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Organophosphorus pesticide residues in market foods in Shaanxi area, China

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Abstract

The aim of this study was to investigate the organophosphorus (OP) pesticide residues in market foods (cereals, vegetables, and fruits) in the Shaanxi area of China. The concentrations of eight OP pesticides were determined by gas chromatography with flame photometric detection (GC-FPD). In 18 of 200 samples, five OP pesticides, including dichlorvos, dimethoate, parathion-methyl, pirimiphos-methyl and parathion, were found in concentrations ranging from 0.004 to 0.257 mg/kg. The mean levels of dimethoate in fruits and parathion in vegetables exceeded the maximum residue limits (MRLs) allowed by the Ministry of Health, of China. Other detectable OP pesticide residues levels were below their MRLs. Demeton, diazinon and sumithion were not found in any sample. The results provide important information on the current contamination status of a key agricultural area in China, and point to the need for urgent action to control the use of some excessively applied and potentially persistent OP pesticides, such as dimethoate and parathion.

Keywords: Organophosphorus pesticide residues; Market foods

1. Introduction

The use of pesticides in agriculture has continuously increased after World War II, which leads to increased world food production. Nevertheless, this use and additional environmental pollution due to industrial emission, during their production, have resulted in the occurrence of residues of these chemicals and their metabolites in food commodities, water and soil. OP pesticides are widely applied in agriculture. Organochlorine pesticides were banned in China in 1983 (Yang & Fang, 1997). OP pesticides act by binding to the enzyme acetylcholinesterase, disrupting nerve function, resulting in paralysis and death (Liu, Olivier, & Pope, 1999), yet their persistence in the environment is not well understood. The general population is mainly exposed to OP pesticides through the ingestion of contaminated foods (such as cereals, vegetables, and fruits), which are directly treated with OP pesticides or are grown in contaminated fields. Therefore, contamination of the environment and food by pesticide residues is a dramatically topical issue in many areas of the world. Any preventive action greatly depends upon international differences, but the common final goal is still to reduce air, water, soil and food contamination, as well as to prevent both acute and chronic adverse effects for manufacturers, consumers and the world community as a whole.

The objective of this study was to investigate the OP pesticide residues in market foods (cereals, vegetables and fruits) in the Shaanxi area of China. The data collected are to be used as a reference point for future

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monitoring as well as for providing a basis for developing sustainable natural resource management practices and for taking preventive measures to minimize human health risks.

2. Materials and methods

2.1. Samples

OP pesticide residues were determined in 200 samples of cereals, vegetables, and fruits obtained from the local market of Shaanxi area of China in 2003. All samples were collected in labelled dark glass bottles, transported to the laboratory and stored for a short time at 4 °C until they were analyzed.

2.2. Materials and reagents

All organic solvents were products of Xi'an city of China and re-distilled before using. Standard OP pesticides of purity 99.0–99.9% were provided by the Institute of Food Safety, the Ministry of Health, of China. Stock standard solutions of each OP pesticide was prepared in methylene chloride at 1000 mg/l. An intermediate solution of the mixture of all pesticides was also made up in methylene chloride.

Table 1
Mean percent recovery ± RSD of eight OP pesticides in cucumber samples at 0.1 and 0.5 mg/kg fortification levels ($n = 10$)

Organophosphorus pesticides	Mean % recovery ± RSD at different fortification levels (mg/kg)	
	0.1	0.5
Dichlorvos	107 ± 4	108 ± 5
Demeton	96 ± 6	97 ± 7
Diazinon	88 ± 7	91 ± 8
Dimethoate	97 ± 5	98 ± 4
Parathion-methyl	91 ± 7	89 ± 8
Pirimiphos-methyl	94 ± 4	96 ± 3
Sumithion	96 ± 3	95 ± 2
Parathion	90 ± 6	89 ± 5

2.3. Extraction and determination of OPs

Extraction, clean-up and analysis of food were performed according to the Chinese standard method (Wang, 2002). Eight OP pesticides: dichlorvos, dimethoate, parathion-methyl, pirimiphos-methyl, parathion, demeton, diazinon, and sumithion were analyzed using gas-chromatographic method. Three microliters of extract were injected into a gas chromatograph (Shimadzu-9A) equipped with the following instrument parameters and operating conditions: flame photometric detector; columns, glass 3.0 m × 2.5 mm packed with a mixture of 200 + 2.0% OV-17 and 4.5% DC, chromosorb WAW, column temperature, 240 °C; detector temperature, 275 °C.

2.4. Recovery experiments, quantitative evaluation and detection limits

Cucumber samples were fortified at 0.1 and 0.5 mg/kg, by adding intermediate pesticide solutions. The recovery assays were replicated ten times and the data are presented in Table 1. The detection limits (DLs), calculated by using a signal-to-noise (S/N) ratio of 3, were in the range 0.002–0.006 mg/kg. The quantity of each OP was calculated by applying the external standard method.

3. Results and discussion

OP pesticides are used worldwide in agriculture for the control of various insects. These compounds have higher acute toxicities than organochlorine pesticides. A study of the possible contamination of cereals, vegetables and fruits in the Shaanxi area of China with eight OP pesticides was carried out during the crop year 2003. The target compounds were selected among those commonly used for controlling agriculture production in the Shaanxi area of China. The mean levels of eight OP pesticides in cereals, vegetables, and fruits samples are presented in Table 2.

Table 2
The mean levels of eight OP pesticides in foods in the Shaanxi area (China)

Pesticides	Cereal ($n = 60$)		Vegetable ($n = 80$)		Fruit ($n = 60$)	
	Mean value (mg/kg)	No. of positive samples	Mean value (mg/kg)	No. of positive samples	Mean value (mg/kg)	No. of positive samples
Dichlorvos	Nd	–	0.004	6	Nd	–
Demeton	Nd	–	Nd	–	Nd	–
Diazinon	Nd	–	Nd	–	Nd	–
Dimethoate	Nd	–	0.004	5	0.002	1
Parathion-methyl	Nd	–	0.003	2	Nd	–
Pirimiphos-methyl	0.002	1	0.002	1	Nd	–
Sumithion	Nd	–	Nd	–	Nd	–
Parathion	Nd	–	0.006	2	Nd	–

Table 3
The levels of parathion-methyl, pirimiphos-methyl and parathion in foods

Food	Mean value (mg/kg)					
	Parathion-methyl		Pirimiphos-methyl		Parathion	
	2003[a]	2000[b]	2003[a]	2000[b]	2003[a]	2000[b]
Cereal	Nd	0.005	0.002	0.005	Nd	0.009
Vegetable	0.003	0.004	0.002	0.008	0.006	0.008
Fruit	Nd	0.005	Nd	0.005	Nd	0.009

[a] This study.
[b] The national value.

Table 2 shows that dichlorvos residues were detected in six vegetable samples with a mean level of 0.004 mg/kg. Dimethoate residues were detected in five vegetable samples and one fruit sample at mean concentrations of 0.004 and 0.002 mg/kg, respectively. Parathion-methyl and parathion were detected in two vegetable samples each. Pirimiphos-methyl was detected in one vegetable sample and one cereal sample. The levels of dimethoate residues in fruits and parathion residues in vegetables are 0.004 and 0.006 mg/kg, respectively, exceeding the national MRLs (The MRLs of dimethoate in fruits and parathion in vegetables laid down by the Ministry of Health of China are non-detectable). Other detectable OP pesticide residues levels were below their MRLs. Demeton, diazinon, and sumithion were not found in any sample.

The mean concentrations of three OP pesticides of this experiment, as compared with those of our country in 2000 (Wang et al., 2003), are listed in Table 3.

Table 3 shows that the mean levels of parathion-methyl, pirimiphos-methyl, and parathion in cereals, vegetables and fruits in this study are decreased, as compared with the national levels in China in 2000.

The most common OP pesticide residues found were dichlorvos, dimethoate, and parathion in vegetables and fruits products in the Shaanxi area. The concentrations of dimethoate in fruits and parathion residues in vegetable products, above their MRLs, may be due to their non-professional use. This observation demands further investigation. In order to improve economical development by providing off-season fresh fruits and vegetables to countries, greater volumes of OP pesticides are used frequently during the growing season in the Shaanxi area and result in serious food contamination. Recent literature reveals that the largest proportion of human acute toxicity data is related to OP pesticide intoxications (Ecobichon, 2001). The World Health Organization (1990) estimated an annual worldwide total of some 3 million cases of acute, severe poisonings matched possibly by a greater number of unreported, with some 220,000 deaths. Furthermore, many OP pesticides are considered as environmental endocrine disruptors (Song & Wang, 2001), and the results of our recent experiment reflect that the mixture of parathion, dimethoate, and methyl-parathion may show reproduction toxicity on the mouse. It is clear that pesticides should be applied correctly according to their recommended volumes, rather than misused. The results also provide important information on the current contamination status of a key agricultural area in China and point to the need for urgent action to control the use of some excessively applied and potentially persistent OP pesticides, such as dimethoate and parathion.

4. Conclusions

(1) The results underline that the OP pesticide residues are present in vegetables and fruits in the Shaanxi area.
(2) Routine monitoring of these pollutants in market foods is required for the prevention, control and reduction of pollution as well as for legal decisions to minimize health risks.

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