Bull. Environ. Contam. Toxicol. (2006) 76:422–428

DOI: 10.1007/s00128-006-0938-6

Bulletin of Environmental Contamination and Toxicology

Organochlorine Pesticide (HCH and DDT) Residues in Dietary Products from Shaanxi Province, People's Republic of China

Y. Bai,[1] L. Zhou,[2] J. Li[3]

[1] Department of Chemistry, Faculty of Science, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China
[2] Department of Public Health, Medical School of Xi'an Jiaotong University, Xi'an 710049, People's Republic of China
[3] Shaanxi Provincial Center of Disease Control and Prevention, Xi'an 710054, People's Republic of China

Received: 5 November 2004/Accepted: 27 December 2005

Organochlorine (OC) pesticides are employed on a massive scale both in agriculture and in public health in China. OC pesticides such as HCH (hexachlorocyclohexanes), and DDT (dichlorodiphenyltrichlorethane), bioaccumulate in the food chain and thus the exposure to OC compounds can occur through the diet, environmental sources, and occupational activities. Due to their high toxicity, lipophilicity, and persistence, the production and use of HCH and DDT have been banned, phased out, or strongly restricted for several decades in most developed countries (Voldner and Li 1995) and it has been the same in China, since 1983 (Chinese Ministry of Agriculture 1989). But the residue levels of HCH and DDT detected in our environment and agricultural produce in some areas of China were higher, as compared with those in developed countries (Li et al. 1998). In recent years, there has been an increase in public concern that chronic low-level exposure to HCH and DDT residues in food might result in serious cancers (Hodgson and Levi 1996) and hormone-disruption activity (Daston 1997).

Shaanxi is one of the largest agricultural areas in China, and plays an important role in national economic development. Although OC pesticide residues in dietary product from Shaanxi Province have been monitored by mixing samples with those from other regions in the Chinese total diet survey at the time intervals since 1973 (Chen and Gao 1993), there is insufficient local documentation, especially for recent years. Thus a growing concern for safer foods has led research into increased monitoring of the pesticide residues. The aim of this study was to investigate the residue levels of HCH, DDT and their metabolites in dietary product from Shaanxi Province of China. The results can help provide a basis for further monitoring so as to take preventive measures to minimize these pesticide residues in dietary product.

MATERIALS AND METHODS

A total of 240 samples of six kinds of dietary product, including cereals, vegetables, fruits, meat, fish, and milk, were collected randomly from the market of Shaanxi Province, China, in 2002 and were stored at 4℃ until analysis was performed.

Correspondence to: Y. Bai

The OC pesticides under investigation were α-HCH, β-HCH, γ-HCH, o,p'-DDT, p, p'-DDT, and p,p'-DDE. All individual standard OC pesticides with a purity of 99.0%-99.9% were provided by the Institute of Food Safety Control and Inspection of the Ministry of Public Health of China. Stock standard solutions of OC pesticides were prepared in hexane at 10 mg/L. All solvents were of pesticide residues analysis grade and the purity of every reagent was carefully checked.

Extraction, clean-up and analysis of HCH and DDT residues in dietary product samples were conducted using the national standard methods (Yang 1998). Samples were analyzed using a gas chromatography (Shimadzu-14B) equipped with a ^{63}Ni electron capture detector (ECD) and 2.5 m column with 1.5% OV-17 and 1.95 QF-1 Chromsorb WAW-DMCS (80-100 mesh). The operating conditions were as follows: column temperature 190℃; injector port temperature 210℃; detector temperature 230℃. The carrier gas was nitrogen (99.99%) at a flow rate of 56 ml/min.

Quality control and quality assurance measures were incorporated in the analytical scheme. Standard curves method was used for the quantification, and good linearity ($\gamma>0.996$) was achieved for tested intervals that included the whole concentration range found in samples. Almost every ten samples were spiked with standard solution. In addition, two duplicates were measured for every sample and the concentrations of pollutants in samples were summarized using the mean values. The detection limits for α-HCH, β-HCH, γ-HCH, o,p'-DDT, p,p'-DDT, and p,p'-DDE were 0.002, 0.002, 0.010, 0.020, 0.010, and 0.010 ng/g, respectively. Certified reference materials supplied by the Institute of Food Safety Control and Inspection of the Ministry of Public Health of China were analyzed, and the reliable results of the individual α-HCH, β-HCH, γ-HCH, o,p'-DDT, p,p'-DDT, and p,p'-DDE in our laboratory deviated less than 7% from reference values. All statistical analysis were carried out using SPSS 10.0 statistical software.

RESULTS AND DISCUSSION

240 samples of six kinds of dietary product from Shaanxi Province of China were analyzed for HCH and DDT residues. Dietary product included cereals, vegetables, fruits, meat, fish, and milk. The number of positive samples as well as the incidence of HCH and DDT residues in 240 samples are shown in Table 1.

From Table 1, we can see that HCH was abundant in all samples, and HCH residues were found in 96.7% of meat samples, followed by 80% of milk samples, 63.3% of fruits, 60% of vegetables, 55% of fish samples, and 53.3% of cereals. As far as DDT was concerned, meat samples were highly contaminated, followed by milk and fish. It can also be found that the incidence of HCH was higher than that of DDT in most samples, especially in botanical samples. Moreover, the frequency of HCH and DDT in zoological products were higher than those in

Table 1. The number of positive samples and incidence of HCH and DDT in dietary product from Shaanxi Province of China.

dietary products	HCH		DDT	
	No.of positive samples	Incidence (%)	No.of positive samples	Incidence (%)
cereal	32	53.3	3	5.0
vegetable	36	60.0	10	16.7
fruit	19	63.3	1	3.3
meat	29	96.7	26	86.7
fish	11	55.0	10	50.0
milk	16	80.0	16	80.0

Table 2. The mean levels of HCH in dietary product from Shaanxi Province in 2002, and those of national values in 1992 and 2000.

dietary products	Mean value of HCH (μg/Kg)			MRLs of China (μg/Kg)
	2002 [a]	2000 [b]	1992 [b]	
cereal	1.1	5.3	4.8	300
vegetable	1.5	4.8	7.1	200
fruit	1.8	1.7	4.0	200
meat	6.2	19.4	25.7	400
fish	1.7	5.0	14.7	500
milk	3.8	13.4	69.5	100

[a] this study
[b] national values

botanical products, except HCH in vegetables and fruits. The high abundance of HCH in fruits and vegetables was probably due to the practices in using pesticide in Shaanxi Province in spite of the banning in its use in 1983.

The residue levels of HCH and DDT in this study, and as compared with those of national values in China in 1992 (Liu et al. 1995) and 2000 (Wang et al. 2002) are presented in Table 2 and Table 3.

From Table 2 and Table 3 we can see that the mean levels for the total of HCH varied between 1.1 and 6.2 μg/Kg, and for DDT ranged from 4.4 to 11.8 μg/ Kg in all samples of this study. The distribution of HCH residues in dietary product was similar to that of DDT, but HCH content was somewhat lower than DDT content, which might be due to the lower persistency, higher biodegradability of HCH than DDT. Table 2 also shows that the residues of HCH detected in dietary product were at decreased levels, as compared with those from the national

Table 3. The mean levels of DDT in dietary product from Shaanxi Province in 2002, and those of national values in 1992 and 2000.

dietary products	Mean value of DDT (μg/Kg)			MRLs of China (μg/Kg)
	2002 [a]	2000 [b]	1992 [b]	
cereal	4.5	25.2	1.9	200
vegetable	4.5	2.9	1.0	100
fruit	4.4	5.8	2.0	100
meat	9.2	8.7	18.6	200
fish	6.8	7.0	13.3	500
milk	11.8	3.2	1.9	100

[a] this study

[b] national values

Table 4. Composition of HCH and DDT isomers (%) in this study.

pesticide	cereal	vegetable	fruit	meat	fish	milk
α-HCH	48.6	40.9	41.2	21.0	39.9	80.9
β-HCH	38.3	47.4	41.2	62.8	42.2	11.4
γ-HCH	13.1	11.7	17.6	16.2	17.9	7.7
o,p'-DDT	34.4	32.1	33.8	12.9	21.1	28.6
p,p'-DDT	54.3	53.1	56.3	27.8	30.5	42.9
p,p'-DDE	11.3	14.8	9.9	59.3	48.4	28.5

survey in 1992 and 2000.

From Table 3, however, we can see that the concentrations of DDT in botanical and milk products are slightly higher than those of national previous values in 1992 and 2000. Probably it is because DDT is still used recently in cereals, vegetables, fruits and milk products or in public health activities, despite of the Ministry's ban its use. The concentrations of HCH and DDT in various dietary product in Shaanxi Province of China in this study are 1 to 1.5 orders of magnitude below the maximum residue limits (MRLs; GB-2763-81) set forth by the Ministry of Public Health of China in 1983 (Wang et al. 2002). This MRLs is relatively higher because large amounts of HCH and DDT were widely used as pesticides in the agricultural produce in China in 1970s and early 1980s. It also indicats that the MRLs should be revised according to the levels of contaminants found today.

Composition of HCH and DDT isomers for 240 samples in six dietary product from Shaanxi Province in this study are listed in Table 4.

In the technical HCH mixtures, the proportions of the isomers are as follows: 60-70% α-HCH, 5-12% β-HCH, 10-12% γ-HCH, and 6-10% δ-HCH. In many cases the removal rates of HCH isomers from a mixture-treated agricultural plot are α- > γ- > δ- > β-HCH (Willett et al. 1998). β-HCH is the predominant accumulation in several biological enzymes (Senthil et al. 2001) and is a HCH isomer released to the environment as a result of the use of technical grade HCH and impurity in the manufacturing of lindane (γ-HCH > 99%). From Table 4 it can be seen that the composition of β-HCH is much higher than what was theoretically expected, accounting for almost 50% in vegetables, fruits, meat, and fish samples, but γ-HCH, on the other hand, was the minimum. This implies that the use of HCH in Shaanxi Province has not been stopped completely.

Technical grade DDT in general, present as a mixture of three forms, i.e., p,p'-DDT (85%), o,p'-DDT (15%), and o,o'-DDT (trace amounts) as reported by the ATSDR (2002). DDT and its break-down product DDE, still persisting in the environment long after it has been banned, may be involved in interfering with the action of male sex hormones (Kelce et al. 1995), and has hazardous effects on other organisms, both terrestrial and aquatic. A recent hypothesis also suggests that DDT may affect the incidence of testicular cancer as one of the most important endocrine disrupters (Skakkebaek et al. 2001). The ratio of p,p'-DDT/ΣDDT and DDT/DDE could be used to estimate the period of DDT application. The data in Table 4 show that the ratio of p,p'-DDT/ΣDDT in cereals, vegetables and fruits is more than half of the total DDT residues and the ratio of DDT/DDE is greater than 1 for cereals, vegetables, fruits and milk. These could be the result of direct exposure through the use of fresh DDT or the past widespread use of DDT in agricultural produce in Shaanxi Province.

The estimated daily intake of HCH and DDT in this study can be calculated according to the daily diet consumption pattern by Chinese (g/person/day) (cereals: 419 g, fruits: 55 g, vegetables: 329 g, fish: 25 g, meat: 33 g, milk, and dairy products: 27 g) (Hou et al. 1998). The estimated daily intake of HCH and DDT in this study is 1.40 and 4.40 μg/person/day, respectively. The comparison between estimated daily intake in this study and Chinese previous study and the acceptable daily intakes (ADIs) recommended by the FAO/WHO are presented in Table 5.

Table 5. The daily intake of HCH and DDT in this study and Chinese previous study and the acceptable daily intakes of FAO/WHO (μg/person/day).

	2002[a]	2000[b]	1992[b]	ADIs[c]
HCH	1.40	3.14	9.28	600 (γ-HCH)
DDT	4.40	2.15	4.93	1200

[a] This study

[b] Chinese study (Zhao et al. 2003)

[c] FAO/WHO. ADIs was expressed as the average body weigh of 60 Kg/person.

The estimated daily intake of HCH and DDT in this study was 1.40 and 4.40 μg/person/day, respectively. They were decreased, as compared with those of the national values in 1992, and were much lower than those of ADIs (FAO/WHO). However, they were still higher than those in developed countries, such as the United States (0.16 μg/person/day for HCH; 1.3 μg/person/day for DDT), and Japan (0.88 μg/person/day for HCH; 1.3 μg/person/day for DDT) (Chen and Gao 1993).

Much research about transport pathway, accumulation, exposure of human, environmental toxicology, and risk assessment and management for OC pesticides have been achieved in developed countries. In contrast to the situation in developed countries, there is a lack of information on the above research in China, especially in Shaanxi Province. This study provides a limited, but hopefully informative snapshot of the pesticide distribution in dietary product within Shaanxi Province. The results of this study show that after banning the use of OC pesticides (HCH and DDT) in China for more than 20 years, they can still be detected in most dietary product samples. This gives further proof that OC pesticides are very persistent organic pollutants in the environment and this implies that the misuse and improper handling of HCH and DDT still occur in Shaanxi Province. Moreover, the possibility of the occasional application should not be ignored due to their least costs and free availability from regional sources with where capabilities of producing chemicals. The HCH and DDT residue contents in dietary samples are well below the national MRLs. However, the concentrations of DDT in botanical samples from Shaanxi Province are somewhat higher than those of national previous survey, which indicates that DDT might be used in cereals, vegetables, and fruits. The estimated dietary intake of HCH and DDT in this study is less than ADIs set by the FAO/WHO, but rather higher than those in some developed countries. Therefore, this kind of situation has slowed down the development of exportation of the agricultural produce in Shaanxi Province. On the other side, exposure to more than one pesticide is common in real life. Interaction among different types of pesticides may induce a wide array of health effects. In animal studies, a number of commercial pesticides has been reported to interact inducing supra-additive effects (e.g., DDT + dimethoate)(Krishnan and Brodeur 1991). Under these circumstances, monitoring OC pesticide residues in dietary product from Shaanxi Province needs to be conducted every few years to determine the trend. We hope that our results will provide a perspective for protection and poisoning surveillance systems and help take preventive measures against the negative impacts on the environment and human health due to pesticide accumulation.

Acknowledgments. We gratefully acknowledge Shaanxi Provincial Center of Disease Control and Prevention for their cooperation and kindly provided partial founding. We also appreciate Dr. Herbert N. Nigg and Dr. John W. Hylin for their suggestions during editing and communication.

REFERENCES

ATSDR(Agency for Toxic Substances and Disease Registry) (2002)Toxicological profile for DDT, DDE, and DDD. US department of Health and Human Services, Public Health Service, Atlante, GA, p 2

Chen JS, Gao JQ (1993) The Chinese total dist study in 1990 Part I. Chemical contaminants. J Hyg Res 22:1-20 (in Chinese)

Chinese Ministry of Agriculture (1989) A new pesticide manual. Agriculture Publisher, Beijing

Daston GP (1997) Advances in understanding mechanisms of toxicity and implications for risk assessment. Reprod Toxicol 11:389-396

Hodgson E, Levi PE (1996) Pesticides: an important but underused model for the environmental health sciences. Environ Health Perspect 104 (Suppl.1) 97-106

Hou WD, Li XH, Zhou QC, Li JH, Jiang SL (1998) A study of dietary component and nutrients in total diet study of Chengdu inhabitant. Modern Preventive Medicine 25:288-300 (In Chinese)

Kelce WR, Christy RS, Laws SC, Gray LE, Kemppaven JA, Wilson EM (1995) Persistent DDT metabolite p,p'-DDE is a potent androgen receptor antagonist. Nature 375:581-585

Krishnan K, Brodeur J (1991)Toxicological consequences of combined exposures to environmental pollutants. Arch Complex Environ Stud 3:1-106

Li YF, Cai DJ, Singh A (1998) Technical hexachlorocyclohexane use trends in China and their impact on the environment. Arch Environ ContamToxicol 35: 688-697

Liu HZ, Chen HJ, Wang XQ (1995) Chinese total diet study in 1992—pesticide residues. J Hyg Res 24:356-360 (in Chinese)

Senthil K, Kannan K, Tamabe S, Subramanian AN (2001) Accumulation of persistent organochlorine pesticides and PCBs in sediments, aquatic biota, birds, eggs and bat collected from South India. Environ Sci Pollut Res 8:35-47

Skakkebaek NE, Rajpert-De Meyts E, Main KM (2001) Testicular dysgenesis syndrome:an increasingly common developmental disorder with environmental aspects. Hum Reprod 16:972-978

Voldner EC, Li YF (1995) Global usage of selected persistent organochlorines.Sci Total Environ 160/161:201-210

Wang MQ, Wang ZT, Bao DY, Ran L (2002) Food contamination monitoring and analysis in 2000 in China. Chinese J Food Hyg 14:3-8 (in Chinese).

Willett KL, Ulrich EM, Hites RA (1998) Differential toxicity and environmental fates of hexachlorocyclohexane isomers. Environ Sci Technol32:2197-2207

Yang HF (1998) Physio-chemical detection handbook in food. Chinese Standard Press, Beijing (In Chinese)

Zhao YF, Wu YN, Wang XQ, Gao JQ, Chen JS (2003) Study on the dietary pesticide residues in Chinese residents. Chinese J Epidemiol 24:661-664 (In Chinese)