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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 ± 134 and 83 ± 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:

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

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