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Distribution, source, and risk of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in urban and rural soils around the Yellow and Bohai Seas, China

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ABSTRACT

Between 1945 and 1983, China was the world's largest producer of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), and the second largest producer of hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs). The provinces of Liaoning, Hebei, Tianjin, Shandong, and Jiangsu around the Yellow and Bohai Seas have a long history of production and usage of OCPs and PCBs. To investigate their residual concentration, distribution, risk level, and temporal degradation, 7 OCPs and 7 indicator PCBs were determined in surface soils collected around the Yellow and Bohai Seas. Residues of the 7 OCPs and 7 PCBs were in the range of 5.89–179.96 ng g^{-1} dry weight (dw) and non-detectable (ND)–385.67 ng g^{-1} dw, respectively. Tianjin and Hebei provinces recorded the highest concentrations of OCPs and PCBs, respectively. Moreover, OCPs residues had a significant relationship with agriculture and orchard land-use types, whereas PCBs residues occurred more in wasteland. Lifetime carcinogenic and non-carcinogenic risks of OCPs and PCBs through ingestion, inhalation, and dermal contact indicated that OCPs and PCBs residues in surface soils are at a low risk level.

1. Introduction

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are well-known persistent organic pollutants (POPs). These pollutants are noted for their persistence, ubiquity, long-range atmospheric transport, bioaccumulation, and adverse effects on environmental and human health (Mamontova et al., 2017; Meng et al., 2017). Among OCPs, hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) have been historically used in agriculture and sanitation (Zhang et al., 2013b). Conversely, PCBs were extensively used for various industrial and commercial applications such as transformers, capacitors, and plasticizers (Dumanoglu et al., 2017). Although OCPs and PCBs were banned in 2004 by the Stockholm Convention treaty, they are still frequently detected in many countries because of their persistence and non-degradable nature (Glüge et al., 2016; Wöhrnschimmel et al., 2016).

China has a long production history of OCPs and PCBs, and was ranked the world's second producer of HCHs and DDTs between 1945 and 1983 (Hu et al., 2009). During this period, China produced approximately 490,000 tons of HCHs, 40,000 tons of DDTs, and 10,000 tons of PCBs (Wang et al. 2005, 2006; Xing et al., 2005b). Among OCPs, production of HCHs and DDTs accounted for 33% and 20% of total global production, respectively (Fu et al., 2003). Due to the significant historical production and usage of these compounds, the residues of these contaminants have been found at high levels in various environmental media such as soil, water, and even food in some places in China (Hu et al., 2010; Li et al., 2016; Luo et al., 2016; Pan et al., 2016; Sun et al., 2016b).

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Coastal areas of the Yellow and Bohai Seas have experienced rapid industrialization, urbanization, and agricultural development (Zhang et al., 2016). The provinces of Liaoning, Hebei, Tianjin, Shandong, and Jiangsu, surrounding the Yellow and Bohai Seas, have a long history of OCPs and PCBs production and use, and high residual concentrations of OCPs and PCBs have been reported in some areas. However, previous research findings are disperse and lack a unified detection standard. Hence, this study aims to determine the distribution, source, and risk of OCPs and PCBs in soils around the Yellow and Bohai Seas.

2. Materials and methods

2.1. Sample collection

Approximately 153 surface (0–10 cm) soil samples around the Yellow and Bohai Seas were collected in September 2013 (Figure S1). Sampling sites included 21 cities from five provinces (Liaoning, Hebei, Tianjin, Shandong, and Jiangsu), which cover an area of approximately 213,000 km^2 along the coast of the Yellow and Bohai Seas in China (Table S1). Soil samples were collected with a stainless steel trowel that had been rinsed with methanol and placed in polypropylene bags. Each sample consisted of five subsamples within a 100 m × 100 m area. All samples were air-dried, homogenized and sieved through a 2 mm mesh in a clean laboratory, and stored in polypropylene bags at room temperature before extraction.

2.2. Sample extraction and analysis

10 g soil samples were spiked with 10 ng chemical surrogates (PCB209 and 2,4,5,6-tetrachloro-m-xylene (TCMX)), and extracted by accelerated solvent extraction (ASE) with mixed solvent (hexane/dichloromethane (DCM), 1:1, v/v). The cleaned extracts were passed through a silica gel/Florisil chromatographic column for OCPs and PCBs analysis. The column was packed with 4 g of 3% deactivated Florisil, 4 g of 3% deactivated silica gel, and 3 g of anhydrous sodium sulfate from bottom to top. The column was prewashed with a 30-mL mixture of hexane: DCM (1:1, v/v) before use. Elution was subsequently conducted using 20 ml of hexane followed by 20 ml of DCM. The elute was concentrated to 0.1 ml by rotary evaporation and a high-purity nitrogen stream. 20 ng of pentachloronitrobenzene (PCNB) was added as internal standards before injection.

For OCPs and PCBs analysis, an Agilent-6890 GC equipped with a 63Ni electron capture detector (micro-ECD) was used. The samples were analyzed using DB-5 capillary columns (30 m*0.25 mm i. d, film thickness 0.25 μm). The temperatures of the injector and detector were set to 250 °C and 300 °C, respectively. 2 μL of the extracts were injected in the pulsed split less mode. High-purity helium was used as the carrier gas with a constant flow of 1 ml/min, and high-purity nitrogen was used as the make-up gas, controlled at 59.9 ml/min. The oven temperature was set to 80 °C for 1 min, increased by 20 °C min^{-1} to 140 °C, held for 1 min, then increased by 10 °C min^{-1} to 300 °C, and held for 5 min. Quantification was conducted by the internal standard method for OCPs and PCBs including α-HCH,β-HCH, γ-HCH, δ-HCH, p,p'-DDE, p,p'- DDD, p,p' -DDT., PCB-28, PCB-52, PCB-101, PCB-118, PCB-153, PCB-138, PCB-180 (El-Shahawi et al., 2010; Rial-Otero et al., 2007; Tang, 2013; Zhang et al., 2013a). Soil organic carbon (SOC) (%) in individual soil samples, measured with a CHN elemental analyzer (MT-5) as in Chi et al. (1999), ranged from 0.1% to 3.62% (average value: 1.73%) (Table S2).

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

All analytical procedures were performed under strict quality assurance and control measures. In order to avoid cross contamination during sampling in the field, the outside of boxes was washed with Milli-Q water after the samples were taken, wiped with clean towel paper and then kept in three-layers of sealed polyethylene (PE) bags. In the pretreatment procedure, we used the glass bottles and clean them up with hexane/DCM (1:1) for the next time. Laboratory blanks for agricultural soil were included at a rate of one for every ten samples, and subjected to the same treatment as samples. The concentration of the lowest calibration standard was taken as the limit of quantitation (LOQ). The LOQs for the DDTs and HCHs were between 0.01 and 0.1 ng g^{-1} based on 10 g dw soil samples. The LOQs for PCBs were between 0.12 and 0.5 ng g^{-1}. Recoveries were between 60% and 121% for TCMX and between 72% and 133% for PCB-209 in the soil samples. Non-detectable data were substituted with ½ LOQ when more than 70% of data were detected. In all the blank samples, the values were lower than the detection value.

2.4. Risk assessment

Potential human health risks caused by OCPs and PCBs in soils were assessed based on Regional Screening Levels (RSL) for residential soils proposed by the USEPA (United States Environmental Protection Agency). The total lifetime carcinogenic risk (TLCR) and total non-carcinogenic hazard quotient (TnHQ, for children) were calculated for these pollutants, covering the exposure routes of incidental ingestion of soil, inhalation of volatiles and particulates emitted from the soil, and dermal contact with the soil (Sun et al., 2016a). The equations and parameters of Sun et al. (2016a) were applied in this study.

3. Results and discussion

3.1. Concentrations of OCPs and PCBs in surface soil

A summary of the statistical mean and range values, and detection frequencies for individual OCPs in the surface soils around the Yellow and Bohai Seas is shown in Table S3 and S4. For individual OCP compounds, detection frequencies were 100%, 99%, 99%, 100%, 100%, 91%, and 99% for α-HCH, β-HCH, γ-HCH, δ-HCH, p,p'-DDE, p,p'-DDD, and p,p'-DDT, respectively. All concentrations are presented as the dry weight. OCPs concentrations in soils ranged from 5.89 to 179.96 ng g^{-1} dw with a mean value of 25.39 ng g^{-1} dw. Concentration ranges were 0.94–16.98 ng g^{-1} dw (average 1.66 ng g^{-1} dw) for α-HCH, non-detectable (ND) to 156.12 ng g^{-1} dw (average 11.02 ng g^{-1} dw) for β-HCH, ND to 16.17 ng g^{-1} dw (average 1.87 ng g^{-1} dw) for γ-HCH, 0.9–56.24 ng g^{-1} dw (average 2.04 ng g^{-1} dw) for δ-HCH, 0.43–91.23 ng g^{-1} dw (average 4.36 ng g^{-1} dw) for p,p'-DDE, ND to 116.2 ng g^{-1} dw (average 2.78 ng g^{-1} dw) for p,p'-DDD, and ND to 10.42 ng g^{-1} dw (average 1.65 ng g^{-1} dw) for p,p'-DDT. Since most of the sampling sites were in farmland, we referred to the second level of China's Soil Environment Quality Standards (GB15618-1995) to assess the pollution level. 6 and 7 samples exceeded the Standards for HCHs (50 ng g^{-1} dw) and DDTs (50 ng g^{-1} dw), respectively. No obvious correlation between the OCPs and SOC ($r<0.8$) was observed in the soil profile. Weak correlations between the OCPs and SOC were also found in the study of Zhangzhou soil in China and Gt. Hungarian Plain in Europe (Dan et al., 2012; Degrendele et al., 2016).

Statistics of PCBs in surface soil samples are shown in Table S3. For individual PCB congeners, detection frequencies were 99%, 71%,