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Monitoring and Risk Assessment of Pesticide Residues in Commercially Dried Vegetables

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ABSTRACT: We tested for residual pesticide levels in dried vegetables in Seoul, Korea. A total of 100 samples of 13 different types of agricultural products were analyzed by a gas chromatography-nitrogen phosphate detector (GC-NPD), an electron capture detector (GC-μECD), a mass spectrometry detector (GC-MSD), and a high performance liquid chromatography-ultraviolet detector (HPLC-UV). We used multi-analysis methods to analyze for 253 different pesticide types. Among the selected agricultural products, residual pesticides were detected in 11 samples, of which 2 samples (2.0%) exceeded the Korea Maximum Residue limits (MRLs). We detected pesticide residue in 6 of 9 analyzed dried pepper leaves and 1 sample exceeded the Korea MRLs. Data obtained were then used for estimating the potential health risks associated with the exposures to these pesticides. The estimated daily intakes (EDIs) range from 0.1% of the acceptable daily intake (ADI) for bifenthrin to 8.4% of the ADI for cadusafos. The most critical commodity is cadusafos in chwinamul, contributing 8.4% to the hazard index (HI). This results show that the detected pesticides could not be considered a serious public health problem. Nevertheless, an investigation into continuous monitoring is recommended.

Keywords: dried, vegetables, pesticide, risk assessment, hazard index

INTRODUCTION

Recently, health-conscious consumers are taking an increasing interest in vegetables. Drying of foods is practiced in Korea to make the products more durable and preserve them during insecure periods. Drying is mainly done on an artisanal scale or through small-scale industrial units (1,2).

Pesticides are used during production and post-harvest treatment of agricultural commodities (3). However, increased use of chemical pesticides has resulted in contamination of the environment and also caused many associated long-term effects on human health (4). Pesticide contamination of foods can negatively affect human health since many pesticides used in agriculture have toxic effects on living organisms. Also pesticides have been associated with a wide spectrum of human health hazards such as headaches and nausea to chronic impacts like cancer, reproductive harm and endocrine disruption (5).

Governments and international organizations regulate the use of pesticides by setting maximum residue levels (MRLs) of pesticide in foods. Pesticide residue monitoring of fruits and vegetables have been conducted to confirm the proper use and exact concentrations of pesticides. MRLs have been established for agricultural products in many countries to avoid the health hazard caused by pesticide residues. Health safety limits for human health are typically expressed as acceptable daily intake (ADI). The standard method to evaluate human exposure is based on the average consumption per person per day, Korean average adult weight, and pesticide residue data (6).

Although many scientists have analyzed pesticide residues in various foods, the analysis of pesticides in dried vegetables has been carried out only by a few studies (7). Dried vegetables have been given a lot of attention in monitoring programs since most of them are concentrated and expected to contain higher pesticide residue levels compared to other food groups of plant origin. Therefore, assessing the risk of pesticide residues in these dried commodities intended for human consumption is necessary.

The aim of the present study is to analyze the presence of 253 pesticides commonly used on dried vegetables and to check their compliance with existing regulations.

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The results of the monitoring program in combination with food consumption data were taken into consideration to evaluate whether the estimated daily intake (EDI) of pesticides through the dried vegetables consumed by the local inhabitants is a cause of toxicological concern according to the recommended dose by the Food and Agriculture Organization (FAO) and World Health Organization (WHO). The results can be used when designing future control programs for this region and taking preventive actions to minimize human health risks.

MATERIALS AND METHODS

Sampling

A total of 100 samples of dried vegetables were collected from June to October 2012 at 8 wholesalers or large supermarkets from each of the 4 districts of Seoul city. The sampling was done according to guidelines of Korea on sampling for official control of pesticide residues. Samples were analyzed within 24 hr and stored at 4°C until the moment of extraction. No degradation of pesticides was detected under the storage conditions.

Chemicals

The 253 pesticide standards were purchased from Ehrenstorfer Gimbh Co. (Augsburg, Germany) and Waco (Osaka, Japan). The purities of standard pesticides ranged from 91.0% to 99.5%. Standard stock solutions were made by dissolving each analytical standard in methanol or acetone to a final concentration of 100 mg/L. The stock and working solutions were stored in completely filled vials closed with parafilm at −20°C until analysis. Acetonitrile, acetone, n-hexane and dichloromethane were purchased from J.T. Baker (Phillipsburg, NJ, USA). Anhydrous sodium chloride for residue analysis was purchased from Fluka (Buchs, Switzerland).

Analytical procedure

The sample extraction procedure was carried out according to the method described in the Korea Food Standards Codex (8) with slight modifications. A portion of sample (300 g) was chopped and homogenized for 3 min at high speed. 20 g of homogenized sample was mixed with 50 mL of distilled water and was homogenized with 100 mL of acetonitrile for 2 min. The sample was filtered through a 12 cm Shark skin filter paper (Whatman, Piscataway, NJ, USA).

Then, 20 g of anhydrous sodium chloride was added to the extract and then vortexed immediately for 3 min. The extract was next centrifuged for 5 min at 4,000 rpm at 4°C (Hanil Co., Seoul, Korea). From the upper layer, a 10 mL aliquot was transferred into a 100 mL beaker. Then, evaporation of the solvent to dryness was carried out with nitrogen gas (35∼40°C). For the gas chromatography analysis, the mixture was passed through a Florisil cartridge (Strata, Harbour City, CA, USA) preconditioned with 5 mL of acetone : hexane (2:8; v/v); the analyte of interest passes through the column while matrix constituents are retained. The solvent in the mixture was then evaporated slowly to dryness at 35∼40°C under a gentle stream of nitrogen. The dried residue was re-dissolved with 2 mL of acetone for GC and GC-MS analysis. For the HPLC analysis, the mixture was passed through SPE NH_2 cartridges (1 g, 6 mL, Phenomenex, CA, USA). Cartridges were activated and conditioned with 5 mL of dichloromethane : methanol (8:2, v/v). 5 mL of dichloromethane : methanol (8:2, v/v) was added both to the sample and for elution through the cartridge. This solvent was evaporated slowly to dryness at 35∼40°C under a gentle stream of nitrogen. The dried residue was re-dissolved in 2 mL methanol for HPLC-UV analysis.

Instrumental analysis

Gas chromatography (GC) analyses were carried out an Agilent Technologies model 7890 A gas chromatograph (Palo Alto, CA, USA) with nitrogen phosphorus detector (NPD) and micro electron capture detector (μECD). The simultaneous analysis of multi-residual pesticides was developed using the GC method shown in Table 1. Any detected residues were confirmed using mass spectrometry to prevent any misinterpretation of results. The spectra were obtained at an ionizing energy of 70 eV in the selected ion-monitoring (SIM) mode. Gas chromatography/mass spectrometry (GC/MS, Agilent Technologies 5975C) has been used in confirmation studies. The high performance liquid chromatography (HPLC) was carried out on an Agilent instrument model 1100 series and diode array detector (Agilent Technologies, Santa Clara, CA, USA). A C18 column (ZORBOX SB-C18 column, 4.6×250 mm, ZORBOX, Tokyo, Japan) was used for separation at 40°C. The injection volume of the sample was 10 μL. Pesticide separation was performed by gradient elution with water (A) and methanol (B) at a flow rate of 1.0 mL/min. UV absorbance was

Table 1. The analytical conditions used for gas chromatography

Detector	μECD	NPD
Inlet temperature	230°C	210°C
Detector temperature	280°C	320°C
Flow rate	1.0 mL/min (N_2)	60 mL/min (Air) 1.2 mL/min (N_2) 3 mL/min (H_2)
Column	DB-1701	DB-1701
Oven temperature	150°C, 1 min 12°C/min 240°C, 2 min 10°C/min 280°C, 12 min	150°C, 1 min 12°C/min 200°C, 8 min 10°C/min 260°C, 8 min

monitored at 254 nm and 280 nm. The gradient elution program was as follows; initial 70% A; 0～15 min, 0% A; and a 15～30 min return to the initial conditions. Processing of the raw chromatographic data and data collection was performed using the ChemStation program (Agilent Technologies).

Method validation

Sample preparation and analytical methods were validated in terms of limits of linearity, repeatability, limits of detection (LOD), quantification (LOQ) and recovery. The linearity of the standard curves was injected at 0.1, 0.5, 1.0, 2.0, 5.0 and 10.0 μg/L concentrations. All standards were injected three times (n=3). The limits of detection (LOD) were measured as analyze concentration based on a signal-to-noise ratio of 3 and limits of quantification (LOQ) was defined as 3.3×LOD. Recovery of pesticide was determined by spiking with a standard pesticide aqueous solution.

RESULTS AND DISCUSSION

Method validation

The 13 pesticides were chosen based on their detection in dried vegetables. Table 2 presents the linearity range, correlation coefficient values, limit of detection (LOD), limit of quantification (LOQ) and recoveries of all pesticides in commodities for the validation study. A linear correlation between pesticide concentrations and peak areas was detected with coefficient correlations in the range of 0.9924～0.9999. Validation of the analytical method was conducted in terms of recovery of the spiked sample. Recoveries were found to be 78.5～97.6%. These results suggest that the experimental procedure including extraction, clean-up and instrumental analysis is suitable for use in the analysis of the targeted pesticide residues in the samples.

Evaluation by commodity

Table 3 gives an overview of the data obtained after the analysis of 100 samples. With regard to all 13 commodities investigated, in 89 samples no pesticide residues were detected. 9 analyzed samples contained pesticide residues at or below MRLs laid down by the Standardization Administration of Korea (8). 2 samples, dried pepper leaves and dried chwinamul, contained pesticide residues above MRLs. Dried bracken, dried eggplant, dried taro, dried radish leaves, dried Siberian gooseberry, dried sweet potato sprout, dried pumpkin, dried mushroom and dried radish were residue-free. The occurrence of pesticide residues in dried vegetables and the total number of commodities containing residues above MRLs are shown in Table 3.

Pesticide levels in dried vegetables

In this monitoring program, pesticide residues were found for 13 different pesticides. The mean levels and

Table 3. Frequency of samples with and without detected pesticide residues, and samples containing residues above MRL for dried vegetables

Commodity	No. of samples analyzed	No. of samples with detectable residues (%)	No. of samples >MRL (%)
Dried bracken	6		
Dried eggplant	6		
Dried taro	6		
Dried radish leaves	6		
Dried chwinamul	14	2	1
Dried Siberian gooseberry	3		
Dried sweet potato sprout	5		
Dried pumpkin	8		
Dried red pepper	8	3	
Dried mushroom	8		
Dried pepper leaves	7	6	1
Dried radish	5		
Others	18		
Total	100	11	2

Table 2. Validation parameters such as limit of detection (LOD), limit of quantification (LOQ) and recoveries of pesticides detected in dried vegetables

Pesticide	Commodity	Range (μg/mL)	Correlation coefficient (r^2)	LOD (mg/L)	LOQ (mg/L)	Recovery (%)
Chlorothalonil	Dried pepper leaves	0.02～10	0.9992	0.02	0.07	96.5±2.2
Bifenthrin	Dried pepper leaves	0.02～10	0.9924	0.05	0.17	93.3±6.8
Tebuconazole	Dried pepper leaves	0.02～10	0.9999	0.05	0.17	78.5±5.0
Isoprothiolane	Dried pepper leaves	0.02～10	0.9980	0.03	0.10	88.2±4.1
Kresoxim-methyl	Dried pepper leaves	0.02～10	0.9999	0.05	0.17	90.5±2.5
	Dried red pepper	0.02～10	0.9999	0.05	0.17	89.6±3.2
Metalaxyl	Dried pepper leaves	0.02～10	0.9945	0.03	0.10	93.8±3.4
Pyridaben	Dried pepper leaves	0.02～10	0.9980	0.03	0.10	90.2±2.8
Chlorfenapyr	Dried pepper leaves	0.02～10	0.9999	0.02	0.07	97.6±1.1
Azoxystrobin	Dried pepper leaves	0.02～10	0.9995	0.05	0.17	80.6±7.2
Pencycuron	Dried red pepper	0.02～10	0.9999	0.05	0.17	81.4±4.4
Diazinon	Dried red pepper	0.02～10	0.9999	0.02	0.07	94.2±2.7
Hexaconazole	Dried chwinamul	0.02～10	0.9999	0.02	0.07	79.6±4.5
Cadusafos	Dried chwinamul	0.02～10	0.9995	0.03	0.10	80.7±3.9

ranges of 13 pesticide residues in dried vegetables are presented in Table 4. Residues of isoprothiolane and cadusafos were found exceeding the Korea MRLs. Isoprothiolane is a fungicide for blast disease and is also used as a dithiolane pesticide and for cultivating rice plant because of its effect on brown planthoppers (9). Cadusafos is an organophosphate insecticide, normally used as a soil treatment (10). Residues of pesticide found most frequently were tebuconazole, followed by chlorothalonil, bifenthrin, kresoxim-methyl, hexaconazole, isoprothiolane, metalaxyl, pyridaben, chlorfenapyr, azoxystrobin, pencycuron, diazinon, cadusafos. Tebuconazole was the residue found most frequently in the 3 dried upper leaf samples analyzed in the concentration range of lower than the detection limit to 4.61 mg/kg. Vegetable safety was estimated considering the detection rate and the disqualification rate of residues. A previous study found that co-occurrence of multiple residues existed in single-erving commodities (11); however, the co-occurrence of pesticide residues was not observed in our work even though multiple residues were detected in a dried vegetable.

Table 4. Pesticide residues detected in dried vegetables

Pesticide	Mean value (mg/kg)	No. of detectable samples	No. of samples >MRL
Chlorothalonil	3.64	2	
Bifenthrin	0.15	2	
Tebuconazole	2.11	3	
Isoprothiolane	8.30	1	1
Kresoxim-methyl	0.60	2	
Metalaxyl	0.81	1	
Pyridaben	5.78	1	
Chlorfenapyr	11.93	1	
Azoxystrobin	8.80	1	
Pencycuron	0.14	1	
Diazinon	0.26	1	
Hexaconazole	2.42	2	
Cadusafos	2.80	1	1

Risk assessment

An exposure evaluation was conducted based on monitoring the results of the pesticide residue to determine the degree of risk by the detected pesticide residues in samples. Risk assessments were performed using the ADI and the EDI. The EDI was calculated from the average consumption per person per day and the pesticide residues data. The percent EDI to ADI ratio was calculated as (EDI/ADE)×Korean average adult weight (55 kg) (12,13). The results of human exposure to pesticides based on dried vegetable intake are shown in Table 5. The EDIs of pesticide range from 1.0×10^{-5} to 8.0×10^{-4} mg/day. Hazard index for cardusafos, diazinon and pyridaben were 8.4%, 5.1% and 3.9%, respectively. Results exceeding 100% indicate a risk potential (14).

The results of this research indicate that the detected pesticides are not harmful to humans. Although the results show a negligible risk associated with exposure via dried vegetables consumption, a special precaution should be taken with the possible total exposure to these chemicals from various foods in the future. Monitoring of the pesticide residue data in dried food has been performed. Therefore, monitoring the residues of pesticide in dried food continuously is necessary because of possible health effects, widespread uses and insufficient residue data. Additionally, monitoring studies must be performed to improve food safety.

Table 5. Exposure assessment parameters of pesticides in dried vegetables

Commodity	Pesticide	ADI[1)] (mg/kgb.w/day)	EDI[2)] (mg/day)	Hazard index[3)] (%)
Dried pepper leaves	Chlorothalonil	0.02	3.0E-04	1.5
	Bifenthrin	0.01	1.0E-05	0.1
	Tebuconazole	0.03	1.4E-05	0.5
	Isoprothiolane	0.1	5.5E-05	0.6
	Kresoxim-methyl	0.4	3.0E-05	0
	Metalaxyl	0.08	5.0E-05	0.1
	Cyhalothrin	0.02	8.0E-05	0.4
	Pyridaben	0.01	3.8E-05	3.9
	Chlorfenapyr	0.026	8.0E-04	3.1
	Azoxystrobin	0.2	5.9E-05	0.3
Dried red pepper	Pencycuron	0.053	1.4E-05	0.3
	Kresoxim-methyl	0.4	7.8E-05	0.2
	Diazinon	0.005	2.6E-05	5.1
Dried chwinamul	Hexaconazole	0.005	4.0E-05	0.7
	Cadusafos	0.0005	4.0E-05	8.4

[1)]Average level of detection.
[2)]Acceptable daily intake.
[3)]Hazard index (%)=EDI/ADI×100.

AUTHOR DISCLOSURE STATEMENT

The authors declare no conflict of interest.

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