



Residue patterns of currently, historically and never-used organochlorine pesticides in agricultural soils across China and associated health risks[☆]



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ABSTRACT

Organochlorine pesticides (OCPs) with different usage states, such as currently, historically or never used, may show different behaviors and potential risks in the environment. It is essential to identify their distribution patterns and fates and to assess their associated health risks to humans. In this study, based on a nationwide sampling campaign across China, we determined the concentrations of currently (endosulfan), historically (chlordane and heptachlor) and never-used (aldrin, dieldrin and endrin) OCPs in agricultural soils. The total residue inventories of Σ Endosulfans, Σ Chlordanes, heptachlor and Σ Drins in soils were 260, 64.3, 54.2 and 88.6 t, respectively. The residues of endosulfan were influenced by current usage, showing a latitude transect trend. Drins were mainly from long-range transport, but the illegal usage in China still affected their residues. This finding indicates that endosulfan and drins in Chinese agricultural soils mainly follow the primary and secondary distribution pattern, respectively. Both primary and secondary distribution have a great impact on the distribution pattern of chlordane, which had been banned for only 4 years at the time we sampled. The health risks of these OCPs were estimated based on their concentrations. There were 0.813% and 1.63% of samples that exceeded the target values for chlordane and endrin according to the Netherlands guideline for unpolluted soil. Their residues in most of the samples posed no or few non-carcinogenic and carcinogenic risks to human beings. The results from this study will provide powerful support for pollution control and management.

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1. Introduction

Persistent organic pollutants (POPs) are a group of toxic, bio-accumulative, biomagnified and persistent contaminants with a potential of long-distance migration in the environment (Jones and de Voogt, 1999). Organochlorine pesticides (OCPs) are an important type of POPs. It has been proven that exposure to OCPs can have adverse effects on human health (Hart and Pimentel, 2002). Among them, chlordane, heptachlor, aldrin, dieldrin and endrin were the first group of POPs to be classified in 2001, and endosulfan was added in the list of POPs in 2011 under the Stockholm Convention. Because of their toxicity, they have also been identified as priority pollutants by the U.S. Environmental Protection Agency (U.S. EPA)

(Keith and Telliard, 1979).

Endosulfan, an insecticide that is used on food crops to control pests, has been widely used in China since 1994 and remains in use (Jia et al., 2009 and China Pesticide Information Network). The estimated endosulfan domestic usage amount was 25,700 t between 1994 and 2004 (Jia et al., 2009). Endosulfan sulfate is the major metabolite of endosulfan under aerobic incubation and is as toxic as the parent α - and β -endosulfan. Due to its less volatile and more persistent properties, endosulfan sulfate was detected along with the parent compounds in various compartments (Guerin, 2001; Jia et al., 2010). Technical chlordane was used as a pesticide for agriculture, home lawns and gardens and as a termiticide for housing foundations around the world (Li et al., 2007). Due to its high risk to humans and wildlife, China began to terminate all use of chlordane in 2009. Wang et al. estimated that the total chlordane usage amount in China was 2745 t from 1988 to 2008, accounting for 80% of the production during the same period (Wang et al.,

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2013). As a component of technical chlordane, heptachlor was not individually used in its purified form in China. Although technical chlordane was banned for many years, chlordane and heptachlor were still detected ubiquitously in the environment due to their semi-volatility and relative persistence (Van Drooge et al., 2004 and Jiang et al., 2009). Drins, including aldrin, dieldrin and endrin, were never produced on an industrial scale and were not introduced in agriculture as pesticides in China (Zhang et al., 2012a). However, previous studies have provided clear evidence for the presence of drins in various media in China, such as soils, water and sediment (Zhou et al., 2006; Zhang et al., 2012a).

Arable soil is one of the biggest reservoirs of organic contaminants. It plays an important role in the global cycling of POPs. The direct use of OCPs during agriculture practices forms their primary sources in soils. After being sprayed in soils, the chemicals will undergo various dissipation pathways, including volatilization, degradation, leaching, adsorption and run-off (Singh et al., 1991). Soil is also considered as a source of these pollutants, which redistribute in the environment as secondary distribution pattern. Primary distribution is governed by the usage patterns, whereas secondary distribution is mainly affected by the soil properties, locations and meteorological conditions (Jia et al., 2010).

The residue levels of endosulfan, chlordane-related compounds and drins in agricultural soils were investigated previously in China (Jiang et al., 2009; Zhang et al., 2012a; Zhou et al., 2013). However, most of these studies were only focused on a regional scale, which resulted in inadequate data to elucidate the large-scale distribution patterns and transport of OCPs. In addition, most of these studies were performed before the restriction of endosulfan and the ban of chlordane. It is essential to conduct a nationwide survey on their occurrence and change in soils and further estimate their associated potential health risks because they have been restricted or phased out for many years. Therefore, in this study, we conducted a sampling campaign in agricultural soils, where these OCPs were extensively applied, across China. We aimed to (a) identify the different residue patterns, (b) explore the influencing factors and (c) estimate the potential health risks of the currently (endosulfan), historically (chlordane and heptachlor) and never-used (drins) OCPs. We hope that our results will aid in better understanding the residue occurrence and fate of these OCPs after their usage following restriction or ban for many years. In addition, these results will provide powerful support for pollution control and management by decision-makers.

2. Materials and methods

2.1. Sample collection

Soil samples were collected from 123 agricultural sites in 31 provinces, autonomous regions or municipalities across China in April and May 2013, as described in our previous study (Niu et al., 2014). The sampling locations are mapped in Fig. S1 (Supporting information).

2.2. Sample extraction and analysis

A mixture of the standard compounds of α -endosulfan, β -endosulfan, endosulfan sulfate, *trans*-chlordane (TC), *cis*-chlordane (CC), heptachlor, aldrin, dieldrin and endrin, the internal standard (pentachloronitrobenzene, PCNB) and the surrogates (TCmX and PCB209) were obtained from AccuStandard Inc. (New Haven, CT, USA). Based on the procedure we described in our previous study (Niu et al., 2013), the concentrated extracts with a known amount of spiked surrogates were cleaned up after being Soxhlet-extracted with dichloromethane (DCM). The clean-up column contained

anhydrous granular sodium sulfate (Na_2SO_4), neutral silica gel, aluminum, and florisil from the bottom to the top. Then, the target analytes were eluted with hexane/DCM (7:3). After being concentrated further, they were spiked with PCNB and then prepared for analysis. The concentrations of these OCPs were measured using an Agilent 7890A gas chromatograph (GC-ECD, Agilent Technologies, Avondale, PA, USA) equipped with a HP-5 column (30 m \times 0.25 mm \times 0.25 μm , Agilent Technologies Inc.). The operating conditions were as follows: initial temperature at 80 $^\circ\text{C}$ and held for 1 min, ramped to 200 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$, then increased at 1 $^\circ\text{C}/\text{min}$ to 225 $^\circ\text{C}$ and held for 1 min, and finally increased to 260 $^\circ\text{C}$ at 15 $^\circ\text{C}/\text{min}$ and held for 5 min; injector temperature, 250 $^\circ\text{C}$; and detector temperature, 300 $^\circ\text{C}$. Nitrogen was the carrier gas at a flow rate of 1.0 mL/min. The concentrations of several randomly selected samples were confirmed using a HP-5MS column (30 m \times 0.32 mm \times 0.25 μm , Agilent Technologies Inc., Santa Clara, CA, USA) on a gas chromatograph-mass spectrometry (Agilent 7890A GC-5975C MS).

2.3. Quality control and quality assurance

Blank controls were administered every 15 soil samples to check for potential cross-contamination and interference. The recoveries of endosulfan, chlordane, heptachlor and drins were in the range of 75.6%–111%. The mean recoveries of the surrogates including TCmX and PCB209 were $93.9 \pm 12\%$ and $89.2 \pm 15\%$, respectively. Three times the signal-to-noise ratio was calculated as the limit of detection (LOD), which ranged from 0.002 to 0.103 ng/g for the target compounds. The concentrations were not blank or recovery corrected. All of the experiments were conducted in duplicate.

2.4. Calculation of OCP inventory in the Chinese soils

The soil burdens of these OCPs were estimated based on their concentrations in the surface soils from each province, autonomous region or municipality according to the following equation.

$$R = \sum ALDC_{\text{soil}} \quad (1)$$

where R is the total residue inventory of these OCPs in farmland soils (kg); A is the provincial area of the cultivated land and provided by the National Bureau of statistics of China (National Bureau of statistics of China, 2013); L is the depth of the soil, which is 20 cm in the present study; D is the density of the soil ($D = 1.16 \text{ g}/\text{cm}^3$ according to the study by Jia et al. (2009)); and C_{soil} is the average individual OCP content in each province, autonomous region or municipality.

2.5. Health risk assessment

Based on the methods recommended by the U.S. EPA (2013), the potential risks of these OCPs were further estimated. It has been reported that endosulfan, chlordane, heptachlor, aldrin, dieldrin and endrin have non-carcinogenic risks, whereas only chlordane, heptachlor, aldrin and dieldrin pose carcinogenic risks to humans (US EPA, 2013). In this assessment, food uptake (only grains and vegetables were involved), soil ingestion, dermal contact and inhalation were the four main exposure routes of the chemicals in soils into human bodies. Detailed calculation equations were listed in our previous study (Niu et al., 2014). The parameters for the assessment of non-carcinogenic and carcinogenic risks are tabulated in Table S1.

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