JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Variation in Concentrations of the Fungicides Tebuconazole and Dichlofluanid Following Successive Applications to Greenhouse-Grown Lettuces

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Residual levels and degradation rates of tebuconazole and dichlofluanid in lettuce plants grown in a greenhouse under agricultural conditions typical of northwestern Spain were studied. Lettuce plants were sprayed four times with a homogeneous 0.2% aqueous solution of Folicur Combi (wettable powder containing 40% dichlofluanid and 10% tebuconazole) at a rate of 2500 g/ha. Samples were collected 1, 5, and 9 days after the first two applications and at times ranging from 1 to 27 days after the last two applications. All samples were stored in a refrigerator at 4 °C. Fungicide levels were determined by solid−liquid extraction (SLE) followed by gas chromatography and mass spectrometry detection (GC−MSD). Recovery was good for tebuconazole (98%) but low for dichlofluanid (29%); precision was good (<10% for both analytes), and quantification limits were low (<1.5 mg/kg). Seven days after the last application, dichlofluanid levels were below the maximum allowed limit established in Spain (10 mg/kg), but tebuconazole levels were above the corresponding limit (5 mg/kg). Tebuconazole concentration dynamics was accurately fitted by zeroth- or combined first- and zeroth-order models (depending on variety), but modeling of the behavior of dichlofluanid was less satisfactory, probably due to its instability.

KEYWORDS: Fungicides; tebuconazole; dichlofluanid; dissipation; lettuce; greenhouse; gas chromatography with mass selective detection.

INTRODUCTION

The warm, humid microclimate of greenhouses favors the development of fungal infections. Prominent among diseases that result in serious losses in lettuce crops (*1*, *2*) are those caused by *Sclerotinia* (spp. *minor* and *sclerotiorum*). Since biological agents are as yet ineffective (*3*, *4*) against infection with these pathogens, the main strategy against them is still preharvest treatment with chemical fungicides such as Bayer's Folicur Combi. This product contains two active ingredients: dichlofluanid (40%) and tebuconazole (10%). Dichlofluanid (DCF, IUPAC name *N*-[(dichlorofluoromethyl)thio]-*N*′,*N*′-dimethyl-*N*-phenylsulfamide; **Figure 1**) is a nonsystemic fungicide that acts by inhibiting the germination of fungal spores and blocking fungal respiration. Its acceptable daily intake (ADI) is 0.3 mg/kg day (*1*), and the maximum residue limit (MRL) established in Spain and the rest of the EU for DCF in lettuces is 10 mg/kg (*5*, *6*). Tebuconazole [TBC, IUPAC name (*RS*)-1-(*p*-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)-pentan-3-ol; **Figure 1**] is a systemic fungicide that acts by inhibiting the synthesis of ergosterol to prevent fungal mycelium development; its ADI is 0.03 mg/kg day (*1*) and its Spanish MRL 5 mg/kg (*6*).

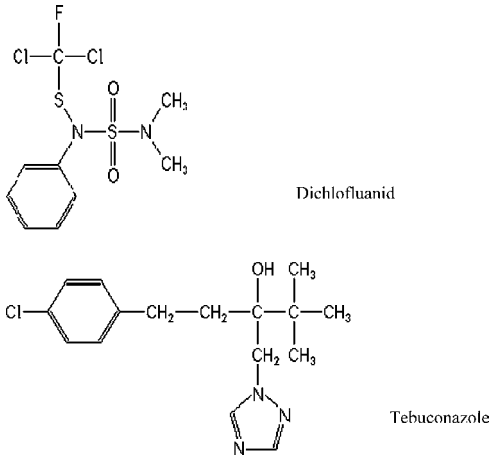

Figure 1. Chemical structures of the fungicides.

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10.1021/jf047848h CCC: $30.25
Published on Web 04/30/2005

Whereas greenhouse vegetables such as tomatoes and eggplants constitute only part of the whole plant, in the case of lettuce it is all of the aerial parts of the plant that constitute the commercial product. Dejonckheere et al. (*7*) and Meloni et al. (*8*) found that fungicide residues accumulated upon repeated applications of the same active ingredient to greenhouse-grown lettuce. Also, pesticide levels measured by Meloni et al. (*8*) in the outer leaves of greenhouse-grown lettuce were much higher than those allowed by Italian laws; although outer leaves are often discarded prior to marketing, and the inner leaves contained no trace of the pesticides studied, compliance with safety time regulations did not ensure that residual levels fell below the legally established limits. Similarly, Sances et al. (*9*) found that at harvest time the highest concentrations of pesticide in pesticide-treated head lettuces were in the basal and outer wrapper leaves. Cabras et al. (*10*) found pesticide levels in lettuce were strongly influenced by plant structure, which depends on cultivar type: immediately after application, the outer leaves of crisphead lettuce were found to contain higher residue concentrations than the inner leaves, which were partially protected by the outer leaves, while the reverse was the case for cos lettuce, although in both varieties it was the outer leaves that subsequently had the higher concentrations.

The dissipation of synthetic fungicides after their application depends on various factors, including plant species, formulation, and application method (*11*, *12*), climatic conditions (especially humidity and temperature), physical phenomena (mainly volatilization), and chemical degradation, in which sunlight plays a prominent role (*13*, *14*). Controlling fungicide residues and preventing them from exceeding established maximum limits requires determination of their dissipation curves. Marín et al. (*15*), who evaluated the dissipation rates of cyprodinil and fludioxonil in lettuce in the field and under cold storage conditions, confirmed that temperature and sunlight have a substantial influence on the dissipation rates of both fungicides. No specific studies on the persistence of DCF and TBC have been reported.

The main purpose of this study was to estimate the rates of disappearance of dichlofluanid and tebuconazole following successive applications to two varieties of lettuce (one a butterhead, one a crisphead) grown in greenhouse conditions.

EXPERIMENTAL PROCEDURES

Active Ingredients and Fungicide Product. Standards of dichlofluanid [CAS Registry No. 1085-98-9] and tebuconazole [CAS Registry No. 107534-96-3] were obtained from Riedel-de-Haën (Seelze, Germany) and were >99% pure. Lindane (97%), used as an internal standard, was purchased from Aldrich (Steinheim, Germany). The fungicide product used was Folicur Combi (Bayer Hispania, S. A., Barcelona, Spain), a wettable powder containing 40% dichlofluanid and 10% tebuconazole.

Plant Material and Fungicide Treatments. The experimental greenhouse was located on the Ourense Campus of the University of Vigo (NW Spain). Two varieties of lettuce (*Lactuca sativa L. var. capitata L*) were grown, the crisphead cultivar Batavia and the butterhead Trocadero. In mid-March 2004, each cultivar was planted in 15 20-compartment 32 × 25 × 5-cm seed trays containing the same substrate (maximum humidity 50%, organic matter 85%, nitrogen 1.7%, phosphorus 0.2%, calcium 1%, potassium 0.2%, pH 5.6) (30 trays in all). During April and May, a 0.2% solution of the fungicide was applied with a leaf sprayer four times at an application rate of 2.5 kg of Folicur Combi/ha. The first application was after the lettuces had grown for a month, and the other three were at regular intervals of 10 days. Immediately following the last application (on day 30), the 60-day-old lettuces were transferred to pots. The preharvest safety interval for lettuce treated with fungicides is 7 days; however, fungicide levels were monitored for 24 days after the last application.

Sampling. Samples were taken from the seed trays following the FAO recommendations (*16*). Whole lettuces were cut 2 h before the first application of fungicide (control samples; day 0) and then on days 1, 5, 9, 11, 15, 19, 21, 24, 27, 30, 35, 40, and 47. On day 30, before the last application of fungicide, the 20 lettuces in one seed tray of each variety were planted individually in pots; these plant lots were sampled on days 4, 8, 12, 16, 20, and 24 after transfer (May−June). Following collection, lettuces were weighed, placed in polyethylene containers, and stored at 0−4 °C until extraction and analysis.

Solid−Liquid Extraction (SLE) Procedure. Samples were homogenized for 5 s in a food processor, and a portion of the homogenate (5 g) was placed in a 250-mL polypropylene carbonate centrifuge tube, where it was extracted with hexane (50 mL) by 5 min in an ultrasound bath at room temperature followed by vigorous back-and-forward shaking for 10 min and centrifugation at 2000 rpm (910*g*) for 15 min at 5 °C. A 30 mL sample of the organic layer was then transferred to a flask and concentrated to dryness in a rotary evaporator at 40 °C and 150 mbar. The residue was dissolved in 2 mL of hexane containing 100 mg/L lindane (used as internal standard to correct for variability in GC−MSD injection and detection).

Fungicide Residue Determination. Gas chromatographic analysis was performed on a Fisons (Rodano, Italy) GC 8000 series gas chromatograph equipped with an MSD 800 mass-selective detector and interfaced to a desktop computer running Masslab-v. 1.4 software (ThermoQuest, Italy). A DB-17 fused-silica capillary column (30 m × 0.25 mm i.d, 0.50 μm film thickness; J&W Scientific, USA) was used, and the oven temperature program was as follows: 10 min at 50 °C, a 15 °C/min ramp to 200 °C, 1 min at 200 °C, an 8 °C/min ramp to 280 °C, and 10 min at 280 °C. A split/splitless injector was initially used for 5 min in the splitless mode and thereafter with a split ratio of 10:1. The carrier gas was helium with a constant column head pressure of 100 kPa. Under these conditions, the flow rate decreased with increasing oven temperature. The injector and transfer line temperatures were 240 and 250 °C, respectively. One microliter of sample was injected.

Mass detection was performed in the single ion monitoring (SIM) mode after a solvent delay of 15 min (ionization energy for electron impact was 70 eV). The selected ions used for detection and quantification were (*m*/*z*) 111, 183, and 219 for lindane (25.2 min); 123, 167, and 224 for dichlofluanid (28.1 min); and 125 and 250 for tebuconazole (32.7 min). The ions were selected from among the fragments with the highest *m*/*z* values and strongest signals, which are highly specific for each compound.

Experiments To Optimize the Analytical Method. *Selection of the Organic Solvent for SLE.* Untreated lettuce leaves were chopped and homogenized, and the homogenate was spiked with 10 mg/kg DCF and 5 mg/kg TBC by adding 1 mL of a mixed solution of both compounds (50 mg/L DCF and 25 mg/L TBC in acetone). After 12 h of equilibration in order to ensure complete evaporation of acetone, samples were extracted with an organic solvent as described above for hexane. The organic solvents tested (in triplicate) were hexane, ethyl acetate, acetonitrile, 1:1 (v/v) ethyl acetate/hexane, 1:3 (v/v) acetone/dichloromethane, and 1:1 (v/v) acetone/hexane.

Evaluation of Matrix Effects and Precision. The proposed method was used to determine the target fungicides in samples of three different varieties of lettuce [Batavia (A), Trocadero (B), and Romana (C)] that had been spiked with 10 mg/kg DCF and 5 mg/kg TBC. Each lettuce was analyzed in triplicate (including the SLE step in each analysis).

Characterization of Performance. The performance of the proposed method was assessed in terms of recovery, linearity and limits of detection, and quantitation. For this purpose, samples of untreated Trocadero were spiked with DCF and TBC at the levels specified below and were treated as described above following 12 h of equilibration. Absolute recoveries were determined by analyzing on the same day 5 untreated lettuce samples, each spiked with 7−20 mg/kg DCF and 1−10 mg/kg TBC, that were measured against fungicide standard solutions with 10.5−30.0 mg/L DCF and 1.5−15.0 mg/L TBC that were directly injected into the GC−MSD apparatus. The linearity of the method for each compound was checked by plotting peak area relative to that of the internal standard against fungicide concentration, using a total of five spiked untreated lettuce samples containing 4−40 mg/kg DCF and

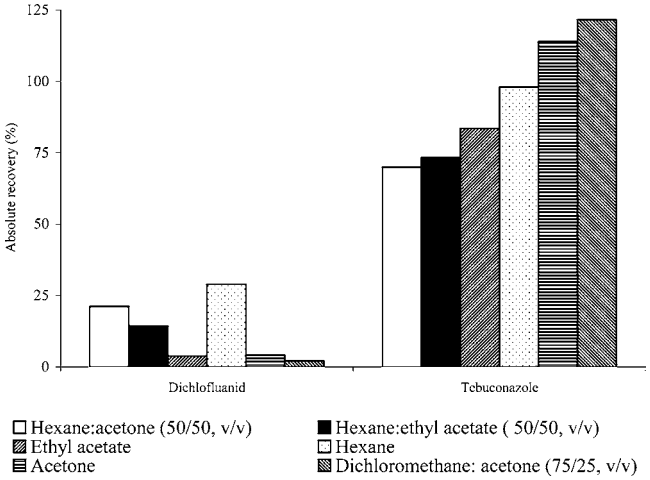

Figure 2. Absolute recoveries of DCF and TBC obtained by solid–liquid extraction with various solvents.

Table 1. Ratios of Fungicide Peak Areas to Internal Standard Peak Area (A_f/A_{is})[a] and Relative Standard Deviation (RSD, %) for DCF and TBC in Lettuce Samples of Different Varieties, As Determined by SLE/GC–MSD

	sample A	sample B	sample C
	Dichlofluanid		
A_{DCF}/A_{is}	0.46	0.44	0.44
RSD (%)	6	10	9
	Tebuconazole		
A_{TBC}/A_{is}	0.21	0.22	0.21
RSD (%)	4	5	6

[a] Means of three analyses, each including the SLE step. Lettuce samples were spiked with 10 mg/kg DCF and 5 mg/kg TBC.

1−30 mg/kg TBC that were analyzed by subjection to the entire procedure. The limits of detection (LOD) and quantitation (LOQ) were calculated from the calibration line and the background noise evaluated using seven unspiked lettuce samples; LOD and LOQ were defined as the concentrations of analyte that provided signal-to-noise ratios of 3 and 10, respectively.

Statistical Analyses and Modeling. Statistical analyses and modeling were performed using the Solver function of the Microsoft Office v. 2000 Excel spreadsheet, which includes routines for optimization of linear and nonlinear models using simplex, generalized reduced gradient, and branch-and-bound methods.

RESULTS AND DISCUSSION

Performance of the Analytical Method. Among the SLE solvents tried, the highest recoveries (see below) were obtained with hexane, which also gave rise to little interference with the GC−MSD chromatograms (**Figure 2**). No matrix effects were detected, there being no significant differences among the three varieties of lettuce as regards the ratios of the fungicide and internal standard peak areas, A_f/A_{is} (**Table 1**). The precision of the method was satisfactory, with relative standard deviations ranging from 4 to 10%.

The mean absolute recovery of TBC was almost quantitative (98%), but that of DCF was low (29%) (**Table 2**). However, relative recoveries must have been about 100% in both cases, since all samples were processed identically and the absolute recoveries may be assumed to have remained constant; since the calibration and test samples underwent exactly the same processing, poor absolute recovery should not have introduced much error into the quantitation of DCF, and this assumption

Table 2. Absolute Recoveries, Linear Ranges, Determination Coefficients (r^2), Limits of Detection (LOD), and Limits of Quantitation (LOQ) of the Optimized SLE/GC-MSD Method

	dichlofluanid	tebuconazole
absolute recovery[a] (%)	29	98
linear range[a] (mg/kg)	2–40	1–30
determination coefficient (r^2)	>0.98	>0.99
LOD[b] (mg/kg)	0.8	0.3
LOQ[b] (mg/kg)	1.5	0.5

[a] From five determinations. [b] From seven determinations.

is supported by the determination coefficients of the corresponding calibration curves, which for both fungicides were >0.98. LODs and LOQs were satisfactorily low, respectively 0.8 and 1.5 mg/kg for DCF and 0.3 and 0.5 mg/kg for TBC.

A Model of Fungicide Concentration Dynamics in Lettuce. On the basis of a review of the literature on the persistence and degradation of pesticides applied to foliage, Willis and McDowell concluded that the factors most strongly influencing the persistence of pesticides on the canopy are droplet size and contact angle, the polarity and degradation rate of the molecules of the pesticide, and the weather (*17*). Of the predictive models that have included pesticide dissipation from plants among the phenomena modeled, the most detailed is the pesticide emission model (PEM) (*18*). However, this model is basically designed for prediction of the dispersion of pesticide in the atmosphere, and in the absence of data on the rate of transfer of pesticides from the waxy cuticle of the plant to deeper cells, where they are metabolized, the only plant structure it considers is the cuticle itself, which it treats simply as a deposit from which pesticide is released, directly or indirectly, into the atmosphere. It is therefore not appropriate for modeling the postapplication dynamics of pesticide concentration in the growing plant. Other authors have reported the area-specific emission rates of dichlofluanid and tebuconazole from wood treated with a solution of these fungicides in a technical solvent (Shellsol AB) to be 0.20 and 0.49 μg m^{-2} h^{-1}, respectively (*19*), but again, these data are of little use for the present study.

In view of the difficulty of identifying the processes that contribute to the dynamics of pesticide levels in growing plants, in this work we chose to try three simple models in which the disappearance of pesticide is due to zeroth- and/or first-order processes, i.e., the model

$$dC/dt = A - K_c C - K_t \quad (1)$$

(where C is the fungicide concentration in the plant (mg kg^{-1}), A is the application rate (mg kg^{-1} day^{-1}), and K_c and K_t are rate constants) and the two special cases in which either K_c or K_t is identically zero. To facilitate identification of the model when fungicide is applied at discrete times, eq 1 was discretized as

$$C_{t+\Delta t} = C_t + A - (K_c C_t + K_t)\Delta t \quad (2)$$

and this discrete model (or the special cases with K_c or K_t identically zero) was fitted to the data by solving eq 2 numerically, with time steps Δt of 1 day, within each loop of a nonlinear least squares curve fitting routine run in Excel (constraints were imposed to prevent trends in the residuals).

Table 3 lists the optimized parameters fitting each of the three models to the TBC data, together with the goodness of fit as evaluated in terms of the slope y/x and coefficient of determination r^2 of a linear regression of fitted concentration values

Table 3. Results of Fitting Fungicide Dynamics Models to the Data for Tebuconazole

model	K_c	K_t	y/x	r^2
	Crisphead Lettuce			
first-order	0.054	–	1.002	0.823
first- and zeroth-order	0.001	0.584	1.065	0.936
zeroth-order	–	0.575	1.009	0.942
	Butterhead Lettuce			
first-order	0.055	–	0.945	0.698
first- and zeroth-order	0.001	0.596	0.970	0.803
zeroth-order	–	0.500	0.976	0.774

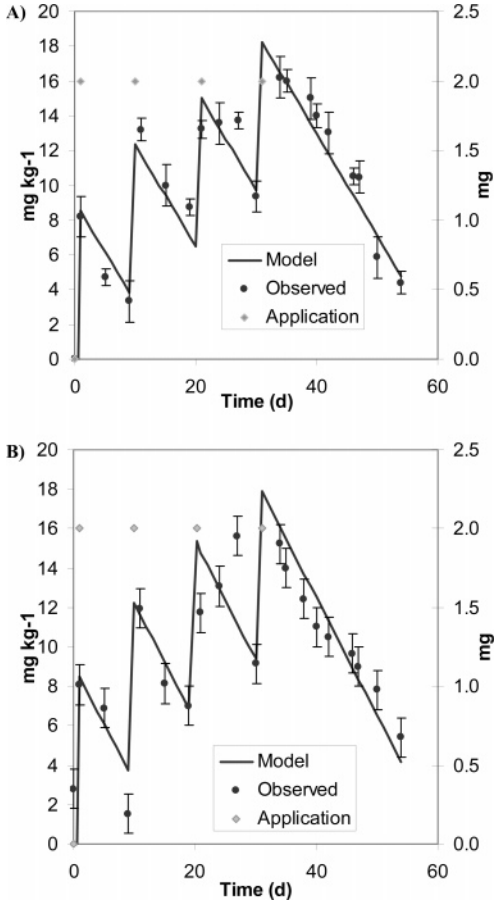

Figure 3. Observed concentrations of tebuconazole (black circles; left *y* axis) in crisphead (**A**) and butterhead (**B**) lettuce, and the results of fitting the zeroth-order model (**A**) or combined first- and zeroth-order model (**B**) of eq 1 (continuous line). Gray circles show the four doses applied (right *y* axis). See **Table 3** for model parameters and goodness-of-fit statistics.

on observed values. Although the crisphead data were fitted better by all models than the butterhead data by any of the three, for both varieties the zeroth-order and combined first- and zeroth-order models fitted better than the first-order model. However, in both cases the value of the first-order decay constant of the combined model, K_c, was very small compared to the zeroth-order constant K_t (0.001 as against 0.584 or 0.596), indicating that the decay of TBC concentration depended fundamentally on factors other than TBC concentration itself. If the disappearance of TBC is assumed to be basically due to loss to the atmosphere, the fitted values of K_t imply area-specific emission rates of about 3 μg m^{-2} h^{-1}, about six times greater than the values for emission from wood (*19*). **Figure 3** shows the data for each lettuce together with the best-fitting model in each case (the zeroth-order model for crisphead, the combined first- and zeroth-order model for butterhead).

Table 4. Results of Fitting Fungicide Dynamics Models to the Data for Dichlofluanid

model	K_c	K_t	y/x	r^2
	Crisphead Lettuce			
first-order	0.106	–	1.040	0.575
first- and zeroth-order	0.081	0.024	1.099	0.621
zeroth-order	–	0.207	0.471	0.364
	Butterhead Lettuce			
first-order	0.120	–	0.765	0.563
first- and zeroth-order	0.213	0.021	1.082	0.633
zeroth-order	–	0.512	0.678	0.287

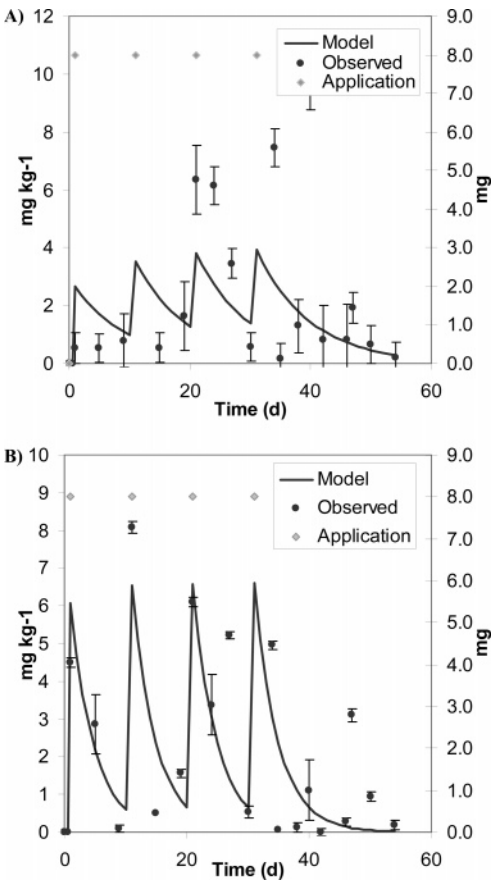

Figure 4. Observed concentrations of dichlofluanid (black circles; left *y* axis) in crisphead (**A**) and butterhead (**B**) lettuce, and the results of fitting the combined first- and zeroth-order model of eq 1 (continuous line). Gray circles show the four doses applied (right *y* axis). See **Table 4** for model parameters and goodness-of-fit statistics.

The results of fitting the three models to the DCF data are listed in **Table 4**. For both crisphead and butterhead lettuces, the best-fitting model was the combined first- and zeroth-order model (with K_t several times smaller than K_c), followed by the first-order model, although in no case was the fit achieved as good as for the TBC data (see **Figure 4**). It seems possible that the poor fit of the models to the DCF data may be due largely to DCF undergoing hydrolysis to dimethylaminosulfanilide (*1*, *20*).

The preharvest safety interval recommended by the manufacturer of Folicur Combi is 1 week. One week after the last application of fungicide in this work the residual concentration of TBC was in both lettuce varieties about 3 times higher than the Spanish MRL, 5 mg/kg. This implies that, in keeping with the findings of Meloni et al. (*6*), the prescribed safety interval is inadequate to ensure compliance with the legally established

limits following repeated applications. The concentrations of DCF were lower than its MRL (10 mg/kg), probably as the result of its hydrolysis.

To sum up, the analytical method used in this work is suitable for determining TBC and DCF in lettuce samples. It has good precision and appears to suffer from no matrix effects. In two different lettuce varieties grown in a greenhouse and treated repeatedly with Folicur Combi, the residual concentration of TBC 1 week after the last application exceeded the Spanish MRL by 3-fold. TBC concentrations during the 7 weeks following the first application of fungicide were accurately fitted by the zeroth- or combined first- and zeroth-order models of eq 1 (depending on variety). The modeling results for dichlofluanid were poorer, probably because of its greater instability.

ACKNOWLEDGMENT

We gratefully acknowledge support of this research by the Xunta de Galicia, Spain, through project PGIDIT03RAG38301PR and through a Parga-Pondal research contract awarded to Dr. Cancho-Grande, and by the Spanish Ministry of Science and Technology through Ramón y Cajal research contracts awarded to Drs. Arias-Estévez and López-Periago.

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Received for review December 21, 2004. Revised manuscript received March 31, 2005. Accepted April 1, 2005.

JF047848H