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Residues of Methamidofos, Malathion, and Methiocarb in Greenhouse Crops

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The diminution of methamidofos, malathion, and methiocarb in different crops grown in greenhouses has been studied, including the presence of metabolites such as malaoxon, methiocarb sulfoxide, and methiocarb sulfone. The analytical method is based on dichloromethane extraction and GC−PFPD analysis. It has been validated establishing performance parameters such as recovery rates, precision, linear ranges, and limits of detection and quantification, which are low enough for ensuring that their corresponding MLRs can be adequately quantified. Samples of treated cucumbers and peppers grown in greenhouses were collected and analyzed during a 15-day period for obtaining the diminution rates of methamidofos and malathion. The behavior of methiocarb in treated green beans and tomatoes has been studied using analysis of variance (ANOVA) as the statistical tool, for establishing the influence of crop, season, application dose, and greenhouse design.

KEYWORDS: Pesticide; residue; methamidofos; malathion; methiocarb; greenhouse

INTRODUCTION

Greenhouse production of crops requires pesticide applications. This treatment may yield accumulation of residues at levels considerably higher than those acceptable by regulations. In the European Union (EU) the legislative basis for establishing the maximum residue levels (MRLs) of pesticides that may be present in food commodities is the Directive 93/58/EEC (*1*), which is adapted by each State member (Royal Order 280; ref *2*) being subjected to the same standards.

When pesticides are properly used and adequately monitored, there is a negligible risk for the consumer's health. However, the required rates of application may vary under different agricultural and climatic conditions, from country to country, and between regions of the same country. Both economic and health reasons make pesticide control necessary.

Methamidofos and malathion are systemic organophosphorus insecticides widely used in the greenhouses of Almeria (Spain), and both are absorbed through the skin, by inhalation, and by ingestion. Methiocarb is a carbamate, which presents a low persistence and also acts as an inhibitor of acetylcholinesterase.

After application, pesticides usually degrade to oxidation products such as malaoxon or, in the case of methiocarb, the sulfoxide and sulfone metabolites. The degradation usually occurs via hydrolysis mediated by physical, chemical, and biological processes as referenced in Mulla et al. (*3*) and Bradman et al. (*4*). Hydrolysis is a likely source of malaoxon in greenhouse conditions, where light and high relative humidity oxidize the thion to oxon compounds on plant surfaces as reported by Seiber et al. (*5*).

Monitoring programs developed by several countries are concerned with the presence of pesticide residues in food; in some cases these programs are focused to ensure the application of MLRs, and in other cases they address the estimated dietary exposure of the population. Results of monitoring programs are periodically published: for example, Yess et al. (*6*) reported pesticide residues in food for a 5-year period in the frame of the Food and Drug Administration (FDA) program for monitoring pesticide residues in foods. The program focuses on residues in raw agricultural products and on table-ready foods. The number of samples monitored was close to 50,000, and, among others, malathion, methiocarb, and methamidofos were found. Similar programs show methamidofos as one of the most commonly found pesticides in agricultural commodities, either from the internal market (*7*), or from imported products (*8*). Residues of malathion were also found in vegetables from various market outlets within Laguna Province in monitoring programs carried out in the Philippines (*9*). Levels of malathion, malaoxon and methamidofos in food are also reported by Leoni et al. (*10*) from total diet studies in Italy.

Residue data from the monitoring programs can be used for the estimation of dietary intake of pesticides; in this way, the International Union of Pure and Applied Chemistry (IUPAC; *11*) reported the optimum use of available residue data in the estimation of dietary intake of pesticides. The paper includes levels of pesticide residues in food commodities that should be included in residue monitoring reports, examples, and analytical methodologies.

Concerning the analytical methods for determining malathion, methamidofos, and methiocarb in vegetables, several reviews report different extraction methods, including solvent extractions

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with ethyl acetate, acetone, ordichloromethane, the most used for routine analysis (*12*, *13*). After extraction, cleanup is usually necessary, and it is typically accomplished with different types of adsorption column chromatography or gel permeation chromatography (*14*).

The Almeria (Spain) region exports vegetable products to the rest of the world, with an annual production valued at close to one thousand million euros. The Spanish government and commercial enterprises monitor about 30,000 vegetable samples per year for pesticide residue, with methamidophos, malathion, and methiocarb residues being the most commonly found. The main goal of this paper is to provide data for supporting adequate preharvest time for greenhouse crops in order to diminish the risk of pesticide dietary intake of consumers. It reports the diminution of methamidofos and malathion in peppers and cucumbers, and the diminution of methiocarb in green beans and tomatoes, including a statistical treatment of the data obtained in order to obtain the influencing factors in diminution, such as crop, greenhouse design, season, and application dose. Residue data have been obtained with a simple and fast analytical method based on dichloromethane extraction, filtration, and concentration. The analytical method has been validated, and performance parameters have been calculated and implemented in a pesticide residues laboratory as a routine method meeting the ISO25 requirements (translated to the member States of the European Union as the European Norme EN45001) where close to 10,000 vegetable samples per year are being analyzed.

EXPERIMENTAL PROCEDURES

Chemicals. The solvents used were acetone and dichloromethane (residue analysis grade, Panreac, Barcelona, Spain). Methiocarb and its metabolites, malathion, and methamidofos standards (99% pure, pestanal quality), obtained from Riedel de Haën (Seelze, Germany), were dissolved separately in acetone (0.2 mg/mL) to obtain the primary calibration solution, from which solutions of lower concentrations were prepared by dilution with acetone or matrix extract when appropriate.

Tamaron 50 SL (methamidofos 50 w/v Bayer Hispania Comercial, Barcelona, Spain), Mesurol 50 WP (methiocarb 50% WP Bayer Hispania Comercial, Barcelona, Spain), and Malathion 90 (malathion 90% w/v Cyanamid Iberica, Madrid, Spain) were used for treating plants in the greenhouses.

Apparatus and Chromatography. The gas chromatograph used was a Varian Star 3400 CX equipped with a pulse flame photometric detector (PFPD), an autosampler, a phosphorus filter for the determination of malathion and methamidofos, and a sulfur filter for detection of methiocarb, methiocarb sulfoxide, and methiocarb sulfone. A fused silica capillary (HP-1701) column containing 14% cyanopropilsyloxane as stationary phase (30-m length, 0.25-mm internal diameter (i.d.), and 0.25 μm film thickness) was used for the separation in the GC.

GC operating conditions were the following: injector temperature, 250 °C; detector temperature, 300 °C; initial oven temperature, 90 °C, raised at 20 °C/min to 150 °C, raised at 10 °C/min to 250 °C, and then held at 250 °C for 15 min. The injection mode was splitless with 2 min splitless time.

The carrier gas was helium (0.9999 pure) at 1.5 mL/min, and hydrogen and air (laboratory grade) were used for the combustions at 13.0 and 27.0 mL/min, respectively.

PFPD Operation. The pulse of the flame in the PFPD occurs in several steps. In the first step, a mixture of air and hydrogen reaches a combustion chamber and follows two different ways: one part of the combustion gases joins with the column carrier and goes into a quartz tube, where the combustion occurs; the other part of the combustion gases circulates outside of the quartz tube through the ignition chamber where an ignitor coil is located. A flame is produced when the mixture of air and hydrogen reach the coil. This flame propagates downward through the combustion chamber and extinguishes at the bottom. During this propagation the molecules of sample contained in the flame break down into simple molecules or atoms. The resulting particles participate in reactions leading to an electronic excitation of the phosphorus and sulfur atoms (in the case that they are present in the sample), which emit light. The appropriate wavelength is selected to filter the light, then it is amplified in a photomultiplier, which covers a range of wavelengths between 300 and 900 nm. While the emission of the flame is complete in 0.3 milliseconds, the emission of P and S_2 is delayed for more time, which improves the sensitivity of the PFPD compared with that of the continuous flame photometric detector.

As the excited molecule of sulfur in the S-mode detection is S_2, the signal given is proportional to the square root of the concentration of S in the sample. The electrometer of the PFPD, through a square root function, converts the quadratic response versus concentration in a linear function.

Field Trial Design. Ten methiocarb applications were conducted in a total of six experimental greenhouses: 600 m^2 surface each, constructed of polyethylene (200 μm thickness), with a lateral window (1.3 m × 30 m) covered with a fine netting; four greenhouses had flat roofs and two had asymmetric roofs. Two of the flat-roofed greenhouses were used for the growth of tomatoes (cultivar Daniela) and the other two were used for growing green beans (cultivar Helda). The greenhouses with asymmetrical roofs were used for the growth of green beans (cultivar Helda). In all cases crops were grown in 1-m rows at 0.5 m between plants. A single application of methiocarb was performed in each greenhouse in spring and winter (in winter, methiocarb was applied only in the flat-roof greenhouses). Methiocarb applications were performed with a high-volume 2-stroke sprayer at the rate of 1000 L/ha at two doses: 1.5 and 0.75 kg of active ingredient per ha, which correspond to the normal and half dose, respectively, as recommended on the label for such crops in greenhouses.

One application of methamidofos and malathion, respectively, was conducted in winter at full dose, in two flat-roof greenhouses similar to these described above, which were used for the growth of cucumber and pepper distributed in 1-m rows at 0.5 m between plants. The application rate in both applications was 1500 L/ha at a dose rate of 0.75 and 2.7 kg/ha for methamidofos and malathion, respectively. They were applied the same day and with the same technique explained above.

In all cases, applications were conducted by persons with more than five years of experience in the field of pesticide application.

Temperature and relative humidity were monitored and registered during the experiments by using a Jules Richard model 16352.47 thermohygrographer (Argenteuil Cedex, France). Average temperatures in winter ranged from 22 °C during the daytime to 12 °C during the night, and from 30 to 16 °C, respectively, in spring. The period of light was 11 h in winter and 13.5 h in spring. Crops were drip irrigated, once per week in winter and twice per week in spring, at a rate of 400 m^3/ha.

Sampling and Storage. For each vegetable, samples were collected as stated in directive 79/700/EEC (*15*), at random, at 0, 0.5, 1, 2, 3, 4, 5, 8, and 15 days after application of methiocarb (Mesurol 50), methamidofos (Tamaron 50 SL), and malathion (Malathion 90). Each sample was chopped and divided into four subsamples (50 g) which were stored in individual polyethylene bags at −24 °C until extraction.

Extraction and Analysis. The extracting method used was similar to that described by Egea Gonzalez et al. (*16*) and Martinez Vidal et al. (*17*), and consisted of mixing (in a safe fume cupboard) 50 g of a chopped sample of tomato, cucumber, pepper, or green bean with 100 g of anhydrous sodium sulfate and 100 mL of dichloromethane. The mixture was homogenized with a Polytron mixer (model PT2100, Kinematica AG, Littan/Luzern, Switzerland) at 10000 rpm for 1 min, and then filtered through a filter paper into a 250-mL round-bottom flask, and the cake was washed twice with 20 mL of dichloromethane each time. The solvent was removed under vacuum at 40 °C in a rotatory evaporator until almost dry and then just to the point of dryness with a slight N_2 stream, after which the internal standard solution (0.5 μg of clorpyrifos) was added, and the volume was made up to 5 mL with cyclohexane, corresponding to 10 g of sample per mL of extract. This solution was injected into the GC−PFPD (1 μL).

Table 1. Calibration Data Obtained with the PFPD

analyte	RTW	detection limit (mg/kg)	determination limit (mg/kg)
methiocarb	13.20–13.30	0.005	0.016
methiocarb sulfoxide	12.32–12.49	0.007	0.023
methiocarb sulfone	11.52–11.69	0.007	0.023
methamidofos	3.20–3.31	0.001	0.003
malathion	9.07–9.19	0.0001	0.0003
chlorpyrifos	10.31–10.45		

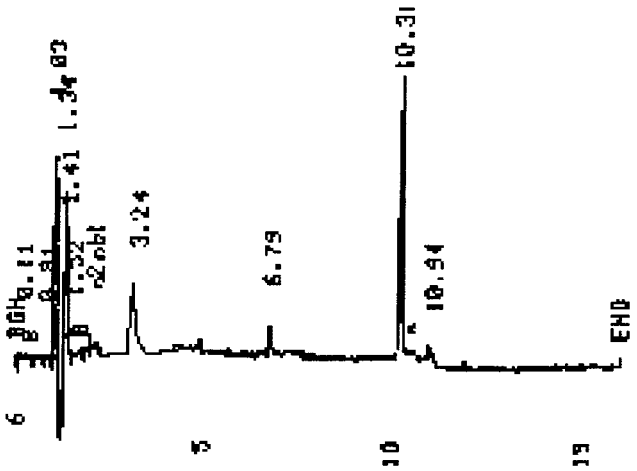

Figure 1. PFPD chromatogram of a green beans extract spiked with methamidofos at 0.050 mg/L concentration (0.005 mg/kg in sample).

Recovery Study. The recovery study was carried out by spiking with 100 μL of methiocarb, methamidofos, and malathion and metabolites standard solutions with 500 g of fresh tomato, cucumber, pepper, and green bean samples that had not been treated with the pesticides. The method was assessed at two different spiking levels: 0.005 mg/kg and 0.1 mg/kg. After evaporation of the solvent using an air stream, the sample was mixed thoroughly and homogenized for 2 min. The samples were then extracted and analyzed as explained above. The method validation was performed by extracting and analyzing 10 replicates of each recovery assay and 10 blank samples of each commodity. In addition to recovery rates, performance parameters of the analytical method were determined such as precision, lower limits, and linear ranges. All calibration solutions used in this study were prepared with pure standards dissolved in blank matrix extract of each commodity.

Analysis of samples was carried out by injecting 1 μL of the sample into the GC−PFPD and including in each batch blank samples, spiked samples, and calibration solutions.

RESULTS AND DISCUSSION

Calibration. Table 1 summarizes the retention time window (RTW) determined for methiocarb, methiocarb sulfoxide, methiocarb sulfone, methamidofos, malathion, and chlorpyrifos. The RTW is defined as the average of the retention times (10 replicates) plus or minus 3 times the standard deviation (SD) of retention time (RT). It can be seen that there is nonoverlapping of the RTWs. Chlorpyrifos was chosen as the internal standard because its characteristics are similar to those of the analytes, and because of its good response in the PFPD detector (either using the P mode or the S mode), with a high repeatability of its chromatographic signal and retention time. **Figure 1** is a chromatogram corresponding to a spiked sample containing 0.005 mg/kg of methamidofos (050 mg/L in the sample extract).

Method Validation. The extraction procedure described above was efficient for extracting the analytes from each commodity (**Table 2**). Recovery rates obtained for the analytes ranged between 87.4% and 105.3% at the high spiking level, with the lowest values being those obtained with methiocarb from tomato (87.4%), methiocarb sulfone from cucumber and pepper (87.6 and 88.7% respectively), and methiocarb sulfoxide from pepper (89.4%). The highest recovery rates were obtained with malathion, which ranged between 100 and 105.3%. The RSDs of recovery rates ($n = 10$) were lower than 10.2% in all cases. The percent recoveries found at the low spiking level were similar to those above, but the RSDs of the measures increased, being in the range of 8−14.2% (malathion and methamidofos, respectively).

Table 2. Recovery Percentages

	% recovery (%RSD)			
analyte	pepper	cucumber	tomato	green bean
methiocarb			87.4 (10.1)	96.1 (8.7)
methiocarb sulfoxide			92.1 (6.4)	91.3 (7.4)
methiocarb sulfone			90.7 (6.4)	91.2 (5.4)
methamidofos	91.2 (8.2)	92.6 (7.6)		
malathion	101.3 (6.4)	100.2 (6.2)		

Detection and quantification limits were calculated as 3- and 10-fold the RSD of the baseline of 10 blank samples' chromatograms and the slope of the calibration plots at low concentration range (*18*, *19*). LOQs obtained were low enough for determining the pesticide residues at the concentration levels stated in the MRLs.

Linear ranges were studied by calculating the response factors of the analytes in the concentration of LOQ and 100 LOQ founding RSDs of the response factors lower than 18%. Calibration plots were established using internal standard calibration and correlation coefficients found were higher than 0.97 in all cases.

Quality Control Procedure. A quality control procedure was established for ensuring that the results obtained were under statistical control. This procedure consisted of incorporating into each batch of samples an uncontaminated matrix extract of each commodity, a matrix-matching calibration plot of each commodity, and three spiked samples at 0.05 mg/kg concentration. A sample control was also incorporated to test whether any pesticide or sample degradation occurred during storage.

Results were considered when the analysis of uncontaminated matrix extracts showed that neither contamination nor degradation of sample had occurred, the recovery rates of spiked samples and the control sample were between 70 and 120%, and the calibration plots fit to lines with correlation coefficients higher than 0.95.

Diminution of Pesticide Residues Levels with Time. The highest residue levels were found in the samples taken just after the pesticide applications, and ranged between 5.2 and 5.8 mg/kg for malathion in cucumbers and peppers, respectively, and between 3.6 and 4.2 mg/kg in the case of methamidofos (**Figures 2** and **3**, respectively). For methiocarb (**Figures 4** and **5**), the highest level was found in tomatoes treated in winter at full dose in the flat-roof greenhouse (2.6 mg/kg). Metabolites of methiocarb were found in several samples at low concentration. In winter, methiocarb sulfoxide was detected in the samples taken between the second and eighth day after the application, withthe maximum concentration found in the samples taken the fourth and fifth day after the application (0.092 and 0.089 mg/kg, respectively). Methiocarb sulfone is detected later than the sulfoxide and at concentration levels lower than 0.052 mg/kg.

In spring the degradation of methiocarb seems faster as both metabolites are found in samples taken the first day after the

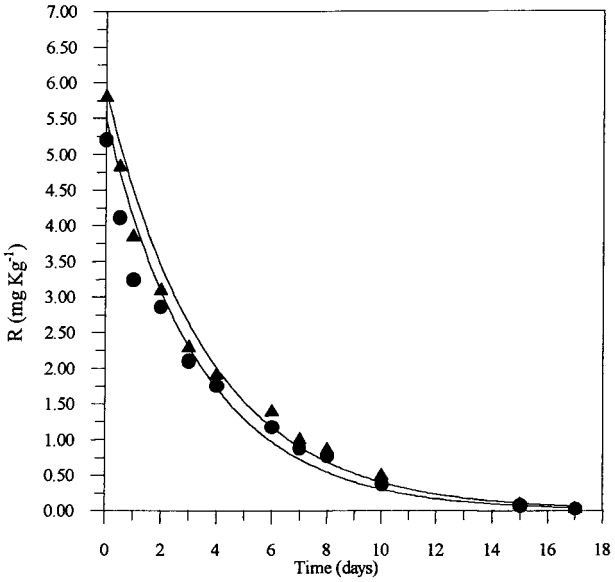

Figure 2. Diminution of malathion in cucumber (●) and pepper (▲).

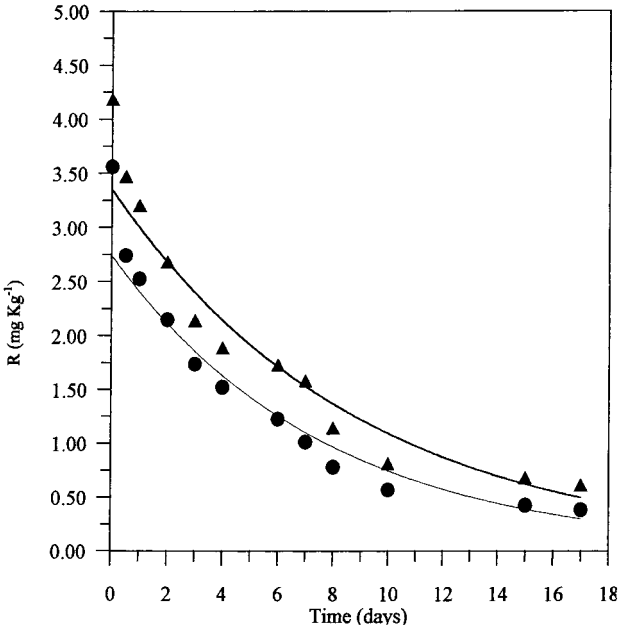

Figure 3. Diminution of methamidofos in cucumber (●) and pepper (▲).

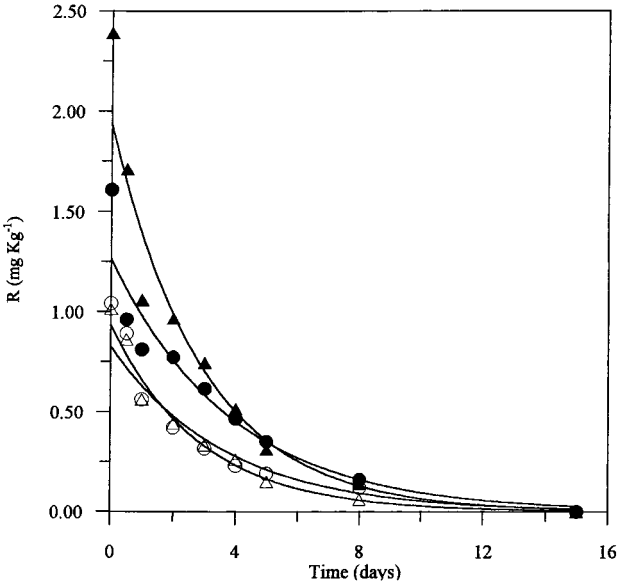

Figure 4. Diminution of methiocarb in tomatoes. Spring-half dose (△), spring-full dose (▲), winter-half dose (○), and winter-full dose (●).

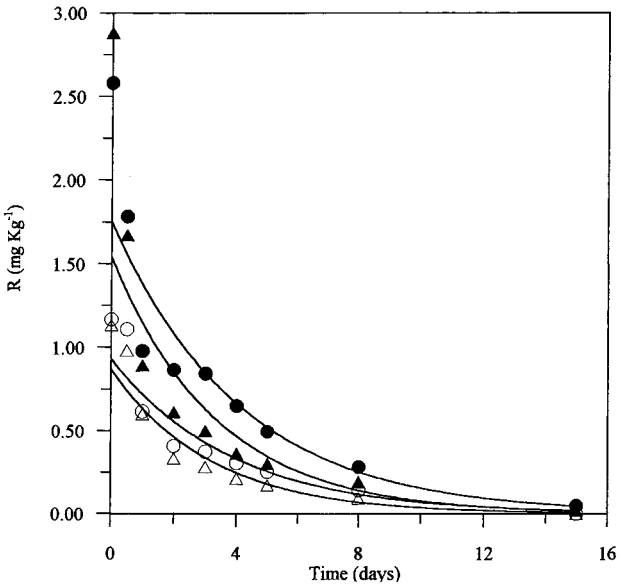

Figure 5. Diminution of methiocarb in green beans. Spring-half dose (△), spring-full dose (▲), winter-half dose (○) and winter-full dose (●).

applications, finding concentration levels similar to those found in winter. Traces of malaoxon (around 0.01 mg/kg) were found in samples taken the second day after applications.

Statistical interpretation of the loss of pesticides in the experimental plots was performed by assuming that the diminution rate of the residues can be described as a pseudo-first-order dissipation according to the aquation $R = R_0\ e^{-kt}$ and can be quantified by a linear semilogarithmic regression analysis, $\ln R = \ln R_0 - kt$, where R is the residue level at t days after pesticide application, R_0 is the residue level at time $t = 0$, and k is the loss rate constant. Their loss parameters are shown in **Tables 3**, **4**, and **5**, respectively. The half-life ($t_{1/2}$) reported in each case corresponds to the average of three $t_{1/2}$ values obtained from the analysis of the samples (three replicates) taken in each field task; the relative standard deviation of $t_{1/2}$ was less than 5% in all cases. In the case of methiocarb, $t_{1/2}$ ranged between 2 and 2.7 days for tomatoes, and between 1.9 and 2.9 days for green beans; in the case of methamidofos, $t_{1/2}$ in peppers was 6.2 days, and was 5.3 days in cucumbers. The half-life ($t_{1/2}$) of malathion in cucumbers is 2.4 days, and in peppers is 2.6 days. Results for the tenth-life ($t_{1/10}$) period of methiocarb were between 6.6 and 9.0 days for tomatoes and between 6.4 and 9.5 days for green beans. In the case of methamidofos, $t_{1/10}$ results were 17.7 days in cucumbers and 20.6 days in peppers; and $t_{1/10}$ results for malathion were 8.0 days in cucumbers and 8.6 days in peppers.

ANOVA was carried out to study the influence on the diminution of methiocarb with the following factors: species grown (tomatoes or green beans), season (spring or winter), doses (full or half), and type of greenhouse (flat or asymmetrical roof), by using the $t_{1/2}$ values obtained in each case (Statgraphics Reference Manual, 1995).

A multiple ANOVA was applied, and the results indicated that the factors species grown, season, and kind of greenhouse have an influence on the loss of methiocarb (yielding significance levels of 0.0008, 0.0000, and 0.0001, respectively), whereas the factor doses has no significant influence in

Table 3. Data on Loss of Methiocarb from Treated Crops

statistical parameters	green beans						tomatoes			
	winter (flat roof)		spring (flat roof)		spring (asymmetrical roof)		winter (flat roof)		spring (flat roof)	
	full dose	half dose	full dose	half dose	full dose	half dose	full dose	half dose	full dose	half dose
K (days $^{-1}$)	0.243	0.259	0.299	0.316	0.354	0.362	0.257	0.273	0.338	0.347
R_0 (mg/kg)	14.752	0.931	1.542	0.870	1.896	1.200	1.265	0.827	1.936	0.934
reg coeff	0.9680	0.9117	0.9500	0.9273	0.9439	0.9535	0.9656	0.9347	0.9748	0.9890
$t_{1/2}$ (days)	2.9	2.7	2.3	2.2	2.0	1.9	2.7	2.5	2.1	2.0
$t_{1/10}$ (days)	9.5	8.9	7.7	7.3	6.5	6.4	9.0	8.4	6.8	6.6
R_{10} (mg/kg)[a]	0.155	0.070	0.077	0.037	0.055	0.032	0.096	0.054	0.066	0.029

[a] R_{10}, residue concentration remaining after 10 days.

Table 4. Data on Loss of Methamidofos from Treated Crops

statistical parameters	cucumber	pepper
K (days^{-1})	0.130	0.112
R_0 (mg/kg)	2.739	3.353
reg coeff	0.976	0.971
$t_{1/2}$ (days)	5.3	6.2
$t_{1/10}$ (days)	17.7	20.6
R_{10} (mg/kg)	0.746	1.094

Table 5. Data on Loss of Malathion from Treated Crops

statistical parameters	cucumber	pepper
K (days^{-1})	0.288	0.267
R_0 (mg/kg)	5.483	5.873
reg coeff	0.989	0.993
$t_{1/2}$ (days)	2.4	2.6
$t_{1/10}$ (days)	8.0	8.6
R_{10} (mg/kg)	0.305	0.403

Table 6. Average Values of Half-Life Times and Standard Errors for the Treatments

level	average (days) ± SE
total	2.27 ± 0.03
green beans	2.36 ± 0.03
tomatoes	2.18 ± 0.05
winter	2.54 ± 0.05
spring	1.99 ± 0.03
flat roof	2.42 ± 0.02
asymmetrical roof	2.12 ± 0.06
full dose	2.31 ± 0.04
half dose	2.22 ± 0.04

agreement with the pseudo first-order kinetics. The cross-effect is not significant, as there are not interactions. The averages of $t_{1/2}$ values and standard errors (SE), either for the total sample or for the different factors in the diminution rate of methiocarb are summarized in **Table 6**. It can be seen that methiocarb disappears more rapidly in spring than in winter; the rate of loss is also lower in green beans than that in tomatoes, which show the highest diminution rate in spring.

Conclusions. A simple and fast analytical method for malathion, methamidofos, methiocarb, and their metabolites malaoxon, methiocarb sulfoxide, and methiocarb sulfone. has been established. Performance parameters calculated during the method validation show the reliability of the analytical method for the analysis of such compounds at the concentrations required by their respective MRLs.

The diminution process of malathion after application in peppers and cucumber shows a pseudo-first-order kinetic with a degradation rate of 0.3 days^{-1}. Malaoxon is detected in some samples, but there is no correlation between the diminution of the parent compound and the presence of malaoxon. Methamidofos is the most persistent pesticide, with a half-life of 5.3 days, taking into account that the MRL of methamidofos in peppers and cucumber is 0.01 mg/kg, and the pre-harvest time is higher than one month. Methiocarb is the least persistent pesticide of the study. The diminution process follows a pseudo-first-order kinetic and ANOVA showed that the main factors influencing its degradation are season and the design of the greenhouse. Nevertheless, the half-life of methiocarb in all cases ranged between 1.9 and 2.9 days, with the faster diminution rate obtained in the application carried out in spring in the asymmetric-roof greenhouse.

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