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Residual Pyrethroids in Fresh Horticultural Products in Sonora, Mexico

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Abstract This study was conducted to evaluate the presence of cyhialothrin, cyfluthrin, cypermethrin, fenvalerate, and deltamethrin in vegetables produced and consumed in Sonora, Mexico. A total of 345 samples were collected from cluster sampling of markets and fields. Approximately 9% of the samples tested positive for pyrethroids (residue range 0.004–0.573 mg kg^{-1}). Based on the results, the potential toxicological risk of human exposure to the pyrethroid insecticides measured in vegetables appears to be minimal, with the estimated exposure being 1,000 times lower than admissible levels.

Keywords Pyrethroids · Insecticides · Vegetables · Toxicological

In Mexico, the most widely used pesticides are herbicides, followed by insecticides and fungicides. There are no clear records documenting the current use of pesticides in Mexico, although 6 years ago it was estimated that about 50,000 tons of pesticide active ingredients are being used by Mexicans each year (Albert 2004).

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The most frequently used pyrethroid insecticides in Sonora include cyhialothrin, cyfluthrin, cypermethrin, fenvalerate and deltamethrin. These five pyrethroids are moderately toxic to humans (CICOPLAFEST 2004). Cypermethrin, has been shown to increase the metabolism of lipids and proteins in the livers of Wistar rats (Aldana et al. 1998) and might cause hazardous effects in different levels to non-target organisms (Yavasoglu et al. 2006). Additional studies have reported toxic effects in the liver in vivo and in vitro (Aldana et al. 2001; Grajeda-Cota et al. 2004).

Based on this information and considering that there is little data on pyrethroid residues in vegetables in Mexico, the objective of the present study was to determine the concentration of the pyrethroids in vegetables and legumes produced and consumed in Sonora, especially those with potential for chronic human health impacts.

Materials and Methods

For this study, vegetables were sampled at production, storage and point of sale sites. The pyrethroids studied were cyhialothrin, cyfluthrin, cypermethrin, fenvalerate and deltamethrin. These compounds were chosen because of their heavy use on agricultural commodities, persistence in the environment and toxicity to humans, animals and other organisms.

The selection of the vegetables and legumes for this study was based on a survey documenting the main food products consumed by people living of the state of Sonora (Valencia et al. 1998).

The sampling was conducted during two different seasons (March–April and October–November, 2008) and used a cluster sampling design, with simple random sampling of sites within each cluster, and simple random sampling of vegetables within each site. The size of each sample collected was 5 kg. Within the laboratory, sample management procedures followed the Manual of Training for Laboratory of Pesticides AOAC (Meloan 1998).

The pyrethroids and its mixture of isomers used in this research were supplied by Sigma-Aldrich Co. (St. Louis, MO; with purity >96%). Hexane and dichloromethane HPLC grade were obtained from J.T Baker (USA), and Burdick & Jackson (USA), respectively.

The samples were packed in polyester bags (20–40 g) and stored at −15°C until analyzed. Samples were typically analyzed within 1 week of preparation.

In this study, the matrix solid-phase dispersion (MSPD) described by Valenzuela-Quintanar et al. (2006) was used. Briefly, 0.5 g of silica gel was added to each sample (0.5 g of green onion, potato, tomato saladette, lettuce, tomato, green pepper, and 0.1 g of onion). The mixture of silica gel and sample was crushed and homogenized in a mortar until a dry powder was obtained. Sample cleanup was accomplished by adding 0.042 g of activated carbon to the samples except to onion; 0.01 g of activated carbon was used. The homogenized sample was transferred to a column packed with glass fiber and 0.5 g of silica gel. Dichloromethane was used to elute the pyrethroids. The extract was collected (35 mL) in a glass tube and the extract was evaporated to dryness under air at 30°C. The extract was resuspended in 100 µL of hexane.

Quantification of pyrethroids was performed using Agilent GC (Agilent Technologies, 6890 N, Network GC System) with an EC detector (USA). The pyrethroids were separated using DB-35MS (30 m × 0.32 mm, 0.25 µm i.d., USA) capillary column (35% phenylmethylpolysiloxane). The injection volume was 1 µL. Nitrogen (purity 99.99 %) was used as the carrier gas at a flow of 2.3 mL min^{-1}. The injector temperature was 275°C and the detector temperature was 325°C. The temperature program was as follows: initial temperature 110°C, increasing temperature at 15°C min^{-1} until the final temperature of 300°C was reached.

Statistics for the recovery include percentage means and standard deviations. Pyrethroid residues detected on the vegetable samples are presented as ranges (minimum and maximum) for each pyrethroid and each vegetable.

The pyrethroid residues risk evaluation was based on a study conducted by Aldana-Madrid et al. (2008a, b). The results were compared with the allowed daily ingested dose for each pyrethroid as published in the CICOPLAFEST (2004).

Results and Discussion

There were 345 samples collected in total, with 163 samples collected in the first season, and 182 samples collected in the second season. Of the 345 samples, 237 were from corresponded storage and point of sale sites and 108 were from production sites.

Regarding the origin of the vegetables, 62% were from Sonora and 38% were from other states or imported. The detection was linear in the range of 50–200 µg kg^{-1}. The coefficients of variation for cyhialothrin, cyfluthrin, cypermethrin, fenvalerate, and deltamethrin were of 0.97, 0.99, 0.94, and 0.95, respectively. The retention times observed for Cyhialothrin isomers were 8.364 and 8.528 min, for Cyfluthrin isomers were 10.368, 10.470 and 10.590 min, for Cypermethrin isomers were 10.961, 11.096 and 11.220 min, for Fenvalerate isomers were 12.763 and 13.156 min and for Deltamethrin was 14.678 min. The limit of detection and quantification for all pyrethroids studied were 0.625 and 1.25 µg kg^{-1}, respectively. The analyte peaks were well resolved from pyrethroids and the chromatograms were comparable to those provided by standard certification.

The recovery was determined by comparing the peak areas obtained from fortified samples with 100 µL of pyrethroids mix (n = 6) before and after the extraction procedure. The concentrations added to samples were based on the Maximum Residual Limits (MRL) and the *Codex Alimentarius* (2008, 2009) cyfluthrin 3 mg kg^{-1}, cyalothrin, cypermethrin, fenvalerate and deltamethrin 1 mg kg^{-1}. For validate the methods for low concentrations, samples of tomato and potato were fortified with 2, 50 and 500 µg kg^{-1}

Table 1 Recovery of pyrethroids from vegetables by the MSPD technique

Vegetable	Recovery (% ± SD)[a]				
	Cyalothrin[b]	Cyfluthrin[c]	Cypermethrin[b]	Fenvalerate[b]	Deltamethrin[b]
Green onion	115 ± 4	113 ± 7	89 ± 4	85 ± 9	101 ± 14
Potato	92 ± 11	95 ± 6	110 ± 12	108 ± 1	98 ± 8
Saladette tomato	90 ± 2	92 ± 1	96 ± 10	108 ± 8	103 ± 3
Lettuce	87 ± 10	92 ± 1	111 ± 13	105 ± 12	112 ± 11
Tomato	78 ± 9	101 ± 7	97 ± 2	98 ± 10	92 ± 1
Green pepper	93 ± 5	93 ± 6	95 ± 2	103 ± 6	89 ± 6
White onion	108 ± 11	93 ± 12	87 ± 8	77 ± 4	104 ± 1

[a] n = 6

[b] Samples fortified with 1 mg kg^{-1}

[c] Samples fortified with 3 mg kg^{-1}

Table 2 Residues of pyrethroid insecticides detected in the fresh vegetables studied

Vegetable	Residues (mg Kg^{-1})				
	Cypermethrin	Cyhialothrin	Cyfluthrin	Fenvalerate	Deltamethrin
Green pepper	0.030–0.460	ND	0.010–0.030	ND	ND
White onion	0.040–0.060	ND	0.090*	ND	ND
Tomato	ND	0.010*	ND	ND	0.004–0.020
Lettuce	0.010–0.080	ND	ND	ND	0.010*
Green onion	0.004–0.198	ND	0.170–0.573	0.070*	ND
potato	0.004–0.075	ND	0.038–0.058	ND	ND
Saladette tomato	0.028–0.029	ND	0.007–0.270	0.061*	0.006*

ND not detected

* Only detected value

with every pyrethroid. The recovery percentages for the different matrices in the study were 77%–115%, with coefficients of variation less than 14% (Table 1). The range of recovery for samples of tomate and potato with low levels (2, 50 and 500 μg kg^{-1}) were 94%–104% with SD $\leq$9, 98%–110% with SD $\leq$10, respectively. These results were similar to the recoveries reported by Pinho et al. (2009) for tomato samples (86%–112%), Tianwen and Guonan (2007) for vegetable samples (69.5%–102.5%), Aldana et al. (2008) and Sannino et al. (2003) for samples of grains, fruits and vegetables (71%–128%). Based on these results the MSPD method is an appropriate technique for pyrethroid extraction. The MSPD method is an efficient, fast, cheap and environment friendly procedure and it could serve as a screening protocol for the determination of pyrethroids in vegetables.

The instruments used to determine pyrethroids in fruits and vegetables are gas chromatography (GC), gas chromatography/mass spectrometry, capillary electrochromatography, high performance liquid chromatography and high liquid chromatography/mass spectrometry (Chen and Chen 2007). In the present research GC with electron capture detection was used to determine pyrethroids residues in vegetable due to this method was sufficiently sensitive to levels found in the matrix studied.

Thirty samples (9%) tested positive for different pyrethroids as follows: green onion, potato, tomato saladette, lettuce, tomato, green chili and green onion. The positive samples had concentrations ranging from 0.004 to 0.573 mg kg^{-1}, as shown in Table 2. Cypermethrin was detected (73%) in most of the positive samples, followed by cyfluthrin (37%). Cypermethrin was detected most frequently. These results are similar to those reported by Zawiyah et al. (2007) and Anwar et al. (2011) who found that Cypermethrin was the most frequent insecticide detected in vegetables in local markets of Malaysia and Pakistan, respectively. Deltamethrin residues appeared in tomato and lettuce (17%) and fenvalerate (7%) and cyhialothrin (3%) were detected in green onion and tomato. Cyfluthrin was detected in green onion at a high concentration of 0.573 mg kg^{-1}, followed by cypermethrin at 0.460 mg kg^{-1} and fenvalerate 0.070 mg kg^{-1}. Only cyhialothrin was detected in tomato (0.010 mg kg^{-1}, ten times less than the MRL). In green onion and potato, the levels of pyrethroids exceeded the MRL allowed by the *Codex Alimentarius* (2008, 2009). A green onion sample contained cypermethrin (0.198 mg kg^{-1}) and two potato samples contained cyfluthrin (0.058 and 0.038 mg kg^{-1}), exceeding the limits stated by the Mexican norms (NOM-050-FITO-1995 1996) and CICOPLAFEST (2004). The pyrethroid residues found in the present study are lower than those reported by Zawiyah et al. (2007), Anwar et al. (2011) and Lee Fook Choy and Seeneevassen (1998). It is important to mention that a MRL for cyfluthrin in green onion has not been published to date.

To determine exposure levels and potential health damage that can be caused by insecticide residues on food products, it is necessary to know the composition of the typical daily Mexican diet. Based on this information, daily consumption can be estimated *per capita* of the vegetable products included in this study. Since no complete information exists about the daily Mexican diet composition, it not possible to calculate the exposure level to pyrethroids. However, the amount of pyrethroid residues quantified in the present research does not appear to represent a risk to consumer health, because the daily uptake in relation to the acceptable dose is minimal (1,000 times less). Therefore, there appears to be a very low toxicological risk of human health effects from the ingestion of pyrethroid residues detected on the vegetables studied from Sonora, Mexico.

Since the capacity of pyrethroids to degrade decreased in the presence of pesticides such as organophosphates, further studies are necessary to ascertain the potential human health risks that may be associated with such mixtures in fresh fruits and vegetables.

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