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Monitoring of Organophosphorus Pesticide Residues in Vegetables of Agricultural Area in Venezuela

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Abstract The purpose of this study was to determine the residues of seven pesticides organophosphorus (methamidophos, diazinon, chlorpyriphos, parathion-methyl, dimethoate, malathion and tetrachlorvinphos), in some vegetables like: potato, lettuce, tomato, onion, red pepper and green onion cultivated in José María Vargas County in Táchira State, Venezuela. The research permitted to detect that 48.0% of the samples were contaminated with some of the pesticides studied. Methamidophos was founded in the vegetables in the rank of 6.3%–65.5%. The results show that 16.7% of the samples tested have residues higher than the maximum limits permitted.

Keywords Monitoring vegetables · Pesticides organophosphorus

The organophosphorus pesticides have an important role in the agricultural pest control, in spite of the toxicological problem its efficiency has been demonstrated in leaf miners, fruit flies, acarus and aphids (Torres and Capote 2004). The continued use of organophosphorus pesticides increases the possibility that residues of these compounds could be found in some vegetables affecting the alimentary security; that is the reason for the commitment between the public health and the sanitary defense of the crops, to fight against the pest and the illness.

Part of the Venezuelan economy is based on the agricultural production, for that reason the use of pesticide is a basic necessity for the commercialization and development of vegetables crops (Quintero et al. 2002; Ettiene et al. 2006). This situation is a result of an agricultural model that prevail in Latin America, where crop rotation is not common; besides an intense production and mechanization which drive us to a high demand of agrochemicals. For this reason it is urgent to develop programs related to the monitoring of pesticides residues in food to protect consumers in the country. These programs could determine the magnitude of the contamination problem and identify a way to solve the situation. Pesticide organophosphorus residue monitoring studies have been reported in fruits and vegetables (Kumari et al. 2006; Mukherjee 2003). In Venezuela, the researches about these pesticides are few (Ettiene et al. 2006; Prieto et al. 2002). Pesticides in vegetables cultivated in José María Vargas County were studied for the first time. A monitoring of seven organophosphorus pesticides (methamidophos, diazinon, chlorpyriphos, parathion-methyl, dimethoate, malathion and tetrachlorvinphos) in vegetables which are included in the Venezuelan's staple diet were taken into account. These vegetables are: onion, potato, tomato, red pepper, lettuce and green onion.

Materials and Methods

Standard pesticides of high purity: methamidophos (98.0%), diazinon (92.5%), dimethoate (99.0%), parathion-methyl (98.5%), chlorpyriphos (98.5%), malathion (99.5%)

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and tetrachlorvinphos (99.5%) Dr. Ehrenstorfer GMBH (Germany), were used to prepare the initial solutions (2000.0 μg/mL) of each pesticide in HPLC grade ethyl acetate (Baker, USA). Calibration solutions and spiked solutions were derived from these initial solutions, diluted in grade HPLC ethyl acetate.

Triphenyl phosphate (99.5%, Riedel de Haën) was used as an internal standard. An initial solution of 1000 μg/mL was prepared in ethyl acetate. Analytical reagent grade anhydrous sodium sulfate (Riedel de Haën) was used to eliminate water residue during extraction process. Acetone HPLC (Fisher) was used to prepare the ethyl acetate/acetone (90:10 v/v) solution. Air, He, H_2 and N_2 of high purity were supplied by AGA from Venezuela.

José María Vargas County located in Táchira State, Venezuela, was selected for this research because is an area of high agriculture production. The County is formed by ten villages, seven of them (Río Arriba, Venegará, Playitas, Pernía, San Agustín, Angostura and Mangaria) were selected for the research due to their high production of onion, potato, tomato, red pepper, lettuce and green onion. The County shows an annual average precipitation between 900–1200 mm and an average of temperature which varies between 15–18°C. This zone was classified according to Holdridge like wet woodland montano low (INE 2002).

A stratified sampling was applied to each crop. The villages were subdivided randomly in four sites of sampling with a total of 16 samples by crop.

Figure 1 shows the area of data collection for crops studied. In the sampling area, a total of 96 questionnaires were applied to the farmers to obtain information about the kinds of pesticides used; as well as, the techniques worked by them; kinds of vegetables cropped and agriculture practices used. The samples of vegetables were collected at the moment of harvest, using the methods recommended by Food and Agriculture Organization/World Health Organization (FAO/WHO 1999) related to the determination of pesticides residues for compliance with MRLs.

The pesticide extraction was performed modifying the method reported by Prieto et al. (2002), without centrifugation of the matrix with the solvent and the cleanup of the extract. A representative sample (200.0 g) was chopped in a food processor. Sub samples were weighed (4.0 g) in triplicate. A solution (10.0 mL) of ethyl acetate/acetone (90:10 v/v) was used to extract the pesticides and anhydrous sodium sulfate (5.0 g) was used to eliminate water residues. They were stirred (10 min) and then were kept at rest (10 min) until getting the solvents separation from the organic matter. The solvents were concentrated in order to obtain the final volume of 2.0 mL. One milliliter was transferred to a vial and spiked with triphenyl phosphate (Internal Standard), then injected (1.0 μL) in duplicate samples in the gas chromatograph for its quantification.

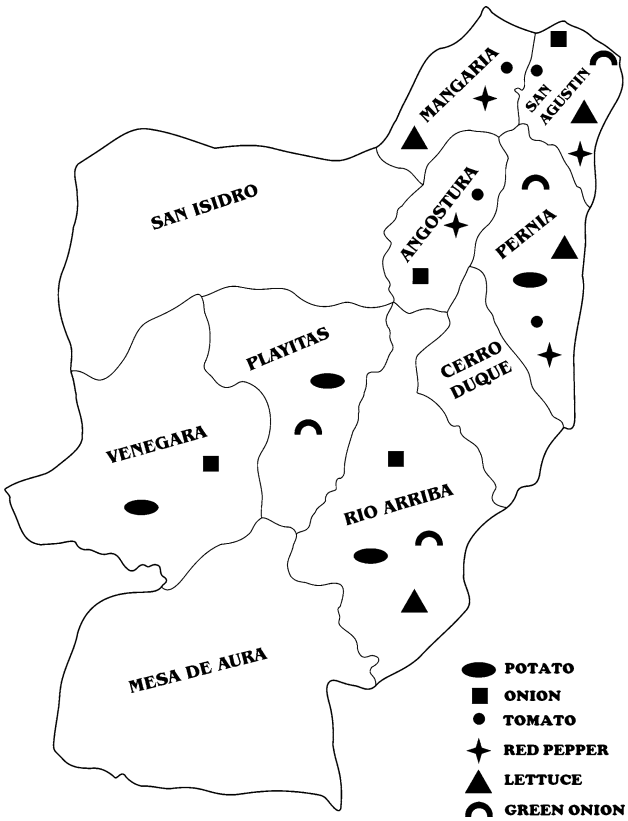

Fig. 1 Sampling sites at the County José María Vargas

Pesticide residues were analyzed using an Auto System Perkin-Elmer gas chromatograph, equipped with a Nitrogen-Phosphorus detector at 280°C, a Perkin-Elmer automatic sampler and a capillary column of 30 m × 0.53 mm × 1.2 μm film thickness, of 50% phenyl-methyl polisiloxane DB-17 (J & W Scientific, USA). The injector temperature was 250°C and splitless injection was used; temperature program: 60°C for 0.80 min, 40°C/min to 160°C, 3.5°C/min to 230°C, 5°C/min to 250°C hold for 4 min; carrier gas flow, helium at 10 mL/min; detector gas flow, H_2 at 2 mL/min, air at 100 mL/min with threshold of 0.75 mV. A personal computer equipped with Turbochrom Navigator 4.1 software was used to record chromatograms and integrated peak areas.

The efficiency of the method was validated statistic with recoveries studies, fortification samples without pesticides residues at two concentration levels (0.2 and 2.0 μg/g), following the same method of extraction and recovery applied in this study. The repeatedly of the method was analyzed by standard deviation relative for recoveries test.

Results and Discussion

The questionnaires applied to the farmers permitted to identify the pesticides used for them in José María Vargas

Table 1 Pesticides used in the cultivation of vegetables

Product	Pesticide	Chemical group
Amidor, Tamaron	Methamidophos	Organophosphorus
Carbodan	Carbofuran	Carbamate
Corsario	Diazinon + Cypermethrin	Organophosphorus
Decis	Deltamethrin	Pyrethroid
Drago	Cypermethrin	Pyrethroid
Furadan	Carbofuran	Carbamate
Lannate	Methomyl	Carbamate
Lorsban	Chlorpyriphos	Organophosphorus
Methion	Parathion-methyl	Organophosphorus
Difos	Dimethoate	Organophosphorus
Malathion	Malathion	Organophosphorus
Gardona	Tetrachlorvinphos	Organophosphorus
Marshal	Carbosulfan	Carbamate

County, Táchira State, Venezuela. Table 1 shows the kinds of pesticides commonly used in the zone by them and the seven organophosphorus pesticides selected for this research.

Table 2 shows the recoveries percentages of pesticides in each vegetable. The recoveries study of methamidophos, diazinon, chlorpyriphos, parathion-methyl, dimethoate, malathion and tetrachlorvinphos shows an average efficiency for the seven vegetables in range 72%–110%, for the two concentration levels tested (0.2 and 2.0 mg/kg). The standard deviations are less than 12%. The detection limits for all the pesticides under study were between 0.0027–0.0081 mg/kg, calculated according to Miller and Miller (2002). Similar results were reported by others authors (Ueno et al. 2003; Gobo et al. 2004).

As a result of the extraction procedure used in this monitoring and the selective application of nitrogen-phosphorus detector a cleanup of extracts was not necessary even though it was possible to get satisfactory recoveries. Analysis of extracts obtained without a cleanup procedure was reported by Torres et al. (1996) and Gobo et al. (2004). The application of this method reduces costs and time of analysis.

Table 3 shows that 46 of the 96 samples were contaminated with some of pesticides studied. The organophosphorus pesticide metamidophos was found in all the vegetables analyzed: tomato (62.5%), red pepper (37.5%), lettuce (37.5%), potatoes (31.3%), onion (12.5%) and green onion (6.3%). Diazinon was detected only in onion (12.5%), chorpyriphos only in tomato (12.5%), malathion in red pepper (31.3%), tetrachlorvinphos in red pepper (18.8%) and in lettuce (25%). dimethoate and parathion-methyl was not detected in any of the samples analyzed.

In agreement to the FAO/WHO (2005), the maximum residues limits (MRLs) of the metamidophos values found in the samples of potato, onion and green onion did not exceed the levels permitted. Nevertheless, in tomato 80.0% of the samples contaminated are above of the MRLs, in red pepper 100.0% and in lettuce 33.3%. The samples of vegetables contaminated with diazinon, chlorpyriphos and

Table 2 Recovery values and RSD for two different fortification levels

Pesticides		% Recovery (RSD) $n = 6$					
		Potato	Onion	Tomato	Red pepper	Lettuce	Green onion
Methamidophos	a	107(3)	90(10)	98(9)	95(5)	77(8)	77(4)
	b	106(3)	84(12)	85(9)	86(7)	70(3)	98(5)
Diazinon	a	83(12)	92(12)	107(5)	83(12)	93(4)	91(5)
	b	86(12)	110(4)	105(3)	103(4)	88(4)	87(3)
Dimethoate	a	94(6)	82(11)	82(7)	90(12)	77(8)	98(4)
	b	84(10)	96(9)	90(9)	82(8)	71(3)	103(4)
Parathion-methyl	a	100(8)	93(10)	100(5)	96(7)	89(11)	104(2)
	b	90(8)	82(5)	78(3)	89(2)	78(1)	98(4)
Chlorpyriphos	a	104(5)	102(3)	107(9)	90(7)	87(12)	89(1)
	b	94(12)	110(5)	109(2)	106(5)	83(10)	87(4)
Malathion	a	109(1)	104(3)	102(6)	110(2)	95(9)	101(2)
	b	108(4)	102(5)	97(3)	105(2)	78(3)	92(3)
Tetrachlor-vinphos	a	91(13)	96(9)	94(8)	99(7)	77(8)	96(5)
	b	105(3)	105(6)	108(2)	104(4)	71(1)	89(6)

a: Fortification level (0.2 mg/kg)

b: Fortification level (2.0 mg/kg)

n: No. of sample

RSD: Relative standard deviation

Table 3 Residues of organophosphorus pesticides in vegetables

Vegetables (samples analyzed)	Pesticides	Samples contaminated	Samples violating MRLS	Residue level Range (mg/kg)	MRLs (mg/kg)
Potato (16)	Metamidophos	5	0	0.01–0.03	0.1
Onion (16)	Metamidophos	2	0	0.01–0.04	0.1
	Diazinon	2	0	0.01–0.07	0.5
Tomato (16)	Metamidophos	10	8	0.04–2.40	0.1
	Chlorpyriphos	2	0	0.14–0.16	0.3
Red pepper (16)	Metamidophos	6	6	0.31–12.06	0.1
	Malathion	5	0	0.02–0.07	1.0
	Tetrachlorvinphos	3	–	0.04–0.64	–
Lettuce (16)	Metamidophos	6	2	0.01–0.23	0.1
	Tetrachlorvinphos	4	–	0.01–0.23	–
Green onion (16)	Metamidophos	1	0	0.09	0.1

MRLs: Maximum residue limits (FAO/WHO 2005)

–: Without comparative values

malathion are between the maximus residues limits. The Codex Alimentarius doesn't report maximums residues of tetrachlorvinphos; because of that, it was not possible to make a comparison with the results obtained in this research.

The results obtained in this study are generally in agreement with the other studies on the evaluation organophosphorus pesticides in the vegetables (Gebara et al. 2005; Abbassy 2001).

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References

Abbassy M (2001) Pesticide residues in selected vegetables and fruits in Alexandria City, Egypt, 1997–1998. Bull Environ Contam Toxicol 67:225–232

Ettiene G, Ortega S, Sepúlveda J, Medina D, Buscema I, Sandoval L (2006) Dissipation of organophosphorus pesticides in green onion (*Allium Fistulosum* L), cultivated in forced system called "barbacoas". Bull Environ Contam Toxicol 76:415–421. doi:10.1007/s00128-006-0937-7

FAO/WHO (1999) Codex alimentarius. Recommended methods of sampling for the determination of pesticide residues for compliance with MRLs, vol 2A

FAO/WHO (2005) Codex alimentarius Commission. Joint FAO/WHO food standards programme. Report of the thirty-seventh session of the Codex Committee on pesticide residues. The hague, The Netherlands

Gebara A, Ciscato C, Ferreira M, Monteiros S (2005) Pesticide residues in vegetables and fruits monitoreo in Sao Paulo City Brazil, 1994–2001. Bull Environ Contam Toxicol 67:163–169. doi:10.1007/s00128-005-0733-9

Gobo A, Kurz M, Pizzutti I, Adaime M, Zanella R (2004) Development and validation of methodology for the determination of residues of organophosphorus pesticides in tomatoes. J Braz Chem Soc 15:945–950. doi:10.1590/S0103-50532004000600024

INE-Instituto Nacional de Estadística (2002) Censo general de población y vivienda año 2001 Venezuela (on line). http://táchira.gov.ve/táchira/estadisticas/Estadisticas_Municipios/josema_vargas.pdf

Kumari B, Mandan V, Kathpal T (2006) Monitoring of pesticide residues in fruits. J Environ Monit Asses 123:407–412. doi:10.1007/s10661-006-1493-7

Miller JN, Miller JC (2002) Estadística y quimiometria para química analítica. Pearson educación, S. A, Madrid

Mukherjee I (2003) Pesticide residues in vegetables in and around Delhi. J Environ Monit Asses 86:265–271. doi:10.1023/A:1024057420937

Prieto A, Molero D, González G, Buscema I, Ettiene G, Medina D (2002) Persistence of methamidophos, diazinon and malathion in tomatoes. Bull Environ Contam Toxicol 69:479–485. doi:10.1007/s00128-002-0087-5

Quintero A, de González CN, Ettiene G (2002) Determinación de plaguicidas organofosforados en tomate y pimentón de El Cobre-Táchira. Rev Acta Cient Venez 53:15

Torres C, Picó Y, Mañes J (1996) Determination of pesticide residues in fruits and vegetables. J Chromatogr A 754:301–331. doi:10.1016/S0021-9673(96)00407-4

Torres D, Capote T (2004) Agroquímicos un problema ambiental global: uso del análisis químico como herramienta para el monitoreo ambiental. Rev Ecosistemas 13:2–6

Ueno E, Oshima H, Saito I, Matsumoto H (2003) Determination of nitrogen-and phosphorus-containing pesticide residues in vegetables by gas chromatography with nitrogen-phosphorus and flame photometric detection after gel permeation chromatography and a two-step minicolumn cleanup. J AOAC Int 86:1241–1250