

LEVEL AND GAS-PARTICLE PARTITIONING OF OCPs IN ATMOSPHERE OF WUXI, CHINA

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Introduction

Organochlorine pesticides (OCPs) are one of the POPs have been recognized as causing adverse effects on humans and the ecosystem in Stockholm Convention 2001. OCPs are semi-volatile organic compounds characterized by their physical and chemical properties, including moderate vapor pressure, high lipid solubility with persistence, ability to bioaccumulation in the food chain, toxic properties, and ability to be transported to remote areas. Because of these characteristics, OCPs have been detected in environmental and biological samples all over the world¹⁻³. Gas-particle partitioning influences the fate, transport, atmospheric residence time, and removal processes of OCPs in atmospheric environments⁴. In the present work, the concentrations of OCPs in both gas and particle phases in the atmosphere of Wuxi, China were measured to obtain information about the levels of OCPs in Wuxi air and to understand the gas-particle partitioning.

Materials and methods

Air samples were collected at Wuxi (31.5501° N, 120.2836° E), Jiangsu province, China from August 1st, 2010 to 6th by using a modified high-volume sampler (Tisch Environmental, Inc.). Total suspended particles (TSP) were collected on 10.2-cm-diameter quartz filters and the gas phase compounds were collected in a cartridge containing polyurethane foam (PUF) (6.2-cm diameter, 7.8-cm length). According to the sampling time, samples were named as PUF-1(August 1st, 2010, gas phase) to PUF-6 and TSP-1(particle phase) to TSP-6. Prior to sampling, quartz filters were baked at 500 °C for 6h. Then, they were allowed to cool to room temperature in desiccators. PUF were cleaned by Dionex ASE 300 Accelerated Extractor with Solvent Controller (P/N 056764): 64mL Extraction Cell, Single Extraction with hexane/ acetone (1:1, v), 100 °C, 4 cycles and 6minutes for each cycle. After sampling, quartz filters and PUF cartridges were stored at -18 °C until analysis.

Samples spiked with internal standards containing ¹³C₆-Hexachlorobenzene, ¹³C₆-β-HCH, ¹³C₆-γ-HCH, ¹³C₁₀-tans-Nonachlor, ¹³C₁₂-4,4'-DDE, ¹³C₁₂-4,4'-DDT, ¹³C₁₂-2,4'-DDT, ¹³C₁₂-Dieldrin, ¹³C₁₀-Heptachlor Epoxide, B isomer, ¹³C₁₀-Oxychlorane and ¹³C₁₀-Mirex were extracted with 200mL hexane/ acetone (1:1, v:v) for 24h by Soxhlet extraction apparatus. All sample extracts were concentrated to about 2mL by rotary evaporator. Then, the concentrated extracts were cleaned with a multilayer 12-mm i.d. silica/alumina column packed from the bottom with anhydrous sodium sulfate (2cm, 450 °C baked), neutral silica gel (12cm, deactivated with 3% water) and neutral alumina (6cm, deactivated with 3% water) topped with anhydrous sodium sulfate (2cm, 450 °C baked). Then, pre-elute the column with 50mL hexane and elute the OCPs with 100mL hexane: dichloromethane (7:3, v/v), and all the elutes were concentrated to 100 μL by rotary evaporator

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and gentle nitrogen flow for GC-MS analysis.

OCPs(HCB, α -HCH, β -HCH, γ -HCH, δ -HCH, Heptachlor, Aldrin, Isodrin, Oxychlordane, Heptachlor Epoxide A, Endosulfan I, Endosulfan II, trans-Chlordane, cis-Chlordane, Dieldrin, Endrin, p,p'-DDT, o,p'-DDT, p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD, Methoxychlor, Mirex) were detected by GC-MS (Agilent 5975 mass spectrometer equipped with a 6890 gas chromatograph) with a fused silica capillary column (5% phenyl, 95% methyl silicone, 30m \times 0.25mm i.d.; 0.1 μ m film thickness; J&W Scientific). Oven temperature was initiated at 80 $^{\circ}$ C (held for 3min) and increased to 260 $^{\circ}$ C at a rate of 6 $^{\circ}$ C /min, and post run for 5min. Injector and interface temperature were 250 $^{\circ}$ C and 300 $^{\circ}$ C, respectively. The carrier gas was helium at a flow rate 1.0mL/min. Samples were injected in splitless mode (1 μ L) operate with negative chemical ionization source and selected ion monitoring mode was used for quantitative analysis.

Results and discussion

The concentrations of the total OCPs in all the samples ranged from 9.43-556.84 pg m^{-3} with a mean of 133.69 pg m^{-3} , and in all the PUF samples ranged from 84.70-556.84 pg m^{-3} with a mean of 252.47 pg m^{-3} , and in all the TSP samples ranged from 9.43-28.47 pg m^{-3} with a mean of 14.91 pg m^{-3} . The concentrations of the selected OCPs are depicted in Figure 1. The concentrations of each OCP in all the samples varied from n.d. (not detectable) to 404.78 pg m^{-3} (PUF-1 for cis-Chlordane & Endosulfan II). PUF samples have much higher concentration than TSP samples, which means OCPs are mainly present in the gas phase of the atmosphere. Among all the samples, PUF samples have much higher average concentration than TSP samples (Fig. 2), and it testified the former conclusion that OCPs are mainly present in the gas phase of atmosphere.

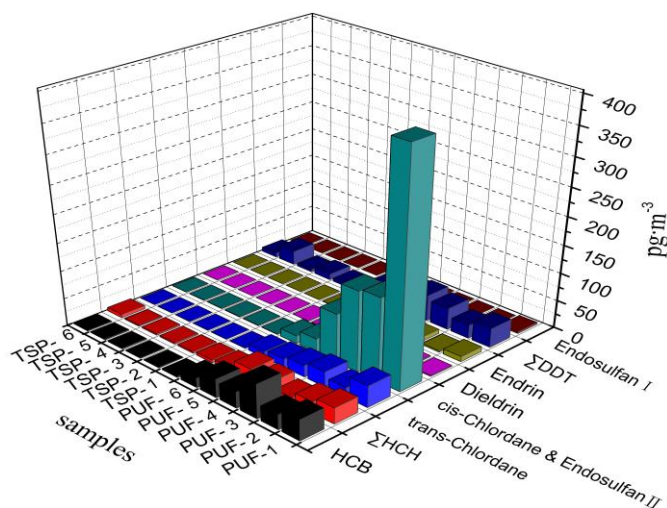


Fig.1 Concentrations of HCB, Σ HCH^a, Chlordane, Endosulfan, Dieldrin, Endrin and Σ DDT^b in atmosphere of Wuxi

a Sum of α -HCH, β -HCH, γ -HCH and δ -HCH.

b Sum of p,p'-DDT, o,p'-DDT, p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD.

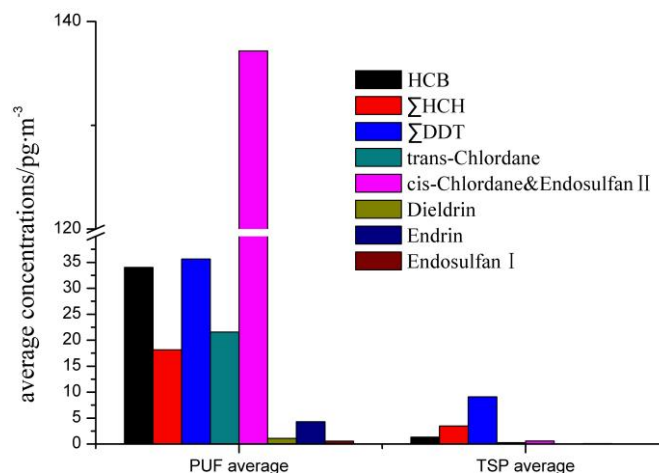


Fig.2 Average concentrations of HCB, Σ HCH, Σ DDT, Chlordane, Endosulfan, Dieldrin and Endrin in gas and particle phase in atmosphere of Wuxi

Compositional differences in HCH isomer or DDT congener profiles in the environment could indicate different sources of contamination. Technical grade HCH consists of five isomers: α -HCH (55-80%), β -HCH (5-14%), γ -HCH (8-15%), δ -HCH (6-10%) and ϵ -HCH (3-4%)⁵ or purified lindane only. Hence, the ratios of α -HCH to γ -HCH (α/γ) would be between 5 to 7 for the technical mixture and nearly zero for lindane⁶. When technical HCH is released into the environment, the ratio of α -HCH/ γ -HCH will increase because α -HCH is more stable than γ -HCH and γ -HCH may isomerizes to α -HCH photolytically. In contrary, the release of lindane will reduce the ratio of α -HCH/ γ -HCH in the environment. As a result, the corresponding values of α -HCH/ γ -HCH for environmental samples can be used to monitor whether the source is from the technical HCH or lindane²⁻³. The average HCH isomer compositions detected in air samples in this study are α -HCH: 22.9%, β -HCH: 27.4%, γ -HCH: 28.2%, δ -HCH: 21.5% (Fig. 3a), which is very different from the HCH technical mixture. The ratio of α -HCH/ γ -HCH among all the samples varied from 0.06-3.92 with a mean of 1.05 (Fig. 4). This fact shows that the HCHs in Wuxi are mainly present as a result of long-range transport or new lindane input²⁻³.

The compositions of DDTs in the atmosphere of Wuxi are depicted in Fig.3b. The main DDT congener was p,p'-DDT, followed by o,p'-DDT+ p,p'-DDD, p,p'-DDE, o,p'-DDE and o,p'-DDD. It was reported that the ratio of p,p'-DDT/p,p'-DDE less than 1 is indicative of aged DDT, while ratio more than 1 means its fresh inputs⁷. The average DDT congener compositions measured in this study were 44.3%, 29.7%, 2.3%, 15.3%, 8.4% for p,p'-DDT:, o,p'-DDT + p,p'-DDD:, o,p'-DDD:, p,p'-DDE, o,p'-DDE, respectively (Fig. 3a). The ratio of p,p'-DDT/p,p'-DDE among all the samples varied from 1.15-31.9 with a mean of 7.05 (Fig. 4), reflecting the fact that the DDTs were mainly present as a result of its fresh input.

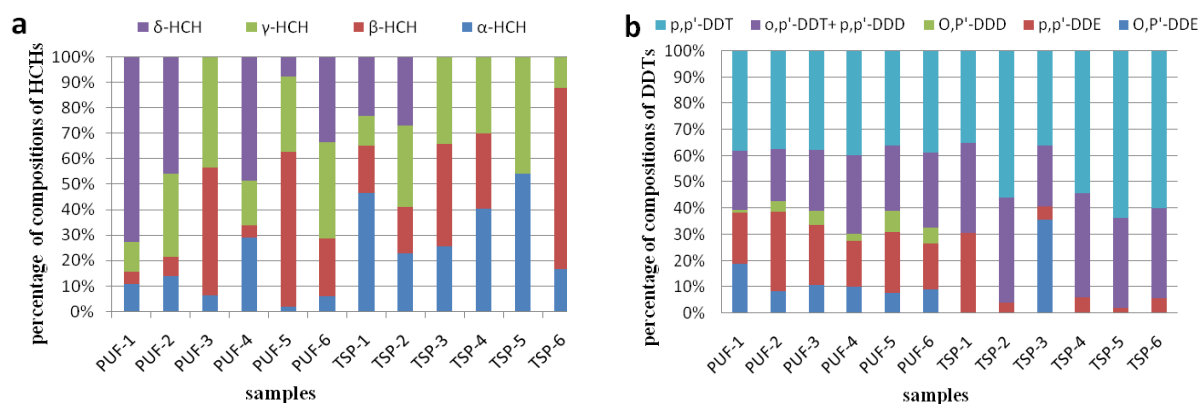


Fig. 3. Percentage compositions of HCHs and DDTs in the atmosphere of Wuxi: (a) HCHs, (b) DDTs

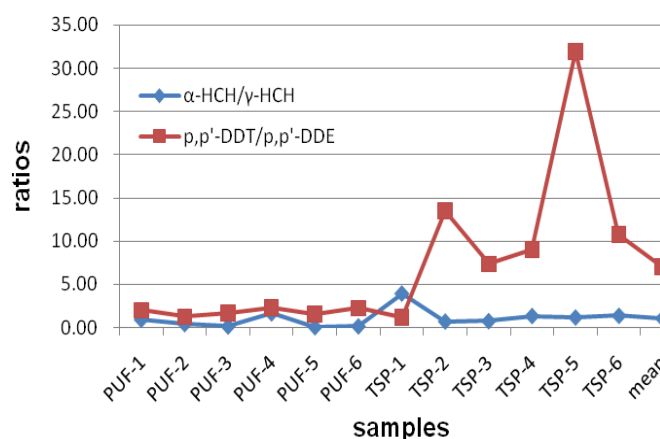


Fig.4 The ratios of α -HCH/ γ -HCH and p,p'-DDT/p,p'-DDE

Acknowledgements

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