A PRELIMINARY INVESTIGATION OF ORGANOCHLORINE PESTICIDES IN ATMOSPHERE OF FIVE PROVINCES AND CITY IN CHINA

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Abstract

Air samples were collected for characterization of organochlorine pesticides (OCPs) such as aldrin, chlordane, *o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB) and mirex during the spring and autumn of 2005 in Beijing, Anhui, Hubei, Hunan and Jiangsu Provinces. The analysis of samples collected in Beijing (sampling site n=7), Anhui (n=7), Hubei (n=9), Hunan (n=12) and Jiangsu (n=11) shows that chlordane, DDE, DDT, hexachlorobenzene were detected in all samples along with aldrin, heptachlor and DDD in some few samples. Higher concentration levels were observed in the sites near pesticide factories.

Introduction

Among the important classes of POPs chemicals, there are many families of chlorinated aromatics, including polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and –furans (PCDDs/PCDFs) and different organochlorine pesticides (OCPs) (e.g. DDT and its metabolites, toxaphene, chlordane, etc.). Some are accidental by-products of combustion or the industrial synthesis of other chemicals (e.g. the PCDD/Fs) not produced deliberately. Many have been synthesized for industrial uses (e.g. PCB, chlorinated paraffin's) or as agrochemicals (e.g. DDT, lindane, chlordane). As a result of large production and usage volumes throughout the world in the past, pollution has spread and caused problems in wide areas and across country borders. At present, chemicals such as DDT, mirex and toxaphene are still being produced and used because of lack of cheap and effective alternatives developing countries.

The intensive uses of organochlorine pesticides (OCPs) in industry and agriculture have led to a global contamination of the environment. Most of organochlorine molecules are resistant to physical, chemical and biological degradation and then tent to be transported over long distance and accumulate in both the aquatic and terrestrial food webs. The atmosphere is well known to be a good pathway for the dissemination of POPs sometimes in zones far from their emissions like Antarctica or high altitudes mountains lakes. Most POPs are now banned or severely restricted in many countries, nevertheless they are commonly detected in air and precipitations of rural, urban or remotes areas. In addition to long range transport from areas where POPs are still in use, volatilization from contaminated soils and water is another import source for their presence in the atmosphere.

OCPs have been used broadly in China's past, yet very little is known about their atmospheric concentrations and transportation[1]. During the spring and autumn of 2005, some OCPs were measured in the atmosphere of Beijing, Anhui, Hubei, Hunan and Jiangsu Provinces in China. The focus of the monitoring is on 14 individual OCPs. The targeted compounds include aldrin, trans-chlordane, cis-chlordane, *o,p'*-DDE, *p,p'*–DDE, *o,p'*-DDD, *p,p'*–DDD, *o,p'*-DDT, *p,p'*–DDT, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB) and mirex, etc.

Materials and Methods

During the spring and autumn of 2005, high-volume samplers were used to collect air samples in Beijing, Anhui, Hubei, Hunan, and Jiangsu Province. The number of sampling sites was 11, 7, 9, 12 and 11 in the five provinces and city, respectively. Air was pulled through a quartz micro-fiber filter, a primary and secondary pre-cleaned polyurethane foam (PUF) plug at a rate of 700ml/min for 24h. The flow rates were checked before and after sampling. Filters and PUF plugs were pressurized fluid extracted using acetone and hexane (1:1, v/v), respectively. Extracts were concentrated by rotary evaporation, blown down with a gentle stream of nitrogen and exchanged into hexane. Extracts were cleaned up and fractionated on a florisil cartridge (2000mg). The samples were analyzed for OCPs by GC-MS on a Shimadzu QP-2010 operated in electron ionization mode using selected ion monitoring.

All procedures used strict quality control measures. Each batch of samples included field and laboratory blanks and matrix spikes to monitor extraction efficiency. Surrogate standards were used in each sample to

monitor recovery.

Results and Discussion

DDTs

Between the 1950s and 1980s, DDT was used principally in China as an agricultural pesticide(2). Accumulated consumption of DDT in China to 1983 was more than 430,000 tones. During the 1970s-1980s, there were 11 local DDT producers but only 2 factories, the Tianjin Chemical Factory and the Yangzhou Pesticide Factory, are thought to remain in production. Total annual production of DDT of these factories is in the range 4,000-6,000 t.

DDTs was one of the major OCPs dominating air concentration. DDT and DDE, the metabolites of DDT, were detected in all samples in this study. During the sampling period the mean concentrations of total DDTs, sum of *p,p'*-DDT + *o,p'*-DDT + *p,p'*-DDD + *o,p'*-DDD + *p,p'*-DDE + *o,p'*-DDE (ΣDDT) were 183 pg/m^3 (ranged from 16.3 to 407pg/m^3), 318 pg/m^3 (from 8.45 to 1890 pg/m^3), 336 pg/m^3 (from 146 to 873 pg/m^3), 1110 pg/m^3 (from 122 to 9170 pg/m^3) and 772 pg/m^3 (from 90.3 to 5420 pg/m^3) for samples collected in Beijing, Anhui, Hubei, Hunan and Jiangsu, respectively. The average ratios of (DDE + DDD)/ΣDDT for samples collected from Beijing and Hubei were 0.68±0.12 and 0.85±0.09, respectively, which means the residues of DDT in ambient air was mainly from past uses and decomposition. However, for samples collected from Anhui, Hunan and Jiangsu, the average ratios of (DDE + DDD)/ΣDDT were 0.43±0.10, 0.46±0.15 and 0.46±0.13, respectively, which mean there were some new source emission that contained DDT in the environment.

Hexachlorobenzene

With the highest vapor pressure among the OCs, HCB was observed in all samples during the sampling period, with concentrations in the range of 18.5–180pg/m^3, 36.6–669pg/m^3, 65.0–236pg/m^3, 21.4–81.0pg/m^3, and 41.1–183pg/m^3 for samples collected in Beijing, Anhui, Hubei, Hunan and Jiangsu, respectively. HCB has multiple sources; it was not only employed as fungicide on seeds and cereals but still also used for industrials applications as solvents, dielectric fluids and the synthesis of organic compounds. Moreover, it is also emitted by waste incineration and the manufacturing of paintings, coal, still, and pulp paper. HCB was relatively uniformly distributed in the five provinces and city.

Chlordane

Chlordane including trans- and cis-chlordane (TC and CC) was monitored in almost all samples collected in the five provinces/city. The mean concentrations of chlordanes during the sampling period were 6.91 pg/m^3 (from 2.32 to 13.8 pg/m^3), 62.4 pg/m^3 (from nd to 722 pg/m^3), 5.48 pg/m^3 (from 2.95 to 9.11 pg/m^3), 54.6 pg/m^3 (from 2.52 to 420 pg/m^3) and 132 pg/m^3 (from 16.4 to 1840 pg/m^3) for samples in Beijing, Anhui, Hubei, Hunan and Jiangsu, respectively. In the environment, TC degrades more rapidly than CC and a ratio of TC/CC＜1 is generally taken to be indicative of aged chlordanes[3]. The proportions of TC/CC in ambient air from the mean concentrations measured in this study were 1.32, 1.70, 2.05, 1.92 and 1.94, respectively; indicating fresh chlordane emission existed in environment.

Aldrin, dieldrin, endrin and heptachlor

Heptachlor was only detected in samples collected in one site located near a pesticide factory in Jiangsu Province, with higher concentration of 918 pg/m^3. At the same time, aldrin was merely observed in five sites in Jiangsu Province, with concentration ranging from 2.77 to 31.2 pg/m^3. No dieldrin, endrin and mirex could be detected in all samples in this study. These OCPs were not measured above detection limit concentrations providing evidence that these pesticides were not used in the areas studied.

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