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Dissipation Rates of Cyprodinil and Fludioxonil in Lettuce and Table Grape in the Field and under Cold Storage Conditions

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Two fungicides (cyprodinil and fludioxonil) have recently been used in southeast Spain to control disease in lettuce and grape. Gas chromatography with a nitrogen–phosphorus detector (GC-NPD) was used to study the disappearance of these compounds from crops under field conditions and during refrigeration. Residual values 21 days after application were below the maximum residue limit (MRL = 0.05 mg kg^{-1}) established by Spanish law in the field experiment for both compounds. However, with the exception of fludioxonil in lettuce, residues were above the MRL in the refrigerated farm produce for both fungicides. The half-lives were 3–6 times greater under refrigeration.

KEYWORDS: Refrigeration; lettuce; table grape; fungicides; dissipation

INTRODUCTION

The province of Murcia (southeast Spain) has a large agricultural sector, much of which is dedicated to horticultural produce and grapes. Of the 605 950 ha planted to agriculture, 11 676 ha (1.92%) are dedicated to lettuce and 4982 ha (0.82%) are dedicated to table grapes. Approximately 75% of the lettuce crop and 80% of the grapes are exported, mainly to the EU, representing a yearly total of 211 million Euros (*1*, *2*).

To maintain market share in the face of foreign competition offering cheaper produce, an effort should be made to improve quality and, if possible, to obtain produce free of pesticide residues (*3*). However, the grower is obliged to continue using chemical fungicides as the main recourse against infection and disease despite the existence of cultivation techniques and biological agents that are not yet as effective (*4*, *5*).

Synthetic fungicides are gradually dissipated after application and dissipation rate depending on several factors including (i) the species cultivated; (ii) the chemical formulation and application method (*6*, *7*); (iii) climatic conditions, especially rainfall and temperature; (iv) physical causes, mainly volatilization; and (v) chemical degradation, in which sunlight plays an important part (*8*, *10*). This means that dissipation curves are only valid for a given crop in the specific conditions of each growing area.

Among the diseases that produce serious losses in the two crops under study are gray mold (*Botrytis cinerea*) in table grape and Sclerotinia (*Sclerotinia minor* and *Sclerotinia sclerotiorum*) in lettuce (*11*, *12*). A new fungicide, SWITCH (Syngenta, Basel, Switzerland), has recently been used in southeast Spain to control both diseases. This product contains two active ingredients, cyprodinil (37.5%) and fludioxonil (25%). The double action of this product is due to its containing active ingredients of two different families, anilinopyrimidine (cyprodinil) (*13*, *14*) and phenylpyrrole (fludioxonil) (*15*, *16*). The first inhibits the biological synthesis of methionine, one of the principal components of the fungus protein synthesis (*17*, *19*), while fludioxonil stimulates the synthesis of glycerol, which blocks the cell growth in the fungus (*19*, *20*).

The aim of the study described in the paper was to increase our knowledge of the above-mentioned fungicides, which have recently been used in southeast Spain to treat lettuce and grape crops. The experiment was carried out in the field and in a cold chamber. The cold chamber simulated the refrigerated conditions of shipment for both crops to decrease residual degradation.

MATERIALS AND METHODS

Plant Material. The table grape studied (var. Superior) was planted in 1994 in a sandy clay soil using American vines as rootstock in a 3 m × 3 m layout. The experimental plot was situated in Alhama (Murcia, southeast Spain). Pot-grown lettuce plants (var. Iceberg) were planted in 1999 in the same type of soil in a 0.75 m × 0.25 m layout. The experimental plot, in this case, was situated in El Mirador (Murcia, southeast Spain).

Phytosanitary Treatments. For the field experiment, six 15 m^2 plots were chosen for each crop. Three were treated with the two fungicides, while the other three plots were left untreated (control). In the case of lettuce, the phytosanitary product SWITCH (37.5% cyprodinil and 25% fludioxonil) was applied in February 1999 using a backpack leaf sprayer (Maruyama) with a nozzle size of 0.8 mm in a dose of 1 kg ha^{-1}. During application, the windspeed was 0.47 m s^{-1}, temperature 18 °C,

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and relative humidity (RH) 45%. No rainfall occurred during the 21 days the experiment lasted. The table grape was treated with the same doses and application method in June 1999. The windspeed during application was 0.56 m s^{-1} with a temperature of 27 °C and RH of 46%. Once again, no rainfall occurred during the 21 day experiment period. Preharvest times for fungicides are 7 and 21 days for lettuce and table grape, respectively.

Sampling, Refrigeration Assay, and Sample Preparation for Analysis. One sample of each plot was taken following FAO recommendations (*21*); bunches that were taken formed all depths, heights, and orientations in the case of grapes and randomly for lettuce. Samples were taken 2 h after application and then after 1, 3, 7, 14, and 21 days. The total weight was 2 and 3 kg for grapes and lettuce, respectively, except on day 21 when 25 kg of each was collected. In each sampling control, samples were taken to determine whether the grower had carried out an unsupervised treatment.

Immediately after collecting the samples on day 21, the plots were treated again, and 2 h later, 25 kg samples for both grapes and lettuce were placed in the cold chamber at 4 °C and in darkness. Samples for analysis were taken 1, 7, 14, and 21 days after they were placed in the chamber.

After the stems of the grapes and the withered leaves of the lettuce were sampled and removed, the samples were homogenized in a food processor (Osterizer, Pulsematic 16). The homogenate of each sample was then placed into polyethylene containers and frozen at −30 °C until its analysis.

Active Ingredients. Cyprodinil [N-(4-cyclopropyl-6-methylpirimidin-2-yl)aniline] and fludioxonil [4-(2,3-difluoro-1,3-benzodioxol-4-yl)pyrrole-3-carbonitrile] were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Both compounds were higher than 98% pure.

Extraction Procedure. For the extraction of fungicide residues from table grapes and lettuce, a micro off-line method was used. The vegetable material was extracted with ethyl acetate, followed by filtration and concentration of the extract.

Ten grams of sample was homogenized with 60 mL of ethyl acetate at 8000 rpm for 3 min in a high-speed electric mixer (Polytron-Aggregate, Kinematica, Germany). The mixture was filtered through a porous plate funnel (pore size no. 4), and the filtrate was passed through Phase Separator Paper (Whatman 2100150 1 PS) into a washing flask with 10 mL of ethyl acetate. All of the fractions were collected in a concentration flask and concentrated to dryness by rotary vacuum evaporation. The dry extract was dissolved in 10 mL of isooctane−toluene (1:1, v/v). Pesticide grade solvents were purchased from Panreac (Barcelone, Spain).

Fungicide Residue Analysis. A Hewlett-Packard 6890 gas chromatograph equipped with a nitrogen−phosphorus detection (NPD) system, autosampler (6890 Hewlett-Packard), and split-splitless injector connected to a HP ChemStation (Hewlett-Packard) was used. The capillary column was a HP-5 (30 m × 0.32 mm i.d.) with 5% diphenyl/95% dimethylsiloxane (film thickness 0.25 μm) (Hewlett-Packard). The injector and detector were operated at 250 and 300 °C, respectively. The sample (2 μL) was injected in the splitless mode (0.75 min). The oven temperature was programmed as follows: 70 °C for 1 min, raised to 100 °C (15 °C min^{-1}), to 210 °C (10 °C min^{-1}) for 1 min, to 270 °C (15 °C min^{-1}), and held for 7 min. Nitrogen was used as the carrier and makeup gas at 1.9 and 8.9 mL min^{-1}, respectively. Hydrogen and air were used as detector gases at 3 and 60 mL min^{-1}, respectively.

Recovery Assays. Untreated grape and lettuce samples were crushed and homogenized before being spiked with fungicides. Recovery assays were performed in the 0.01−0.5 mg kg^{-1} range. The quantification of recovery was carried out with standards dissolved into pure solvent (there is not a matrix effect with the detector used, NPD). The samples were processed according to the above procedure. At each fortification level, five replicates were analyzed.

Statistical Analysis. Statistical analyses were done using the Statistical Package for Social Sciences (SPSS 10.0) program.

RESULTS AND DISCUSSION.

Analytical Determination. The linearity of the method was tested using standard solutions in the 0.01−2 mg L^{-1} range for cyprodinil and the 0.05−2 mg L^{-1} range for fludioximil. The method was linear for both fungicides with satisfactory precision (>0.99).

The reproducibility of the GC response was evaluated by repeating the injection of the same standard seven times under constant operating conditions. The values found for the coefficient of variation (CV) were 1.1 for cyprodinil and 8.6 for fludioxonil.

The method recovery factors obtained in table grape and lettuce are presented in **Table 1**. Mean recovery ($n = 5$) in lettuce ranged from 81 to 94%. The CV ranged from 3.7 to 18.8% in the most unfavorable case. In table grape, the recoveries from fortified samples were in the range of 81−99% with a CV of 6.2−17.5%. These results demonstrate the good performance of the method.

The limits of quantitation (LOQ) for table grape and lettuce were 0.01 and 0.05 mg kg^{-1} for cyprodinil and fludioxonil, respectively. These limits are, in all cases, below the maximum residue limit (MRL) established by the different legislation for those compounds (0.05 mg kg^{-1} for both fungicides in both crops).

Dissipation Study. Table 2 shows the residual values of both fungicides in the field samples of lettuce and table grape. It can be seen that in lettuce, 7 days after treatment, fludioxonil levels were below the LOQ (0.05 mg kg^{-1}), a value that coincides with Spanish MRL levels. In grape, the residual level of fludioxonil was below the MRL after 14 days. The dissipation of cyprodinil showed a similar curve for both crops, although residual levels remain high for longer (7 days in lettuce and 21 days in table grape).

The greater persistence in grape than in lettuce was probably due to the “dilution effect” brought about by the rapid growth of the latter since the residue is expressed as a proportion of weight (mg kg^{-1}). As the weight of vegetable material increases, then the proportion of residue decreases. This is known as “apparent elimination” and is important in rapidly growing crops (lettuce can easily double its weight in a few days) (*22*). The greater degradation of fludioxonil than of ciprodinil is probably due to the different chemical structures of the compounds.

Because these products have been recently used, we have found no studies concerning their dissipation except that carried

Table 1. Mean Recovery Test ($n = 5$)

fungicide	fortification level (mg kg^{-1})	lettuce recovery (%)	lettuce CV (%)	table grape recovery (%)	table grape CV (%)
cyprodinil	0.01	81.0	18.8	93.5	17.5
	0.1	92.3	3.7	94.7	8.8
fludioxonil	0.05	86.1	17.1	98.6	17.2
	0.5	94.4	14.5	80.8	6.2

Table 2. Dissipation of Cyprodinil and Fludioxonil Residues (mg kg^{-1}) in Lettuce and Grape under Field Conditions[a]

days	lettuce cyprodinil (± SD)	lettuce fludioxonil (± SD)	table grape cyprodinil (± SD)	table grape fludioxonil (± SD)
0	0.345 ± 0.024	0.222 ± 0.043	0.633 ± 0.043	0.406 ± 0.045
1	0.312 ± 0.030	0.223 ± 0.039	0.534 ± 0.032	0.347 ± 0.030
3	0.198 ± 0.036	0.067 ± 0.026	0.432 ± 0.019	0.243 ± 0.026
7	0.048 ± 0.019	ND	0.183 ± 0.026	0.141 ± 0.026
14	ND	ND	0.069 ± 0.011	ND
21	ND	ND	0.030 ± 0.007	ND

[a] ND, not detected (<LOQ).

Table 3. Dissipation of Cyprodinil and Fludioxonil Residues (mg kg^{-1}) in Lettuce under Cold Storage Conditions[a]

	cyprodinil (± SD)		fludioxonil (± SD)	
days	GAP[b]	2nd treatment[c]	GAP[b]	2nd treatment[c]
0	ND	0.450 ± 0.020	ND	0.388 ± 0.034
3	ND	0.375 ± 0.028	ND	0.348 ± 0.035
7	ND	0.330 ± 0.020	ND	0.168 ± 0.020
14	ND	0.180 ± 0.026	ND	0.080 ± 0.023
21	ND	0.075 ± 0.022	ND	ND

[a] ND, not detected (<LOQ). [b] GAP (good agricultural practice). Samples were gathered 21 days after the first phytosanitary treatment and stored in cold chamber according to GAP. [c] Samples treated twice, once 21 days before harvest and 21 days before stored in the cold chamber.

Table 4. Dissipation of Cyprodinil and Fludioxonil Residues (mg kg^{-1}) in Table Grape under Cold Storage Conditions

	cyprodinil (± SD)		fludioxonil (± SD)	
days	GAP[b]	2nd treatment[c]	GAP[b]	2nd treatment[c]
0	0.030 ± 0.010	0.705 ± 0.032	ND	0.420 ± 0.030
3	0.028 ± 0.011	0.650 ± 0.028	ND	0.393 ± 0.028
7	ND	0.540 ± 0.026	ND	0.243 ± 0.040
14	ND	0.473 ± 0.026	ND	0.225 ± 0.062
21	ND	0.435 ± 0.032	ND	0.192 ± 0.074

[a] ND, not detected (<LOQ). [b] GAP (good agricultural practice). Samples were gathered 21 days after the first phytosanitary treatment and stored in cold chamber according to GAP. [c] Samples were treated twice, once 21 days before harvest and 21 days before stored in the cold chamber.

out by Cabras et al. (*23*) in grapes intended for producing wine. That study involved much higher doses than we used. Their residue levels 21 days after treatment were 19.5 and 64.5% of initial values for cyprodinil and fludioxonil, respectively, indicating a much higher dissipation rate for cyprodinil than for fludioxonil, contrary to our findings. Higher dose and different variety and application and weather conditions can be responsible for the different dissipation rates of the two fungicides.

The data concerning the behavior of both fungicides in refrigerated conditions and darkness (**Tables 3** and **4**) show that except for fludioxonil in lettuce, the values remaining 21 days after the second treatment were considerably above the MRL of both fungicides (0.05 mg kg^{-1}). The higher dissipation rate in lettuce than grape in cold conditions can only be due to the influence of the plant material itself (water content, chemical composition, and enzyme content) (*22*).

The residue dissipation rate in lettuce and table grape was derived by fitting the experimental data to a pseudo-first-order kinetic function (*24*). To test the correlation coefficient (r) obtained, a test quantity (D) was calculated to ascertain whether there was a correlation between residue and time; that is, whether the correlation coefficient differed significantly from zero:

$$D = r - \frac{t}{\sqrt{t^2 + (n-2)}}$$

where r is the absolute value of the correlation coefficient and t is the value of t, for $n - 2$ d.f., in the table of Student-t distribution at the contrasted level of probability.

The statistical values calculated for the two compounds are shown in **Table 5**. As can be observed, the quantity (D) was in all cases (except for fludioxonil in the field experiment involving in lettuce) greater than 0, which confirms that there was a correlation between residual level and time.

The values found for the rate constants (k) show that in all cases dissipation rates were higher in the field at ambient temperature and with natural light than in cold conditions and darkness. This was particularly evident in the case of cyprodinil. Such findings were not unexpected since it is known that the

Table 5. Linear Fit of the Data for the Dissipation of Both Fungicides in Lettuce and Table Grape

	parameter					
fungicide	*r*	*R*	TEE[a]	*a* ± CI (95%)	*k* ± CI (95%)	*D*[b]
			lettuce in field			
cyprodinil	−0.9873	0.9747	0.1718	−0.938 ± 0.429 (*)	−0.281 ± 0.138 (*)	0.0873
fludioxonil	−0.9424	0.8832	0.3154	−1.341 ± 3.384	−0.411 ± 1.855	−0.0453
			table grape in field			
cyprodinil	−0.9960	0.9921	0.1227	−0.499 ± 0.198 (**)	−0.148 ± 0.018 (***)	0.2667
fludioxonil	−0.9965	0.9930	0.0486	−0.911 ± 0.150 (**)	−0.153 ± 0.039 (**)	0.0965
			lettuce in cold storage room			
cyprodinil	−0.8884	0.7893	0.3653	−0.667 ± 0.805	−0.072 ± 0.068 (*)	0.0829
fludioxonil	−0.9874	0.9750	0.1417	−0.853 ± 0.463 (*)	−0.119 ± 0.058 (*)	0.0874
			table grape in cold storage room			
cyprodinil	−0.9728	0.9464	0.0546	−0.390 ± 0.120 (**)	−0.023 ± 0.010 (**)	0.1673
fludioxonil	−0.9219	0.8499	0.1587	−0.936 ± 0.3497 (**)	−0.038 ± 0.030 (*)	0.1164

[a] Typical error of estimate. [b] Test quantity for correlation. *p (≤0.05); **p (≤0.01); ***p (≤0.001).

Table 6. Theoretical Values (R_0) Corresponding to the Initial Residue Levels (mg kg^{-1}), Residual Concentration in the Preharvest Time (R_{PT}) (mg kg^{-1}), Half-Life Times ($t_{1/2}$) (Days), and Time Necessary to Reach the MRLs (t_{MRL}) (Days) for the Two Fungicides Studied

		field				cold storage room			
vegetal stuff	fungicide	R_0	R_{PT}[a]	$t_{1/2}$	t_{MRL}[b]	R_0	R_{PT}	$t_{1/2}$	t_{MRL}
lettuce	cyprodinil	0.391	0.054	2.46	7.31	0.513	0.310	9.64	32.39
	fludioxonil	0.261	0.015	1.68	4.02	0.426	0.184	5.80	17.93
table grape	cyprodinil	0.607	0.027	4.68	16.85	0.677	0.415	29.75	111.8
	fludioxonil	0.402	0.016	4.53	13.61	0.392	0.175	18.05	53.63

[a] PT, preharvest time (7 days for lettuce and 21 days for table grape). [b] MRL (0.05 mg kg^{-1}) for lettuce and table grape.

most important factor in pesticide dissipation is chemical degradation, especially that caused by high temperatures and solar radiation (*22*). However, during cold storage, decreases of weight are nonsignificant, evaporation and photodegradation appear negligible, and the only way to interpret the high rate of residue disappearance seems to be the enzymatic degradation.

On the basis of the linear fit carried out, **Table 6** shows the values of the theoretical initial residue (R_0), half-life ($t_{1/2}$), theoretical residual level corresponding to the preharvest times (R_{PT}), and time necessary for the concentrations to reach the MRLs permitted by Spanish law (t_{MRL}). The above findings show that the preharvest times established by Spanish law are longer, except for cyprodinil in lettuce, in which case they coincided, than the time we found necessary for MRL to be reached (t_{MRL}). In the refrigeration experiment, the t_{MRL} was 10−20 times longer than in the field, with up to 4 months necessary for cyprodinil in table grape to fall below MRL.

The study confirms the substantial influence of temperature and sunlight on the dissipation rates of the fungicides studies. The presence of residues at the time of harvesting, particularly in table grape, may be problematic if the crop is stored or transported in cold conditions for a given time.

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