



## Dissipation rates of iprodione and thiacloprid during tomato production in greenhouse

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### ABSTRACT

The behaviour of the insecticide thiacloprid and the fungicide iprodione was investigated in greenhouse tomato fruits, when both pesticides were applied in two different rates (normal dose-ND, and double dose-DD). Thiacloprid residues were below the already established EU MRLs (0.5 mg/kg) 2 and 7 days after ND and DD application, respectively. Iprodione residues were always below EU MRLs (5 mg/kg) in both application rates. The impact of storage on pesticide residues in tomatoes was also assessed. Significantly higher iprodione residue levels were observed during post harvest storage compared with those determined in fresh harvested tomatoes. Mean residue levels determined in fresh harvested tomatoes 12 days after iprodione application were 0.69 mg/kg whereas, in post harvest tomatoes stored for the same period was 0.86 mg/kg. On the contrary, no differences were noticed in thiacloprid residues between post harvest stored and fresh harvested tomatoes. Model equations that best describe the dissipation curves obtained from the experimental data of iprodione and thiacloprid in tomatoes showing different behaviour of the two pesticides. Half-life period of iprodione in ND treatment, calculated by the best fitted experimental data, (2nd order model) was 6.8 days, whilst for thiacloprid the best fitted to experimental data, model equation (R.F. 1st order model) gave a half-life of 1.9 days.

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### 1. Introduction

Iprodione, a dicarboximide contact fungicide, 3-(3,5-dichlorophenyl)-N-isopropyl-2,4-dioximidazolidine-1-carboxamide with protective and curative action, is usually employed to control *Botrytis cinerea* in greenhouse and field crops (Cabras, Meloni, Pirisi, & Cabitza, 1985; Tomlin, 1994). Thiacloprid (Z)-3-(6-chloro-3-pyridylmethyl)-1,3-thiazolidin-2-ylidenecyanamide is a new member of neonicotinoid pesticides. It is the first chloronicotinyl insecticide which does not only have activity against sucking insects such as aphids, whiteflies and some jassids, but it is also active against weevils, leaf miners and various species of beetles (Elbert et al., 2001). Iprodione residues are commonly detected residues in agricultural products (Cabras & Angioni, 2000; Cabras et al., 1985; Lentza-Rizos, 1995; Lopez & Riba, 1999; Ripley, Ritcey, Harris, Denomme, & Lissemore, 2003; Stensvand & Christiansen, 2000). On the contrary, there are limited literature references to our knowledge about the presence of thiacloprid residues in agricultural products (Agüera et al., 2004; Ticha et al., 2008).

Greenhouse production is of great concern in Greece and tomato is one of the most important greenhouse crops with annual production equal to 234 thousand tones. Tomato fruits ripen gradually

and are usually harvested weekly. In practice fruits can be harvested in two different physiological stages, at “green ripen” or “red ripen” stage, depending on the time intervene between harvesting and consumption. “Green ripen” stage tomatoes can be consumed 4–6 days after harvesting whilst “red ripen” are mature enough for consumption. Most of the times, “green ripen” gathered tomatoes are transferred in a short distance from the production area (Ware & McCollum, 1980).

With the intensive use of pesticides in greenhouse crops, residues may be accumulated at levels higher than those permitted by the EU (Regulation (EC) No. 396/2005) or international MRLs. The dissipation rate of a pesticide after application is a useful tool for the assessment of the behaviour of its residues. Additionally, residues dissipation curves can be used to estimate the time required for decreasing the residues levels below MRLs (Castillo-Sanchez, Aguilera-del Real, Rodriguez-Sanchez, & Valverde-Garcia, 2000; Fenoll, Ruiz, Hellín, Lacasa, & Flores, 2009; Lantos & Ambrus, 2002). To the best of our knowledge there is limited data in the literature concerning the dissipation rate of the above mentioned pesticides. In Greece both active ingredients were widely used especially, during the last years because of the withdrawal of “traditional greenhouse pesticides” according to Council Directive 91/414 EEC. MRLs established in Greece for iprodione and thiacloprid in tomatoes are 5 mg/kg (with PHI 7 days) and 0.5 mg/kg (with PHI 3 days), respectively (Regulation (EC) No. 396/2005).

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The objectives of this work were: (a) to determine the residue levels of iprodione and thiacloprid in greenhouse tomatoes after normal and double dose application (b) to define the pesticide residue behaviour in tomato fruits with the use of dissipation curves and (c) to determine the behaviour of these pesticides in trade post harvest conditions.

## 2. Experimental procedure

### 2.1. Reagents and instrumentation

Dichloromethane, petroleum ether, ethyl acetate and methanol of pro-analysis grade, acetonitrile of Pestanal grade were purchased from Merck (Darmstadt, Germany). Florisil with particle size of 0.150–0.250 mm was obtained from Merck (Darmstadt, Germany) and was deactivated with 5% water prior to use. Distilled water was filtered throughout millipore membranes 0.45 µm (USA). Analytical standards of thiacloprid of 98.7% purity were donated by Bayer CropScience (Thessaloniki, Greece) and iprodione of 99% purity was purchased from Dr. Ehrensstorfer (Augsburg, Germany). Stock solutions (1 mg/ml) were prepared by dissolving the appropriate amounts of analytical standards in acetonitrile and stored in darkness at  $-18^{\circ}\text{C}$ . After several dilutions, working standard solutions of 0.1, 1, 5, 10, 20, 50 and 100 µg/ml were prepared.

Pesticide residues were analysed by using high performance liquid chromatography (HPLC) system that consisted of a Marathon IV Rigas Labs (Thessaloniki, Greece) HPLC pump, a Midas Spark Holland (AJ Emmen, The Netherlands) autosampler and chromatographic analysis was carried out on a Nucleosil 100-5 C18,  $150 \times 4.6$  I.D. (K.G. Duren, Germany) column. Also, a Mistral Spark Holland (AJ Emmen, The Netherlands) oven was used to achieve stable column temperature ( $30^{\circ}\text{C}$ ). Detections of thiacloprid and iprodione were made at 242 and 210 nm, respectively by using SSI Model 500 UV/Vis detector.

### 2.2. Experimental design and sampling procedures

The experiment was carried out in the greenhouse of the Horticultural Department, Aristotle University of Thessaloniki. Tomato cv. Belladonna, plants were employed from Agris Co. (Verioia, Greece) and transplanted in 12 l pots (perlite) in an open hydroponic system. The greenhouse temperature and relative humidity were controlled by a heating system and measurements were taken by a data logger during the course of the experiment. During this period the mean temperature and relative humidity inside the greenhouse environment were  $19.4 \pm 1.1^{\circ}\text{C}$  and  $76.3 \pm 0.8\%$ , respectively.

A random block design was used, with two treatments. Each block contained 15 plants of tomato spaced 0.5 with 0.9 m between the rows. Tomato plants of the first treatment, amongst the routine horticultural treatments were once sprayed with Calypso 480SC (thiacloprid 48%) at a dose of 30 ml/hl and Rovral 50%WP (iprodione 50%) at a dose of 100 g/hl according to the good agricultural practice (ND, normal dose). The tomato plants of the second treatment were sprayed with double dose (DD) pesticide solution to estimate the worst case scenario.

Pre marked tomato fruits of the same ripen stage and size were harvested randomly "on time" at 0.125, 1, 1.4, 2, 4, 7, 12, and 20 days intervals after pesticides application for both treatments. For post harvest residue screening, "green ripen" and "red ripen" fruits were collected and placed in darkness simulating trade conditions just after spraying (temperature  $15 \pm 0.5^{\circ}\text{C}$ , and relative humidity  $75 \pm 0.3\%$ ). Post harvest samples were taken after 0.125, 4, 7 and 12 days of storage. Control samples were collected before pesticide application. Each sample (1 kg) was chopped and divided

into three sub samples which were stored in individual polyethylene bags at  $-18^{\circ}\text{C}$  until extraction. Fifty gram of each sub sample were extracted and analysed by HPLC.

### 2.3. Extraction, clean up and HPLC analysis

Thiacloprid and Iprodione residues in tomatoes were determined by HPLC coupled with UV/Vis detector after liquid–liquid extraction with dichloromethane followed by a clean-up procedure with florisil columns.

Briefly, 50 g of chopped tomato was blended with 150 ml acetone for 2 min. The mixture was filtered through a 12 cm-Buchner filter. The filter was rinsed with another 30 ml of acetone and the filtrate was transferred in a separate funnel (500 ml) and 160 ml of dichloromethane and petroleum ether (1:1) were added. The separating funnel was shaken vigorously for 2 min. After separation of the two phases, organic phase was collected in a round bottom flask after passing through anhydrous sodium sulphate. The aqueous phase was re-extracted with 80 ml of dichloromethane, the organic phase was passed through anhydrous sodium sulphate and collected to the same round bottom flask (500 ml) as previously described. Afterwards, the filtrate was divided in two equally portions in order to perform the clean-up procedure for thiacloprid determination. The extracts were concentrated in rotary vacuum evaporator to dryness using a  $40^{\circ}\text{C}$  water bath. The residue of the first flask (predestinated for iprodione analysis) was redissolved in 4 ml acetonitrile and was analysed by HPLC. The residue of the second flask was redissolved in 2 ml ethyl acetate and loaded onto a florisil column for the clean-up procedure. Clean-up columns were packed with 2 g of deactivated, with 5% water, florisil. One millilitre of the sample was loaded onto the pre-washed with 10 ml ethyl acetate florisil column. Afterwards, the column was washed with 15 ml ethyl acetate and the eluate was discarded. Thiacloprid was eluted with 30 ml of acetonitrile. The eluate was collected in a round bottom flask (100 ml) and concentrated in rotary vacuum evaporator. The residue finally was redissolved in 1 ml of acetonitrile and was analysed by HPLC.

Thiacloprid and iprodione were analysed separately. A 20-µl of each sample was injected into HPLC system. Analytes separation was obtained by using gradient mobile phase consisted of acetonitrile and water. The mobile phase components were filtered through 0.45-µm membrane filters (millipore) in an all glass filtration apparatus operated under reduced pressure and degassed for 15 min in an ultrasonic bath before use. The % acetonitrile gradient regime during thiacloprid analysis was: 25% (0–2 min), 90% (2–12 min), and 100% (12–15 min); an equilibration time of 5 min was set to achieve initial gradient conditions. Similarly, for iprodione analysis the % acetonitrile gradient regime was: 10% (0–4 min), 50% (4–12 min), 70% (12–17 min), 90% (17–23 min) and 100% (23–27 min); the equilibrium time was 3 min. The flow rate for both gradient mobile phases was 1 ml/min.

### 2.4. Method validation

Calibration curves and tomato fortified samples were prepared by using working standard solutions. Tomato samples fortified at 0.05, 0.1, 0.5 and 1 mg/kg were processed as previously described and analysed by HPLC to evaluate the accuracy and the precision of the analytical procedure. Recovery tests were replicated three times for each fortification level. The limit of detection (LOD mg/kg) of each analyte was determined as the lowest concentration giving response of three times the standard deviation of the baseline noise defined from the analysis of three control samples. The limit of quantification (LOQ mg/kg) was determined as the lowest concentration of a given compound giving a response that could be

quantified with relative standard deviation lower than 20% (Vryzas & Papadopoulou-Mourkidou, 2002).

### 2.5. Data analysis

Dissipation studies of pesticide residues were carried out by linear regression. One way analysis of variance of pesticide residue levels by ripen stage was calculated. The means with significant differences ( $\alpha < 0.05$ ) were separated by Student's *t*-test. Statistics were performed by JMP IN 5.1 statistical packages (SAS, Institute Inc., 2005).

## 3. Results and discussion

### 3.1. Method performance

The analytical method was developed as to provide a rapid accurate and efficient means of determining iprodione and thiacloprid residues in tomatoes. Mean recovery values obtained for thiacloprid and iprodione were >84% and 90%, respectively with relative standard deviation (RSD%) <12% in the fortification range from 0.05 to 1 mg/kg. Calibration for quantification was carried out by use of external standard calibration curves; calibration curves were linear with correlation coefficients being better than 0.999 for both analytes. The LOQ and LOD for both analytes in tomatoes fruits were 0.05 and 0.005 mg/kg, respectively ensuring LOQ values significantly lower than the MRLs established by the European Union.

Sample chromatograms from the analysis of control and fortified (0.05 mg/kg) tomato samples are shown in Fig. 1. The chromatograms of fortified and field treated samples were clean of co-extractives and solutes were eluted well resolved.

### 3.2. Pesticide residue levels in fresh "on time" harvested tomatoes

Mean residue levels of both pesticides during the sampling period for each application dose (ND and DD) derived from the extraction and analysis of three tomato sub samples are shown

**Table 1**

Mean residue levels of thiacloprid and iprodione (SD) of fresh harvested (ND and DD treatments) and stored tomato fruits harvested at different maturity stages.

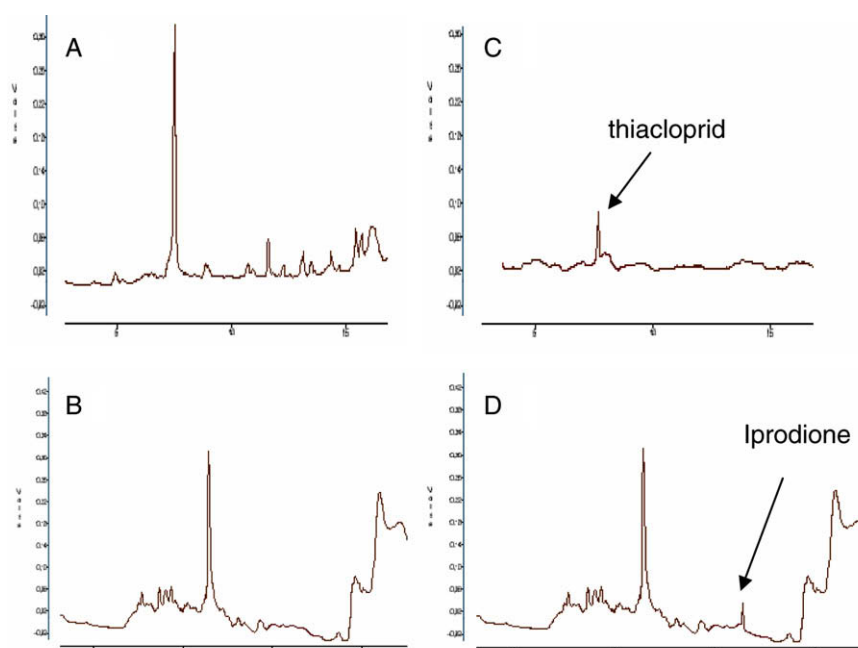
| Time (days) <sup>a</sup>      | Iprodione <sup>b</sup> , mg/kg (SD) |             | Thiacloprid <sup>b</sup> , mg/kg (SD) |             |
|-------------------------------|-------------------------------------|-------------|---------------------------------------|-------------|
|                               | Normal dose                         | Double dose | Normal dose                           | Double dose |
| <i>Fresh harvested fruits</i> |                                     |             |                                       |             |
| 0.125                         | 1.71 (0.12)                         | 3.69 (0.17) | 0.74 (0.03)                           | 1.56 (0.05) |
| 1                             | 1.56 (0.08)                         | 3.43 (0.24) | 0.52 (0.03)                           | 1.38 (0.10) |
| 1.4                           | 1.42 (0.11)                         | 3.03 (0.18) | 0.46 (0.03)                           | 1.18 (0.06) |
| 2                             | 1.29 (0.08)                         | 2.68 (0.20) | 0.41 (0.03)                           | 1.14 (0.06) |
| 4                             | 1.06 (0.09)                         | 2.16 (0.17) | 0.34 (0.03)                           | 0.78 (0.06) |
| 7                             | 0.84 (0.08)                         | 1.80 (0.21) | 0.28 (0.02)                           | 0.53 (0.06) |
| 12                            | 0.69 (0.05)                         | 1.33 (0.15) | 0.19 (0.03)                           | 0.40 (0.04) |
| 20                            | 0.42 (0.04)                         | 0.96 (0.15) | 0.07 (0.01)                           | 0.23 (0.03) |
| <i>Stored fruits</i>          |                                     |             |                                       |             |
| Time (days) <sup>a</sup>      | Ripen red                           | Ripen green | Ripen red                             | Ripen green |
| 0                             | 1.67 (0.11)                         | 1.80 (0.13) | 0.76 (0.10)                           | 0.71 (0.08) |
| 4                             | 1.05 (0.07)                         | 0.99 (0.06) | 0.41 (0.03)                           | 0.39 (0.03) |
| 7                             | 0.86 (0.06)                         | 0.87 (0.05) | 0.30 (0.03)                           | 0.24 (0.02) |
| 12                            | 0.84 (0.03)                         | 0.77 (0.06) | 0.27 (0.01)                           | 0.21 (0.02) |

<sup>a</sup> Days after pesticide application.

<sup>b</sup> Mean residue values and standard deviation (SD) of the extraction and analysis of three tomato sub samples.

in Table 1. Mean residue levels of iprodione both at ND and DD application rates were below the EU established MRLs (5 mg/kg) throughout the experimental period. The highest residue levels in both treatments were determined in samples taken in the first sampling (day 0.125) just after pesticide application. Mean residue values determined for iprodione at this sampling were 1.71 and 3.69 mg/kg at ND and DD, respectively. Residue levels of iprodione had been decreasing throughout the experiment reaching levels below 0.5 and 1 mg/kg 20 days after application in ND and DD, respectively.

A similar behaviour of thiacloprid residue levels was also observed. The highest residue levels of thiacloprid were observed at 0.125 days in ND treatment (0.74 mg/kg) whilst at the same sampling, residue levels in DD treatment were 1.56 mg/kg. Thiacloprid



**Fig. 1.** Sample chromatograms from the analysis of control and fortified (0.05 mg/kg) tomato fruits samples; chromatograms of untreated tomato fruits at 242 nm (A) and 210 nm (B). Chromatograms of fortified (0.05 mg/kg) with thiacloprid tomato fruits after clean-up at 242 nm (C) and iprodione without clean-up at 210 nm (D).

residues determined in both treatments were higher from the EU established MRLs (0.5 mg/kg) just after application (Table 1). In particular, thiacloprid residue levels determined at ND were higher than MRLs one day after application (0.52 mg/kg). Moreover, when thiacloprid applied at double dose the residue levels found in tomato fruits remained higher than MRLs 7 days after application (0.53 mg/kg).

### 3.3. Post harvest – residues

Iprodione and thiacloprid mean residue levels for the post harvest treatments derived from the extraction and analysis of three tomato sub samples are presented in Table 1. No significant differences on residue levels were observed between the different ripen stages determined just after (0.125 days) and until the seventh day after application. Significant differences for iprodione residues between the fresh harvested and the stored tomatoes were observed 12 days after application. The mean residue levels determined in fresh harvested tomatoes were 0.69 mg/kg whilst in stored tomatoes they were 0.86 mg/kg (Table 1). This is probably related with the photodegradation of iprodione, since tomato fruits were stored in dark chambers after harvesting, simulating the marketing procedure (Burrows, Canle, Santaballa, & Steenken, 2002; Schick, Moza, & Hustert, 1999; Schwack, Bourgeois, & Walker, 1995). On the contrary, no significant differences were observed between thiacloprid residues, found in tomatoes ripened in the greenhouse and from those harvested earlier during the “ripen green” and “ripen red” stage and which were kept in storage conditions (Table 1). This

behaviour of thiacloprid residues is likely related with the stability of the active ingredient to UV radiation (Krohn, 2001).

Similar to the fresh harvested tomatoes, residue levels of iprodione were below the EU MRLs both in ripen “green” and “red” harvesting stage throughout the sampling period whereas, thiacloprid residues were below EU MRLs four days after pesticide application.

### 3.4. Dissipation studies

Mean residue data gathered from each sampling date and treatment were subjected to linear regression analysis following the

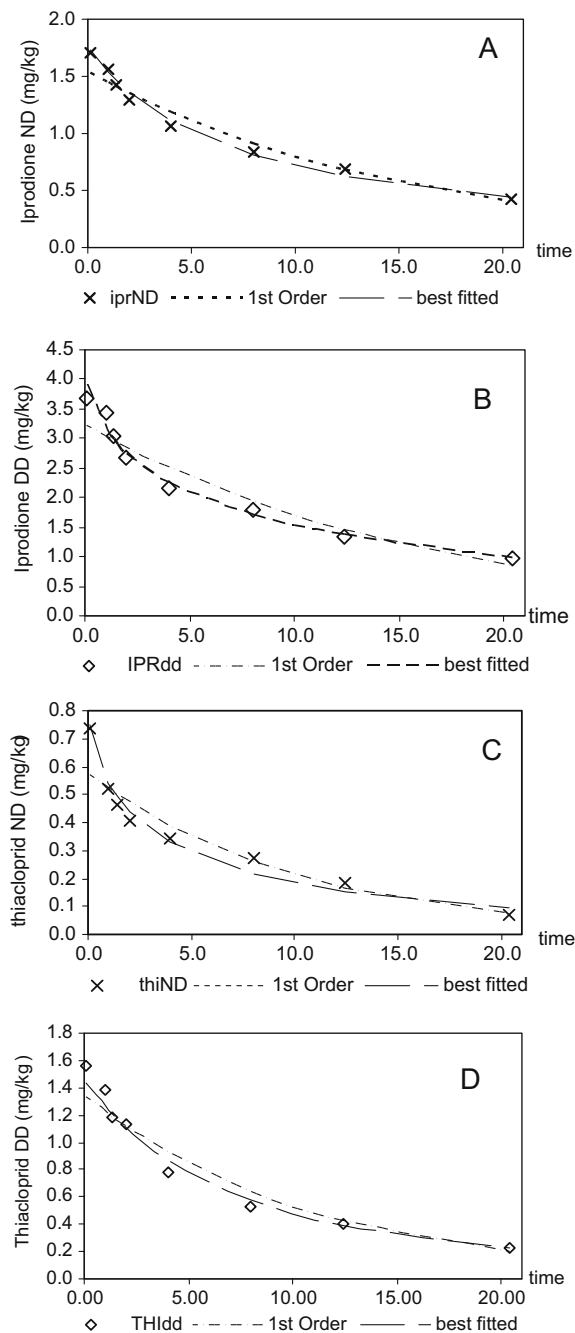
**Table 2**  
Dissipation model equations that describe the disappearance of thiacloprid and iprodione in tomato fruits (ND, DD treatments).

|                      | Normal dose (ND)                   | Double dose (DD)                 |
|----------------------|------------------------------------|----------------------------------|
| <b>Iprodione</b>     |                                    |                                  |
| 1st Order model      |                                    |                                  |
| Dissipation curve    | $R = 10^{0.189 - 0.0286t}$         | $R = 10^{0.515 - 0.0286t}$       |
| $r^{2a}$             | 0.952                              | 0.919                            |
| $D^b$                | 0.244                              | 0.212                            |
| 1.5th Order model    |                                    |                                  |
| Dissipation curve    | $R = 1/(0.787 + 0.0366t)^2$        | $R = 1/(0.545 + 0.0243t)^2$      |
| $r^2$                | 0.978                              | 0.949                            |
| $D$                  | 0.270                              | 0.242                            |
| 2nd Order model      |                                    |                                  |
| Dissipation curve    | $R = 1/(0.569 + 0.0841t)$          | $R = 1/(0.279 + 0.0374t)$        |
| $r^2$                | 0.989                              | 0.973                            |
| $D$                  | 0.282                              | 0.269                            |
| R.F. 1st order model |                                    |                                  |
| Dissipation curve    | $R = 10^{0.317 - 0.145\sqrt{t}}$   | $R = 10^{0.643 - 0.144\sqrt{t}}$ |
| $r^2$                | 0.979                              | 0.978                            |
| $D$                  | 0.271                              | 0.271                            |
| <b>Thiacloprid</b>   |                                    |                                  |
| 1st Order model      |                                    |                                  |
| Dissipation curve    | $R = 10^{-0.239 - 0.0439t}$        | $R = 10^{0.129 - 0.0409t}$       |
| $r^{2a}$             | 0.877                              | 0.880                            |
| $D^b$                | 0.170                              | 0.475                            |
| 1.5th Order model    |                                    |                                  |
| Dissipation curve    | $R = 1/(1.212 + 0.113t)^2$         | $R = 1/(1.212 + 0.1145t)^2$      |
| $r^2$                | 0.920                              | 0.938                            |
| $D$                  | 0.213                              | 0.533                            |
| 2nd Order model      |                                    |                                  |
| Dissipation curve    | c                                  | $R = 1/(0.543 + 0.178t)$         |
| $r^2$                | c                                  | 0.944                            |
| $D$                  | <0                                 | 0.539                            |
| R.F. 1st Order Model |                                    |                                  |
| Dissipation curve    | $R = 10^{-0.0472 - 0.219\sqrt{t}}$ | $R = 10^{0.314 - 0.208\sqrt{t}}$ |
| $r^2$                | 0.972                              | 0.942                            |
| $D$                  | 0.265                              | 0.537                            |

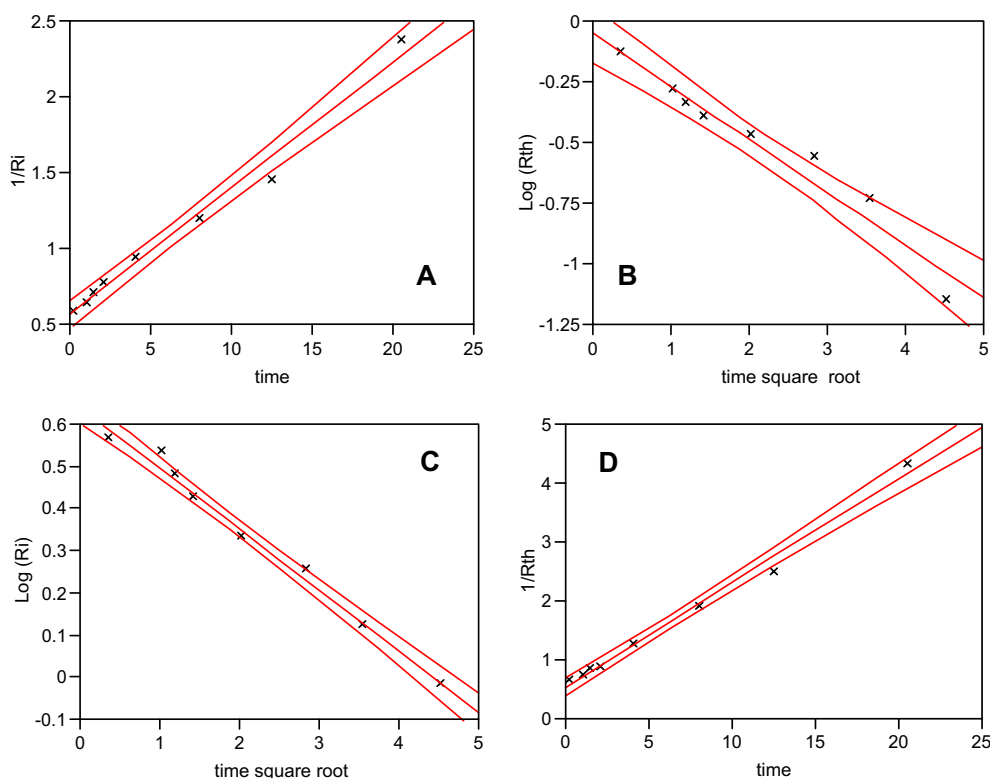
<sup>a</sup> Modified coefficient of determination.

<sup>b</sup> Test of quantity at significance level of 95%.

<sup>c</sup> Not applied  $D < 0$ .



**Fig. 2.** Dissipation curves of iprodione and thiacloprid residues from experimental data, in ND (A and C) and DD (B and D) treatments respectively. Where – X – indicates the experimental data in ND and – ◊ – the experimental data in DD. – – – – indicates the back-transformed dissipation curve (1st order model equation in A–D) and – – – – indicates the back-transformed dissipation curve (2nd order model equation for A and D, R.F. 1st order model equation for B and C).



**Fig. 3.** Transformed residue data of the best fitting model equations. (A) 2nd order model equation (best fitted to experimental data) obtained from the mean iprodione ND treatment data (Ri). (B) R.F. 1st order model equation (best fitted to experimental data) obtained from the mean thiacloprid ND treatment data (Rth). (C) R.F. 1st order model equation (best fitted to experimental data) obtained from the mean iprodione DD treatment data (Ri). (D) 2nd order model equation (best fitted to experimental data) obtained from the mean thiacloprid DD treatment data (Rth).

methodology proposed by Timme, Frehse, and Laska (1986). This procedure allows evaluating various “model” equations which describe the loss of pesticide residues in agricultural products versus time. Briefly, the following steps were used in order to evaluate and describe the dissipation procedure in tomatoes.

Mean experimental residue data were transformed in order to achieve 1st, 1.5th, 2nd order and the corresponding Root Factor (R.F.) model equations. Then linear equations 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 determined. Intercept and slope were back-transformed in order to estimate the “model” residue values from the corresponding model equations. The evaluation of model fit was achieved by the modified coefficient of determination ( $r^2$ ) and the correlation between residues and time determined by the use of the quantity test as proposed elsewhere (Timme & Frehse, 1980; Timme et al., 1986).

The bigger the  $r^2$  is, the better the model equation fit and can predict the experimental data. Negative values of  $r^2$  or values equal with nil indicate that the model equation does not respond to the experimental data. The correlation between the residues and the time is verified when  $D > 0$ .

Model equations which predict better the experimental data for the examined pesticides both at ND and DD treatments in tomatoes with their corresponding  $r^2$  and  $D$  are presented in Table 2. The equations which predicts better the experimental data of ND and DD treatments of iprodione were the 2nd order and R.F. 1st order model, respectively. Thiacloprid ND and DD experimental data were better fitted by the R.F. 1st order and 2nd order model equations, respectively. Dissipation curves obtained for iprodione and thiacloprid treatments are presented in Fig. 2. Transformed residue data of the best fitting model equations for both pesticides and all treatments are presented in Fig. 3.

**Table 3**

Data on dissipation studies of thiacloprid and iprodione residues in tomato fruits.

|                           | Iprodione             |                       |                       |                 | Thiacloprid          |                      |                   |                 |
|---------------------------|-----------------------|-----------------------|-----------------------|-----------------|----------------------|----------------------|-------------------|-----------------|
|                           | 1st Order model       |                       | Best fitted model     |                 | 1st Order model      |                      | Best fitted model |                 |
|                           | ND                    | DD                    | ND                    | DD              | ND                   | DD                   | ND                | DD              |
| $K$ (days <sup>-1</sup> ) | $2.86 \times 10^{-2}$ | $2.82 \times 10^{-2}$ | $8.41 \times 10^{-2}$ | 0.144           | $4.3 \times 10^{-2}$ | $4.1 \times 10^{-2}$ | 0.219             | 0.178           |
| $R_3$ C.I.                | $1.27 \pm 0.3$        | $2.68 \pm 0.08$       | $1.22 \pm 0.09$       | $2.55 \pm 0.07$ | $0.43 \pm 0.2$       | $1.02 \pm 0.2$       | $0.23 \pm 0.1$    | $0.98 \pm 0.2$  |
| $R_7$ C.I.                | $0.97 \pm 0.02$       | $2.06 \pm 0.04$       | $0.87 \pm 0.1$        | $1.85 \pm 0.01$ | $0.28 \pm 0.06$      | $0.70 \pm 0.06$      | $0.24 \pm 0.16$   | $0.63 \pm 0.01$ |
| $t/2$ C.I.                | $10.5 \pm 1.1$        | $10.6 \pm 1.4$        | $6.8 \pm 0.5$         | $4.3 \pm 0.7$   | $6.9 \pm 1.3$        | $7.5 \pm 1.5$        | $1.9 \pm 0.9$     | $2.1 \pm 0.4$   |

$K$ , dissipation rate of pesticide residue in days.

$R_3$  and  $R_7$  estimated pesticide residue (mg/kg) 3 and 7 days after application and its confidence intervals (C.I.) in mg/kg (P.H.I. of thiacloprid and iprodione are 3 and 7 days, respectively).

$t/2$  Estimate half-life and its confidence intervals (C.I.) in days.

As expected, in the 1st and R.F. 1st order model, the pesticide dissipation rate ( $K$ ) – which is the slope of the transformed straight line – was not influenced by the treatment dose (Castillo-Sanchez et al., 2000; Galera, Garcia, Lallena, Lopez, & Vidal, 2003; Hernandez Torres, Egea Gonzalez, Castro Cano, Moreno Frias, & Martinez Vidal, 2002; Timme et al., 1986). Therefore, the dissipation rate of iprodione and thiacloprid residues, as described by the 1st order model equations, is independent from pesticide initial concentration. The dissipation rates obtained from the other model equations were different according to the treatment dose (Table 3). Moreover, the half-life of pesticides obtained with best predicted model equations were lower than those obtained by the 1st order model. Iprodione and thiacloprid half-life values determined at ND treatment from the 1st order model were  $10.5 \pm 1.7$  and  $6.9 \pm 1.3$  mg/kg, respectively, in comparison with  $6.8 \pm 1.4$  and  $1.9 \pm 0.9$  mg/kg half-life values which were obtained from the best predicted model.

#### 4. Conclusions

The mean residue levels of iprodione during the course of the experiment after normal and double dose application were lower than the EU MRLs unlike thiacloprid. Mean residue levels of thiacloprid were lower than EU MRLs 2 days after ND application and 7 days after DD application. The pesticide residue levels during storage were not affected by the fruit physiological stage. The dissipation study of iprodione after ND application in tomatoes shows that the model that best fits the experimental data was the 2nd Order model with dissipation rate of  $0.084 \text{ days}^{-1}$ . On the other hand, thiacloprid applied at ND showed that the best fit model was R.F. 1st order model with dissipation rate of  $0.219 \text{ days}^{-1}$ . Half-life of iprodione and thiacloprid after ND application was 6.8 and 1.9 days, respectively according to the model that best fits the experimental data. Finally, the Pre Harvest Intervals which have already been established by the EU competent authorities are safe enough for greenhouse tomatoes for both pesticides.

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