JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Disappearance of Azoxystrobin, Pyrimethanil, Cyprodinil, and Fludioxonil on Tomatoes in a Greenhouse

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The disappearance of azoxystrobin, pyrimethanil, cyprodinil, and fludioxonil on tomatoes in greenhouse was studied. At the preharvest interval, except for cyprodinil, the pesticide residues were below the MRL fixed in Italy. The mechanism of disappearance studied with model systems shows that the decrease in residues was due to codistillation and photodegradation in pyrimethanil, to photodegradation in fludioxonil, and to evaporation and codistillation in cyprodinil. Azoxystrobin residues were stable during all experiments.

KEYWORDS: Azoxystrobin; pyrimethanil; cyprodinil; fludioxonil; residues; disappearance; tomatoes

Long-cycle tomatoes grown in a greenhouse develop during all of winter and part of spring. Fruits ripen gradually and are usually harvested weekly. Therefore, to protect tomatoes from pathogens, such as gray mold *(Botrytis cinerea)* and gray mildew *(Phytophtora infestans)*, pesticides with a short preharvest interval (PHI) of 1 week or less are required. Conventional fungicides (*1*, *2*) have shown resistance phenomena due to their extensive use. Therefore, they do not give sufficient protection and the PHI of most of these pesticides is too long and unsuitable for greenhouse harvesting periods.

Recently, some new fungicides, such as azoxystrobin, pyrimethanil, cyprodinil, and fludioxonil, were introduced on the market. These compounds have both fungicide action and PHIs meeting the protection requirements of greenhouse tomatoes. Studies on the degradative behavior of these fungicides on grapes are reported in the literature (*3*, *4*), while to our knowledge no study has been carried out on tomatoes. A trial was carried out to assess whether in operative conditions the disappearance kinetics of two active ingredients (a.i.) with a PHI of 3 days (azoxystrobin and pyrimethanil) and two a.i. with a PHI of 7 days (cyprodinil and fludioxonil) applied with repeated treatments allows one to harvest tomatoes with pesticide residues lower than their MRL. Pesticides decrease on account of fruit growing, evaporation, codistillation, thermodegradation, and photodegradation. Experiments on model systems have been carried out to clarify which of these mechanisms was responsible for the disappearance of the a.i.

MATERIALS AND METHODS

Field Trial. The trials were carried out in a farm owned by C. R. A. S., located at Uta (CA) in a greenhouse of an area of 500 m^2, made of iron and glass, equipped with a hot blast heating system and a localized irrigation system. The trials started at the end of August, with tomatoes of the cultivar Camone cch (Slui and Groot), planted with a plant spacing of 40 cm × 80 cm. A random block scheme was used with four replications for each test; each block contained 16 plants in a single row. Treatments were carried out with a Carpi portable motor sprayer (Modena, Italy) using the following commercial formulation: Quadris (25% of azoxystrobin), Scala (37.4% of pyrimethanil), and Switch (37.5% of cyprodinil and 25% of fludioxonil).

Two treatments were carried out on February 28 and March 7, 2001 at the doses recommended by the manufacturers. Before the first treatment, samples of tomatoes with the same ripening stage, size, and shape were localized and tagged. Samplings (15 kg) were made before and after the treatments and repeated after 2, 4, 7, and 10 days.

Chemicals. Acetone and petroleum ether were pesticide grade solvents (Carlo Erba, Milano, Italy). Chloroform was an high-performance liquid chromatography solvent (Carlo Erba, Milano, Italy). Regenerated cellulose membranes (diameter 2.5 cm and mesh 0.45 μm) were purchased from Sartorius (Sartorius, Gottingen, Germania).

Pyrimethanil, cyprodinil, fludioxonil, and azoxystrobin were analytical standards kindly donated by the manufacturers (Hoechst Schering, AgrEvo Italia, Ciba-Geigy, and Zeneca). Standard stock solutions (∼500 mg/kg) were prepared in acetone. Working standard solutions were obtained by dilution with untreated tomato extracts and prepared daily.

Apparatus and Chromatography. An HRGC Mega 5160 (Carlo Erba, Milan, Italy), equipped with a nitrogenous-phosphorus detector NPD-40, an autosampler AS 550 (Fisons), a split-splitless injector, and an HP 3396 integrator (Hewlett-Packard, Avondale, PA) was used. The capillary column was a Durabond DB-5 (15 m × 0.25 mm id × film thickness 0.1 μm; J&W Scientific, Folsom, CA). The injector and the detector were operated at 220 and 300 °C, respectively. The samples (2 μL) were injected in the splitless mode (60 s), and the oven temperature was programmed as follows: 100 °C for 1 min, raised to 120 °C (3 °C/min), raised to 300 °C (15 °C/min), and held for 5 min. Helium was the carrier and makeup gas at 120 and 80 kPa, respectively. Hydrogen and air were at 150 and 100 kPa, respectively.

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10.1021/jf011219f CCC: $22.00
Published on Web 02/21/2002

Extraction Procedure. A 5 g aliquot of chopped and homogenized tomatoes was weighed in a 40 mL screw-capped tube; 2 g of NaCl and 10 mL of acetone/petroleum ether (1/1; v/v) mixture were added. The tube was agitated for 30 min in a rotating shaker, the phase was allowed to separate, and the organic layer was placed in a vial with 1 g of anhydrous Na_2SO_4 and then injected for gas chromatography (GC) analysis.

Recovery Assay. Untreated tomato samples were fortified with known amounts of pesticides (2.00, 1.00, 0.50, 0.20, and 0.05 mg/kg) and processed according to the above procedure. Every recovery was done in four replicates.

Extraction Procedure of Fruit Waxes. Tomato wax extraction was performed as described by McDonald et al. (*5*). Untreated tomatoes of a known volume and weight were dipped in chloroform for 2 min; the quantity of wax on the fruit surface was determined by evaporation of 10 mL of chloroform extract to dryness (60 μg/cm^2 on tomatoes).

Model System. *Test A.* The fungicide was dissolved in acetone and poured on a regenerated cellulose membrane. After the solvent was evaporated, the membrane was placed in a 10 mL screw-capped vial. The vial was then placed in a thermostatic stove at 50 °C for 24 h. It was then removed and put in a freezer at −20 °C for 5 h to allow the a.i. in the gaseous state to condense on the inner side of the vial. The membrane was then transferred to another vial and extracted following the above procedure. This analysis allows one to determine the pesticide residue in the membrane. In the vial, 5 mL of the extraction mixture was added, shacked, and analyzed. Because of the presence of residues on the inner side of the vial, the amount of pesticides evaporated from the membrane can be determined, while the pesticides in the control vial less the sum of the residues in the membrane and those on the vial indicate the amount of thermodegraded pesticides. A control vial was stored in the dark and at room temperature.

Test B. The fungicide was dissolved in acetone and poured on membranes of regenerated cellulose. After the solvent was evaporated, the membranes were placed on top of the vials and closed with a screw-holed cap. The 10 mL vial was filled with 5 mL of water and placed in a thermostatic stove at 50 °C for 24 h. A control vial without water was stored in the dark at room temperature. When the vial returned to room temperature, it was weighed to determine the amount of water evaporated. During the evaporation, the water passing through the membrane could entrain the pesticide residues from the membrane (codistillation process). From the amount of pesticides on the membrane after this experiment, the loss in a.i. can be assessed as a result of the codistillation process. A correct estimation of the codistillation is obtained considering the losses due to evaporation and thermodegradation determined with test A.

Sunlight Photodegradation Experiments. The fungicide was dissolved in acetone and poured into Petri quartz dishes of 5 cm diameter. The solvent was let to dry at room temperature. The dishes were then exposed to sunlight and removed at prefixed intervals for analysis. Control samples were stored in the dark at room temperature. The residues in the dishes were solubilized with 5 mL of the extracting mixture and analyzed by GC. To simulate photodegradation in the greenhouse, the dishes were covered with a glass plate and then exposed to sunlight. A correct estimation of the photodegradation is obtained considering the losses due to evaporation and thermodegradation determined with test A.

All of the experiments of the A and B test and of photodegradation were carried out also in the presence of tomato epicuticular waxes (60 μg/cm^2) and using the commercial formulation. Every trial was conducted in four replicates.

Statistical Analysis. Analysis of variance was performed by "MSTAT-C" (1991), when appropriate ($p < 0.05$); analysis was followed by the Duncan post hoc test.

RESULTS AND DISCUSSION

Analytical Method. The analysis of the pesticide residues was carried out by adapting a method already used in the analysis of pesticides on grapes (*6*, *7*). **Figure 1** shows the chromatogram of the untreated tomato extract. Because it does not show any interfering peaks, no clean up was needed. The recovery assay yielded good recoveries in the extracting process (from 86 to 114%) with a maximum standard deviation of 16%.

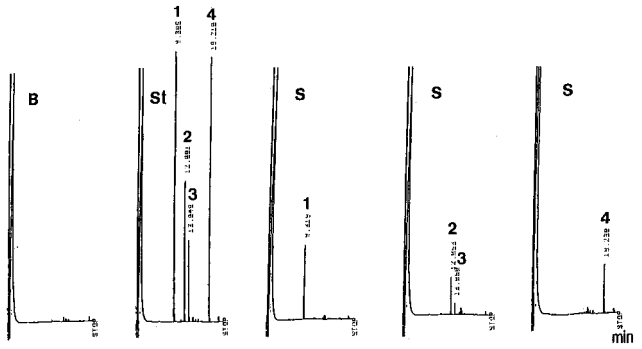

Figure 1. Chromatograms obtained following the conditions reported in the text: untreated tomato (B), standard of pyrimethanil (1), cyprodinil (2), fludioxonil (3), and azoxystrobin (4) at concentrations equal to the MRLs in untreated tomato extract (St) and in samples of treated tomatoes (S).

Table 1. Disappearance of Pesticides in Greenhouse after the Treatments

	pyrimethanil (mg/kg)	fludioxonil (mg/kg)	cyprodinil (mg/kg)	azoxystrobin (mg/kg)
	days after first treatment			
0	1.08 ± 0.09	0.42 ± 0.03	0.52 ± 0.17	0.19 ± 0.04
2	0.80 ± 0.16	0.40 ± 0.05	0.53 ± 0.13	0.21 ± 0.03
4	0.49 ± 0.09	0.28 ± 0.03	0.43 ± 0.08	0.14 ± 0.01
7	0.19 ± 0.04	0.20 ± 0.00	0.26 ± 0.04	0.15 ± 0.01
	days after second treatment			
0	1.39 ± 0.24	0.51 ± 0.16	1.12 ± 0.23	0.36 ± 0.06
2	1.15 ± 0.34	0.49 ± 0.09	1.25 ± 0.41	0.36 ± 0.06
4	0.55 ± 0.06	0.37 ± 0.04	0.89 ± 0.06	0.37 ± 0.05
7	0.32 ± 0.06	0.30 ± 0.04	0.56 ± 0.12	0.36 ± 0.03
10	0.22 ± 0.03	0.21 ± 0.02	0.30 ± 0.06	0.30 ± 0.03
MRL (PHI)	2.0 (3 days)	1.0 (7 days)	0.5 (7 days)	2.0 (3 days)

Table 2. Half-Life and Correlation Values of Fungicides after the First Treatment and after the Second Treatment

	first treatment		second treatment	
	r	$t_{1/2}$ (days)	r	$t_{1/2}$ (days)
pyrimethanil	−0.9885	2.8	−0.9834	3.5
fludioxonil	−0.9755	6.1	−0.9869	7.6
cyprodinil	−0.9305	6.7	−0.9581	4.9
azoxystrobin				

Residue Degradation. The evaporation of water from tomatoes, calculated on fruit detached from the plant at room temperature, was 1.12% on a daily basis. Because the fruit weight was constant (100 ± 6 g) during the experiment, there was a balance between the amount of liquid provided to the fruits by the plant and the evaporation effect. Therefore, there was no dilution effect on the residue content. To evaluate the mechanism responsible for pesticide decrease, trials with model systems were carried out. With these experiments, we studied the effect of evaporation, thermodegradation (test A), codistillation (test B), and photodegradation. The half-life of pesticide residues was calculated as pseudo first-order kinetics.

Pyrimethanil. After the first treatment, the residue level on tomatoes was 1.08 mg/kg (**Table 1**), which degraded with a half-life of 2.8 days (**Table 2**). Before the second treatment, the residue level on the fruit was 0.19 mg/kg, and after, it increased to 1.20 mg/kg. After the second treatment, the decrease rate was similar to that after the first, with a half-life of 3.5 days. At harvest time, the residue was 0.22 mg/kg, while 3 days

Table 3. Test A for the Determination of the Effect of Evaporation and Thermodegradation on Pesticides[a]

pesticide	waxes	control (c) (μg/cm^2)	vial (v) (μg/cm^2)	filter (f) (μg/cm^2)	difference c − (v + f) (μg/cm^2)
pyrimethanil	without	1.88 ± 0.17	0.91 ± 0.19	0.71 ± 0.15	ns
	with	1.84± 0.21	0.01 ± 0.01	1.61 ± 0.06	ns
cyprodinil	without	0.45 ± 0.04	0.18 ± 0.03	0.23 ± 0.03	ns
	with	0.44 ± 0.07	0.10 ± 0.00	0.40 ± 0.03	ns
fludioxonil	without	0.87 ± 0.07	0.03 ± 0.00	0.78 ± 0.08	ns
	with	0.88 ± 0.13	0.03 ± 0.01	0.75 ± 0.04	ns
azoxystrobin	without	1.86 ± 0.15	nd	1.88 ± 0.21	ns
	with	2.07 ± 0.18	nd	1.94 ± 0.14	ns

[a] nd = not determinable and ns = not significant.

Table 4. Test B for the Determination of the Effect of Codistillation on Pesticides[a]

pesticides	waxes	control (c) (μg/cm^2)	filter (f) (μg/cm^2)	difference (c − f) (μg/cm^2)
pyrimethanil	without	1.88 ± 0.17	nd	1.88
	with	1.84± 0.21	0.09 ± 0.01	1.75
cyprodinil	without	0.45 ± 0.04	nd	0.45
	with	0.44 ± 0.07	0.04 ± 0.01	0.40
fludioxonil	without	0.87 ± 0.07	0.65 ± 0.02	0.22
	with	0.88 ± 0.13	0.70 ± 0.07	ns
azoxystrobin	without	1.86 ± 0.15	1.72 ± 0.13	ns
	with	2.07 ± 0.18	1.97 ± 0.06	ns

[a] nd = not determinable and ns = not significant.

after treatment (PHI) it was already abundantly under the MRL (2.0 mg/kg).

The model system (**Table 3**) showed that in absence of waxes, 48.4% of a.i. evaporates from the filter, while in their presence evaporation was null. On average, the sum of residues in the filter and in the vial was lower than in the control (15%), but the differences were not statistically significant. This experiment showed that in real conditions, evaporation and thermodegradation process do not affect residue levels. The amount of water passing through the membrane in 24 h is 1.01 g. The residues decrease almost completely by the effect of codistillation (**Table 4**). The presence or absence of waxes does not affect the amount of water evaporated and the quantity of pesticides entrained. Because the area of the hole in the vial cap was 2 cm^2, every square centimeter was crossed by 500 mg of water in 24 h. A tomato weighing 100 g had an area of 134 cm^2 and lost 1.12 g every day due to evaporation; consequently, the surface of a tomato is crossed by 8.3 mg of water/cm^2. Therefore, it would need 60 days to be crossed by 500 mg of water. In field trials, the residues decreased from 1.39 to 0.22 mg/kg in 10 days, with a loss of 1.17 mg/kg, equivalent to a codistillation of pesticides of 8.7 μg/cm^2. The model system shows that due to codistillation, the fruit should have a daily loss of pesticides of 0.03 μg/cm^2; therefore, it should lose 0.3 μg/cm^2 in 10 days, that is, 0.4 mg/kg, corresponding to one-third of the total loss in a greenhouse. The pesticides exposed to sunlight have a high tendency to degrade (**Table 5**). In fact, in absence of waxes, the formulation degrades after 4 h by 90%, with a half-life of 1.1 h. Screening the radiation with a glass cover caused a decrease in the photodegradation effect, with a half-life of 5.6 h. In the presence of waxes, the a.i. shows a disappearance rate slower by a factor of 3. This experiment shows that photodegradation plays an important role in the disappearance of pesticides and that the glass screen can decrease the effect of the sun radiations by a factor of 5. Because the residue decrease on tomatoes is considerably lower, it can be assumed that the pesticides went beyond the cuticle layer allowing a greater protection from sunlight radiations. These data show that codistillation and photodegradation are responsible for the decrease in pyrimethanil in tomatoes and that photodegradation should be the main degradation effect.

Table 5. Photodegradation of Pyrimethanil at Sunlight

		formulation without waxes		formulation with waxes	
time (hours)	control (mg/kg)	field (mg/kg)	greenhouse (mg/kg)	field (mg/kg)	greenhouse (mg/kg)
0	1.06 ± 0.11	1.06 ± 0.11	1.06 ± 0.06	1.03 ± 0.12	1.01 ± 0.05
4	1.06 ± 0.08	0.09 ± 0.02	0.45 ± 0.03	0.50 ± 0.08	0.83 ± 0.11
8	1.06 ± 0.12	nd	0.21 ± 0.02	0.30 ± 0.06	0.74 ± 0.06
12	1.05 ± 0.13	nd	0.10 ± 0.02	0.07 ± 0.01	0.68 ± 0.03
21	0.95 ± 0.04	nd	0.08 ± 0.01	nd	0.45 ± 0.05
$t_{1/2}$		1.1	5.6	3.2	18.8

Table 6. Photodegradation of Cyprodinil at Sunlight

		formulation without waxes		formulation with waxes	
time (hours)	control (mg/kg)	field (mg/kg)	greenhouse (mg/kg)	field (mg/kg)	greenhouse (mg/kg)
0	0.93 ± 0.07	0.93 ± 0.07	0.95 ± 0.02	1.03 ± 0.10	1.00 ± 0.06
4	0.99 ± 0.06	0.13 ± 0.03	0.49 ± 0.04	0.62 ± 0.06	0.76 ± 0.03
8	1.08 ± 0.08	0.03 ± 0.01	0.23 ± 0.01	0.47 ± 0.06	0.54 ± 0.06
12	1.04 ± 0.06	nd	0.09 ± 0.03	0.33 ± 0.01	0.38 ± 0.03
21	1.02 ± 0.03	nd	0.06 ± 0.01	0.08 ± 0.05	0.40 ±0.05
$t_{1/2}$		1.6	5.0	5.8	8.5

Cyprodinil and Fludioxonil. Because these compounds have the same formulation, they are considered together in the discussion. After the first treatment, the decrease rate of the two pesticides was similar (6.7 and 6.1 days for cyprodinil and fludioxonil, respectively), while after the second treatment the decrease rate of cyprodinil was significantly higher than that of fludioxonil (4.9 vs 7.6 days). A week after treatment, the residue level of cyprodinil was above the MRL (0.5 mg/kg), while fludioxonil was below it (1 mg/kg) immediately after treatment. The data shown in these trials raise doubts as to the MRL values established for these 2 fungicides; in particular, the MRL for fludioxonil is twice that for cyprodinil, while the concentration in the formulation is 1.5 times higher in cyprodinil.

Data from the model system show that both fungicides are not thermodegraded and have little evaporation in the presence of waxes (20% for cyprodinil and 3% for fludioxonil; **Table 3**). Cyprodinil was codistilled almost completely in test B. Considering the same arguments as for pyrimethanil, with cyprodinil, the loss of fungicide in 60 days should be 0.4 μg/cm^2 in the presence of waxes (**Table 4**). Therefore, after the 10 days of the experiment, the loss should be 0.07 μg/cm^2, corresponding to 0.09 mg/kg. These data corrected for evaporation (20%) are 0.07 mg/kg. Fludioxonil in the presence of waxes does not show any codistillation effect.

Photodegradation of cyprodinil with waxes is slower than without (**Table 6**). This means that waxes could adsorb the radiations responsible for photodegradation. A similar effect is obtained if the sunlight is screened with a glass plate. In pseudo real conditions (formulation, waxes, and greenhouse), the half-life is 8.5 h. The half-life of fludioxonil in pseudo real conditions

Table 7. Photodegradation of Fludioxonil at Sunlight

		formulation without waxes		formulation with waxes	
time (hours)	control (mg/kg)	field (mg/kg)	greenhouse (mg/kg)	field (mg/kg)	greenhouse (mg/kg)
0	1.08 ± 0.05	1.06 ± 0.05	1.09 ± 0.02	1.06 ± 0.03	1.10 ± 0.07
2	1.08 ± 0.05	0.29 ± 0.07	0.29 ± 0.04	0.29 ± 0.07	0.26 ± 0.05
4	1.18 ± 0.07	0.22 ± 0.01	0.24 ± 0.02	0.18 ± 0.01	0.22 ± 0.02
8	1.02 ± 0.06	0.14 ± 0.02	0.14 ± 0.05	0.10 ± 0.00	0.10 ± 0.03
12	1.10 ± 0.07	nd	nd	nd	nd
$t_{1/2}$		3.0	3.0	2.5	2.5

Table 8. Photodegradation of Azoxystrobin at Sunlight

		formulation without waxes		formulation with waxes	
time (hours)	control (mg/kg)	field (mg/kg)	greenhouse (mg/kg)	field (mg/kg)	greenhouse (mg/kg)
0	1.50 ± 0.10	1.50 ± 0.10	1.50 ± 0.06	1.48 ± 0.11	1.53 ± 0.08
4	1.45 ± 0.10	0.07 ± 0.02	0.71 ± 0.06	0.63 ± 0.02	1.00 ± 0.09
8	1.47 ± 0.24	nd	0.43 ± 0.04	0.56 ± 0.11	0.60 ± 0.15
12	1.58 ± 0.04	nd	0.17 ± 0.05	0.45 ± 0.10	0.50 ± 0.08
21	1.47 ± 0.02	nd	0.14 ± 0.03	0.27 ± 0.04	0.29 ± 0.08
$t_{1/2}$		0.9	6.0	9.6	8.9

is 2.5 h, and it is not affected by waxes or by a glass screen (**Table 7**).

From the data obtained, we can state that the decrease in fludioxonil is due only to photodegradation, while in cyprodinil there is a combination of evaporation and codistillation. Because cyprodinil is a fungicide with a systemic action, the effect of photodegradation could be less effective.

Azoxystrobin. This a.i. was unchanged after both treatments. Because the residue level was below the MRL (2.0 mg/kg) immediately after treatment, this limit seems an over-estimation. The data from the model system show no evaporation, thermodegradation, or codistillation effects for this fungicide. The photodegradation experiment shows that waxes have a stronger screen effect than glass, 9.6 vs 0.9 h (**Table 8**). The a.i. is sensible to photodegradation, but absence of any decrease in operative conditions is due to the systemic activity of azoxystrobin, as in cyprodinil.

CONCLUSION

The degradation trials on fungicides in a greenhouse have shown that, except for cyprodinil, pesticide residues at the PHI are below the MRL. The presented data show that for cyprodinil it would be appropriate to increase the PHI at 10 days or the MRL, considering that higher MRLs are established in other crops (2 mg/kg in strawberry and lettuce). The model systems have been useful to understand the mechanisms responsible for the disappearance of the pesticides.

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Received for review September 18, 2001. Revised manuscript received December 17, 2001. Accepted December 18, 2001.

JF011219F