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Persistence of Methamidophos, Diazinon, and Malathion in Tomatoes

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The organophosphorus pesticides diazinon (o,o-diethyl o-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate), malathion (s-1,2-dicarbethoxyethyl-o,o-dimethyl-dithiophosphate) and methamidophos (o,s-dimethyl phosphoramidothioate) are active ingredients in the organophosphorus pesticide formulations used in many parts of the world to control a range of pests on an array of crops, including tomatoes (Adnan et al.1998, Arellano, 1998). These pesticides are used widely in Venezuela to suppress the population of several common pests, such as the white fly (Bemesia tabaci), aphids and cutworms, which infest tomato plants (lycopersicum esculetum Miller) and cause serious economic damage (Chirinos et al. 1996, Geraud-Pouey et al.1997).

Due to the high ambient temperature (about 40 ºC) reached throughout the dry season in the tomato cultivated area (Zulia state), volatility could be a primary means of loss for diazinon and malathion from the pesticide sprayed tomatoes, since both are non-systemic pesticides. This environmental condition establishes a safety interval before harvest. Persistence pesticide studies have been conducted in other countries (Adnan et al. 1988, Antonious et al.1994, Liapis et al.1994), however research of this type in tomatoes has not been carried out in our country, although the persistence for pesticides on other kind of matrix has being developed (Ettiene et al. 1997, Medina et al. 1999), such as must and grape wine and also in river water. This work deals with the study of the dissipation rates of two non-systemic pesticides (diazinon and malathion) and the systemic pesticide methamidophos applied on physiologically ripe tomatoes. Small volume of samples and reagents were used in the extraction-clean up procedure, prior to gas chromatographic analysis.

MATERIALS AND METHODS

Stock solutions (1000 µg/mL) of high purity standards: methamidophos, diazinon and malathion (Dr. Ehrenstosfer GmbH) pesticides, and 500 µg/mL triphenyl phosphate (99% purity, Riedel de Haen) were prepared in ethyl acetate (Beaker). Anhydrous sodium sulphate (Riedel de Haen) analytical-reagent grade was used to get dryness during the extraction process. Acetone (Fisher), methanol (Baker) and ethyl acetate grade

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pesticides were used. Clean up of the sample extracts was performed through 100 mg non porous (120-400 mesh) graphitized carbon black cartridges (supelclean Envi-Carb, Supelco).

Pesticide residues were analysed using an Auto system Perkin Elmer gas chromatograph; equipped with a NPD at 280 °C , autosampler (Perkin Elmer), and a 30m x 0.53mm x 1.2 µm AT-5 capillary column (Alltech) containing 5 % phenyl- 95% methyl silicon. The injector temperature was 250 °C and splitless injection was used; temperature program: 60 °C for 0.80 min, 40 °C/min to 100 °C, 3.5 °C/ min to 280 °C hold for 1 min; carrier gas flow, helium at 10 mL/min; detector gas flow, H_2 at 2 mL/min, air at 100 mL/min with a work umbral of 0.75 mV.

Commercial formulations of pesticides at 1.5 L/ha in the dose recommended by the manufacturer (Amidor 60: Methamidophos 60 % at 900 g/ha; Danol 60: Diazinon 58.6 % or 879 g/ha and Malathion 57: Malathion 57 % i.e. 855 g/ha) were applied once on 0.04 ha plots of ripe tomatoes in April 1996 (dry season). Tomato plants (lycopersicum esculentum mill) cv. Rìo Grande were grown at the Mara area located in the Zulia State (Venezuela). Four plots of 0.01 ha were studied, one of them was left untreated as a control plot.

Tomato samples were taken from all plots at 0, 1, 2, 4, 6, 8, 10, 16, 23 and 30 days after the application. Samples designated as 0 day post-application were taken 1hr after the application, as soon as the water from the spray application had evaporated. At each sampling date, one bulk field sample (500 g) was taken from each plot. Samples were transported to the laboratory each day for processing and analysing in persistence studies.

Sub-samples (4 g tomatoes) were blended for 10 min with 10 mL of acetone/ ethyl acetate 10:90 v/v and 5 g anhydrous sodium sulphate for the studied pesticides extraction. The small extraction solvent volume used in this step allows us to describe it as a mini-extraction method. After centrifugation at 1200 rpm for 4 min, a 2.00 mL aliquot of the organic layer was cleaned up through a graphitized carbon black cartridge, by gravity. This is an additional application of the graphitized carbon black which, as far as the authors concern, has not been previously reported. The partially retained pesticides during the clean up steps were then eluted from the cartridge with 2.00 mL of 10:90 v/v acetone/ethyl acetate (elution solvent). This last step avoided that nearly 50 % of the pesticides were retained on the cartridge, thus improving pesticide recovery. Furthermore, colourless extracts were obtained by mixing both the 2.00 mL cleaned aliquot sample and the 2.00 mL elution solvent. The extracts were concentrated to 2.00 mL with the aid of a stream of nitrogen. Triphenyl phosphate (TPP) as internal standard was added to each extract. Sub samples were prepared in triplicate and 1 µL aliquots of each one was injected into the chromatograph, in order to study the persistence of methamidophos, diazinon and malathion.

Untreated tomatoes samples were fortified with methamidophos, diazinon and malathion at 1 and 5 µg/g. The extraction was carried out as described above. The quantitative recovery study was perfomed in order to establish the validity of the extraction process.

RESULTS AND DISCUSSION

Sample chromatograms from the analysis of methamidophos, diazinon and malathion in tomatoes are shown in Figure 1. The TPP peak is also shown. The recoveries from fortified samples at 1 and 5 µg/g were in the range of 75-105 %. The mean RSD was 7 %. These results demonstrate that the procedures used for extraction, clean up through graphitized carbon black cartridge and the quantitation of the 3 organophosphorus pesticides were reliable and provided clean chromatograms, free of interference and good recoveries. The limits of detectability for the pesticides was considered to be 0.01µg/g. The developed mini-extraction and clean up procedures, were performed with small volume (12 mL/sample) of organic solvents, and they were carried out in 14 min, using less volume and consuming less time than other methods previously reported (Carabias et al.1992, Holstege et al. 1994).

Residues of methamidophos, diazinon and malathion remaining in treated tomatoes are shown in Table 1. The initial residue level of methamidophos was higher than those of diazinon and malathion, and it dropped less rapidly during the following days. These results demonstrate an extremely rapid absorption of methamidophos into the tomato tissues. Percentage of residue levels decreased steadily over the 30-day period of the study, in this order methamidophos followed by diazinon and malathion. The persistence of malathion was lower than that of the other pesticides studied. Both diazinon and malathion are documented as non-systemic pesticides (Adnan et al. 1988, International Regulatory Aspects For Pesticide Chemical.1981), while methamidophos is systemic (International Regulatory Aspects For Pesticide Chemical.1981, Antonious et al. 1994).

This difference probably accounts for the persistence of methamidophos in tomatoes, since similar behaviour has being reported (Antonious et al. 1994) for this pesticide in comparison to other pesticides, although the experiments were carried out under different production systems, climates, farming, conditions, etc. The residue levels of diazinon and malathion were below the limit of determination (0.01 µg/g) for this procedure at day 23; while methamidophos remained at 0.60 µg/g , being lower than the M.R.L (International Regulatory Aspects For Pesticide Chemical.1981) of 2 µg/g.

Logarithmic dissipation plots of methamidophos, diazinon and malathion are shown in Figure 2. As expected, according to non-systemic behaviour; the half-life of diazinon and malathion were similar.

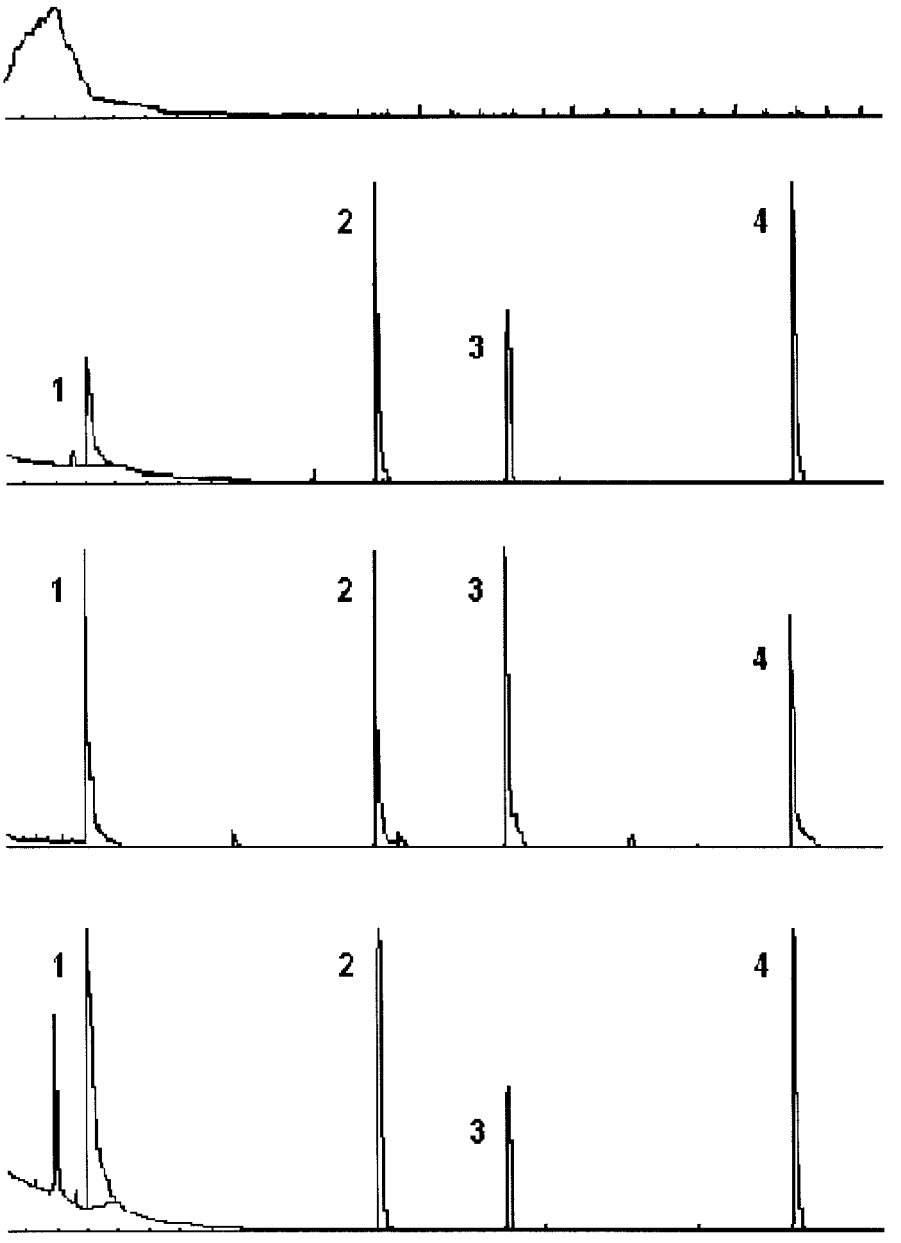

Figure 1. Sample Chromatograms from the analysis of organophosphorus pesticides in tomatoes. one µL injection of: **a** control sample, **b** fortified control sample at 1 µg/g, **c** fortified control sample at 5 µg/g, **d** field treated sample 0 day application. **1**: methamidophos, **2**: diazinon, **3**: malathion, **4**: triphenyl phosphate internal standard.

Table 1. Persistence of the pesticides in tomatoes samples.

Mean (n=3) residue concentration (µg/g X ± S) and % Residue						
Time days	Methamidophos	%	Diazinon	%	Malathion	%
0	8.57 ± 4.71	-	3.65± 1.79	-	7.32 ± 4.61	-
1	6.76 ± 1.57	21.1	1.58 ± 0.59	56.7	2.13 ± 0.90	70.9
2	3.90 ± 2.80	54.5	0.53 ± 0.41	85.5	0.32 ± 0.22	95.6
4	3.30 ± 0.99	61.5	0.34 ± 0.21	90.7	0.16 ± 0.14	97.8
6	2.87 ± 0.79	66.5	0.30 ± 0.13	91.8	0.17 ± 0.08	97.7
8	3.32 ± 2.32	61.3	0.16 ± 0.13	95.6	0.09 ± 0.04	98.8
10	2.91 ± 1.74	66.0	0.11 ± 0.06	97.0	0.04 ±0.02	99.5
16	2.40 ± 2.14	72.0	0.04 ± 0.02	98.9	0.02 ± 0.01	99.7
23	0.60 ± 0.30	93.0	ND	-	ND	-
30	ND	-	ND	-	ND	-

ND = Not detected < 0.01 µg/g
- = It does not apply

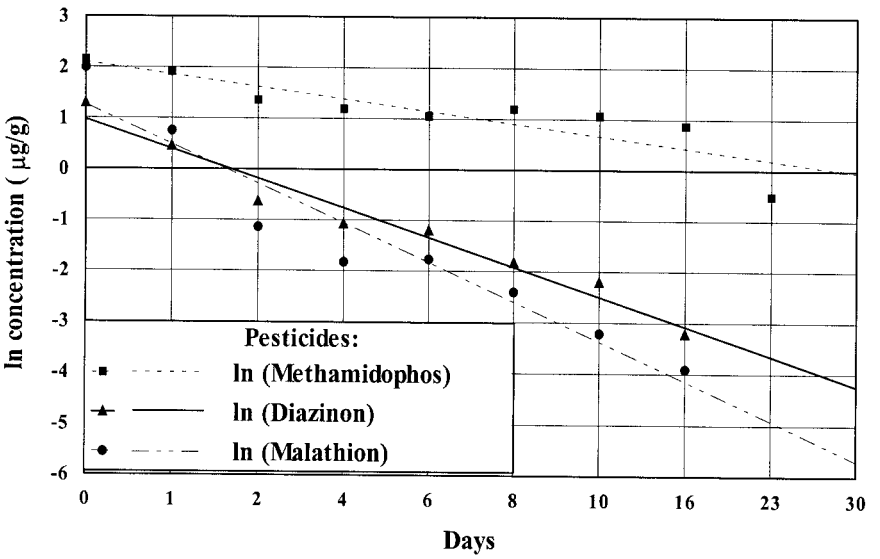

Figure 2. Logarithmic dissipation of methamidophos, diazinon and malathion in tomatos samples

The maximum residue limits (MRL) for the studied pesticides are shown in Table 2. Comparison of Tables 1 and 2 shows that the residue levels of diazinon and malathion at the fourth and first-day sampling, respectively were below the published maximum residue limits. These results would suggest that a safety interval in the range of 1-4 days should be allowed after the application of diazinon and malathion on tomatoes, and more than 16 days after the application of methamidophos.

Table 2. Approximate waiting time for residues to reach Maximum Residue Limits (MRL) after one application on tomato fruit.

Pesticide	Application Rate (g/L)	Residue recovered at 1 h after application (µg/g)	K day^{-1}	Half-life $t_{½}$ (days)	MRL (Codex tolerance) µg/g	Approximate waiting time (days)
Methamidophos	2.3	8.57	0.37	1.87	2.0	23
Diazinon	0.9	3.65	0.61	1.14	0.5	4
Malathion	1.4	7.32	0.61	1.14	3.0	1

MRL= Maximum residue limits recommended by FAO/ WHO

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