Analysis and Risk Assessment of Pesticides in Korean Agricultural Products

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ABSTRACT

The objective of this study was to establish an analytical method to measure pesticides and to analyze pesticide residue levels of Korean agricultural products such as yuza (Citrus junos Sieb. ex Tanaka), yuza tea, and ginseng products. Risk assessments were also performed by calculating estimated daily intake (EDI) and acceptable daily intake (ADI). In addition, kinetic study such as the degradation order of pesticides in yuza tea was carried out. Acequinocyl, spirodiclofen and carbendazim were detected in yuza samples in the concentration range of 0.07–0.15 μg/g, 0.11–1.89 μg/g, and 0.03–5.15 μg /g, respectively, whereas chlorpyrifos, prothiofos, phosalone, and deltamethrin were not detected in yuza or yuza tea. The concentrations of acequinocyl, spirodiclofen and carbendazim ranged from 0.18–1.05 μg/g, 0.13–0.29 μg/g, and 0.17–2.36 μg/g, respectively, in yuza tea samples. The percent ratios of EDI to ADI for acequinocyl, spirodiclofen, and carbendazim were 24.6%, 22.7%, and 58.5%, respectively. The degradation order of the seven pesticides in yuza tea was as follows: acequinocyl > chlorpyrifos > spirodiclofen > carbendazim > deltamethrin > phosalone, prothiofos. For the accurate analysis of Korean ginseng products a new analytical method was developed based on gas chromatography-triple quadrupole tandem mass spectrometry (GC-MS/MS). The analytical method was validated and the most frequently detected pesticide was tolclofos-methyl. Tolclofos-methyl was detected in 86.4 % of fresh ginseng (18.25-404.5 μg/kg), 91.7 % of red ginseng (13.14-119.4 μg/kg), and 87.5 % of dried ginseng (23.15-3673 μg/kg).

Keywords: Pesticide; Residue; Yuza; Yuza tea; Risk assessment; Ginseng; Validation; GC-MS/MS

INTRODUCTION

Yuza, *Citrus junos* Sieb. ex Tanaka, is a citrus fruit harvested in Korea, China, and Japan. Particularly in Korea, the fruit is commonly processed into beverages and herbal medicines due to its special flavor and effectiveness against colds. Most parts of yuza fruit such as the peel, juice, and seeds have been used (Lan-Phi et al., 2009). The beneficial health effects of flavonoids in yuza such as antioxidant, anti-carcinogenic, anti-viral, and anti-inflammatory activities have been reported (Fujihara and Shimizu, 2003; Yoo et al., 2004).

Ginseng (*Panax ginseng C.A. Mayer*) is a valuable herb that has been used extensively in Eastern Asian countries, such as Korea, China, and Japan, for more than 5,000 years. Ginseng as a medicine has been studied thoroughly. Ginsenosides are major components having pharmacological and biological activities, including immune, cardiovascular, central nervous system, endocrine, anti-diabetic, anti-tumor, and antioxidant activities (Attele et al., 1999). Ginseng is generally harvested after a 5- or 6-year cultivation period, or even a 10-year period.

Such a long cultivation period combined with the widespread use of pesticides in ginseng production has led to the presence of pesticide residue in ginseng (Kim and Lee, 2002).

A number of pesticides have been widely used for pest control in crops and fruits at various stages of cultivation. Pesticides are used for better yields and quality during post-harvest storage. However, pesticide residues are of concern, because these substances are potential health hazards (Taylor et al., 2002). In particular, pesticide residues may persist in plant tissues and appear in the pulp and juice of fruits and vegetables. Determining pesticide concentrations is important, as people who eat relatively large quantities of these foods are more at risk than others. In Korea, the pesticides authorized by Korea Crop Protection Association for yuza production are chlorpyrifos, prothiofos, phosalone, deltamethrin, acequinocyl, spirodiclofen and carbendazim (Korea Crop Protection Association, 2009). Pesticide residue monitoring of fruits and vegetables has been conducted to confirm the proper use and exact concentrations of pesticides. Maximum residue limits (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 (Park et al. 2010).

Tandem mass spectrometry (MS/MS) provides a much higher degree of assurance in the identification of an analyte than any other single stage mass spectrometry technique. One of the advantages of MS/MS is to increase S/N ratio and selectivity. Due to the power of MS/MS, the confirmation of target compounds can be achieved with a higher level of confidence. Among the various mass analyzers that can perform tandem mass spectrometry, triple quadrupole mass spectrometers have recently been recommended for the analysis of pesticide residues in crops (Walorczyk, 2007).

Although many scientists have analyzed pesticide residues in various fruits, the analysis of pesticides in yuza has been carried out a few. Yamamoto et al. (1982) reported acaricide residue on yuza fruits grown in vinyl houses. Goto et al. (2003) reported on a simple and rapid method to identify pesticides in citrus fruits by electro-spray ionization tandem mass spectrometry. Micro-extraction procedures were compared to determine pesticides in oranges using liquid chromatography–mass spectrometry by Blasco et al. (2002).

The objective of this study was to establish an analytical method for seven pesticides often used for yuza and to analyze pesticide residue levels in yuza and yuza tea produced in Goheung, Korea. A risk assessment of pesticides in yuza tea was also conducted by determining the estimated daily intake (EDI) and ADI. In addition, the kinetic parameters for the degradation of pesticides were investigated. Regarding to the ginseng, a robust multiresidue method for the analysis of 32 pesticides of different classes was studied using GC/MS/MS.

MATERIALS AND METHOD

Chemicals

Pesticides,acequinocyl, chlorpyrifos, spirodiclofen, carbendazim, deltamethrin, phosalone, and prothiofos, were purchased from Sigma-Aldrich (Germany) and stored at room temperature.

Sampling and Storage

Yuza sampling was conducted from October to November 2009. Yuza samples, grown in Goheung, Korea, were placed in polyethylene bags and transported to the laboratory immediately after harvest and stored at -20°C. Yuza teas samples (n = 25) were collected from Hansung Food Inc., Goheung, Korea during 2009 and 2010. Ginseng samples (fresh ginseng, red ginseng, dried ginseng) were obtained from local ginseng agricultural cooperative

federations located in Seoul. All samples were produced in South Korea. Samples were analyzed within 24h and stored at 4℃ until the moment of extraction. No degradation of pesticides was detected under the storage conditions.

Extraction and purification

Extraction and purification of various pesticides were carried out by the previously published papers (Lee and Lee, 2012; Lee and Jo, 2012; Nam et al., 2015).

Analytical method

Gas chromatography (GC) analyses were carried out on an Agilent Technologies Model 6890N gas chromatograph with nitrogen phosphorus detector (NPD) and auto-sampler (Model 7683). Data acquisition and analysis were performed with the G1035 Wiley Library. Separation was performed on a DB-5 capillary column (30 m × 0.250 mm i.d × 0.25 μm film thickness, Agilent Technologies). Injection temperature was held at 260°C. The injection mode and volume were split mode and 1 μl, respectively. Helium was used as the carrier gas at a flow rate of 1.0 ml/min. The oven temperature program was initially 120°C (hold 2 min), increased to 220°C at 10°C/min, to 250°C at 7°C /min, and then to 280°C at 7°C /min (hold 15 min). The NPD temperature was maintained at 280°C.

Gas chromatography/mass spectroscopy (GC/MS) analyses were carried out on an Agilent Technologies Model 6890N gas chromatograph with a mass selective detector (Model 5975, Agilent Technologies). Data acquisition and analysis were performed with the Chemstation (Agilent Technologies). Deltamethrin separation was performed on a DB-5 MS capillary column (30 m × 0.250 mm i.d × 0.25 μm film thicknesses, Agilent Technologies). Injection temperature was held at 260°C. The injection port was heated to 260°C, and the splitless injection mode was used. Injection volume was 2 μl. Helium was used as carrier gas at a flow rate of 1.0 ml/min. The oven temperature program initially consisted of 120°C (hold 2 min), increased to 220°C at 10°C /min, to 250°C at 7°C /min, and then to 280°C at 7°C /min (hold 15 min).

The high performance liquid chromatography (HPLC) was carried out on a Waters Instrument Model 1525 consisting of an auto-sampler (Model 717, Waters) and a photodiode array detector (Model 2998, Waters). A C_{18} column (Zorbax Eclipse XDB, Agilent Technologies, 4.6 × 250 mm, 5 μm particle size,) was used for separation at 40°C. The injection volume of the sample was 10 μl. Acequinocyl separation was carried out with water and acetonitrile (13%: 77%) at a flow rate of 0.8 ml/min for 30 min. The UV absorbance of acequinocyl was monitored at 250 nm. Separation of sprodiclofen and carbendazim was performed by gradient elution with water (A) and methanol (B) at a flow rate of 1.0 ml/min. UV absorbance of spirodiclofen and carbendazim was monitored at 254 nm and 279 nm, respectively. The gradient elution program was as follows: initial 50% A; 0–45 min, 10% A; and a 45-50 min return to the initial conditions. Processing the raw chromatographic data and data collection were performed using the Empower 2 Pro program (Waters, Milford, MA, USA).

Pesticide analysis was performed using a Varian 3800 gas chromatograph equipped with an electronic flow control (EFC) and fitted with a triple quadrupole mass spectrometer (GC-MS/MS) (Varian Instrument, Sunnyvale, CA, USA). Chromatographic separation was performed on Varian VF-5ms Columns (30 m × 0.32 mm, 25 μm film, Walnut Creek, CA. USA). Injection temperature was held at 250°C, and injection volume was 1 μl. The oven temperature was held for 2 min at 70°C, ramped to 200 °C at 20°C/min, increased to 220°C at 2°C/min, and then held for 3 min and finally increased to 300℃ (hold 3min) at 10℃/min (total run time equaled 35 min) with a flow of 1.0 ml/min. Helium (99.999 %) was used as the carrier gas and the linear velocity was 30 cm/s. Triple quadruple system was operated in electron impact ionization mode (EI, 70 eV). Argon (99.999 %) was used as the collision gas. The dwell time was 0.5 s. The trap, manifold, and transfer line temperatures were set at 200°C, 40°C, and 280°C, respectively. Split ratio and split vent valve state were programmed as follows: initial (open, 5:1); 0 min

(closed, off); 1.5 min (open, 100:1); 3.0 min (open, 30:1). The MS/MS system entails two fundamental steps between the formation and detection of ions. In the first step, the precursor ion or an entire cluster of parent ions is isolated in the trap, and in the second step, the dissociation of the precursor ion or ions is performed by collision with an inert gas.

Method validation

Sample preparation was validated in terms of linearity, repeatability, limits of detection (LOD) and quantification (LOQ), and recovery. The evaluation of linearity was conducted by injecting a solution containing six standard chemicals (0.02, 0.1, 0.5, 1.0, 5.0, and 10.0 µg/ml). All standards were injected three times (n = 3). LOD was measured as the analyte concentration based on signal to-noise ratio of 3, and LOQ was defined as 3.3 × LOD. To determine recovery of pesticide, each pesticide standard solution (10.0 µg/ml) was spiked to the homogenized sample. The recovery rate was calculated as (pesticide weight in spiked sample–pesticide weight in unspiked sample) × 100/spiking pesticide weight. The assay procedure was repeated five times, and relative standard deviation values were obtained within the same day to evaluate intra-day precision. To evaluate inter-day precision this assay was carried out over five different days.

Experimental design for the kinetic model

Yuza cultivated in the conventional way was sprayed with a mixture of chlorpyrifos, prothiofos, phosalone, deltamethrin, acequinocyl, spirodiclofen, and carbendazim at the recommended normal doses with a sprayer. The amounts of 7 pesticides dissolved in 30mL aqueous solution of the mixture were from 0.003g to 0.03g. Yuza sprayed with 30mL of pesticide mixture was processed for yuza tea in the laboratory, because we usually consume yuza tea rather than yuza worldwide. The sprayed yuza was sliced and the seed was separated. Table sugar was added to the sliced yuza (1:1) and aged for 1 week in the shade. Sampling was conducted after 2 h, and 1, 2, 3, 5, 7, and 10 days from the last pesticide spraying. The weight of yuza did not increase during the sampling period; thus, the dilution of pesticide residue was not affected by growth. Kinetic models employed to estimate the half-life of the pesticide residues in yuza tea after pesticide treatment such as first-order (FO), zero-order (ZO), and second-order (SO) models are empirical formulas for estimating the correlations between time (t) and concentration (µg g^{-1}) of pesticide residue.

RESULTS AND DISCUSSION

Method validation

Seven pesticides (chlorpyrifos, prothiofos, phosalone, deltamethrin, acequinocyl, spirodiclofen, and carbendazim) were chosen because of their frequent use during yuza cultivation. The maximum residue levels (MRLs) for yuza are shown in Table 1. The slopes, Correlation coefficient values, Limit of detection (LOD), and Limit of quantification (LOQ) are also summarized in Table 1 for the validation study. An excellent linear correlation was observed between the pesticide concentration and peak areas, with coefficient correlations values of 0.9750–0.9999. Percent recoveries were 80.4–109.9% for all pesticides. The standard deviation of recovery rate were <6.9%, suggesting that the extraction procedure was suitable for routine analysis of the targeted pesticide residues. The LOQs of the method were 0.06–0.33 µg/ml. The intra-day variability was assayed at five replications on the same day. For inter-day variability the assay was carried out during 5 sequential days to test precision of each pesticide. The relative standard deviation (RSD) of intra-day and inter-day variability was <15.9% and 16.9%, respectively

(Table 1).

Pesticide levels in yuza and yuza tea samples

The results of the pesticide analysis in yuza cultivated by ordinary and environmentally friendly cultures (2010–2011) and the maximum residue limits (MRLs) are summarized in Table 2. Prothiofos and deltamethrin were not detected in yuza cultivated by ordinary culture in 2010. Chlorpyrifos was found at up to 0.108 mg kg^{-1} in a single sample of yuza cultivated by ordinary culture. Spirodiclofen revealed a range of contamination of up to 1.889 mg kg^{-1} in 16 of 50 yuza plants cultivated by ordinary culture. The 37 yuza cultivated by ordinary culture contained the highest level of carbendazim at 5.148 mg kg^{-1}. In 2011, spirodiclofen and carbendazim were detected at lower than 0.334 and 3.840 mg kg^{-1}, respectively. The other pesticides were not detected or quantified. Chlorpyrifos, prothiofos, phosalone, deltamethrin and acequinocyl were not detected or quantified in yuza cultivated by environmentally friendly culture in 2010. Spirodiclofen and carbendazim were found in eight of 30 yuza samples at up to 0.801 mg kg^{-1} and in 13 of 30 yuza samples at up to 2.907 mg kg^{-1}, respectively. Carbendazim was detected in eight samples at concentrations ranging from ND to 0.340 mg kg^{-1} in 2011. The remaining pesticides were not detected or quantified. Carbendazim was detected in all samples. The pesticide residues in all yuza samples were lower than the MRLs established by Korean legislation. However, because of possible health effects and widespread use, continuous monitoring of carbendazim is necessary in the future. In addition, higher levels of the tested pesticides were present in yuza samples produced in 2010 than in 2011.

Risk assessment

The results of human exposure to pesticides based on yuza tea intake are shown in Table 3. The EDIs of acequinocyl, spirodiclofen, and carbendazim were 6.6438×10^{-3}, 3.1733×10^{-3}, and 1.7562×10^{-2} mg/day, respectively. The percent ratios of EDI to ADI for acequinocyl, spirodiclofen and carbendazim were 24.6, 22.7, and 58.5%, respectively. Results of EDI/ADI exceeding 100% indicates a risk potential. Therefore, 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 yuza tea consumption, a special precaution should be taken with the possible total exposure to these chemicals from various foods in the future. Monitoring of pesticide residue data in yuza has not been performed. Therefore, it is necessary to monitor the residues of acequinocyl, spirodiclofen, and carbendazim in yuza continuously because of possible health effects, widespread use, and insufficient residue data. Additionally, further monitoring studies must be performed to improve food safety.

Pesticides levels in ginseng

The validated method was applied to the routine pesticide analysis of ginseng samples. Fresh ginseng (n = 118), red ginseng (n = 24), and dried ginseng (n = 10) were analyzed following the sample preparation method described above. Detailed data on the pesticide levels measured in fresh ginseng are shown in Table 4. We detected 16 different pesticides in fresh ginseng samples. Especially, tolclofos-methyl was detected in 102 samples (ranging from 18.25 to 404.5 μg/kg). The detection level of fludioxonil was 56.62 μg/kg and detection frequency was 49.2%. The residue level of chlorothalonil was higher than its MRLs, but detection frequency was not very high at 0.9%. Detailed data of the residue pesticide detected in red ginseng are shown in Table 5. The results show that the most frequently detected pesticide was tolclofos-methyl, which was detected in 22 out of 24 samples at concentrations ranging from 13.14-119.4 μg/kg. The detection frequencies of cyprodinil, fludioxonil, and difenoconazole were 79.0, 57.9, and 57.9%, respectively, which were lower than their MRLs.

Table 6 shows residue levels detected in dried ginseng. The results indicate the existence of quintozene, tolclofos-mehyl, cyprodinil, and difenoconazole. The detection frequencies of these pesticides were relatively higher than those of others. The residue level of tolclofos-methyl was higher than its MRL.

Kinetic parameters for pesticide degradation

Ten days after spraying, the degradation rates of chlorpyrifos and acequinocyl exceeded 90% and 100%, respectively. The degradation order of the seven pesticides was as follows: acequinocyl > chlorpyrifos > spirodiclofen > carbendazim > deltamethrin > phosalone , prothiofos. Because the half-lives of prothiofos, phosalone, and deltamethrin were longer than those of the others, their application doses should be reduced. The doses of acequinocyl and chlorpyrifos could be increased to improve productivity as they were under the MRLs. Three kinetic models were employed to characterize the best-fit kinetic model. Among the theoretical models, FO and SO models were the best-fit models for the pesticides residues, judging from the significance of the coefficient of determination and the standard error. Therefore, it is recommended that the half-life of the pesticide be assessed from the best-fit model rather than from the FO kinetic model.

CONCLUSION

In this study establishment of an analytical method to measure pesticides and to analyze pesticide residue levels of Korean agricultural products such as yuza (*Citrus junos* Sieb. ex Tanaka), yuza tea, and ginseng products was carried out. Risk assessments were also performed by calculating estimated daily intake (EDI) and acceptable daily intake (ADI). In addition, kinetic study such as the degradation order of pesticides in yuza tea was carried out. Acequinocyl, spirodiclofen and carbendazim were detected in yuza samples in the concentration range of 0.07–0.15 μg/g, 0.11–1.89 μg/g, and 0.03–5.15 μg /g, respectively. The percent ratios of EDI to ADI for acequinocyl, spirodiclofen, and carbendazim were 24.6%, 22.7%, and 58.5%, respectively. The degradation order of the seven pesticides in yuza tea was as follows: acequinocyl > chlorpyrifos > spirodiclofen > carbendazim > deltamethrin > phosalone, prothiofos. For the accurate analysis of Korean ginseng products a new analytical method was developed based on gas chromatography-triple quadrupole tandem mass spectrometry (GC-MS/MS).

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Table 1. Validation parameters: Linearity, Limit of detection (LOD), Limit of quantification (LOQ), and Recoveries of pesticides used during yuza cultivation

Pesticides	Linearity			LOD	LOQ	MRL[1]	Recovery (%)	Precision[2] (%)	
	Range (μg/ml)	Equation	Correlation coefficient (r^2)	(μg/ml)	(μg/ml)	(μg/g)		Intra-day (n = 5)	Inter-day (n = 5)
Chlorpyrifos	0.02-10	y = 16.682x-0.9356	0.9992	0.02	0.06	0.5	109.9 ± 3.9	10.0	9.4
Prothiofos	0.02-10	y = 18.722x-2.7729	0.9972	0.03	0.10	2.0	99.4 ± 4.2	10.3	5.9
Phosalone	0.02-10	y = 18.116x-2.9475	0.9974	0.02	0.06	0.05	96.0 ± 3.9	8.8	11.3
Deltamethrin	0.02-10	y = 22180x-72217	0.9750	0.02	0.06	0.5	103.2 ± 5.9	6.4	6.5
Acequinocyl	0.02-10	y = 7773x-3737	0.9999	0.10	0.33	0.1/3.0[a]	93.8 ± 6.9	15.9	6.9
Spirodiclofen	0.02-10	y = 11818x-7.3200	0.9999	0.03	0.10	2.0	93.2 ± 2.7	12.1	7.2
Carbendazim	0.02-10	y = 42955x-560.10	0.9999	0.02	0.06	7.0	80.4 ± 5.8	14.8	16.9

[1]Maximum Residue level

[2] Relative standard deviation (RSD:%) of recovery rates from intra-day (n=5) and inter-day (n=5) experiments.

Table 2. Results of the pesticide residue analysis in Yuza cultivated by ordinary and environmentally-friendly culture

Detected pesticide	Yuza cultivated by ordinary culture					Yuza cultivated by environmentally-friendly culture					Korean MRLs[3] (mg kg^{-1})
	No. of samples Analyzed per year	Samples with residues		Detection range (mg kg^{-1})		No. of samples analyzed per year	Samples with residues		Detection range (mg kg^{-1})		
		2010	2011	2010	2011		2010	2011	2010	2011	
Chlorpyrifos	50	1 (2%)	0 (0%)	t [1] -0.108	t	30	0 (0%)	0 (0%)	ND[1]	ND	0.50
Prothiofos	50	0 (0%)	0 (0%)	ND[2]	t	30	0 (0%)	0 (0%)	ND	ND	0.05
Phosalone	50	0 (0%)	0 (0%)	t	t	30	0 (0%)	0 (0%)	ND	t	2.00
Deltamethrin	50	0 (0%)	0 (0%)	ND	ND	30	0 (0%)	0 (0%)	ND	ND	0.50
Acequinocyl	50	0 (0%)	0 (0%)	t	t	30	0 (0%)	0 (0%)	t [2]	t	1.00
Spirodiclofen	50	16 (32%)	5 (10%)	0.299 -1.889	0.274 -0.334	30	8 (27%)	0 (0%)	0.283 - 0.801	t	2.00
Carbendazim	50	37 (74%)	27 (54%)	0.113 -5.148	0.088 -3.840	30	13 (43%)	8 (27%)	0.029 - 2.907	0.111 -0.340	7.00 [4]

[1] t: LOD < values < LOQ
[2] ND: values < LOD
[3] MRLs: maximum residue limit of yuza tea
[4] MRLs: maximum residue limit of other citrus fruits

Table 3. Exposure assessment parameters of pesticides in yuza tea samples

Pesticide	ALD[a] (mg/kg)	EDI[b] (mg/day)	EDI/ADI[c]×100
Acequinocyl	0.4271	0.36541	24.6
Spirodiclofen	0.2040	0.17453	22.7
Carbendazim	1.1293	0.96592	58.5

[a] average level of detection.
[b] estimated daily intake.
[c] acceptable daily intake

Table 4. Pesticides levels detected in fresh ginseng (n=118)

Pesticides	Mean(㎍/kg)	Frequency (%)	Detection range(㎍/kg)
EBDC	N.D.	N.D.	N.D.
Cadusafos	N.D.	N.D.	N.D.
α-BHC	N.D.	N.D.	N.D.
β-BHC	N.D.	N.D.	N.D.
Quintozene	21.15	28.81	20.15-23.25
γ-BHC	N.D.	N.D.	N.D.
Tefluthrin	7.34	0.85	7.34
Chlorothalonil	132.11	0.85	132.11
Tebupirimfos	N.D.	N.D.	N.D.
δ-BHC	N.D.	N.D.	N.D.
Tolclofos-methyl	34.62	86.44	18.25-404.52
Metalaxyl	17.62	40.68	10.25-36.62
Diethofencarb	27.62	4.00	26.25-28.62
Aldrin	N.D.	N.D.	N.D.
Cyprodinil	16.26	24.58	15.62-24.25
Tolyfluanid	N.D.	N.D.	N.D.
Flutolanil	38.63	35.59	26.92-65.62
Fludioxonil	56.62	49.15	7.69-56.29
p,p-DDE	N.D.	N.D.	N.D.
Thifluzamid	20.63	6.78	7.20-47.29
Kresoxim-methyl	N.D.	N.D.	N.D.
Dieldrin	N.D.	N.D.	N.D.
Endrin	N.D.	N.D.	N.D.
p,p-DDT	N.D.	N.D.	N.D.

p,p-DDD	N.D.	N.D.	N.D.
o,p-DDT	N.D.	N.D.	N.D.
Trifloxystrobin	28.26	1.69	20.29-36.29
Carbosulfan	104.62	18.64	25.62-213.35
Fenhexamid	21.22	8.47	15.14-31.38
Cypermethrin	122.26	4.24	90.93-147.29
Difenoconazole	32.73	31.36	25.25-82.29
Azoxystrobin	18.36	3.39	4.29-34.17

Table 5. Pesticides levels detected in red ginseng (n = 24)

Pesticides	Mean(㎍/kg)	Frequency (%)	Detection range(㎍/kg)
EBDC	N.D.	N.D.	N.D.
Cadusafos	N.D.	N.D.	N.D.
α-BHC	N.D.	N.D.	N.D.
β-BHC	N.D.	N.D.	N.D.
Quintozene	36.23	42.11	25.14-114.27
γ-BHC	N.D.	N.D.	N.D.
Tefluthrin	N.D.	N.D.	N.D.
Chlorothalonil	N.D.	N.D.	N.D.
Tebupirimfos	N.D.	N.D.	N.D.
δ-BHC	N.D.	N.D.	N.D.
Tolclofos-methyl	51.14	91.66	13.14-119.38
Metalaxyl	16.15	47.37	13.15-23.35
Diethofencarb	34.17	15.79	32.15-37.98
Aldrin	N.D.	N.D.	N.D.
Cyprodinil	29.25	78.95	19.38-115.18
Tolyfluanid	N.D.	N.D.	N.D.
Flutolanil	44.14	26.32	32.14-71.38
Fludioxonil	56.25	57.89	71.18-79.46
p,p-DDE	N.D.	N.D.	N.D.
Thifluzamid	20.25	6.78	7.16-47.62
Kresoxim-methyl	N.D.	N.D.	N.D.
Dieldrin	N.D.	N.D.	N.D.
Endrin	N.D.	N.D.	N.D.
p,p-DDT	N.D.	N.D.	N.D.
p,p-DDD	N.D.	N.D.	N.D.
o,p-DDT	N.D.	N.D.	N.D.
Trifloxystrobin	N.D.	N.D.	N.D.
Carbosulfan	113.11	4.16	113.11
Fenhexamid	109.35	4.16	109.35
Cypermethrin	N.D.	N.D.	N.D.
Difenoconazole	54.64	57.89	33.62-234.11
Azoxystrobin	26.24	4.16	26.24

Table 6. Pesticides levels detected in dried ginseng (n = 10)

Pesticides	Mean(㎍/kg)	Frequency (%)	Detection range(㎍/kg)
EBDC	N.D.	N.D.	N.D.
Cadusafos	N.D.	N.D.	N.D.
α-BHC	N.D.	N.D.	N.D.
β-BHC	N.D.	N.D.	N.D.
Quintozene	25.14	50.00	25.14
γ-BHC	N.D.	N.D.	N.D.
Tefluthrin	N.D.	N.D.	N.D.
Chlorothalonil	N.D.	N.D.	N.D.
Tebupirimfos	N.D.	N.D.	N.D.
δ-BHC	N.D.	N.D.	N.D.
Tolclofos-methyl	523.12	87.50	23.15-3673.25
Metalaxyl	N.D.	N.D.	N.D.
Diethofencarb	33.14	10.00	33.14
Aldrin	N.D.	N.D.	N.D.
Cyprodinil	23.35	75.00	20.14-34.35
Tolyfluanid	N.D.	N.D.	N.D.
Flutolanil	33.35	10.00	33.35
Fludioxonil	71.41	37.50	71.13-71.73
p,p-DDE	N.D.	N.D.	N.D.
Thifluzamid	N.D.	N.D.	N.D.
Kresoxim-methyl	N.D.	N.D.	N.D.
Dieldrin	N.D.	N.D.	N.D.
Endrin	N.D.	N.D.	N.D.
p,p-DDT	N.D.	N.D.	N.D.
p,p-DDD	N.D.	N.D.	N.D.
o,p-DDT	N.D.	N.D.	N.D.
Trifloxystrobin	N.D.	N.D.	N.D.
Carbosulfan	N.D.	N.D.	N.D.
Fenhexamid	N.D.	N.D.	N.D.
Cypermethrin	N.D.	N.D.	N.D.
Difenoconazole	37.32	50.00	35.26-39.52
Azoxystrobin	5.92	10.00	5.92

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