Organochlorine Pesticides Residues in Foodstuffs: China Status of Contamination, Historical Trend, and Human Dietary Exposure

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Introduction

In the past several decades, the intensive use of persistent organochlorines (POCs) for agricultural and other purposes has resulted in significant contamination in food. In China, POC pesticides, such as DDTs and HCHs, were first used during the 1950s, reaching a maximum in the 1970s. The total amount of HCH production was estimated as 4.46 million tones in China, suggesting it as the largest producer/user of technical HCHs in the world[1]. The occurrence of POCs in foodstuffs has been investigated to understand the status of contamination and to evaluate the possible impacts of its exposure to humans. Since the 1970s, most of the countries have observed a steady decline of contaminants levels, reflecting a reduction, restrictions, and banning of their use[2]. Though the production of DDTs and HCHs was banned in 1983 in China, their levels in foodstuffs remained relatively high in 1990s, and dietary intakes in Chinese were still much greater than those in developed countries[3]. However, recent information of DDT and HCH levels in Chinese foodstuffs is limited and fragmentary. Therefore, we try to comprehend the extent of DDT and HCH contamination as well as to elucidate the historical trend of their residues.

Materials and Methods

Samples

The Chinese total diet study was carried out in 2000. The overall study design and experimental methods were similar to that carried out in 1990[3]. In brief, the food composite approach was used to study the total diet in 4 regional market baskets; each region comprised 3 provinces, which compassed more than 47% population in China. The food composition pattern of a standard man (18-45 years old, 60 kg body weight) in each of 12 provinces was determined by a 3-day household dietary survey. All the foods, beverages, and water consumed by the standard man were integrated into 12 food groups: meats, eggs, fishes, milk, cereals, legumes, tubers, vegetables, fruit, sugar, beverages and water, and alcoholic beverages. Food samples were collected and prepared (cooked) in 3 sampling sites for each province according to the local food habits. Twelve food group composites were made for each province; the same food composites from each of the 3 provinces were combined to formulate regional market baskets. The composite samples were subjected to analysis of POC pesticides. The historical trends of DDT and HCH levels can be obtained by comparing foodstuff concentrations between 1970s, 1990s, and 2000. An attempt was also made to estimate the average daily intake of POC pesticides in Chinese and compared with the acceptable daily intakes (ADIs) recommended by the FAO/WHO and other organizations.

Chemical Analysis

Approximately 5 g of foodstuffs were ground with sodium sulfate and extracted with mixed solvents of 80 ml acetone and 60 ml hexane. The concentrated hexane layer was treated with sulfuric acid. An aliquot of hexane extract was taken out and injected into GC-MS and GC-ECD for quantification of organochlorine pesticides, respectively. The packed columns of GC-ECD were 1.5%OV17 and 2% QF coated on Chromosorb WHP (80-100 mesh). The oven temperature was 185°C. The temperatures of the injector and detector were set at 220°C and 225°C, respectively. Nitrogen were used as carrier and makeup gases, respectively. The capillary columns of GC-MS were DB-1 (0.25 mm *30 m, 0.25 μm film thickness). The oven temperature was programmed from 70°C to 160°C at a rate of 10°C/min and held for 10min. Then the temperature increased to 260°C at a rate of 2°C/min with a final hold of 20 min. The injector temperature was set at 260°C. Helium was used as carrier gases. MS was operated at EI mode.

Results and Discussion

Contamination of Foodstuffs and Historical Trend

Several large-scale surveys of HCH and DDT residues in foods have been carried out in China during last thirty years. From 1973 to 1978, the first national survey on HCH and DDT residues in foods was carried in China, it was obtained that the data of the dietary residues of HCH and DDT in representative population covered the most areas in China. After that, 3 Chinese total diet studies and a national food contamination monitoring survey were carried out in 1990, 1992 and 2000. In order to acquire the comparable data, the levels of DDTs and HCHs in cooked samples were transferred into the equivalence to that in raw samples. Temporal trend of residues in Chinese foodstuffs is shown in Table 1.

Compared to the result in 1970s, the level of the residues of HCHs and DDTs in foods in 1990 and 1992 decreased greatly, especially on animal food. In general, DDT and its metabolites were predominant among POCs, and these residues for meats, eggs, fishes and milks respectively remained as 26.2%, 10.0%, 9.7% and 11.6%, of that in 1970s; while for the residue levels of HCHs in only 1.0%, 2.2%, 0.7% and 1.9% remained respectively. The declining rates of HCH levels in foodstuffs seemed to be faster than that of DDTs, which may due to the low persistency, high biodegradability, and volatility of HCHs than DDTs. In 2000, the residue levels of HCHs and DDTs continues to decrease except to HCHs in fishes, which is consistent to the result from the national food contamination monitoring survey conducted in 10 provinces in 2000. The level of HCH residues in meats and eggs in 2000 is respectively 19.9% and 11.8 % of that in 1990s, and 4.5%t, 22.1%, 18.2% respectively for DDT residues in meats, eggs and fishes. However, the residue level in milks remained stable without significant decline.

In China, DDTs was a widely used POC pesticide during the 1960s and 1970s, with an estimated total amount of 43,520 tones[4]. Greater contamination by DDTs in foodstuffs was reported in the 1970s, and the level decreased until the early 1990s[3,5]. There is difference among the levels of residues in foods in different times. In 1990, the levels of HCH and DDT residues in meats is the highest, and they are 19.10μg/Kg and 227.53μg/Kg, and it is a little higher in eggs and fishes. In 1992, it is still in meats, eggs and fishes that the levels of HCH and DDT residues is higher than others, moreover, fruits also attracting some attention. In 2000, the highest one is that of fishes. The reason is that the high amount of HCH residues in the second south areas and in the first north areas. If the data are excluded from these two areas, the amount of HCH residues in fish 2000 is 4.3μg/Kg, which is 52.7 percent of that of 1990.

Compared to the revised Chinese extraneous maximum residue limit (EMRL) standard for DDTs and HCHs in foods, the levels of HCH and DDT residues in foods are lower than the two EMRLs. The HCH residues in fishes is 64% of EMRL, others are less than 10%. Although the levels of HCH residues in the north China 1 area and south China 2 are 170.7% and 76.0% of EMRL. Earlier studies reported that China is one of the biggest producers/consumers of technical HCHs in the world. The amount of HCHs in production (4,460 kt during 1952 and 1983) was somewhat greater than those for India (1,000 kt), Japan (400 kt), and the United States (350 kt)[1]. Until 1983, the technical HCH mixture was used instead of Lindane in the form of γ-HCH congeners in China. So, the order of predominant HCH congeners is α-HCH>β-HCH>γ-HCH in plant foods in 1990s, which consistent with the corresponding proportions in the commercial products of HCH in China[1], while β-HCH >α-HCH >γ-HCH in animal food because environmental and animal metabolism. These higher ratios of β-HCH indicated that residues likely from the results of widespread use of this pesticide for agriculture during the past.

The contamination source identification study of γ-HCH in fishes in 2000 Chinese total dietary study

The level of HCH residues in South China 2 area (including Hubei, Sichuan, Guangxi Zhuang autonomic region) and in north China 1 (including Heilongjiang, Liaoning, Heibei) is respectively 76.0μg/Kg and 170.72μg/Kg, and the ratio of γ-HCH is 90% of the total HCHs residues. To explain the reason for fishes polluted by γ-HCH, further individual province composite samples were analyzed. The HCHs residues in fishes was found at the level up to 401.56μg/Kg in one area in Hubei province in south China 2, while γ-HCH is 400.6μg/Kg which is 99.8% of the total HCHs residues. The HCHs residues in fishes was found at the level up to 631.0μg/Kg in one area in Heilongjiang province in north China 1, while γ-HCH is 603.56μg/Kg which is 95.7% of the total HCHs residues.

The individual fish samples from individual province fishes composite were further analyzed in Hubei and Heilongjiang, finally it was identified that the main contributor of the exposure source was from the two fresh water fishes. The level of γ-HCH in bream (*Megalobrama amblycephala*) sample in Huibei province is 546.4μg/Kg (exceeding the 0.1mg/Kg HCHs EMRL in fish), which is 98.3% of all HCHs; the level of γ-HCH in carp (*Cyprinus carpio Linnaeus*) sample in Heilongjiang province is 602.4μg/Kg, which is 97.1% of all HCHs. The result were confirmed by GC-MS. Although Lindane is not commercially manufactured in China, it is still manufactured in some appointed export factories. In 1990, the Ministry of Agriculture registered to restrict the use of Lindane in grasshopper calamity areas. Afterwards, Lindane has been used irregularly in some areas in China, e.g., airplanes occasionally sprayed Lindane to kill grasshopper in forest areas in Northeast areas. The result from present study suggests less recent input of HCHs into the Chinese environment could not be ignored although the possibility of the occasional application. EU has repealed the register of Lindane in the latter part of 2001, and also regulated to ban use of deposit Lindane by Jun 20, 2002. Now Llindane has been ranked as restrictedly administered pesticide, and more restrictedly maximal residue limit in farm products is needed in China.

Dietary Intakes and Time Trend

According to the food consumption and levels of HCH and DDT residues in foods in different areas, the dietary intakes of HCH and DDT in different foods were estimated for Chinese population in Table 2.

Compared with the result of 1990, the Chinese dietary intake for HCHs and DDTs in 2000 decreased continuously. The total intake of HCH decreased from 5.04μg in 1990 to 3.11μg in 2000, and the total intake of DDTs decreased from 20.47μg in 1990 to 2.15μg in 2000. If transferred into bdaily intake as body weight, both intakes of HCHs and DDTs are below 1% of provisional tolerance daily intake (PTDI) recommended by FAO/WHO Joint Meeting on Pesticide Residues (JMPR) in 2000. Nevertheless, it is difficult to exclude the heavier contamination of special food in particular area. For example, carps in the fresh water in Hubei and Heilongjiang province in 2000.

Conclusions

The residue levels of DDTs and HCHs were assessed in food collected from China. In general, POCs contamination was less significant in most of foodstuffs; nevertheless, China was one of the largest producers/consumers of these compounds in the world. Otherwise, some foodstuffs (such as carps from fresh water) recorded higher concentrations of Lindane, suggesting the possibility of sporadic use of the pesticide for both agriculture and aquaculture. A comparison of DDT and HCH residue levels reported for previous studies suggested a drastic decline in foodstuffs over the past 30 years. The residue levels of DDTs and HCHs in Chinese food did not exceed the EMRLs set forth by the Chinese government. The average daily intakes were also below the allowance daily intake (ADI, herein as PTDI) authorized by FAO/WHO, and it was comparable to that of other developed countries.

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Table 1**.** Historical trends of DDTs and HCHs levels (ng/g wet weight) in Chinese foodstuffs

Food	HCH					DDT				
	2000 survey	2000 TDS	1992 TDS	1990 TDS	73-78 Survey	2000 survey	2000 TDS	1992 TDS	1990 TDS	73-78 survey
cereals	5.30	1.92	5.62	3.62	146.00	25.20	1.17	1.82	0.96	24.40
vegetables	4.80	0.89	6.31	2.20	23.40	2.90	1.02	3.10	5.59	16.20
fruits	1.70	0.31	2.67	2.28	17.90	5.80	0.23	20.45	2.68	19.00
meats	19.40	3.27	49.16	19.10	2006.60	8.70	8.71	24.40	227.53	868.30
eggs	5.00	1.91	47.48	18.75	861.00	7.00	8.26	28.28	40.51	406.10
fishes	14.30	64.15*	13.97	8.16	1171.90	4.50	30.49	29.45	118.97	1227.40
milks	0.80	1.97	4.06	2.90	152.80	32.50	1.16	2.77	2.77	23.80

Note: TDS total diet study.
* if the data from north China 1 and south China 1 were omitted, the HCH level in fishes is 4.3μg/kg.

Table 2**.** Historical trends of daily dietary intake for DDTs and HCHs in Chinese (μg/ day)

food	HCH			DDT		
	2000	1992	1990	2000	1992	1990
cereals	0.7	2.57	2.06	0.21	0.83	0.54
potatoes	0.04	0.33	0.15	0.01	0.19	0.12
legumes	0.18	0.35	0.15	0.03	0.26	0.08
vegetables	0.32	2.03	0.76	0.36	0.82	1.75
fruits	0.05	0.35	0.29	0.01	0.38	0.27
meats	0.21	2.23	1.04	0.52	1.12	11.64
eggs	0.06	0.96	0.31	0.22	0.59	0.68
fishes	1.45	0.39	0.24	0.72	0.71	5.37
milks	0.13	0.07	0.04	0.07	0.03	0.03
all food	3.14	9.28	5.04	2.15	4.93	20.48
daily intake (μg/kg bw·d)[1]	0.05	0.16	0.08	0.04	0.09	0.34
ADI % [2]				0.4	0.9	3.4

Note 1. Calculated as body weight, adult (60kg).
2. JMPR 2000 recommended provisional tolerance daily intake (PTDI) for DDT is 0.01 mg/kg bw·d

Abbreviation: maximum residue limit (MRL)

Provisional tolerance daily intake (PTDI)
acceptable daily intake (ADI)
FAO/WHO Joint Meeting on Pesticide Residues (JMPR)
X is replaced by daily intake (μg/kg bw·d)