Dissipation of Fungicides, Insecticides, and Acaricide in Tomato Using HPLC-DAD and QuEChERS Methodology

Sherif Hussein Abd Al-Rahman · Monir M. Almaz · Nevin S. Ahmed

Abstract Excessive use of pesticides in tomato cultivation could lead to impact on environment and health. Here, dissipation rate of six widely used pesticides in growing tomatoes, namely, chlorothalonil, pymetrozine, metalaxyl-m, metalaxyl, abamectin, and propamocarb hydrochloride, was evaluated. Tomato samples were collected within 2 weeks after pesticides application, and the pesticide residues extracted by an optimized QuEChERS method and quantified by high-performance liquid chromatography combined with diode array detection. The half-life of these pesticides was found to be 2.06, 1.65, 19.8, 4.88, 1.06, and 1.29 days for chlorothalonil, pymetrozine, metalaxyl-m, metalaxyl, abamectin, and propamocarb hydrochloride, respectively. Preharvest intervals (PHI) for these pesticides ranged from 3 to 9 days, with the longest being for metalaxyl (9 days), followed by chlorothalonil and abamectin (6 days). Pymetrozine metalaxyl-m, and propamocarb hydrochloride had PHIs of 3, 4, and 4 days, respectively. Due to the immediate consumption of the tomatoes after harvest, the persistence of metalaxyl, chlorothalonil, and abamectin in the environment is expected to have an adverse health effect.

Keywords Pesticides · Dissipation · QuEChERS · Preharvest interval · Tomato

Introduction

Pesticides play an inevitable role in modern agriculture. Rising concern about food safety and environmental impact

S. H. Abd Al-Rahman (✉) · M. M. Almaz · N. S. Ahmed
Pesticides Residues and Environmental Pollution Department,
Central Agricultural Pesticide Laboratory, Agricultural Research
Center,
Giza 12618, Egypt
e-mail: drsherif_hussein@yahoo.com

has led to increasing number of studies on the impact of pesticide residues in agricultural products consumed by humans (Cun-Zheng Zhang et al. 2010; Mestres 1988; Rozemeijer and Broers 2007).

Tomatoes are cultivated over a large area in Egypt. This important dietary component is used fresh or processed and canned for later use. (El Nabarawy et al. 1992).The cultivation of tomatoes demands frequent application of a large number of pesticides, and >100 pesticides have been recommended for use in Egypt to control a variety of pests and diseases (APC 2010).

Agricultural committees are required by law to safeguard the interests of consumers, and hence, regulations have been formed and stringently implemented to eliminate harmful pesticide residues in foods. The management of pesticide residues in tomatoes is challenging because of direct application of pesticides over fruits, pesticides accumulated in the soil and absorbed through the roots, and drifting pesticides from adjoining fields of other agricultural crops. The intensive use of pesticides on tomato crop may cause accumulation of pesticide residues more than the permitted levels and hence needs frequent field evaluations. Accurate measurements of dissipation or degradation rates of various pesticides under field conditions will be helpful in their optimal application (Fenoll et al. 2009; Omirou et al. 2009)

The dissipation/degradation of various pesticide compounds after their application depends on various factors, including plant species, chemical formulation, and mode of application (Cabras et al. 1989; Ebert et al. 1999; Womac et al. 1994), climatic conditions, physical phenomena (mainly volatilization), and photodegradation, in which sunlight plays a prominent role (Garau et al. 2002; Minelli et al. 1996; Papadopoulos et al. 1995). Therefore, dissipation studies for a given crop under the open field conditions of each growing area are necessary to test if the pesticide residue levels soon after the preharvest interval (PHI) are

below the maximum residue limit (MRL). PHI, which is defined as the period between the last pesticide application and harvesting the crop, after which the pesticide residue level is expected to be below the established maximum residue level (MRL), is one of the important pesticide registration requirements in Egypt.

The QuEChERS (quick, easy, cheap, effective, rugged, and safe) method is well known for its applicability in simultaneous analysis of a large number of pesticides in a variety of food matrices (Anastassiades et al. 2003; Lehotay et al. 2005). The method has received worldwide acceptance because of its simplicity and high throughput, enabling a laboratory to process significantly larger number of samples in a given time as compared to the earlier methods (AOAC 2000; Luke et al. 1975). Recently, the QuEChERS method has received the distinction as an AOAC official method for measuring multiple pesticide residues in fruits and vegetables (Lehotay 2007).

The objectives of this study were to: (a) determine the residue levels of six most commonly used pesticides in tomato cultivation in Egypt, (b) define the individual pesticide residue behavior in tomatoes using dissipation curves, and (c) determine the preharvest interval for each of these pesticides which may be suggested as a registration requirement. For this purpose, the QuEChERS method has been applied prior to high-performance chromatography (HPLC connected with photodiode array detector (DAD)).

Material and Methods

Plant Material

Pesticide residues of metalaxyl, abamectin, and propamocarb hydrochloride were studied in 200 m² of open field, on tomato (*Solanum lycopersicum*) planted in January 2008, and pymetrozine, chlorothalonil, and metalaxyl-m were studied on tomato planted in July 2008, in certain governorates of Egypt.

Chemicals

Reference standards of all pesticides were of >98% purity and obtained from Central Agricultural Pesticides Laboratory (Egypt). Stock solutions of pesticides were prepared in acetonitrile and stored at −18 °C. All HPLC grade organic solvents, methanol, and acetonitrile were purchased from Sigma (Sigma GmbH, Germany). Primary secondary amine (PSA, 40 μm Bondesil) sorbent was purchased from Supelco (Supelco, Bellefonte, USA). Sodium acetate and anhydrous magnesium sulfate were of analytical reagent grade and purchased from Merck Ltd. These were activated by heating at 150 °C overnight and kept in desiccators.

Field Trial

For the field experiment, a random block scheme was used with three replications for each test. Pesticide treatments were carried out with a backpack motorized sprayer with an adjustable nozzle size of 1 mm. The following commercial formulations were used: Chess (50% of pymetrozine), Folio Gold (50% of chlorothalonil and 37.5% of metalaxyl-M), Ridomil Gold (537.5 metalaxyl-M), Previcure-N (72.2% of propamocarb hydrochloride), Vacomil plus (20% of metalaxyl and 50% of copper), and Vapcomic (1.8% abamectin); characteristics and details about the commercial formulations, the doses employed, a.i., and MRL are summarized in Table 1. The applications were carried out on January 9th and July 4th, 2008, respectively, at doses prescribed by the manufacturers. The relative humidity during the application period of January and July was 67.1% and 58.5%, and temperatures were 35.5 °C and 20.1 °C, respectively. Before application, samples of tomato of similar ripening stage, size, and shape were located and tagged. Samples,

Table 1 General characteristics of investigated pesticides

Pesticide name	Trade name	Formulation Type	Registration number	Main use	Rate of application	Toxicity class	LD$_{50}$ (Oral:Rat) (mg/kg)	Tomato MRL (ppm)	Ref.
Abamectin	Vabcomic	EC 1.8%	584	Acaricide	40 ml/100 L	High 1b	1.5	0.02	Codex
Chlorothalonil	Folio Gold	SC 537.5 (50%)	—[a]	Fungicide	300 ml/100 L	class C	>5000	5.00	Codex
Metalaxyl	Vacomil plus	WP 50% (35%)	1,001	Fungicide	150 g/100 L	Low III	669	0.50	Codex
Metalaxyl -M	Folio Gold	SC 537.5 (3.75%)	—[a]	Fungicide	300 ml/100 L	M o d II	2084	0.50	Codex
Propamocarb hydrochloride	Previcur-N	SL 72.2%	270	Fungicide	250 ml/100 L	Low III	3050 1.00	1.00	Codex
Pymetrozine	Chess	WG 50%	1,235	Insecticide	240 g/Fed.	Low III	5820	0.50	Switzerland

[a] Under registration

1 kg, were collected 1 h after application at intervals of 1, 2, 3, 5, 7, 9, 12, and 15 days. During the experiment, a control sample was also collected after each sampling time interval. Immediately after collecting the tomatoes, all samples were put into plastic bags, transported to the laboratory, and homogenized using a food processor (Thermomix, Vorwerk). The homogenate of each sample was then placed into 50-ml polypropylene centrifuge tubes and frozen at −20 °C until further analysis.

Sample Preparation

The entire sample (1 kg) of tomatoes was chopped and homogenized for 5 min at high speed in a laboratory homogenizer and extracted according to the procedure described and modified by Lehotay (Lehotay et al. 2010). 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; the screw cap was 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 were added, then extract by shaking vigorously on vortex for 2 min and centrifuged 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-μm PTFE filter (Millipore, USA) and then analyzed by Agilent 1100 HPLC-DAD.

Apparatus and Chromatographic Analysis

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, flow rate, and detection wavelength of each pesticide are mentioned in Table 2. Data analysis was performed using Chemistation software.

Statistical Analysis

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

Results and Discussion

Analytical Performance

The analytical method was validated as per the single laboratory validation approach (Thompson et al. 2002). The performance of the method was evaluated considering different validation parameters that include the following items: the calibration curves of all of the compounds in pure solvent, and matrix were obtained by plotting the peak area against the concentration of the corresponding calibration standards at seven calibration levels ranging between 10 and 200 μg kg^{-1}.

The limits of detection (LOD) were set to a signal-to-noise ratio of 3 with reference to the background noise obtained from blank sample, whereas the limits of quantification (LOQ) were set to a signal-to-noise ratio of 10. The LODs and LOQs obtained from six studied pesticides are presented in Table 3. The accuracy and precision of method were evaluated via recovery experiments with fortified samples at two fortification levels, 10 and 200 μg kg^{-1}, each replicated thrice. The limits of quantification were, in all cases, lower than MRLs established by Codex Committee and Switzerland (FAO/WHO 2006a).

Table 2 Typical HPLC analysis of conditions used for investigated pesticides

Pesticide	Column type	Mobile phase	Flow rate (ml/min)	Detection	Reference
Chlorothalonil	C 18 (150×4.6 mm, 5 μm)	Acetonitrile/water 30:70 v/v	0.5	HPLC-UV 230 nm	(Lesueura et al. 2008)
Metalaxyl	C 18 (150×4.6 mm, 5 μm)	Acetonitrile/methanol/water 15:40:45 $v/v/v$	0.5	HPLC-UV 202 nm	(Lesueura et al. 2008)
Metalaxyl -M	C 18 (150×4.6 mm, 5 μm)	Acetonitrile/methanol/water 15:40:45 $v/v/v$	0.5	HPLC-UV 202 nm	(Lesueura et al. 2008)
Pymetrozine	C 18 (150×4.6 mm, 5 μm)	Acetonitrile/water 40:60 v/v	1.0	HPLC-UV 240 nm	(Lesueura et al. 2008)
Abamectin	C 18 (150×4.6 mm, 5 μm)	Acetonitrile/methanol/water 15:40:45 $v/v/v$	1.0	HPLC-UV240 nm	(Diserens and Henzelin 1999)
Propamocarb hydrochloride	C 18 (150×4.6 mm, 5 μm)	Methanol/water 30:70 v/v	0.75	HPLC-UV 260 nm	(Lehotay et al. 2005)

Accuracy and Recovery Experiments

Tomatoes obtained from the untreated area (which did not receive any treatment of the test pesticides) were used as blanks. Recovery experiments were carried out on fresh untreated tomatoes by fortifying the samples in three replicates of each pesticide separately at two concentration levels, 10 and 200 µg kg^{-1}. The results are reported in Table 3.

Residual Behavior of Pesticides

Degradation rate of six pesticides (chlorothalonil, pymetrozine, metalaxyl, metalaxyl-M, abamectin, and propamocarb) was studied after one application of these pesticides on tomatoes in open field trials, at the recommended doses of 300 ml/100 L, 240 g/Fed., 150 g/100 L, 200 g/100 L, 40 ml/100 L, and 250 ml/100 L for chlorothalonil, pymetrozine, metalaxyl, metalaxyl-M, abamectin, and propamocarb hydrochloride, respectively. Table 3 shows the values of the residues of all studied pesticides, maximum residues limit (MRL), half-life ($t_{1/2}$), and preharvest interval of each pesticide.

In this study, curve fitting for various pesticides was achieved by the modified coefficient of determination (r^2), and the correlation between residues and time was determined by the equation as proposed elsewhere (Timme and Frehse 1980; Timme et al. 1986). The correlation coefficient was calculated as follows:

$$r^2 = 1 - \frac{\sum_{i=1}^{n}(C_i - C_i, \text{mod})^2}{\sum_{i=1}^{n}(C_i - \overline{C})^2}$$

where C is the mean of the residue values and C_i, mod are the modified residue values calculated starting from the equation of the adjusted decline curve. By definition, $r^2 \leq 1$; and the higher this coefficient, the better the decline curve fits the data in the sense of the least squares. Briefly, the following steps were used to evaluate and describe the dissipation process in tomatoes: the linear, quadratic, and cubic curves were obtained by plotting transformed residue values versus time; the coefficient of determination (r^2), the intercept, and the slope of each one line were also determined.
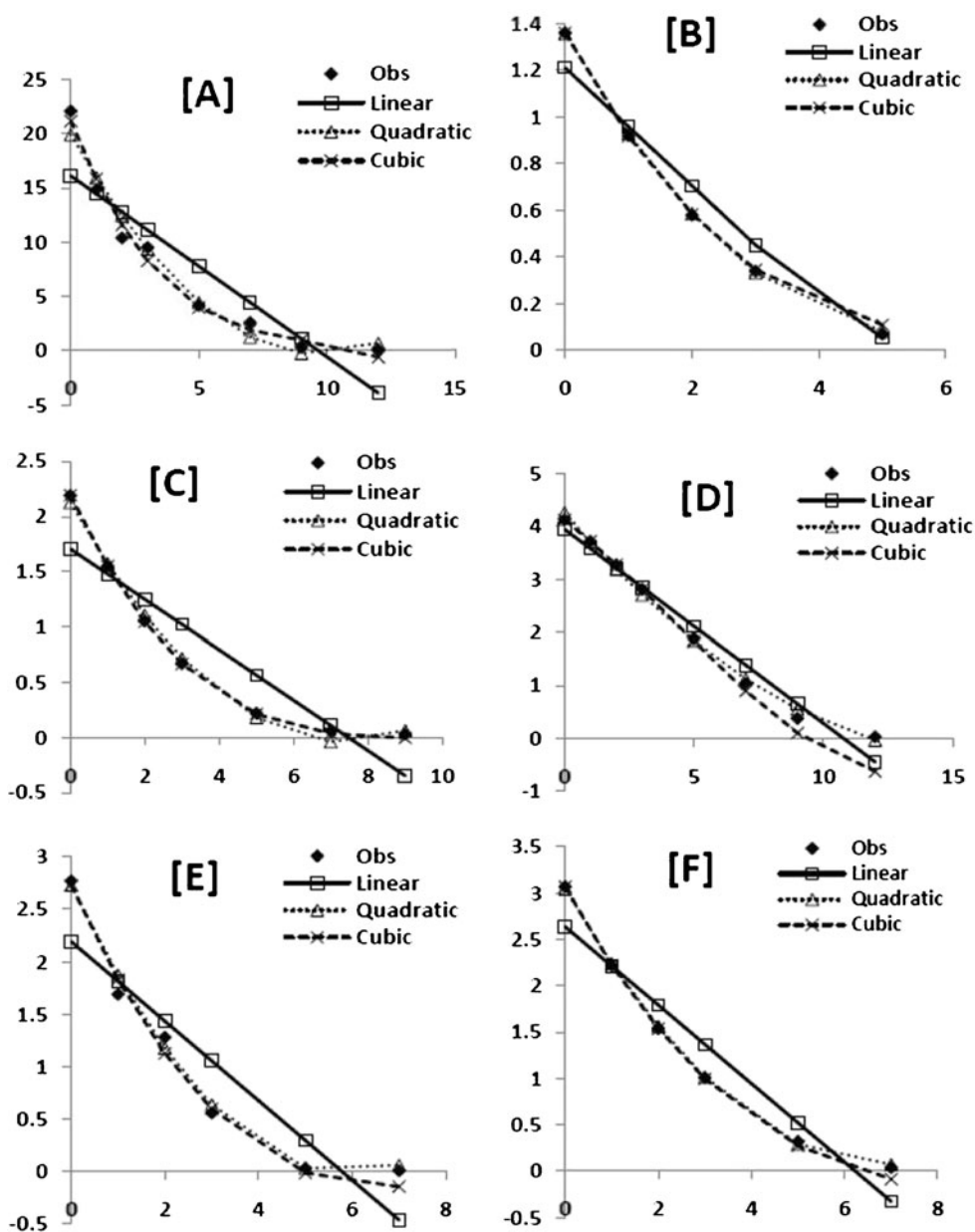
Fungicides

Tomato samples were collected during a 2-week period after the application of fungicides chlorothalonil, metalaxyl, metalaxyl-M, and propamocarb hydrochloride. The residue level of these fungicides tended to decrease with time (Fig. 1). Metalaxyl and chlorothalonil were the most stable fungicides showing first-order kinetics (r^2=0.889 and 0.954) with half-lives ($t_{1/2}$) of 4.88 and 2.06 days for metalaxyl and chlorothalonil, respectively. Residue level of these fungicides decreased with time from the initial concentration of 22.08 and 4.12 mg kg^{-1}to 0.09 and 0.03 mg kg^{-1} in 15 days. Residues of metalaxyl and chlorothalonil decreased gradually from initial concentration of 22.08 and 4.12 mg kg^{-1} to 0.09 and 0.03 mg kg^{-1} during the experiment period of 15 days. Metalaxyl-M and propamocarb hydrochloride had shorter half-lives than the other fungicides of 1.98 and 1.29 days, respectively, and showed first-order kinetics (r^2=0.991 and 0.903). Residues of these two fungicides decreased from the initial 2.13 and

Table 3 Dissipation rate of pesticides residues, mean±SD (mg kg^{-1}) detected in tomatoes under open field condition

Time (day)	Chlorothalonil	Pymetrozine	Metalaxyl-M	Metalaxyl	Abamectin	Propamocarb hydrochloride
0 (1 h)	22.08±0.042	1.36±0.029	2.19±0.034	4.12±0.044	2.77±0.023	3.07±0.042
1	14.84±0.025	0.92±0.037	1.55±0.024	3.71±0.032	1.69±0.024	2.22±0.034
2	10.39±0.031	0.58±0.026	1.05±0.024	3.27±0.041	1.28±0.021	1.54±0.034
3	9.5±0.023	0.34±0.02	0.67±0.021	2.81±0.029	0.56±0.032	1.01±0.029
5	4.16±0.033	0.07±0.009	0.22±0.021	1.88±0.018	0.03±0.011	0.32±0.023
7	2.6±0.019	nd	0.06±0.008	1.04±0.018	0.009±0.004	0.04±0.005
9	0.3±0.014		0.03±0.003	0.38±0.016	nd	nd
12	0.09±0.013		nd	0.03±0.002		
14	nd			nd		
Mean recovery %	92.6 (91.2–94.0)	88.0 (88.0–89.0)	86.3 (84.6–88.0)	92.0 (90.8–93.0)	89.0 (88.0–91.0)	84.5 (83.4–85.6)
LOD (mg/kg)	0.003	0.003	0.004	0.004	0.001	0.005
LOQ (mg/kg)	0.01	0.01	0.01	0.01	0.005	0.02
MRL (ppm)	5.0	0.5	0.5	0.5	0.02	1.0
$t_{1/2}$	2.06	1.65	1.98	4.88	1.06	1.29
PHI	6.0	3.0	4.0	9.0	6.0	4.0

LOD limit of detection, *LOQ* limit of quantification, *MRL* acceptable maximum residue limit, $t_{1/2}$ half-life period, *nd* not detected

Fig. 1 Dissipation rate of chlorothalonil (**a**), pymetrozine (**b**), metalaxyl-m (**c**), metalaxyl (**d**), abamectin (**e**), and propamocarb hydrochloride (**f**) after application on tomato using different curves

3.07 mg kg^{-1} to 0.03 and 0.02 mg kg^{-1} in 12 and 9 days, respectively (Fig. 1 and Table 3). The preharvest interval (PHI), during which the residue level was below the maximum permitted residues level (MRL), of these fungicides was 6, 9, 4 and 4 days for chlorothalonil, metalaxyl, metalaxyl-M, and propamocarb hydrochloride, respectively. Different dissipation rates and half-lives ($t_{1/2}$= 6.5 days) for chlorothalonil were obtained by Gabacorta et al. (2005), Gil Garcia et al. (1997), and Zhang et al. (2007).

Insecticides

This study included one insecticide, pymetrozine. Figure 1 shows the residual behavior and degradation rate of this compound. Pymetrozine had a short $t_{1/2}$ of 3 days. The

coefficient of regression of degradation curve was r^2=0.92. The insecticide pymetrozine had an initial deposit of 1.36 mg kg^{-1} after 1 h from the application and reached 0.07 mg kg^{-1} after 5 days. It required about 3 days for pymetrozine residue to be less than the established MRL of 0.5 mg kg^{-1}. Same trend of pymetrozine dissipation rate was reported, and that the initial residues and half-life were 1.11 mg kg^{-1} and 0.89 day, respectively (Fenoll et al. 2009; Li et al. 2011; Shen et al. 2009; White et al. 2010).

Acaricide

One acaricide, abamectin, was included in this study. The results are presented in Table 2 and show that the initial deposit of abamectin on tomatoes of *S. lycopersicum*

variety was 2.77 mg kg^{-1} which gradually decreased with time until the residue reached 0.009 mg kg^{-1} 7 days after application. This is less than the upper limit of the maximum allowed residue set by the Codex Committee on Pesticide Residues under the Joint FAO/WHO Food Standards Program at 0.02 mg kg^{-1} for fruits (FAO/WHO 2006b). Half-life ($t_{1/2}$) of abamectin was 1.06 day and the PHI was 6 days to have a residue less than MRL 0.02 mg kg^{-1}. Dissipation rate of abamectin (Fig. 1) had a coefficient of regression of r^2=0.904. A different dissipation rate was reported in cases where the initial deposit of abamectin and residues after 7 days of application were 0.09 and 0.03 mg kg^{-1}, respectively (Kamel 2007).

Conclusion

In this study, the dissipation rates of six pesticides after a single application at recommended doses on tomatoes were evaluated. We used an improved method (QuEChERS) for sample preparation. The half-life and PHI were determined for all pesticides. Different dissipation rates, ranging from 3–9 days, were seen for these pesticides. The long PHIs might lead to a higher risk of exposure to pesticides, especially that of metalaxyl, chlorothalonil, and abamectin. Further studies are required to assess the residual behavior, exposure risk, and the environmental fate of these pesticides, especially chlorothalonil, as a new fungicide.

References

Anastassiades M, Lehotay SJ et al (2003) Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. J AOAC Int 86(2):412–431

AOAC (2000) Official methods of analysis (2000) 17th edn. AOAC International, Gaithersburg

APC, Agricultural Pesticide Committee (2010) Pesticides registration. Ministry of Agriculture, Cairo, Egypt

Cabras P, Meloni M et al (1989) Pesticide residues in lettuce. 2. Influence of formulations. J Agric Food Chem 37:1405–1407

Cun-Zheng Zhang Z-YZ, Liu X-J, Jiang W, Wua Y-D (2010) Dissipation and environmental fate of herbicide H-9201 in carrot plantings under field conditions. Food Chem 119:874–879

Diserens H, Henzelin M (1999) Determination of abamectin residues in fruits and vegetables by high-performance liquid chromatography. J Chromatogr A 833:13–18

Ebert TA, Taylor RA et al (1999) Deposit structure and efficacy of pesticide application. Interactions between deposit size, toxicant concentration and deposit number. Pestic Sci 55:783–792

El Nabarawy IM, Abou-Donia MA, Amra HA (1992) Determination of profenofos and malathion residues in fresh tomatoes and paste. Egypt J Appl Sci 7(4):106–111

FAO/WHO (2006a) Joint FAO/WHO food standards program. Codex Committee on Pesticide Residues CX/PR 06/38/5, February 177

FAO/WHO (ed) (2006b) FAO/WHO, Joint FAO/WHO food standards program

Fenoll J, Ruiz E et al (2009) Dissipation rates of insecticides and fungicides in peppers grown in greenhouse and under cold storage conditions. Food Chem 113:727–732

Gambacorta G, Faccia M et al (2005) Pesticide residues in tomato grown in open field. Food Control 16:629–632

Garau VL, Angioni A et al (2002) Disappearance of azoxystrobin, cyprodinil, and fludioxonil on tomato in a greenhouse. J Agric Food Chem 50:1929–1932

Gil Garcia MD, Martinez Vidal JL et al (1997) Determination and degradation of methomyl in tomatoes and green beans grown in greenhouses. J AOAC Int 80(3):633–638

Kamel ASA-DSIMAA (2007) Degradation of the acaricides abamectin, flufenoxuron and amitraz on Saudi Arabian dates. Food Chem 100:1590–1593

Lehotay SJ (2007) Determination of pesticide residues in foods by acetonitrile extraction and partitioning with magnesium sulfate: collaborative study. J AOAC Int 90(2):485–520

Lehotay SJ, de Kok A, Hiemstra M and Van Bodegraven P (2005) Validation of a fast and easy method for the determination of residues from 229 pesticides in fruits and vegetables using gas and liquid chromatography and mass spectrometric detection. J AOAC Int 88(2):595–614

Lehotay SJ, Son KA et al (2010) Comparison of QuEChERS sample preparation methods for the analysis of pesticide residues in fruits and vegetables. J Chromatogr A 1217(16):2548–2560

Lesueura C, Knittla P, Gartnera M, Mentlerc A, Fuerhacker M (2008) Analysis of 140 pesticides from conventional farming foodstuff samples after extraction with the modified QuECheRS method. Food Control 19:906–914

Li C, Yang T et al (2011) Residues and dynamics of pymetrozine in rice field ecosystem. Chemosphere 82(6):901–904

Luke M, Froberg JE et al (1975) J Assoc Off Anal Chem 58:1020

Mestres R (1988) L_analisi dei residui tossici; il suo interesse e i suoi limiti; esempio dei residui di pesticidi. Tossicologia e sicurezza degli alimenti. Tecniche Nuove, Milan, pp 111–132

Minelli EV, Cabras P et al (1996) Persistence and metabolism of fenthion in orange fruit. J Agric Food Chem 44:936–939

Omirou M, Vryzas Z et al (2009) Dissipation rates of iprodione and thiacloprid during tomato production in greenhouse. Food Chemistry 116:499–504

Papadopoulos E, Kotopoulou A et al (1995) Dissipation of cyproconazole and quinalphos on/in grapes. Pestic Sci 45:111–116

Rozemeijer JC, Broers HP (2007) The groundwater contribution to surface water contamination in a region with intensive agricultural land use (Noord-Brabant, The Netherlands). Environ Pollut 148(3):695–706

Shen G, Hu X et al (2009) Kinetic study of the degradation of the insecticide pymetrozine in a vegetable-field ecosystem. J Hazard Mater 164(2–3):497–501

Thompson M, Ellison SL, Wood R (2002) Harmonized guidelines for singlelaboratory validation of methods of analysis. Pure Appl Chem 74(5):835–855

Timme G, Frehse H (1980) Statistical interpretation of the degradational behavior of pesticide residues I. Pflanzenschutz-Nachrichten Bayer 33:47–60

Timme G, Frehse H, Laska V (1986) Statistical interpretation and graphic representation of the degradation behavior of pesticide residues II. Pflanzenschutz-Nach. Bayer 39:187–203

White PM, Potter TL et al (2010) Fungicide dissipation and impact on metolachlor aerobic soil degradation and soil microbial dynamics. Sci Total Environ 408(6):1393–1402

Womac AR, Mulrooney JE et al (1994) Influence of oil droplet size on the transfer of bifenthrin from cotton to tobacco budworm. Pestic Sci 40:77–83

Zhang Z-Y, Liu X-J, Yu X-Y, Zhang C-Z, Hong X-Y (2007) Pesticide residues in the spring cabbage (*Brassica oleracea* l. var. *capitata*) grown in open field. Food Control 18:723–730