecticide soil–air exchange

Soil–air diffusive exchange is an important process indicating the direction for organic pollutants to move between soil and air (Meijer et al., 2003; Tao et al., 2008). In the PRD and surrounding areas, individual HCHs tended to evaporate from soil to air with escaping diffusive fluxes in the ranges of 3.8–62 μg m^{-2} yr^{-1} in the central PRD and 0.20–18.7 μg m^{-2} yr^{-1} in the PRD's surrounding areas (Table 1). This result implicating soil as a secondary source of atmospheric HCHs was consistent with the findings of several previous studies conducted in Haihe Plain of China (Tao et al., 2008), Tibet (Wang et al., 2012), Hami of Xinjiang (Ma et al., 2013), the Central and South Europe (Růžičková et al., 2007), and Mexico (Wong et al., 2010). Moreover, the escaping fluxes of individual HCHs in the central PRD were 3.3–26 times of those in the surrounding areas of the PRD, implying that the central

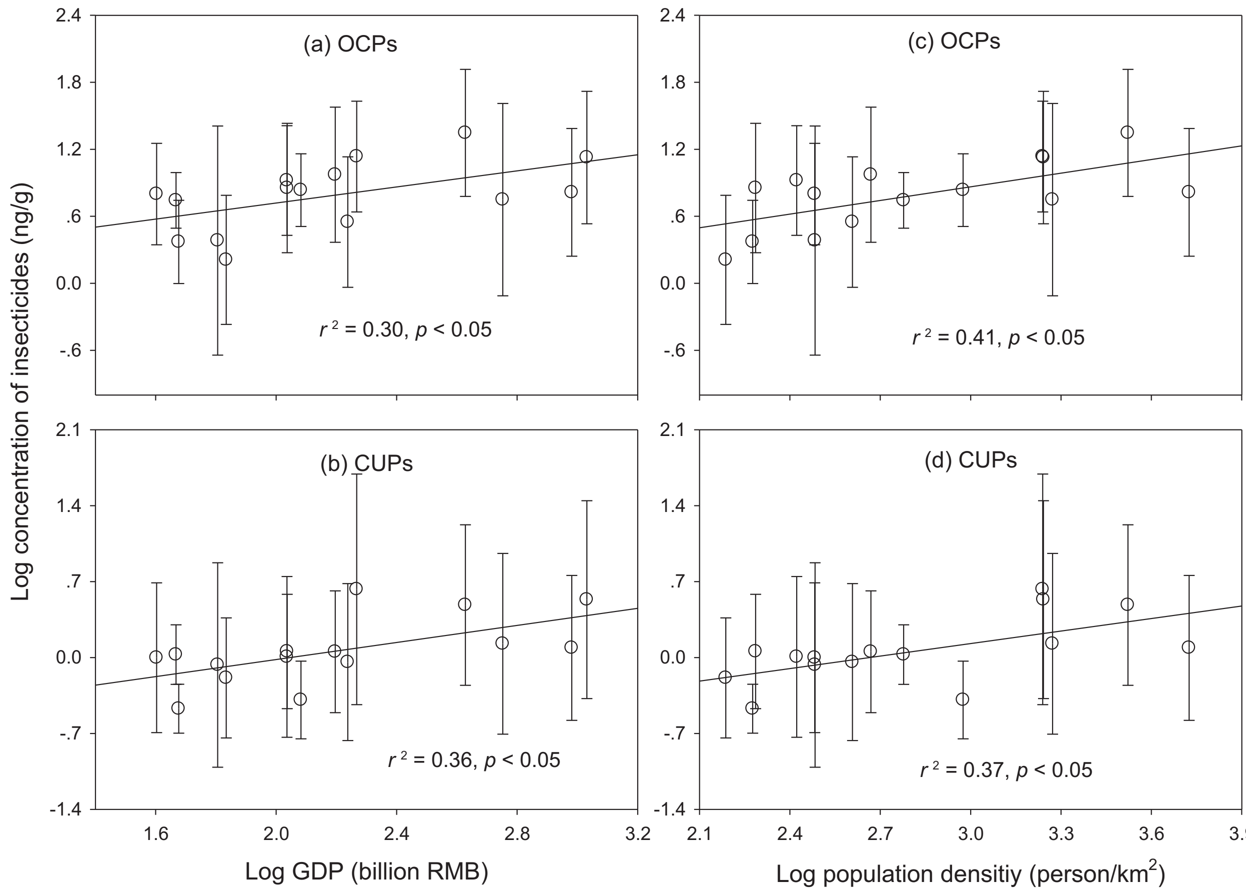

Fig. 3. Regressions of log-transformed of gross domestic production (GDP; in billion yuans (RMB)) or log-transformed population density (person/km^2) and log-transformed concentrations (ng/g dry weight) of insecticides in 15 administrative districts from the Pearl River Delta and surrounding areas (Fig. S1).

PRD's soil may serve as a secondary source of HCHs, which may be transported to its surrounding areas through the atmosphere.

On the contrary, atmospheric transport appeared to be the main input mechanism for *o,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD and *o,p′*-DDT in soil with average depositing fluxes ranging from 0.06 to 2.1 μg m^{-2} yr^{-1}. The fugacity fractions of *p,p′*-DDE (0.33–0.47), calculated by the fugacity in soil divided by the sum of fugacities in soil and air, are in the range of 0.3–0.7, indicating the likelihood of soil–air partition equilibrium (Harner et al., 2001; Meijer et al., 2003). It is interesting to note that *p,p′*-DDT tended to escape from soil to the atmosphere with an average diffusive flux of 0.39 μg m^{-2} yr^{-1} in the central PRD and 1.28 μg m^{-2} yr^{-1} in the PRD's surrounding areas (Table 1). The different directions of soil–

Table 1
Fugacity fractions (f_f, mean ± standard deviation (SD)) and soil–air diffusive exchange fluxes (F_{sa}, mean ± SD; μg m^{-2} yr^{-1}) of individual OCPs in the central Pearl River Delta (PRD) and surrounding areas, South China (Fig. S1). Negative flux values indicate the direction from air to soil.

	f_f		F_{sa}	
	Central PRD[d]	PRD's surrounding areas[e]	Central PRD	PRD's surrounding areas
α-HCH	0.93 ± 0.14	0.74 ± 0.23	10.6 ± 95	0.41 ± 0.99
γ-HCH	0.85 ± 0.15	0.73 ± 0.21	62 ± 122	18.7 ± 38
β-HCH	0.95 ± 0.10	0.97 ± 0.05	61 ± 310	12.6 ± 21
δ-HCH	0.64 ± 0.29	0.46 ± 0.28	3.8 ± 29	0.20 ± 1.92
o,p′-DDE	0.02 ± 0.05	0.02 ± 0.05	−3.2 ± 1.72	−1.19 ± 0.98
p,p′-DDE	0.47 ± 0.29	0.33 ± 0.27	0.07 ± 0.74	0.03 ± 0.68
o,p′-DDD	0.12 ± 0.18	0.04 ± 0.06	−0.47 ± 1.21	−0.51 ± 0.28
p,p′-DDD	0.12 ± 0.17	0.18 ± 0.21	−0.40 ± 0.39	−0.06 ± 0.11
o,p′-DDT	0.06 ± 0.11	0.04 ± 0.10	−2.1 ± 1.56	−1.13 ± 0.83
p,p′-DDT	0.51 ± 0.29	0.58 ± 0.33	0.39 ± 2.3	1.28 ± 6.1
p,p′-DDMU	NA[f]	NA	NA	NA
$\sum_7$DDX[a]			−5.7 ± 3.4	−1.6 ± 8.7
$\sum_4$HCH[b]			138 ± 280	32 ± 44
$\sum_{11}$OCP[c]			133 ± 280	30 ± 45

[a] $\sum_7$DDX included *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDT, *p,p′*-DDT, and *p,p′*-DDMU.
[b] $\sum_4$HCH included α-HCH, γ-HCH, β-HCH, and δ-HCH.
[c] Sum of $\sum_7$DDX and $\sum_4$HCH.
[d] Included the administrative districts of Guangzhou, Dongguan, Shenzhen, Zhuhai, Foshan, and Zhongshan (Fig. S1).
[e] Included Yangjiang, Yunfu, Zhaoqing, Qingyuan, Jiangmen, Shaoguan, Heyuan, Huizhou, and Shanwei (Fig. S1).
[f] Not available.

air exchange for *p,p*′-DDT and its metabolite *p,p*′-DDD may be attributed to the different half-life times of *p,p*′-DDT in soil and air. Meijer et al. (2001) found that the half-life time of *p,p*′-DDT in Luddington soils of the United Kingdom is 11.8 years, which is longer than those (8.2 ± 1.4 and 7.1 ± 1.0 years, respectively) in the atmosphere of Sleeping Bear Dunes and Sturgeon Points around the Great Lakes (Buehler et al., 2004). Hence, it is speculated that *p,p*′-DDT would degrade into *p,p*′-DDD faster in air than in soil, making soil a secondary source of *p,p*′-DDT and a sink of atmospheric *p,p*′-DDD.

3.5. Prognosis of soil insecticide inventory

Soil inventories of $\sum_4$HCH, $\sum_7$DDX, $\sum_9$PYRE, and $\sum_3$OP varied in the ranges of 0.90–18.9, 0.36–32, 0.06–8.2, and 0.02–1.28 tons in different administrative districts (Table S4). Unexpectedly, the total soil inventory of legacy $\sum_{11}$OCP (183 ± 160 tons) was much greater than that of $\sum_{12}$CUP (67 ± 71 tons). It should be noted that the total amount of legacy $\sum_{11}$OCP (including HCHs and DDT) used in China was 5.3×10^6 tons (Hua and Shan, 1996), considerably less than that of $\sum_{12}$CUP (1.4×10^7 tons) from 1991 to 2012, if the annual usage amounts of organophosphates and pyrethroids accounted for 49% of total amounts of insecticides (Li et al., 2014; National Bureau of Statistics of China, 2014; Tang et al., 2008). Two reasons may be used to explain the disparity between soil inventories and usage amounts for OCPs and CUPs. First, organophosphates and pyrethroids have shorter half-life times (0.012–0.45 yr; Table S5) (Laskowski, 2002; Mackay, 2001) than DDTs and HCHs (2.0–41 yr; Table S5) (Dem et al., 2007; Mackay et al., 2006; Meijer et al., 2001) in soil, which would lead to relatively lower soil inventory of $\sum_{12}$CUP. Second, the ratio of (DDD + DDE)/DDT (all the *o,p*′ and *p,p*′-isomers) in soil was in the range of 0–48 with the mean value at 3.3. In particular, 24% of the ratio values were below 1.0, indicating that there were fresh inputs of DDTs, such as illegal use of technical DDTs (Metcalf, 1973) and antifouling paints containing DDTs (Yu et al., 2011).

Our previous study predicted the temporal trend of soil inventory for *p,p*′-DDT in the PRD based on literature data (Zhang et al., 2011). With the empirical box model, the temporal changes in soil inventories of insecticides were also modeled with the comprehensive data of soil insecticides acquired in the present study. Specifically, we assumed that the annual decay ratio of soil legacy OCPs without fresh inputs was 3% (Zhang et al., 2011). The annual amounts of CUPs used in the PRD and surrounding areas would increase at a rate of 2.2%, estimated from the total masses of pesticides in 1985 (7.3×10^4 tons) and 2010 (1.04×10^5 tons) in Guangdong Province (Statistical Bureau of Guangdong Province, 1990, 2011). Due to the lack of atmospheric data for all CUPs, only five CUP compounds were included in the box modeling, which is described in the Supplementary data.

The projected soil inventories of legacy OCPs and five CUP compounds in the PRD and surrounding area for the next 100 years are profiled in Figs. 4 and S6. As expected, the temporal trends for the soil inventories of legacy OCPs are opposite to those for CUPs. The amount of DDTs in soil is projected to decrease to half of its current value after 18 years, which was consistent with our pervious results (Zhang et al., 2011), whereas the soil inventory of HCHs is predicted to reduce to zero after 98 years. Interestingly, the amounts of five CUP compounds in soil will decrease in the first few years and then increase to twice as much as the current values for four pyrethroids and 1.0 ton for chlorpyrifos after 100 years. In this scenario, residents in the PRD and surrounding area may expose to high soil concentrations of pyrethroids (7.4 ng/g), deduced by soil inventory in 2109.

Sensitivity analysis in prognosis of soil insecticide inventories (Table S7) provides useful hints for implementing effective preventive

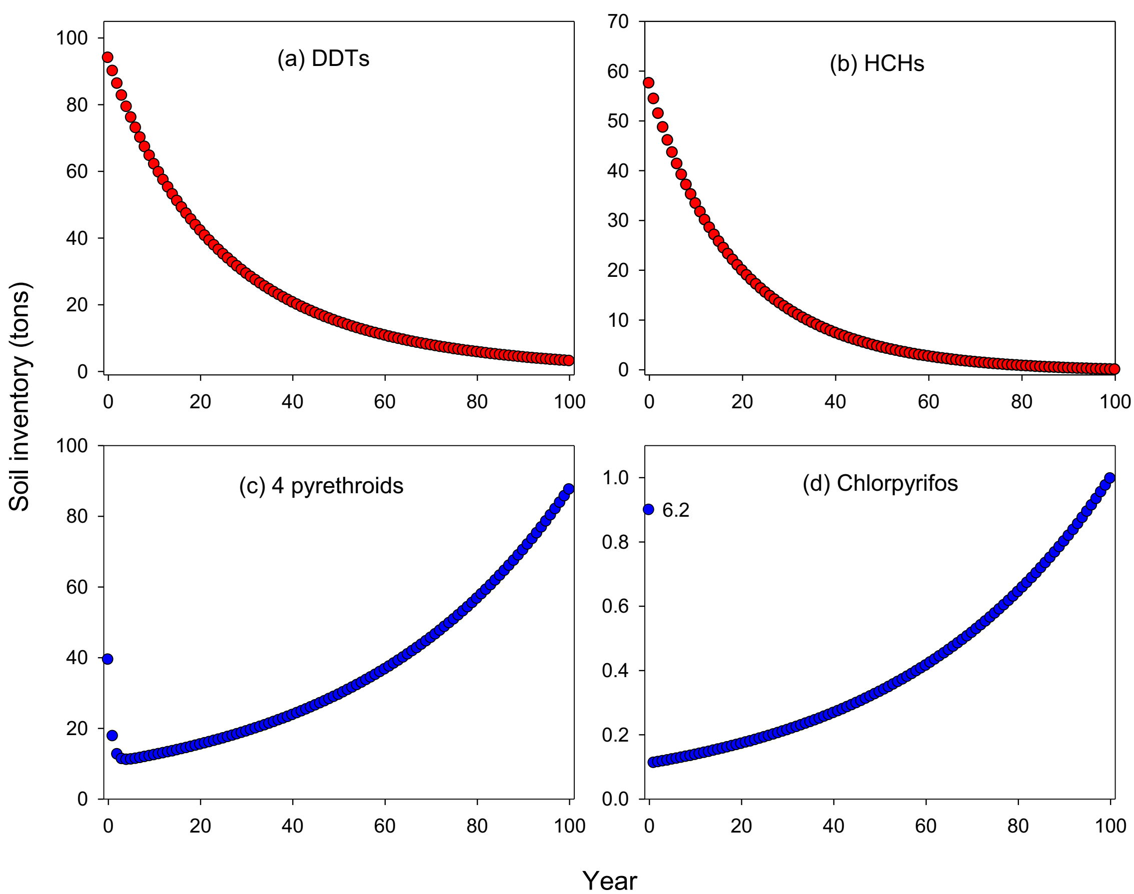

Fig. 4. Projected soil inventories of HCHs, DDTs, pyrethroids, and chlorpyrifos in the Pearl River Delta and surrounding areas (Fig. S1).

measures in the study region. Specifically, the initial inventory in 2010 is the major contributor to individual OCP inventories with the sensitivity distributions in the ranges of 77–100% before 2020. The uncertainties of soil inventories of most DDT and HCH compounds (*p,p′*-DDD, *o,p′*-DDD, *o,p′*-DDT, α-HCH, and γ-HCH) are accounted for by their atmospheric concentrations with the sensitivity distributions varying between 45% and 98% in 2110. On the other hand, the soil inventories of five CUP compounds are mainly impacted by their annual dry and wet depositions for the entire simulation period, and the sensitivity distributions range from 69% to 98% after 2015 except 39% dry and wet deposition sensitivity distribution of chlorpyrifos in 2110. In our other studies, wet deposition was identified as a major mechanism for removal of atmospheric PAHs and polybrominated diphenyl ethers (Guo et al., 2014a,b). However, it is nearly impossible to control dry and wet depositions of atmospheric insecticides into soil. Therefore, the key to mitigating insecticide pollution in soil is decreasing their usage amounts. Strict law implementation on banning the use of technical DDTs and HCHs and anti-fouling paints containing DDTs may be efficient in reducing the soil inventories of DDTs and HCHs. Furthermore, Li et al. (2014) pointed out that high pesticide application dosage in China may be attributed to the serious overuse and improper use of pesticides; thereby, training farmers for proper use of insecticide should also be a part of the strategy in minimizing the health effects of insecticides.

4. Conclusions

Soil contamination by legacy OCPs and CUPs was more serious in the central PRD than in the PRD's surrounding areas. Anthropogenic impacts may play a moderate role in shaping the spatial patterns of soil insecticide concentrations. Soil was a sink of atmospheric *o,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD, and *o,p′*-DDT, and was a significant secondary source of HCHs and *p,p′*-DDT to the atmosphere. The amounts of DDTs and HCHs in soil (100 ± 134 and 83 ± 70 tons) were expected to decrease to half of their current values after 18 and 13 years, respectively, while soil inventories of pyrethroids and organophosphates (39 and 6.2 tons) were estimated to decrease after 4 and 2 years and then would increase moderately to 87 and 1.0 tons after 100 years. Mitigating insecticide pollution in the environment required strict ban on the use of technical DDTs and HCHs and training of famers to use insecticide properly.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.01.111.

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