ORIGINAL ARTICLE

Dissipation of methomyl residues in tomato fruits, soil and water using LC-MS/MS

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Abstract

Tomato is an economically important vegetable crop which is attacked heavily by insect pests leading to reduction of yield and quality of the fruits. Field experiments were carried out to investigate the dissipation of methomyl (a common insecticide) used mainly on tomato fruits. LC-MS/MS coupled with the QuEChERS method were used for the determination of methomyl. The results showed that the recovery using matrix-matched standards ranged from 87.8 to 101.3%, with relative standard deviation of 2.5 to 7.5%. Kinetics equation, Log R = log R_0 – 0.434 Kt, was used to calculate the rate of degradation in tomato, soil and water. Residue half-life calculated using kinetic rate ranged from 1.95 to 1.63 days in tomato and soil, respectively. From the results it was concluded that tomato fruits can be safely harvested for consumption after 15 days of application based on estimated pre-harvest interval (PHI). It is advisable to re-estimate the PHI regularly owing to data from the EU and Codex.

Keywords: dissipation, LC-MS/MS, methomyl, tomato, QuEChERS

Introduction

Tomato is considered to be an important vegetable crop in Egypt in terms of market value, productivity and area coverage. Tomato is a basic component of the Egyptian diet and is consumed almost daily fresh, cooked or processed (canned product or paste). Egypt produces about seven million tons of tomato each year which represents 34% of the average area of all vegetables (Malhat *et al.* 2012). However, the productivity and quality of tomatoes are affected by the level of attack of insect pests, which results in lower yield and fruit quality (Gambacorta *et al.* 2005; Filho *et al.* 2006).

Chemical insect control using conventional insecticides is widely used by tomato farmers and producers in Egypt. Methomyl under several commercial formulations is one of the major insecticides commonly used for controlling many lepidopterous insect pests particularly, cotton leaf worm which attacks tomato and also cotton (Agricultural Pesticides Committee 2018).

However, its use in vegetable crop protection poses a serious risk to humans, as it is often used near the maturing stages of the crops (Liu *et al.* 2005; Chowdhury *et al.* 2012). For many years the determination of insecticide residues in agricultural products has been of worldwide concern due to potential detrimental impacts on human health and the environment, particularly if the produce is being consumed immediately or within a few days of harvest. Insecticide residues can also remain as environmental pollutants in the soil. They have become a matter of environmental concern because of their potentially adverse effects on flora and soil microorganisms (Araújo *et al.* 2003), and can be reflected in soil fertility (Schuster and Schröder 1990).

QuEChERS is a sample preparation method, which is quick, easy, cheap, effective, rugged and safe, introduced by Anastassiades *et al.* (2003). It involves pesticide dispersive solid phase extraction (dSPE), with primary secondary amine (PSA) sorbent. Compared

to other procedures, the QuEChERS method is very fast and cheap and therefore it is used worldwide for minimizing matrix effects in different samples (Lehotay *et al.* 2005a; Lehotay *et al.* 2005b; Hernández-Borges *et al.* 2009; Fernandez-Alvarez *et al.* 2009; Cunha *et al.* 2009; Furlani *et al.* 2011). In studies with tomato samples analyzed by the QuEChERS method, acceptable results were found for a wide range of pesticides with lower limit of detection (LOD) and limit of quantification (LOQ) values and good analytical precision (Wang *et al.* 2007; Lesueur *et al.* 2008; Kmellár *et al.* 2008; Andrade *et al.* 2011).

LC-MS/MS analysis is a powerful technique used efficiently to determine pesticides in environmental and food matrices with high sensitivity and selectivity. It is especially well-suited for the identification and quantification of polar and thermally labile pesticides down to mg · kg⁻¹ levels. Therefore, the objectives of this study were to use LC-MS/MS for the quantitative determination of methomyl residues in tomato fruits and in the soil under the plants. The pre-harvest interval (PHI), based on kinetic studies of dissipation rate, and the residue half-life were also calculated.

Materials and Methods

Standards and reagents

Methomyl reference standard was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany), with >99% purity. All other reagents and solvents were obtained from Sigma Aldrich and were LC/MS grade. A stock solution of methomyl was prepared at a concentration of 1 mg · ml⁻¹ in acetonitrile and kept in a refrigerator (0–5°C). Calibration standard and working solutions in concentrations ranging from 0.01 to 6.0 mg · kg⁻¹ were prepared by serial dilution of the stock solution.

Field trials

The experiment was conducted in April, 2018 at a farm in Meet Ghamr district, located in Dakahlyia Governorate (Egypt). The average maximum and minimum temperatures during the experiment were 30°C and 19°C, the relative humidity was 47% and there was no rainfall during the experimental period. The tomato variety Rama 888 was transplanted in an open field in double rows 1.0 m wide and 0.5 m apart in the row and grown in an area of 175 m². The experimental area was divided into three plots with a randomized complete block design with three replicates. When tomato fruits were close to ripeness, plants were sprayed with a commercial formulation of methomyl (wanet 90% SP; TrustChem Agrochemicals) as

a single application at the field recommended rate. The treatment was performed using a knapsack sprayer fitted with one nozzle boom. A separate plot was used to obtain untreated tomatoes for assessing the accuracy of the method developed for residues.

Sample processing

Samples of tomato fruits (2 kg) of the same ripening stage and size were harvested at random separately from each replicate of the treated and control plots at the following time intervals: 0 (1 hour after spraying), 1, 3, 7, 10, 15 and 21 days after insecticide application. Soon after collection, samples were put in labeled polyethylene bags and transported in an ice box to the laboratory and kept at 4°C. The tomatoes were homogenized and the homogeneous matrix was stored in a deep freezer at –20°C until further analysis. The soil texture was clay and soil parameters were: silt 10%, clay 64%, soft sand 18.9%, hard sand 5%, calcium carbonate 2%, salts 0.1% and organic matter 3.6%. Soil samples were collected 1, 3, 7 and 10 days after insecticide application. A soil probe, 1 inch diameter and 10 inches deep, was used for soil sampling with three replicates with 2 kg of soil for each replicate. After collection, samples were transported in labeled polyethylene bags in darkness at 4°C to the laboratory where they were processed. Soil samples were air-dried, placed in polyethylene bags and frozen at –20°C until analysis. Water samples were taken at the same intervals as soil from various sources e.g. the nearest irrigation and waste water canal, and the drinking water system located within the farms. The nearest water source was 250 m away. Three replicates for each interval were used. The water samples were placed in an icebox, and delivered to the laboratory within 24 h. The samples were extracted immediately when they reached the laboratory and were analyzed using LC-MS/MS.

Sample preparation

The tomato samples were prepared according to the QuEChERS method (Anastassiades *et al.* 2003). Whole samples were first chopped with a stainless-steel knife with dry ice using a Hobart Food Chopper (Model: 84181D, Serial: 11-257-552) and stored in jars at –20°C until analysis. After homogenization, a 10.0 g sample was weighed into a 50 ml centrifuge tube and extracted using 10 ml acetonitrile (ACN)/1% acetic acid. Tubes were shaken by hand for 1 min. A QuEChERS liquid extraction salt packet, containing magnesium sulfate anhydrous, sodium chloride, sodium citrate dibasic sesquihydrate and sodium citrate tribasic dehydrate supplied from Interchim (USA) was added to the tube. Sample tubes were capped tightly

and shaken vigorously for 1 min by hand. Then the tubes were centrifuged at 4000 rpm for 5 min at 4°C. One ml of upper ACN layer was transferred to 1 ml Agilent dispersive tube which contained 25 mg PSA and 150 mg MgSO$_4$ for cleanup. The tubes were capped and vortexed for 1 min, then centrifuged at 4000 rpm for 5 min at 4°C. The supernatants were transferred to a clean vial after being filtered through a 0.22 μm Polytetrafluoroethylene (PTFE) filter (Millipore, Billerica, MA). The samples were directly injected into the LC system for analysis (Fu and Zhai 2013). Fortified samples were prepared by adding different standard solution concentrations to 10 g of control samples of tomato, soil and 10 ml of water samples resulting in the levels of 0.01 to 6.0 mg · kg⁻¹ for tomato samples, and 0.1 to 2.0 mg · kg⁻¹ for soil and water samples. The fortified samples were left for 30 min at room temperature to allow the pesticide to penetrate into the matrix before extraction. Each fortification level was analyzed through six replicates.

Analytical instrumentation and conditions

An aliquot of the sample extract was chromatographed on a C18 column using gradient elution at 1 ml · min⁻¹ flow. An electro spray ionization probe (ESI) source was used in the positive mode, with nitrogen as nebulizer curtain gas. Other gas settings were optimized according to recommendations made by the manufacturer; source temperature was 400°C, ion spray potential was 5,500 V, de-cluster potential and collision energy were optimized using a Harvard apparatus syringe pump by introducing the pesticide solution into the MS instrument to allow optimization of the MS/MS conditions. LC-MS/MS System 6500 QTRAP, Applied Biosystem equipped with Ekspert UPLC system was used. The column was Phenomenex Analytical HPLC column Luna® with 3 μm C18 100 Å, LC, column 50 × 2 mm (internal diameter) and the column temperature was 40°C. Mobile phase A (2 mM ammonium formate in water), and Mobile phase B (methanol) were used. Injection volume was 2 μl, auto sampler temperature was 4°C, source temperature was 400°C, ion spray potential was 5,500 V, and the mode electron spray ionization was positive mode.

Method validation

The recovery experiment was carried out on fresh untreated tomatoes, soil and water by fortifying the samples with methomyl standards at five levels ranging from 0.01 to 6.0 mg · kg⁻¹ for fruit samples and from 0.1 to 2.0 mg · kg⁻¹ for soil samples. The fortified samples were analyzed in six replicates, with two injections for each replicate. The fortified samples were processed and analyzed as previously described to evaluate the accuracy and the precision of the method. Blank samples were analyzed under the same chromatographic conditions. Recovery percentage was calculated by the following equation:

% Recovery = [(μg) found/(μg) added] × 100.

The correlation coefficient was calculated for residues in tomato fruits, soil and water. Linearity was studied by creating calibration curves using standard solutions. The range of concentration was from 0.01 to 6.0 mg · kg⁻¹ and two injections were made for each of the five concentration levels. Accuracy was calculated as the percentage between the found and the known concentrations and precision was determined as the relative standard deviation (% *RSD*), which is the ratio between standard deviation and average concentration obtained. Relative standard deviation was calculated as follows:

$$\% \ RSD \ = \ S \ \times \ 100/\overline{x},$$

where: *RSD* % – relative standard deviation, *S* – standard deviation, $\overline{x}$ – mean of found concentration in n samples.

The precision and accuracy were considered adequate for validating the method according to Filho *et al.* (2006). Matrix effect (*ME*) was evaluated by comparison between both the slope of calibration curve of standard in the extract and standard in the solvent and was calculated as follows:

$$ME \ (\%) = [(S1/S2) -1] \times 100,$$

where: *S1* – the slope of matrix-enriched standard, *S2* – the slope of matrix-free standard in solvent.

Negative values of matrix effects signify suppression of the signal, and positive values signify enhancement. For better understanding of the results, the values were categorized into three groups: (i) soft matrix effect ≤20%, (ii) medium ≥20 and ≤50%, and (iii) strong ≥50%. Values <20% indicated no *ME* or its insignificance, and values >20% were considered as a high *ME* (Łozowicka *et al.* 2017).

LOD for methomyl was calculated as the minimum level at which the analyse can be reliably detected and LOQ is set by determining the analyse at different detectable concentrations based on SANTE (2017).

Residue calculations

The residues were calculated by the following equation (Möllhoff 1975):

$$\text{ppm } [\text{mg} \cdot \text{kg}^{-1}] \ = \ \frac{Ps \times B \times V}{Pst \times G \times C} \times F,$$

where: *F* (recovery factor) – 100/*R*, *R* – average of recovery, *Ps* – sample peak area, *B* – amount of standard injected (ng), *V* – final volume of sample solution (ml), *Pst* – standard peak area, *G* – sample weight (g), *C* – amount of sample injected (μl).

Kinetic studies

The degradation rate was calculated mathematically according to Timme *et al.* (1980), following the first-order kinetic using common logarithms as in the following equation:

$$\text{Log } R = \log R_0 - 0.434 \, Kt,$$

where: R_0 – residue level at the initial time (zero time), *R* – residue level at interval (days) after application, *Kt* – degradation rate constant at the successive intervals in days.

Residue half-life value (RL_{50}) was calculated mathematically according to Moye *et al.* (1987) from the following equation:

$$RL_{50} = \text{Ln}2/K = 0.6932/K.$$

Statistical analysis

The analytical determinations were made in three replicates for each sampling. Mean values and standard deviations were calculated and analyzed by Microsoft Excel Program. All other calculations were made using the above-mentioned equations.

Results and Discussion

Validation study

Recovery was carried out on untreated samples that were spiked with methomyl at five levels for tomato fruits and four levels for soil and water samples in six replicates. The method trueness and precision parameters in terms of average recovery and relative standard deviation were calculated and measured according to the European Union guidelines (SANTE 2017). The percentage recovery of methomyl from the fortified tomato samples is presented in Table 1. Data showed that the average recovery percent ranged from 87.8 to 101.3% with %RSD ranging from 2.5 to 7.5%. Recovery rate from soil was in the range of 81–94.2% with %RSD of 3.68–8.50%. The recovery percentage from water ranged from 82.61 to 103.27% with %RSD from 4.50 to 9.17% (Table 2). The recovery and the RSD for tomato fruits, soil and water were within the acceptable limits for routine analysis of methomyl residues

Table 1. Recovery percentages of methomyl in tomato fruits

Fortification level [mg · kg⁻¹] n = 6	% Recovery	% *RSD*
6.0	101.33 ± 2.59	2.56
3.0	95.97 ± 4.30	4.49
1.0	91.47 ± 6.91	7.55
0.1	89.80 ± 5.04	5.61
0.01	87.83 ± 3.27	3.73

n – number of replicates
RSD – relative standard deviation

Table 2. Recovery percentages of methomyl in soil and water

Fortified levels [mg · kg⁻¹] n = 6	Soil Rec.% ± SD	% *RSD*	Water Rec.% ± SD	% *RSD*
2	94.27 ± 3.47	3.68	103.27 ± .65	4.50
1	89.34 ± 7.64	8.55	93.14 ± 6.74	7.24
0.5	85.31 ± 6.40	7.50	90.51 ± 8.30	9.17
0.1	81.01 ± 6.21	7.67	82.61 ± 5.16	6.21

n – number of replicates
RSD – relative standard deviation

leading to high precision. Data indicated that the recovery from the tomato and water samples was slightly higher than that from the soil. Methomyl showed linearity in the concentration range used when analyzed in the pure solvent matrix extract with determination coefficient (R^2) higher than 0.99, showing better analytical sensitivity and accuracy. The detection and quantification limit were calculated considering the matrix match calibration slope. The LOD and LOQ for methomyl were 0.01 and 0.03 mg · kg⁻¹, respectively, indicating good analytical precision. Regarding matrix effect, the relative responses were −16.60 and −18.53 for tomatoes and soil, respectively. It can be concluded that the matrix did not-significantly suppress or enhance the response of the instrument. These results showed that there was no interfering endogenous peak and good performance of analysis was also achieved, indicating that this method meets the criteria of the European Union. Hence, this method can be used for routine residue analysis of methomyl in tomato, soil and water matrices.

Dissipation of methomyl residues in tomato fruits

Mean residue levels of methomyl detected in tomato fruits at different time intervals are presented in Table 3. Data showed that residues of methomyl, applied at the recommended rate, after 1 hour of application

Table 3. Methomyl residues in tomato fruits and soil after treatment

Days after treatment	Tomatoes			Soil		
	residue* ± SD [mg · kg⁻¹]	% dissipation	% *RSD*	residue ± SD [mg · kg⁻¹]	% dissipation	% *RSD*
Initial	2.06 ± 0.08	0	3.92	0.77 ± 0.10	0	13.49
1	1.92 ± 0.11	7.11	6.18	0.42 ± 0.05	45.88	13.21
3	0.85 ± 0.05	58.64	5.54	0.33 ± 0.01	56.27	4.53
7	0.21 ± 0.01	89.82	4.76	0.11 ± 0.01	84.84	13.09
10	0.07 ± 0.01	96.41	12.50	NT	–	–
15	0.009 ± 0.003	99.58	6.66	NT	–	–
21	0.003 ± 0.001	99.84	7.95	NT	–	–
MRL	0.01 mg · kg⁻¹			NA		
PHI	15 days (recommended)			NA		

*average of three replicates, NT – not taken, NA – not applicable, *RSD* – relative standard deviation,
SD – standard deviation of 3 replicates

were 2.1 mg · kg⁻¹. The insecticide dissipated rapidly 3 days after application to reach almost a loss of 59%. Twenty-one days after spraying, the residue amount declined by 99.8%. The decomposition rate of methomyl in tomato is presented in Table 4. The coefficient of determination (R^2) resulted >0.98 indicating a high level of fitting. The first-order kinetic parameter calculated showed that the degradation rate of methomyl (K) was 0.36. Results also revealed that the RL_{50} of methomyl in tomato fruits was almost 2 days and the estimated pre-harvest interval (PHI) was 15 days. The maximum residue limit (MRL) of methomyl residues was 0.01 mg · kg⁻¹ according to European Union 2016. Major factors influence insecticide dissipation in the environment such as: physicochemical properties, the frequency and amount of insecticide used, mode of application, occurrence of insect pests, biotic and abiotic characteristics of the environment and weather conditions, as well as tomato characteristics, e.g. roughness and content of cuticular waxes (Romeh and Mekky 2009; Andrade *et al.* 2011). Studies indicated that tomato treated with methomyl should remain in the field about 15 days before harvesting in order to be consumed and marketed safely for human consumption. These results are in agreement with Malhat *et al.* (2015) who calculated residue half-life of methomyl in tomato fruits as 1.34 days. Since methomyl has a systemic action, it can migrate inside the cuticle of the

tomatoes and it may create different bonds with the inner media compounds of tomatoes (Rasolonjatovo *et al.* 2017). However, higher growth rates of tomato fruits that dilute the insecticide play a significant role in the degradation rate of methomyl (Walgenbach *et al.* 1991; Bisen and Ghosh2000; Khay *et al.* 2008; Malhat 2013). In addition, the residues of methomyl in soybean pods were decreased after direct exposure to sunlight and UV radiation (Massoud *et al.* 2014). Data obtained are also consistent with those found by Ramadan *et al.* (2015), who reported that tomato fruits could be safely consumed after 15 days of application of chlorpyrifos, a conventional insecticide belonging to a similar group of insecticides applied at the recommended rate. In contrast to our findings, PHI of carbaryl (another carbamate insecticide) in tomato under greenhouse conditions was 21 days (Kinyunzu 2015) which is longer than the estimated value in our work. In greenhouses, the diverse weather conditions and different agroecosystem may alter the degradation profile of an insecticide and also the growth pattern of tomato.

Decline rate in soil under the plants

Residues of methomyl in contaminated soil under the treated plants decreased with the sampling time (Table 3). The initial deposit was lower than that in fruits with a value of 0.77 mg · kg⁻¹. The rate of disappearance gradually decreased on all sampling dates to present no detectable limit after 10 days post application. The residue half-life time of methomyl calculated in soil was 1.63 days, indicating that the insecticide remains for a relatively shorter time in the soil compared with that in plants. This result was confirmed by calculating the degradation rate (K) as it was 0.42 (Table 5). This agrees with Malhat *et al.* (2015) who also found that the

Table 4. Decomposition rate (*K*) and half-life (*RL*₅₀) of methomyl in tomato fruits

Regression equation	$y = 0.144x + 0.3413$
Regression coefficient (R^2)	0.9884
K	0.36
*RL*₅₀ (Days)	1.95

Table 5. Decomposition rate (K) and half-life (RL_{50}) of methomyl in soil

Regression equation	$y = 0.1157x - 0.1342$
Regression coefficient (R^2)	0.9266
K	0.42
RL_{50} (Days)	1.63

half-life of methomyl in soil was 1.8 days. Methomyl has fairly low persistence in the soil environment due to its high solubility in water, and low affinity for binding to soil (Howard 1991). It is also rapidly degraded by soil microbes and its residues are not expected to be found in treated soil after the growing season in which it is applied (Howard 1991). On the contrary, carbaryl remained longer in three different soils from Kenya as the dissipation half-life ranged from 5.29 to 7.19 days (Kinyunzu 2015). This could be attributed to different soil pH, soil organic matter, soil moisture, rate of application, environmental and growth conditions in the greenhouse used in his study. The loss of insecticide in the soil in an open field happens relatively more rapidly due to volatilization which occurs within a few days after application. Also there is quick chemical and biological degradation, run-off and leaching (Spynu 1989; Fang and Qiu 2002; Malhat and Hassan 2011).

Conclusions

This study validates a method for the dissipation of methomyl in tomato using LC-MS/MS. This technique has recently become more popular for the quantitative determination of pesticides. It offers several advantages such as improved higher sensitivity, accuracy, precision, better selectivity, standard applicability and very low analytical interference. From our findings, it can be concluded that residue levels of methomyl in tomato were in the safe limits for human consumption when applied at the recommended rate. Furthermore, allowing 15 days from application to harvest was adequate for keeping the methomyl residues below the current MRL. Since farmers do not usually consider the prescribed safety period before harvesting the fruit particularly at the fruiting stage, efforts should be made to educate both farmers and consumers as to the health implications. Thus, selective use of insecticides mainly at the fruiting stage and ensuring the safe waiting period would lead to the disappearance of pesticide residues from consumable vegetables to levels lower than that of acceptable MRL. This study is a step towards rationalization of tomato protection against insect pests under field conditions. The results can be used when designing future control programs

and taking preventive actions to minimize human health risks. The monitoring of these programs should be conducted to ensure safe dietary components. It is noteworthy that the correlation between PHI and MRL values could be changed according to data from the EU and Codex (data not shown). Data revealed that PHI of methomyl in tomatoes was 7 days in 2008 when MRL was 0.2 mg · kg⁻¹, then increased to 15 days in 2009, 2010 and 2016 when MRL changed to 0.02 and 0.01 mg · kg⁻¹, respectively. These data indicate that MRL decreased 20 times during 8 years, while the PHI value increased only eight times. The MRL value in 2009 was 1 mg · kg⁻¹ according to Codex, however, the estimated PHI value was only 3 days. Consequently, it is advisable to re-estimate and update PHI values recorded for each pesticide on each crop and for each pest in order to ensure human food safety.

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