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Degradation of Propamocarb-hydrochloride in Tomatoes, Potatoes and Cucumber Using HPLC–DAD and QuEChERS Methodology

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Abstract Propamocarb-hydrochloride is a widely used fungicide around the world. The dissipation of propamocarb-hydrochloride in tomatoes, potatoes and cucumber were evaluated. QuEChERS methodology before quantification using HPLC–DAD was used. Preharvest interval and maximum residue limit were 4 days and 1.0 mg kg^{-1} for tomatoes, 3 days and 0.5 mg kg^{-1} for potatoes and 7 days and 1.0 mg kg^{-1} for cucumber. Half-lives ($t_{1/2}$) were 1.29, 2.26 and 9.05 days for tomatoes, potatoes and cucumber, respectively.

Keywords Degradation · Fungicide · Propamocarb-hydrochloride · QuEChERS

Agricultural pesticides are increased the concerns because of their adverse effects on human health as these residues in varying levels agricultural products such as vegetables and fruits. Propamocarb-hydrochloride [propyl 3-(dimethyl-amino) propylcarbamate hydrochloride, a systemic carbamated fungicide with protective action against phycomycetous diseases (Phythium, Phytophthora spp.) and used particularly against Aphanomyces, Phytophtora and Phytium (Fernandez-Alba et al. 2001). This pesticide is used on a wide variety of mainly greenhouse vegetables and fruits (Tomlin 2000), and is registered in Egypt for application on many greenhouse-based vegetable crops, such as tomatoes, potatoes and cucumber.

Due to intensive use of pesticides in vegetable farming, residues may be accumulated at levels higher than those permitted by the international MRLs. Assessment of dissipation rate of a pesticide after application is a key process for determining of the residual behavior of pesticides in agricultural crops and for detecting pre-harvest interval (PHI). Additionally, residues dissipation curves can be used to estimate the time required for decreasing the residues below MRLs (Ambrus and Lantos 2002; Castillo-Sanchez et al. 2000; Fenoll et al. 2009).

QuEChERS (quick, easy, cheap, effective, rugged and safe) is a method which has been mainly applied for the extraction of different classes of pesticides (Abd-Alrahman et al. 2011a; Garrido Frenich et al. 2008; Lehotay et al. 2005; Paya et al. 2007). This method achieved the status of Official Method of AOAC International (Lehotay 2007). The objectives of this work were: (a) to determine the residue levels of propamocarb-hydrochloride in tomatoes, potatoes and cucumber after normal dose application (b) to define the pesticide residue behavior in these fruits with using dissipation curves and (c) to determine the pre-harvest intervals of this pesticide required for each fruit.

Materials and Methods

Certified reference standard of Propamocarb-hydrochloride >99 % purity was obtained from central agricultural pesticides laboratory (CAPL). Acetonitrile (MeCN) and methanol (MeOH) of HPLC grade were purchased from Merck. Bulk primary secondary amine (PSA) sorbent (Bondesil-PSA, 40 μm) was bought from Subelco. Ammonium acetate

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(cryst. Extra pure), acetic acid and sodium chloride were purchased from Merck. Magnesium sulphate anhydrous fine powder, trisodium citrate dihydrate (Extra pure) and disodium hydrogencitrate sesquihydrate (Extra pure) were purchased from Merck Ltd.

For the field experiment, a random block scheme was used with three replications for each test. Propamocarb-hydrochloride was applied with a backpack motorized sprayers with an adjustable nozzle size of 1 mm using the commercial formulation Previcur-N 72.2 % SL. The pesticide application was carried out in Feb. 27th, Nov. 21th and 31th Dec. 2008 for cucumber, potatoes and tomatoes, respectively, at the dose recommended by the manufacturers 250 cm^3 100 L^{-1} water. Before the application, samples of tomatoes, potatoes and cucumber with similar ripening stage, size, and shape were located and tagged. Samples 1 kg were collected 1 h after application and then after 1, 3, 5, 7, 10 and 15 days. A control sample was also taken at each sampling time. Immediately after collecting the samples, each individual sample were put into plastic bags and transported to the laboratory, the samples were homogenized using a food processor (Thermomix, Vorwerk). The homogenate of each sample was then placed into polyethylene 50 mL centrifuge tube and stored frozen at -20 ± 2°C until further analysis.

Stock solution of Propamocarb-hydrochloride was prepared by dissolving 50 mg of the analyte (of accurate weight) in 50 mL MeOH to obtain solution concentration 1 mg/mL (Fig. 1). A working standard solution of 10 μg mL^{-1} was prepared by appropriately diluting the stock solution with MeOH. Stock solution was stored at -20 ± 2°C, and working standard solutions were stored in the dark ≤ 4°C when not in use.

All samples (1 kg each) of tomatoes, potatoes and cucumber were chopped and homogenized for 5 min at high speed in a laboratory homogenizer and extracted according to the procedure described and modified by Lehotay et al. (2010) and validated by Sherif (Abd-Alrahman et al. 2011b). Briefly, 10 g of the homogenized sample was weighed into a 50-ml centrifuge tube. Ten milliliters of 1.0 % acidified acetonitrile with acetic acid was added; closed and vigorously shaken for 1 min using a vortex mixer at maximum speed. Afterwards, 4 g of anhydrous MgSO4, 1 g of NaCl, 1 g sodium citrate dihydrate, and 0.5 g disodium hydrogen citrate sesquihydrate

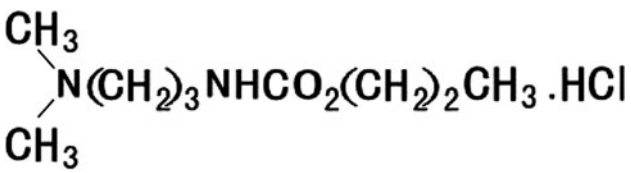

Fig. 1 Propamocarb-hydrochloride structure

were added, then extracted by shaking vigorously using vortex for 2 min following centrifugation for 10 min at 5,000 rpm. An aliquot of 3 mL was transferred from the supernatant to a new clean 5-mL centrifuge tube and cleaned by dispersive solid-phase extraction with 75 mg of PSA and 500 mg of magnesium sulfate. Afterwards, centrifugation was carried out at 6,000 rpm for 5 min. An aliquot (2 mL) from the supernatant was filtered through a 0.2-ìm PTFE filter (Millipore, USA) and then analyzed by Agilent 1100 HPLC–DAD.

Pesticide residue analysis was performed with Agilent technologies HP-1100 series high-performance liquid chromatographic system (Agilent Technologies, USA) equipped with a diode array detector and quaternary pump. The separation was performed on a C18 column (150 × 4.6 mm, 5 μm). The mobile phase was (MeOH: Water 70:30 v/v) with flow rate 0.8 mL min^{-1} and detection wavelength of 260 nm Data analysis was performed using Chemistation software.

Data were statistically evaluated by one-way analysis of variance (ANOVA). Determination the differences among means were carried out by using the least significant differences (LSD) test. All statistical analyses were done using the Statistical Package for social sciences (SPSS 16.0) program.

Results and Discussion

Control (without pesticide application) samples of tomatoes, potatoes and cucumber were used for the evaluation of selectivity. The absence of any signal at the retention time of Propamocarb-hydrochloride indicated that no matrix compounds are present, which could give false positive signal. The calibration curve of propamocarb-hydrochloride showed a good linearity and strong correlation between concentrations and area in the studied range (0–100 ng mL^{-1}) ($r^2 \geq 0.996$). Recoveries for propamocarb-hydrochloride (Table 1), ranged from 84.8 % to 87.2 %, 85.5 % to 90.1 % and 85.2 % to 88.8 %, in tomatoes, potatoes and cucumber, respectively. Precision was studied by performing repeatability studies, expressed as RSD. Satisfactory precision was obtained for Propamocarb-hydrochloride. Repeatability was lower than 7 % for all three levels assayed. Similarly, with the examination of the matrix effect, a general tendency was observed towards higher values of RSDs at low spiking concentrations. Instrumental LOD based on S/N of 3:1 and LOQ based on S/N of 10:1 was (1.2 and 4.5 μg kg^{-1}) (0.9 and 2.7 μg kg^{-1}) and (0.5 and 2.3 μg kg^{-1}) for tomatoes, potatoes and cucumber, respectively.

Propamocarb-hydrochloride mean residue levels during the sampling period for each application derived from three

Table 1 Dissipation of propamocarb-hydrochloride in/on tomatoes, potatoes and cucumber

Days after application	Tomatoes		Potatoes		Cucumber	
	Residue (mg kg^{-1}) Mean[a] ± SD	Dissipation %	Residue (mg kg^{-1}) Mean ± SD	Dissipation %	Residue (mg kg^{-1}) Mean ± SD	Dissipation %
Zero	3.10 ± 0.15	0.00	0.00	0.00	1.74 ± 0.11	0.00
1	2.17 ± 0.08	30.00	0.99 ± 0.09	0.00	1.41 ± 0.09	18.96
3	1.04 ± 0.04	66.45	0.48 ± 0.06	51.52	1.25 ± 0.08	28.16
5	0.59 ± 0.05	80.96	0.28 ± 0.05	71.72	1.15 ± 0.11	33.91
7	0.32 ± 0.03	89.67	0.11 ± 0.06	88.88	0.94 ± 0.07	45.97
10	0.05 ± 0.04	98.38	0.02 ± 0.05	97.98	0.74 ± 0.05	57.47
15	Nd	–	Nd	–	0.31 ± 0.06	82.18
Mean recovery %	86 (84.8–87.2)		87.8 (85.5–90.1)		87.0 (85.2–88.8)	
MRL (mg kg^{-1})	1.0		0.5		1.0	
$t_{1/2}$ (day)	1.29		2.26		9.05	
PHI (day)	4		3		7	
r^2	0.982		0.9905		0.986	

Nd not detectable

[a] n = 3

sub samples are shown in (Table 1; Fig. 2). Residue levels of propamocarb-hydrochloride were found to be below the MRLs established by the Codex Committee (1.0 mg kg^{-1}), (0.5 mg kg^{-1}) and (1.0 mg kg^{-1}) after the application of recommended dose, which were 250 cm^3 100 L^{-1} water for tomatoes, potatoes and cucumber, throughout the experimental period (FAO/WHO 2006).

The highest residue levels were found in samples taken in the first sampling time 1 h after pesticide application. Mean values of Propamocarb-hydrochloride residue determined with these samples were 3.1, 0.99 and 1.74 mg kg^{-1} for tomatoes, potatoes and cucumber, respectively. Residue levels of Propamocarb-hydrochloride had been decreasing in the following period, reaching levels below 0.05, 0.02 and 0.74 mg kg^{-1} in 10 days after application for tomatoes, potatoes and cucumber, respectively. In cucumber, the residues reached 0.31 mg kg^{-1} in 15 days after application.

The results showed different half-life(s) ($t_{1/2}$) and PHI for propamocarb-hydrochloride of (1.29, 4), (2.26, 3) and (9.05, 7) days for tomatoes, potatoes and cucumber, respectively. A similar behaviour of iprodione and thiacloprid residue levels was observed by Omirou et al. (2009), Mean residue levels of both pesticides were below the EU established MRLs throughout the experimental period. Also Omirou reported that the highest residue levels in both treatments were determined in samples taken in the first sampling just after pesticide application as in our case. In another study by Beouwer was reported that the dissipation of pesticide deposit was a complex process depingding on various environmental factors like temperature, relative humidity and UV irradiation), metabolism and translocation (pesticide penetration and plant growth), application technique and pesticide formulation (Brouwer et al. 1997; Katagi 2004; McCrady and Maggard 1993).

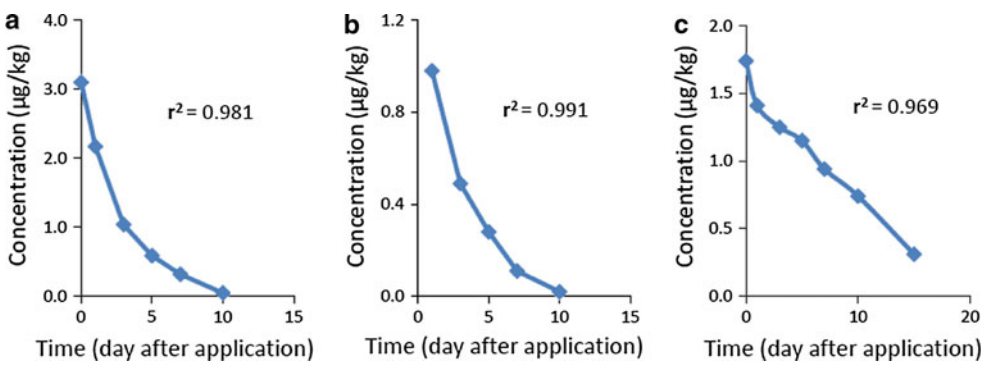

Fig. 2 Dissipation curve of propamocarb-hydrochloride residue in/on **a** tomatoes, **b** potatoes and **c** cucumber

In this study, the fungicide propamocarb-hydrochloride dissipation rates after a single application at recommended dose on tomatoes, potatoes and cucumber were evaluated. We used an improved method (QuEChERS) for sample preparation. Through this method, we achieved a good analytical performance in terms of sensitivity (LODs, 0.5–1.2 μg kg^{-1}; LOQs, 2.3–4.5 μg kg^{-1}) and recovery rates (84.8 %–90.1 %). Thus, this method can be used for residue determination in the detection of propamocarb-hydrochloride residues with low levels. Propamocarb-hydrochloride has shown different dissipation rates: half-life(s) and PHI for propamocarb-hydrochloride were (1.29, 4), (2.26, 3) and (9.05, 7) days for tomatoes, potatoes and cucumber, respectively. From the PHI values was determined, it was noted that the propamocarb-hydrochloride residue did not exceed the MRL recommended by the Codex Committee of 1.0, 0.5 and 1.0 mg kg − 1 for tomatoes, potatoes and cucumber, respectively. However the long PHIs might lead to a higher risk of exposure to Propamocarb-hydrochloride, especially in case of cucumber.

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