Appraisal for Edible Use of Vegetable Crops Cultivated in Egypt after Treatment with Selected Insecticides and Fungicides: Insights of Dissipation Rates and Pre-Harvest intervals

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Abstract

An analytical investigation was carried out to study the dissipation rate of two commonly used pesticides, Thiamethoxam (neonicotinoid insecticide) and propamocarb hydrochloride (carbamate fungicide) applied to four vegetable crops: cucumber, zucchini, lettuce and pepper, after open-field application. Samples were harvested according to a scheduled plan followed by QuEChERS extraction, then thiamethoxam residues were analyzed using a GC-ECD method, while propamocarb HCl residues were analyzed using an HPLC-UV method. Validation parameters were attained for both methods and the kinetic profile was studied which fitted the first –order kinetics where k, t ½ and t90 were calculated. The proper pre-harvest interval (PHI) was studied for each crop to ensure that the residues levels declined to reach below the maximum residue limit (MRL) where the crop is suitable for edible use. These values were found to be different from labelled values which proves that the PHIs are greatly affected by changing weather conditions.

Keywords: Thiamethoxam; Propamocarb; QuEChERS; PHI; MRL.

1. Introduction

Over the past decades, the prevalence of uncontrolled use of pesticides was observed, where about 1% only of the applied pesticides is beneficial, which leads to misspending billions of pounds \(^1\). In addition to that financial loss, uncontrolled exposure to pesticides can be extremely hazardous to humans and other living organisms through inhalation, contact with pesticide or eating foods containing pesticide residue (even in low amounts) \(^2\)–\(^4\).

Egypt occupies the first place among the Arab countries, and the second one in Africa in terms of population which exceeded 100 million. Agricultural activities play an important role in Egypt, due to the high population density which is concentrated among the areas of crop
production, lower and middle areas around the River Nile; in addition to the economic importance of agricultural activities, as it represents around 28% of Egypt’s total national income by the means of exports of agricultural crops which heavily contribute to the country's earnings of foreign currencies. The history of pesticide market in Egypt went through several phases. Prior to the year 1950, the use of pesticides was very limited. Then through years (1952 – 1990), the main agricultural crop was cotton treated with insecticides (mainly toxaphene) which was substituted latter on with other types of insecticides. Starting from year 2005, an increasing demand on fungicides was observed due to the expansion of the greenhouse crop agriculture and it was observed that insecticides and fungicide showed the highest share among different classes in Egyptian pesticide market.

Vegetables occupy the top of the diet pyramid in Egypt because it is considered a low-cost source of balanced and healthy diet as well as its variety. Vegetables are usually attached by different diseases and pests. Accordingly, in developing countries, such as Egypt, farmers would apply intensive pesticide treatment, even one day prior to harvest, in order to protect the crops during the shipment and selling processes. This greatly affect the level of pesticides that may reach the consumers and may cause serious health issues. That’s why serious regulations are adopted for the presence of pesticide residues in different kinds of food. The international food standards legislated by FAO and WHO (Codex Alimentarius) has described what is known by “Maximum Residue Limits” (MRLs). MRL is the amount of pesticide residue that can be found in a food type which is considered to be safe for human and animal use in accordance with Good Agricultural Practice and is accepted through international trade and to ensure that this food supply. Another important term is the pre-harvest interval (PHI) which is the time interval required for the level of pesticide residue in certain sample to decrease till reaching the labelled MRL.
Through the years (2015-2019), Egyptian exports to the European Union were negatively affected due to the ban of 52 vegetables crops where violations to the European Union pesticides limits (MRLs) were recorded. On the top of these banned crop list were pepper and cucumber. The highest percentage of detected pesticide groups in these crops were: insecticides (50%) followed by fungicides (37.5%) \textsuperscript{10}. Following this incident, Egyptian agricultural ministry took several corrective actions including: examinations were conducted in the ministry’s laboratories to check the MRLs of samples withdrawn from major markets, serious actions were taken against any pesticide residues found in exports and Egypt’s plan to drop 50% of used pesticide use to be replaced with biopesticides by 2030 \textsuperscript{11}.

Thus, it is necessary to ensure that pesticide residues levels decline to reach below the maximum residue limit (MRL) by studying the dissipation rate of each pesticide in order to recommend a proper pre-harvest interval (PHI) \textsuperscript{12-14}. For a certain crop, it’s expected that changing the cultivating conditions will highly affect the values of the PHI. So, it is recommended to study the effect of different growing conditions on the dissipation rate of pesticides and when their levels will reach the MRL and become safe to edible use \textsuperscript{15}.

Two commonly used pesticides in Egypt nowadays were selected for this study, thiamethoxam (TMX) and propamocarb HCl (PRB), as examples for insecticides and fungicides, respectively. These two pesticides were applied to four vegetable crops which are widely consumed in the Egyptian market and involved in the export process (cucumber, zucchini, lettuce and pepper) \textsuperscript{10, 16-18}.

Thiamethoxam (TMX), (EZ)-3-(2-chloro-1,3-thiazol-5-ylmethyl)-5-methyl-1,3,5-oxadiazinan-4-ylidene (nitro) amine (Fig. 1), is a nitro-neonicotinoid insecticide which interferes
with the nicotinic acetylcholine receptor and thus affects the insect nervous system \(^{19}\). Several methods were reported for determination of TMX by liquid and gas chromatography alone in honeybees, fruits and vegetables \(^{20,21}\) or with other neonicotinoids \(^{22-25}\). Studies showed that TMX disturbs hepatic and renal functions, provokes an increase in glucose levels and undesirable neurological effects in rats \(^{26}\). It can also cause acute kidney injury by direct tubular toxicity via \(\alpha_7\) nicotinic receptor inhibition in human \(^{27}\).

Propamocarb HCl (PRB), propyl 3-(dimethylamino) propylcarbamate hydrochloride (Fig. 1), is a systemic carbamate fungicide which acquire a protective action against phyco mycetous diseases (Phythium, Phytophthora spp.) \(^{28}\). Literature revealed several chromatographic methods reported for the analysis of propamocarb residues alone or in combinations with other carbamates such as LC-MS \(^{29-32}\), HPLC – DAD \(^{33}\) and GC-MS \(^{34}\). Acute and chronic exposure to propamocarb showed alterations in locomotor activity and behavioral impairments in mice \(^{35}\). In addition, propamocarb was identified as an estrogenic compound which affects \(\alpha\) and \(\beta\) estrogen receptors \(^{36}\).

In 2003, Anastassiades et al.\(^{37}\) firstly introduced QuEChERS method which involves treatment with acetonitrile forming a single extraction phase, followed by shaking with sodium chloride and magnesium sulfate to remove residual water. QuEChERS method has been applied for different types of food and has been validated as the AOAC official method for the extraction of pesticide residues.

The aim of this work was to study the dissipation patterns of two commonly-used pesticides (Thiamethoxam (TMX) and propamocarb hydrochloride (PRB)) after open-field application to four vegetable crops (cucumber, zucchini, lettuce and pepper). This was done by applying
QuEChERS method for extracting the pesticides’ residues from vegetable samples withdrawn from the field on a scheduled time plan, followed by analysis of the residues of TMX by GC-ECD method; and residues of PRB were analyzed using by HPLC-UV method. Both methods were validated per linearity, accuracy, precision, matrix effect parameters. Accordingly, the proper pre-harvest intervals (PHI) would be recommended for each crop treated by either pesticide.

2. Material and methods

2.1. Chemicals and reagents

Certified reference standards of TMX and PRB (purity > 99%) were kindly supplied by Central Agricultural Pesticides Laboratory (CAPL), Egypt. HPLC grade acetonitrile, anhydrous magnesium sulphate, sodium chloride and formic acid were supplied from (Merck, Germany). Distilled water. Bulk primary secondary amine PSA sorbent (Bondesil-PSA, 40 lm) was supplied from (Supelco Analytical, USA). Pesticide’s formulations of Actara® 25% WG containing TMX (Syngenta) and Previcur n® containing PRB (Bayer) were purchased from the local Egyptian market.

2.2. Standard solutions

Stock solutions of TMX and PRB were prepared by dissolving 50 mg of each in 50 mL acetonitrile, to obtain a solution concentration of 1 mg/mL. Working standard solutions were prepared with concentration range of (0.01-10 mg/kg) and (2 – 200 mg/kg) for TMX and PRB, respectively, by appropriately diluting each stock solution with acetonitrile. Stock solutions were stored at -20 ± 2 °C, and working standard solutions were stored in the dark ≤ 4 °C when not in use.
2.3. Chromatographic conditions

**GC.** TMX residues were quantified by a Hewlett-packard series 6890N gas chromatography (GC), equipped with electron capture detector (ECD). The column was PAS-5, (30 m × 0.25 mm × 0.25 µm film thicknesses) and the injection port temperature was 280°C. The oven temperature was programmed as follows: initial temperature 240°C for 2 min, then up to 260°C was held for 5 min and the detector temperature was set at 300°C. The carrier gas was nitrogen at a flow rate of 3 mL/min.

**HPLC.** PRB residues were determined using Agilent 1100 HPLC equipped with diode array detector (Agilent, USA) at wavelength 219 nm. An ODS C_{18} column (4.6 mm × 150 mm × 5µm) was used as the stationary phase. Isocratic elution using a mobile phase of acetonitrile and water (60: 40 v/v) with a flow rate of 0.8 mL/min at room temperature.

2.4. Sample collection

**Field Application:** It was carried out at a farm located at Cairo-Alexandria desert road, Giza Governorate, Egypt. Four fields were chosen to apply the experiment, one field for the cultivation of each crop separately. Each field was subdivided into three areas (total area equals to 150 m²), one area for treatment with each of TMX or PRB, separately and the third area acted as a control which received no treatment. The specified fields were treated with the recommended doses as indicated in the Technical Recommendations for Agricultural Pests Control, Ministry of Agriculture. For TMX, 2.5 gm of Actara 25% WG was diluted with 20 L of water; while for propamocarb HCl, a volume of 100 ml of Previcur N 72.2% was diluted with 20 L of water, and then the diluted pesticides were applied on the specified area with a knapsack sprayer equipped with a nozzle. All crops were sprayed with the same amount of prepared pesticide solutions sufficient to cover all the field area.
**Sampling and storage:** Representative samples were collected randomly from all plants in the field, three replicates weighing one kilogram of each crop (cucumber, zucchini, lettuce and pepper). According to a scheduled time plan over 30 days, the control samples were collected from the untreated fields coinciding with the collection from the treated fields with TMX and PRB. Sampling took place 1 h (zero time) after the initial application of selected pesticide and then repeated 1, 3, 5, 8, 11, and 15 days afterwards to study the dissipation rate the pesticides. Field samples were placed in sterile polythene bags, labelled and placed in iceboxes to avoid contamination and deterioration, and then transported to the laboratory.

### 2.5. Sample extraction and clean-up

Each field sample was subdivided, chopped using a food cutter and then homogenized for 5 minutes using a food processor. Triplets of each representative subsamples of 10 g were weighed and stored in 50 mL Falcon tubes at -20°C in deep freezer until analysis for a maximum of 24 hours. The samples were extracted with modified QuEChERS method \(^{37, 38}\). To the 10 g of the homogenized sample, 10 mL of acetonitrile was added and shaken vigorously for 1 min using a vortex mixer. Then 4 g of anhydrous magnesium sulfate and one gram of sodium chloride were added and shaken by a vortex mixer immediately for 1 min. The extracts were then centrifuged for 3 min at 5000 rpm. 6 mL aliquot of the upper layer were transferred into 15-mL Falcon tube containing 150 mg PSA and 950 mg MgSO\(_4\), and the extracts were centrifuged for 3 min at 5000 rpm. The whole supernatant has been filtered through 0.45 um filter and 1.5 mL of the extract was transferred into an auto sampler vial containing 15 µl of a 5 % formic acid solution for the stabilization of the extracts, then transferred to GC (for TMX) and HPLC (for PRB) analysis. Each sample was analyzed in triplicate and the average concentration was calculated.
2.6. Kinetic study: Dissipation rate and PHI determination

Residual levels of the pesticides have been monitored over the period of the study. Dissipation profiles were then demonstrated and PHIs (Pre-Harvest Interval) estimated. The dissipation rates of TMX and PRB were plotted and the dissipation rates constant \( (k) \) was determined. The half-life \( (t_{1/2}) \), is defined as the time required for the pesticide residual level to fall to half of the initial residue level after application (at zero time) and was calculated from the \( k \) value for each experiment, being \( t_{1/2} = \ln 2/k \) for first order kinetics.

2.7. Method validation

Method validation was performed according to document \(^{39}\) to ensure that the proposed methods are valid for the extraction ad analysis of TMX and PRB in vegetable crops (cucumber, zucchini, lettuce and pepper).

2.7.1. Calibration curves and linearity

Linearity was tested at multi-levels to fit the pesticides residues of (0.01-10 mg/kg) and (2 – 200 mg/kg) for TMX and PRB, respectively in GC-ECD and HPLC-UV analysis. Each experiment was repeated three times, and the calibrations curves relating peak areas against pesticides concentrations were constructed and regression equations were calculated. Linearity was checked using correlation coefficient and calculation of residual percentages \( (\text{Res} \%) \) \(^{40}\).

\[
\text{Res} \% = \frac{S(e) - S(c)}{S(e)} \times 100
\]

where: \% Res is the residual of the point, \( S(e) \) is the signal of the calibration point obtained experimentally and \( S(c) \) is the signal of the calibration provided by calibration function.
2.7.2. Limit of quantitation (LOQ) and specificity

It is defined as the lowest spiked level meeting the method performance criteria for trueness (70-120 %) and precision (RSD ≤ 20%). The LOQ should be less than MRL of both pesticides in the selected vegetables. Specificity is the response to blank control samples to evaluate the interference of matrix components to detector response.

2.7.3. Trueness and Matrix effect

Three levels of concentrations were used for these tests (0.05, 2.5, 7.5 mg/kg) and (5, 50, 150 mg/kg) for TMX and PRB, respectively. Three sets of preparations for each pesticide were used. The first set was prepared by spiking the blank samples before extraction by QuEChERS method; the second one was prepared by spiking the blank samples after extraction; while the third set was pure standard solutions of the same concentrations. For each set, concentrations were plotted against response and the slope of each calibration graph was calculated.

Trueness describes the effectiveness of the proposed extraction procedure, where the slope of the pre-extraction samples is compared to the slope of the post-extraction samples. Matrix effect describes the effect of other matrix constituents on the analyte response. This is done by comparing the slope of the post-extraction samples with the slope of the standard solutions at the same concentration levels. Standard error percentages (SE%) and matrix effects (ME%) were calculated using the equation:

\[
\text{SE}\% = \left| \frac{M(p) - M(m)}{M(m)} \right| \times 100 \tag{2}
\]

\[
\text{ME}\% = \frac{M(m) - M(s)}{M(s)} \times 100 \tag{3}
\]
Where SE\% is the standard error percentage, ME\% is the matrix effect, $M(p)$, $M(m)$ and $M(s)$ are the slopes of the calibration graphs of pre-extraction, post-extraction and pure solution, respectively.

2.7.4. Accuracy and precision

Accuracy is defined as a measurement of bias, where previously mentioned three levels of each pesticide of TMX and PRB in pure standard solutions. Trueness is expressed by the following equation:

$$R\% = \frac{C\text{(exp)}}{C\text{(cal)}} \times 100$$

(4)

Where R\% is the recovery \%, $C\text{(exp)}$ is the experimental concentration in (mg/Kg), $C\text{(cal)}$ is the calculated concentration in (mg/Kg).

The same three levels of concentrations were used for the precision study including: repeatability (intraday precision) and intermediate precision (interday precision). For intraday precision, the samples were extracted and analyzed in triplicate on the same day; while for interday precision, the procedure was performed over three consecutive days.

3. Results and Discussion

3.1. QuEChERS & chromatographic conditions

QuEChERS method was selected for sample extraction and clean-up. Compared to other extraction methods such as solid-phase extraction or liquid-liquid extraction, QuEChERS method has several advantages such as: inexpensive, minimal solvents usage (eco-friendly), few steps (low-labor), fast and has a wide range of applications \textsuperscript{41,42}. 
A well-homogenized sample size of 10 g was reported to be a satisfactory representative sample. Acetonitrile is a suitable solvent for sample extraction because it usually forms single-phase extraction due to its miscibility with water, the extraction of lipids, waxes and fats is minimum; in addition to the possibility of using salts, such as NaCl and MgSO₄ for the clean-up of non-polar substances and residual water. Acetonitrile low volatility and viscosity causes small volume changes and it is suitable for different chromatographic applications (GC, LC...) \(^{37,38}\). The dissipation rates of two selected pesticides: TMX (neonicotinoid insecticide) and PRB (carbamate fungicide) were studied in cucumber, zucchini, lettuce and pepper crops after open-field application.

The chromatographic conditions for both methods (TMX by GC-ECD method, Fig. 2. and PRB by HPLC-UV method, Fig. 3) were optimized by manipulating separating conditions in order to achieve efficient elution of both pesticides. For GC-ECD method, columns with different dimensions and a wide range of temperature were tested. While for HPLC-UV method, C₈ and C₁₈ column with different ratios of the mobile phase: acetonitrile and water, were tested. The assigned chromatographic conditions gave the best results regarding selectivity and accuracy. Both methods are considered to be economic and suitable for routine low-cost analysis when compared to other hyphenated methods such as GC-MS, GC TQ-MS and LC-MS/MS \(^{43-46}\).

### 3.2. Dissipation rates and kinetic profiles

The dissipation rates of TMX and PRB were determined by the first-order kinetic reactions. Linearity was checked by calculating the correlation coefficient “r” for the linear range in dissolution rate plot and it was found to be > 0.97. Fig. 3 and 4 showed the residual values in mg/kg against time in days where a decline was shown for both pesticides.
For TMX, it was observed that the dissipation rate in zucchini was different from the other crops, where the percentage of loss (loss %) of residue reached 60 % after the first day after the application, and reached 74.55 % by the third day of application. For cucumber, the loss % reached 57.14 % by the third day of application. For both zucchini and cucumber, the residue levels were not detected at day 15 of the application. On the other hand, the dissipation rates in lettuce and pepper were quite similar to each other till day 5 (around 50%), but the dissipation rate in lettuce went faster where loss% reached 66.07 % by the 8th day of application and raised up to 87.01 % by the 15th day. For pepper the dissipation rate was much slower where the loss% reached around 77.75 % by the 15th day.

For PRB, the dissipation rates in cucumber and lettuce were similar to each other, showing close values of intercept. The percentage of loss (loss %) of residue reached around 65 % in cucumber and lettuce between the 6th - 7th day of application. On the other hand, the loss % of residue in zucchini reached 72.03 % by the 3rd, but pepper showed the slowest dissipation rate where loss% reached 51.09% by the 5th day. By the 15th day of application, the residues in zucchini and cucumber were not detected, whilst the loss % in lettuce and pepper reached 83 % and 68.5 %, respectively.

It was observed that the pesticide residues (especially PRB) residues in lettuce were higher than the other vegetables. This was previously reported for leafy vegetables and can be contributed to the large surface area of lettuce papers which are capable of capturing much of pesticides\textsuperscript{16,47}.

The values of residual TMX and PRB in all crops and the loss % versus the scheduled time plan were listed in Table 1. The degradation rates constant and half-life were calculated using first order rate equation: 

\[ C_t = C_0 e^{-kt} \] where \( C_t \) represents the concentration of the pesticide residue at
the time of \( t \), \( C_0 \) represents initial deposits after application and \( k \) is the dissipation rate constant in \( \text{days}^{-1} \). All the kinetic parameters including \( k \), \( t \frac{1}{2} \) and \( t_{90} \) were listed in Table 2 and calculated according to the equations: \( t \frac{1}{2} = \frac{0.693}{k} \) and \( t_{90} = \frac{0.105}{k} \).

### 3.3. Pre-harvest intervals (PHI)

The maximum residue levels (MRL) of TMX and PRB were listed in Table 2 according to Codex Alimentarius. According to the previously calculated dissipation rates, the pre-harvest intervals (PHI) for TMX and PRB were calculated where the pesticide residues reach the MRL. The values of MRL (in mg/kg) are substituted in the first-order kinetic linear curve of the dissipation rate of each pesticide and then the time calculated corresponds to the PHI (in days). The parameters for linear first-order kinetic curve are listed in Table 2.

The PHI for both cucumber and zucchini were found to be zero days, in other words, the level of pesticides residues reached the MRL within the first hour of treatment. The PHI of lettuce and pepper were found to be 7 and 2 days, respectively. For PRB, the PHI was found to be 13, 9, 5 and 15 days for cucumber, zucchini, lettuce, and pepper, respectively.

### 3.4. Validation sheet

#### 3.4.1. Linearity, LOQ and specificity

Standard solutions of TMX and PRB, dissolved in acetonitrile, in the range of \((0.01-10 \ \mu g/ml)\) and \((2 – 200 \ \mu g/ml)\), respectively were analyzed by the proposed GC-ECD and HPLC-UV analysis. Linearity was checked via correlation coefficient which were found >0.97 for both pesticides. Moreover, linearity was assessed by calculating residuals \(\%\) using eq.(1) and it was found to be within the acceptance limit of residuals deviation is \(\leq \pm 20\%\) . LOQ values for both pesticides were practically measured as the lowest spiked level meeting with \(R\% = \) 115.23 \(\%\) and \(RSD\% = \)
14.526. LOQ values were accepted because it was lower than MRL of each corresponding pesticide in all samples. The specificity of both GC-ECD and HPLC-UV methods were tested by analyzing blank samples of cucumber, zucchini, lettuce and pepper, where no peaks appeared at the retention time of the eluted pesticides. The previously mentioned validation parameters were listed in Table 3.

3.4.2. Trueness and Matrix effect

Recovery was calculated to assess the suitability of the method for extraction. Relatively low SE% values were calculated using eq (2) which indicated the high extraction power of QuEChERS method to the samples. Meanwhile, Matrix effect is tested to indicate whether the influence of the blank matrix components is positive or negative. By calculating the matrix effect (ME)% using eq (3) to all samples for both pesticides, lettuce showed negative values of ME% for both HPLC-UV and GC–DAD analysis which reflects matrix induced suppression. On the other hand, cucumber, zucchini and pepper showed positive values which indicates matrix induced enhancement. This goes in line with the different nature of lettuce matrix rather than the other samples’ matrices. The SE% and ME% values for these experiments are listed in Table 4 where all values were found to be below or equal to 20%.

3.4.3. Accuracy and precision

Trueness represents the closeness of agreements of pure standard solutions through five replicates of three levels of concentrations of each pesticide through substitution in equation (4). Trueness is expressed by recovery% (R%) and relative standard deviation (RSD%) which were listed in Table 4. The values were found in agreement with the SANTE/11813/2017, where R% lied between 70-120 % and RSD% were below 20% for all samples.
Precision was assessed on two levels on true samples; repeatability (intraday precision) where the five replicated of the three concentration levels were analyzed on the same day, while intermediate precision (interday precision), samples were analyzed on three consecutive days. Both precision levels were expressed as (RSD%) values which were found within the acceptable range ≤ 20% in Table 4.

4. Conclusion

This work introduced two chromatographic approaches for the quantitation of TMX and PRB. Samples were extracted by QuEChERS procedure and the dissipation rates were studied for both pesticides when applied to four vegetable crops which are: cucumber, zucchini, lettuce and pepper, after open-field application. The kinetic profile was studied which fitted the first–order kinetics where k and t½ were calculated. The proper pre-harvest interval (PHI) was recommended for each crop. Validation parameters were attained for both methods including linearity, LOQ, accuracy, precision, trueness and matrix effects.

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The authors have no conflicts of interest to declare that are relevant to the content of this article.
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Fig. 1. The chemical structures for (a) Thiamethoxam and (b) Propamocarb HCl

Fig. 2. The chromatogram of analyzing thiamethoxam (a) standard (b) sample residues using GC-ECD method.
Fig. 3. Chromatogram of analyzing propamocarb HCl (a) standard (b) sample residues using HPLC-UV method.

Fig. 4. The residual values in mg/kg against time in days of thiamethoxam in cucumber, zucchini, lettuce and pepper, after open-field application.
Fig. 5. The residual values in mg/kg against time in days of propamocarb HCl in cucumber, zucchini, lettuce and pepper, after open-field application.
Table 1. Pesticide residues and loss % in field samples as a function of time of application.

| Time after application (days) | Pesticide residue (mg/kg) | Loss % | Pesticide residue (mg/kg) | Loss % | Pesticide residue (mg/kg) | Loss % | Pesticide residue (mg/kg) | Loss % |
|-------------------------------|---------------------------|--------|---------------------------|--------|---------------------------|--------|---------------------------|--------|
|                               | **Cucumber**              | **Zucchini** | **Lettuce**              |        | **Pepper**                |        | **Propamocarb HCl**      |        |
|                               | **Thiamethoxam**          |         |                           |        |                           |        |                           |        |
| 0                             | 0.28                      | 0      | 0.55                      | 0      | 9.43                      | 0      | 7.19                      | 0      |
| 1                             | 0.18                      | 35.71  | 0.22                      | 60.00  | 7.79                      | 17.35  | 4.42                      | 38.53  |
| 3                             | 0.12                      | 57.14  | 0.14                      | 74.55  | 6.16                      | 34.70  | 3.79                      | 47.27  |
| 5                             | 0.08                      | 71.43  | 0.03                      | 94.55  | 4.52                      | 52.05  | 3.55                      | 50.57  |
| 8                             | 0.05                      | 82.14  | 0.02                      | 96.36  | 3.20                      | 66.07  | 3.04                      | 57.71  |
| 11                            | 0.04                      | 85.71  | 0.01                      | 98.18  | 1.88                      | 80.09  | 1.93                      | 73.13  |
| 15                            | ND                        | ----   | ND                        | ----   | 1.23                      | 87.01  | 1.18                      | 77.75  |
|                               | **Propamocarb HCl**       |         |                           |        |                           |        |                           |        |
| 0                             | 20.12                     | 0      | 30                        | 0      | 203.93                    | 0      | 13.00                     | 0      |
| 1                             | 13.92                     | 30.40  | 20.4                      | 32.00  | 141.34                    | 30.69  | 10.00                     | 23.08  |
| 3                             | 9.50                      | 52.50  | 8.39                      | 72.03  | 108.87                    | 46.61  | 8.15                      | 37.33  |
| 5                             | 7.11                      | 64.45  | 6.50                      | 78.33  | 76.41                     | 62.53  | 6.36                      | 51.09  |
| 8                             | 6.25                      | 68.75  | 5.51                      | 81.67  | 62.43                     | 69.38  | 4.70                      | 63.88  |
| 11                            | 5.31                      | 73.50  | 3.22                      | 89.33  | 48.56                     | 76.19  | 3.00                      | 76.92  |
| 15                            | ND                        | ----   | ND                        | ----   | 34.68                     | 83.00  | 2.83                      | 78.27  |
Table 2. Parameters of first-order kinetic dissipation rate of field samples.

| Parameters                  | Thiamethoxam | Propamocarb HCl |
|-----------------------------|--------------|-----------------|
|                             | Cucumber     | Zucchini        | Lettuce | Pepper | Cucumber | Zucchini | Lettuce | Pepper |
| Slope                       | -0.0899      | -0.153          | -0.0595 | -0.0486 | -0.0436  | -0.0843  | -0.045  | -0.0444 |
| intercept                   | -0.6176      | -0.3902         | 0.9621  | 0.799   | 1.2541   | 1.4142   | 2.2022  | 1.0547  |
| Correlation coefficient “r” | 0.9741       | 0.9800          | 0.9965  | 0.9741  | 0.9728   | 0.9868   | 0.9841  | 0.9711  |
| Dissipation rate constant ‘k’ | 0.207        | 0.352           | 0.137   | 0.112   | 0.100    | 0.194    | 0.104   | 0.102   |
| Half-life $t_{\frac{1}{2}}$ | 3.35         | 1.97            | 5.06    | 6.19    | 6.90     | 3.57     | 6.69    | 6.78    |
| $t_{90}$                     | 0.51         | 0.30            | 0.77    | 0.94    | 1.05     | 0.54     | 1.01    | 1.03    |
| MRL $^c$                    | 0.5          | 0.5             | 3       | 7       | 5        | 5        | 100     | 3       |

$^a$ in days$^{-1}$

$^b$ in days.

$^c$ Maximum residue limit (in mg/kg) as listed in Codex Alimentarius.
Table 3. Validation sheet parameters for Thiamethoxam and Propamocarb HCl.

| Parameters                  | Thiamethoxam | Propamocarb HCl |
|-----------------------------|--------------|-----------------|
| Concentration range (mg/kg)| 0.01-10      | 2-200           |
| Slope                       | 3.0691       | 0.1045          |
| intercept                   | 0.5807       | 0.2655          |
| Correlation coefficient “r” | 0.9982       | 0.9972          |
| Res %                       | ±6.40        | ±2.58           |
| LOQ (mg/kg)                 | 0.01         | 0.52            |

*Res% = residual percentage

*LOQ = limit of quantitation*
Table 4. Matrix effect, Recovery, Trueness and Precision of Thiamethoxam and Propamocarb HCl in different matrices.

| Samples  | Thiamethoxam | Propamocarb HCl | Thiamethoxam | Propamocarb HCl | Thiamethoxam | Propamocarb HCl | Thiamethoxam | Propamocarb HCl |
|----------|--------------|-----------------|--------------|-----------------|--------------|-----------------|--------------|----------------|
|          | ME% | ME% | SE% | SE% | R% | RSD% | R% | RSD% | Intra-day | Inter-day | Intra-day | Inter-day |
| Cucumber | + 15.68 | + 20.36 | 12.65 | 14.98 | 92.32 | 2.36 | 92.87 | 3.69 | 6.32 | 8.99 | 10.23 | 13.87 |
| Zucchini | + 15.69 | + 13.24 | 15.85 | 18.58 | 96.52 | 2.66 | 95.85 | 2.87 | 8.44 | 12.55 | 5.62 | 9.87 |
| Lettuce  | - 11.83 | - 20.17 | 13.96 | 15.99 | 91.74 | 1.45 | 103.21 | 2.65 | 11.97 | 14.96 | 8.88 | 18.14 |
| Pepper   | + 8.56  | + 13.86 | 20.45 | 17.96 | 98.63 | 1.39 | 101.32 | 3.98 | 5.88 | 16.99 | 9.74 | 13.15 |

*ME%: Matrix effect, SE%: Standard error, R%: Recovery % and RSD%: Relative standard deviation.
Graphical Index

Dissipation Rates

Thiamethoxam

Propamocarb HCl

Pre-Harvest intervals