

Adsorption–Desorption Dynamics of Cyprodinil and Fludioxonil in Vineyard Soils

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Cyprodinil and fludioxonil are new-generation fungicides that are employed to protect grapevines from botrytis and various rots. In this work, their adsorption and desorption dynamics in eight vineyard soils from Galicia (northwestern Spain) were examined in batch and column experiments. Both fungicides exhibited linear adsorption isotherms, with more ready adsorption (greater K_d) of fludioxonil. K_d values for cyprodinil were significantly correlated with soil organic matter content ($r^2 = 0.675$, $p < 0.01$). Both pesticides exhibited adsorption–desorption hysteresis, but desorption was easier and more variable for cyprodinil (12–21%, RSD = 17%) than for fludioxonil (3–5%, RSD = 13%) and appeared to depend on the formation of irreversible bonds in the former case and on poor solubility in the latter. A linear adsorption model involving nonequilibrium conditions and an irreversible adsorption term was found to reproduce transport behavior accurately.

KEYWORDS: Contamination; cyprodinil; fludioxonil; adsorption–desorption; transport

INTRODUCTION

Grapes are an important crop in Spain (production of 6 million tons in 2003) and worldwide (total 2003 production of 62.1 million tons) (1). In Galicia (northwestern Spain), high relative humidity and spring rains favor fungal grapevine diseases, which are generally fought using antifungal sprays. A proportion of spray inevitably enters the soil, either at spraying time or subsequently (in raindrops falling from fungicide-treated leaves or in fallen plant debris), which is why the upper horizons of many vineyard soils contain substantial levels of copper (2, 3). Fungicides entering the soil in this way can have marked effects on the soil microbiota (4, 5) and, potentially, on organisms in any waters they may reach. The magnitude of such effects depends, inter alia, on the adsorption and desorption processes that affect the mobility of each fungicide in the ecosystem (6).

Over the past 5 years, a number of “new-generation” fungicides with improved efficacy have become commercially available, including cyprodinil and fludioxonil. Cyprodinil (4-cyclopropyl-6-methyl-*N*-phenylpyrimidine) is a systemic fungicide recommended for the prevention and treatment of various rots of fungal origin that can affect fruit plants and vines. Fludioxonil [4-(2,2-difluoro-1,3-benzodioxol-4-yl)-1*H*-pyrrole-3-carbonitrile] is a contact fungicide recommended for the control of *Botrytis cinerea*. These two fungicides are marketed together in a water-dispersible granule form under the name Switch, a preparation that is sprayed on the foliage of vines at

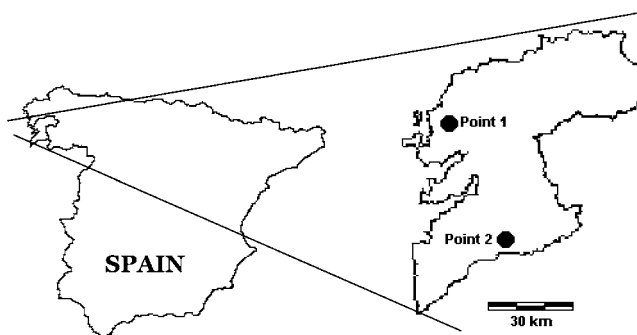


Figure 1. Locations from which the soil samples were taken.

a dosage of 0.6–1.0 kg/ha between two and nine times per season, depending on weather conditions. Because of their recent introduction, there is less information on the dynamics of cyprodinil and fludioxonil in the soil than is available for older pesticides. In this study we performed batch experiments to determine the characteristics of their adsorption on and desorption from samples of Galician vineyard soils. Because they are used together in practice, these characteristics were determined both for the individual fungicides and for a mixture of the two; experiments were also performed in which, to obtain information on their transport under nonequilibrium conditions, they were passed through a column of aggregated vineyard soil by a water flux simulating field conditions.

MATERIALS AND METHODS

Soil Samples. In each of two localities in the Galician province of Pontevedra (**Figure 1**), composite samples of the

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top 0–20 cm of the soil were obtained from four vineyards. Each of these eight composite samples was made up of five initial samples that were collected within 0.5 m of each other using an Edelman auger and were then pooled to average out spatial variation in soil properties. Once in the laboratory, the samples were dried at room temperature, passed through a 2 mm mesh sieve, homogenized, and stored until they were analyzed in duplicate.

Analytical Methods. The pH of 1:2.5 suspensions of soil in water or in 0.1 M KCl was measured with a combined glass electrode. Organic carbon content was determined by elemental analysis on a ThermoFinnigan 1112 series NC instrument. The proportions of sand (the 0.05–2.00 mm fraction), silt (0.002–0.05 mm), and clay (<0.002 mm) were determined by the wet sieving and pipet methods. Exchangeable cations were extracted with 0.2 M NH₄Cl (7) and determined by atomic absorption spectroscopy (Ca_e and Mg_e) or flame emission spectrophotometry (Na_e and K_e). Exchangeable Al was quantified by displacement with 1 M KCl, followed by atomic absorption spectrophotometry. Finally, the cation exchange capacity (CEC) was determined as the sum of bases (Na, K, Ca, and Mg) and exchangeable Al.

Soil cyprodinil and fludioxonil contents were determined as follows. A 10 g sample of soil in 15 mL of pH 8 buffer (3.6 g of sodium carbonate and 0.8 g of sodium polyphosphate in 100 mL of water) was ultrasonicated for 5 min, 10 mL of ethyl acetate was added, and the mixture was shaken in an orbital mixer for 45 min and stored at 4 °C to facilitate the separation of aqueous and organic phases. A 7 mL sample of the latter was then concentrated to dryness in a rotary evaporator at 40 °C and 240 mbar, and the residue was dissolved in 0.5 mL of a 4 mg L⁻¹ solution of internal standard (lindane) in ethyl acetate. This solution was ultrasonicated for 5 min, shaken in the orbital mixer for another 5 min, and analyzed by gas chromatography in a Fisons Instruments GC 8000 apparatus equipped with an MD 800 quadrupole mass spectrometer from the same manufacturer.

Adsorption Curves. Aqueous solutions of cyprodinil (2–12 mg L⁻¹) or fludioxonil (0.7–1.5 mg L⁻¹) were made up by adding the appropriate volume of stock solutions of the individual fungicides (1 g L⁻¹ in methanol) to 0.01 M CaCl₂ and then passing a stream of nitrogen to remove the methanol. A 5 g sample of soil was suspended in 50 mL of each, and these suspensions were shaken end-over-end for 24 h at 50 rpm and 25 ± 1 °C and then centrifuged for 30 min at 2000 rpm in a rotor ~12 cm in diameter. The resulting supernatants were analyzed on a Fisons Instruments HPLC/UV-vis liquid chromatograph, and the amounts of cyprodinil or fludioxonil adsorbed by the soil were calculated as the differences between the amounts in the initial solution and those remaining in solution after centrifugation. To investigate the influence of each fungicide on adsorption of the other, the same procedure was followed using solutions containing both 1.5 or 5 mg L⁻¹ cyprodinil and a concentration of fludioxonil of 1 mg L⁻¹ and also using solutions containing 1 mg L⁻¹ fludioxonil and a concentration of cyprodinil of 5 mg L⁻¹. All analyses were performed in triplicate.

Desorption Tests. After centrifugation of the suspensions described in the previous section that had been made from solutions containing both 1.5 mg L⁻¹ cyprodinil and 1 mg L⁻¹ fludioxonil, and following removal of the supernatant sample taken for HPLC analysis, 40 mL of the remaining supernatant of each sample was replaced with the same volume of a 0.01 M CaCl₂ solution containing no fungicide, and this solution was

shaken and centrifuged as described in the previous section. This procedure was repeated twice (three times in all), and the amounts of cyprodinil and fludioxonil that had desorbed were calculated following determination of the concentrations of the fungicides in the supernatants.

Column Experiments and Modeling. For both cyprodinil and fludioxonil, column experiments were performed on the <2 mm fractions of samples 3 and 7. Each column was set up by packing the soil uniformly between two layers of washed quartz sand (particle size pf 0.5–1.0 mm) in polypropylene tubes that were 1.8 cm long and 1 cm in inner diameter. The experiments were conducted in a chamber thermostated at 20 °C. The columns were preconditioned by percolation with ~100 pore volumes of 0.01 M CaCl₂ to homogenize the composition of cation exchange surfaces and stabilize ionic strength. The resident solution was 0.01 M CaCl₂ and the flushing solution, 5 mg L⁻¹ cyprodinil or 1 mg L⁻¹ fludioxonil in 0.01 M CaCl₂; both were injected into the columns by means of a peristaltic pump. Using a fraction collector, the eluate was collected as 2 mL fractions in Amber Titeseal vials, and the cyprodinil and fludioxonil breakthrough curves (BTCs) for each column were constructed by determining the fungicide contents of each fraction by HPLC using the procedure described above under Cyprodinil and Fludioxonil Adsorption Curves.

The transport of the fungicides through the soil columns was modeled using convection–dispersion equations under three distinct assumptions: LE, that adsorption onto and desorption from the soil were fast enough for local equilibrium to be attained throughout the column; NLE, that sorption processes were too slow for attainment of local equilibrium; and IRR, that sorption processes were too slow for local equilibrium, but adsorbed fungicide was subject to the subsequent formation of irreversible bonds with soil particles, a process modeled as a first-order decay.

Under LE, the convection–dispersion equations for one-dimensional flow may be written in dimensionless form as

$$R\partial C/\partial T = (1/P)\partial^2 C/\partial Z^2 - \partial C/\partial Z \quad (1)$$

(the meanings of the symbols are listed in **Table 1**). Under IRR, this becomes

$$\partial C/\partial T = (1/P)\partial^2 C/\partial Z^2 - \partial C/\partial Z - \omega(C - S) \quad (2)$$

$$(R - 1)\partial S/\partial T = \omega(C - S) - \mu S \quad (3)$$

For NLE, the equations are the same as for IRR except that eq 3 loses the μ term.

In this work, the program CXTFIT v. 2.1 (8) was used to try to fit the above sets of equations to breakthrough data from experiments designed to approximate the following initial and boundary conditions:

$$C(Z,0) = S(Z,0) = 0 \text{ for all } Z \quad (4)$$

$$C(0,T) - (1/P)\partial C(0,T)/\partial Z = C(T) \quad (5)$$

and

$$\partial C/\partial Z(1,T) = 0 \quad (6)$$

where $C(T)$ represents the time course of the concentration of fungicide in a 0.01 M CaCl₂ solution injected into the top of the column at the steady-state rates v listed in **Table 6**. $C(T)$ took the form of a 250 min square pulse (see the first paragraph of this subsection for the concentrations) followed by continuous application of fungicide-free 0.01 M CaCl₂ solution. For the

Table 1. Variables and Parameters of the Models^a

Dimensional Variables		
<i>x</i>	distance down the column	cm
<i>t</i>	time	h
<i>c</i>	concentration of solute in solution	mg/L
<i>s</i>	concentration of solute adsorbed onto soil particles	mg/kg
Dimensional Parameters		
<i>L</i>	column length	cm
ρ	bulk density of soil	kg/dm ³
θ	volumetric water content of soil	L/L
<i>v</i>	average velocity of water through soil pores	cm/min
<i>D</i> ^a	hydrodynamic coefficient of dispersion of the solute in the soil solution	cm ² /min
α ^a	first-order mass transfer coefficient for reversible adsorption of solute	min ⁻¹
<i>K</i> _d	partition coefficient for distribution of fungicide between the solid and liquid phases at equilibrium	L/kg
μ_s ^a	first-order rate constant for the conversion of reversibly adsorbed solute into irreversibly adsorbed solute	min ⁻¹
Dimensionless Variables and Parameters Used in Equations 1–3		
$Z = x/L$	dimensionless distance down the column	
$T = vt/L$	dimensionless time	
$C = c/(1 \text{ mg/L})$	dimensionless concentration	
$S = s/(K_d \times 1 \text{ mg/L})$	dimensionless concentration of adsorbed solute	
$P = vL/D^b$	Péclet number: ratio of convective to diffusive transport	
$R = 1 + \rho K_d/\theta$	retardation factor due to reversible adsorption	
$\omega = \alpha(R - 1)L/v^b$	dimensionless first-order reversible adsorption coefficient	
$\mu = \mu_s(R - 1)L/v^b$	dimensionless first-order constant for "irreversibilization"	

^a Parameters to be calculated from the corresponding fitted dimensionless parameters. ^b Dimensionless parameters that were in principle to be fitted directly using CXTFIT.

Table 2. Characterization of the Soils

sample	C (%)	pH (H ₂ O)	pH (KCl)	CEC (cmol _(c) kg ⁻¹)	sand (%)	silt (%)	clay (%)
1	2.7	6.9	5.8	19.2	70	16	14
2	3.6	7.4	6.6	33.2	46	35	19
3	3.1	7.0	5.4	12.8	67	15	18
4	4.4	6.5	6.1	17.2	59	23	18
5	3.7	5.6	4.9	19.5	69	17	14
6	4.9	5.6	5.0	12.3	51	32	17
7	3.1	5.3	4.6	8.6	53	30	17
8	4.1	5.5	5.0	24.7	65	19	16

relationship between eq 5 and mass balance, and the assumptions involved in eq 6, see ref 12.

Statistical Analyses. All statistical analyses were performed using SPSS v. 12.0 for Windows.

RESULTS AND DISCUSSION

Influence of Soil Properties on Adsorption. The soils studied had C contents ranging from 2.7 to 4.9%, sandy loam textures, and pH_{KCl} values of 4.6–6.6 (Table 2). The higher pH values may be attributed to fertilization and liming; amelioration of pH is usual in this region, the natural soils of which have mostly developed over acid geological materials, and fertilization and liming would explain why Ca and K are the major components of the cation exchange complex.

Adsorption–desorption experiments were preceded by determination of the pre-existing concentrations of cyprodinil and fludioxonil in the soil samples. All were low except the concentration of cyprodinil in sample 4, which was 142 $\mu\text{g kg}^{-1}$ (Table 3). That in all samples the concentration of cyprodinil exceeded that of fludioxonil can generally be attributed to the

Table 3. Initial Concentrations of Cyprodinil and Fludioxonil in the Soils (Means of Duplicate Analyses of the Composite Samples Obtained As Described under Materials and Methods; Relative Standard Deviations Were All <15% for Cyprodinil and <6% for Fludioxonil)

sample	cyprodinil ($\mu\text{g kg}^{-1}$)	fludioxonil ($\mu\text{g kg}^{-1}$)
1	19	9
2	nd ^a	nd
3	3	nd
4	142	nd
5	11	5
6	2	nd
7	2	nd
8	4	nd

^a Not detected.

Table 4. Partition Coefficients (*K*_d) and *K*_{OC} Values (*K*_{OC} = *K*_d × 100/Organic Carbon) for the Distribution of the Fungicides between Soil and Solution in the Adsorption Experiments

sample	<i>K</i> _d (mL g ⁻¹)		<i>K</i> _{OC}	
	cyprodinil	fludioxonil	cyprodinil	fludioxonil
1	54	116	2279	3154
2	61	116	1679	3149
3	82	129	2613	3498
4	91	213	2036	5785
5	80	112	2167	3043
6	110	62	2221	1671
7	79	110	2550	2973
8	93	187	2044	5076
mean	81	131	2199	3544
RSD (%)	22	37	14	37

fact that the commercial product Switch contains more cyprodinil (37.5%) than fludioxonil (25%), although this hardly accounts for the results for sample 4.

The adsorption isotherms of both cyprodinil (Figure 2) and fludioxonil (Figure 3) were linear (C type) throughout the concentration range studied. Although the cyprodinil data were somewhat more linear ($r^2 = 0.9367$ – 0.9995) than the fludioxonil data ($r^2 = 0.9075$ – 0.9732), this may probably be attributed to the poor solubility of fludioxonil in water (1.8 mg L⁻¹ at 25 °C) having restricted the range of initial adsorption solution concentrations (0.7–1.5 mg L⁻¹ for fludioxonil, in contrast to 2–12 mg L⁻¹ for cyprodinil) and hence the range of equilibrium concentrations in solution (0.05–0.16 mg L⁻¹ for fludioxonil in contrast to 0.18–1.6 mg L⁻¹ for cyprodinil). Except in soil 6, fludioxonil was the more avidly adsorbed fungicide, with values of the partition coefficient *K*_d of 62–213 mL g⁻¹ in contrast to 54–110 mL g⁻¹ for cyprodinil (110–213 versus 54–93 mL g⁻¹ if soil 6 is excluded; Table 4), and this greater adsorption may have been substantially due to the higher *pK*_a of fludioxonil, 13.6 in contrast to 5.3 for cyprodinil, because at pH 5–6 the predominantly positively charged fludioxonil molecules would be subject to electrostatic interactions with both organic and inorganic colloids, which possess predominantly negative charges. However, if the main soil–solute interactions were electrostatic, the value of *K*_d would be expected to vary with CEC, and for fludioxonil there was no statistically significant dependence of *K*_d on this or any other of the soil variables investigated (carbon content, clay content, and pH). For cyprodinil, *K*_d depended linearly on carbon content:

$$K_d = 0.0342C + 0.926 \quad (R^2 = 0.675, p < 0.01)$$

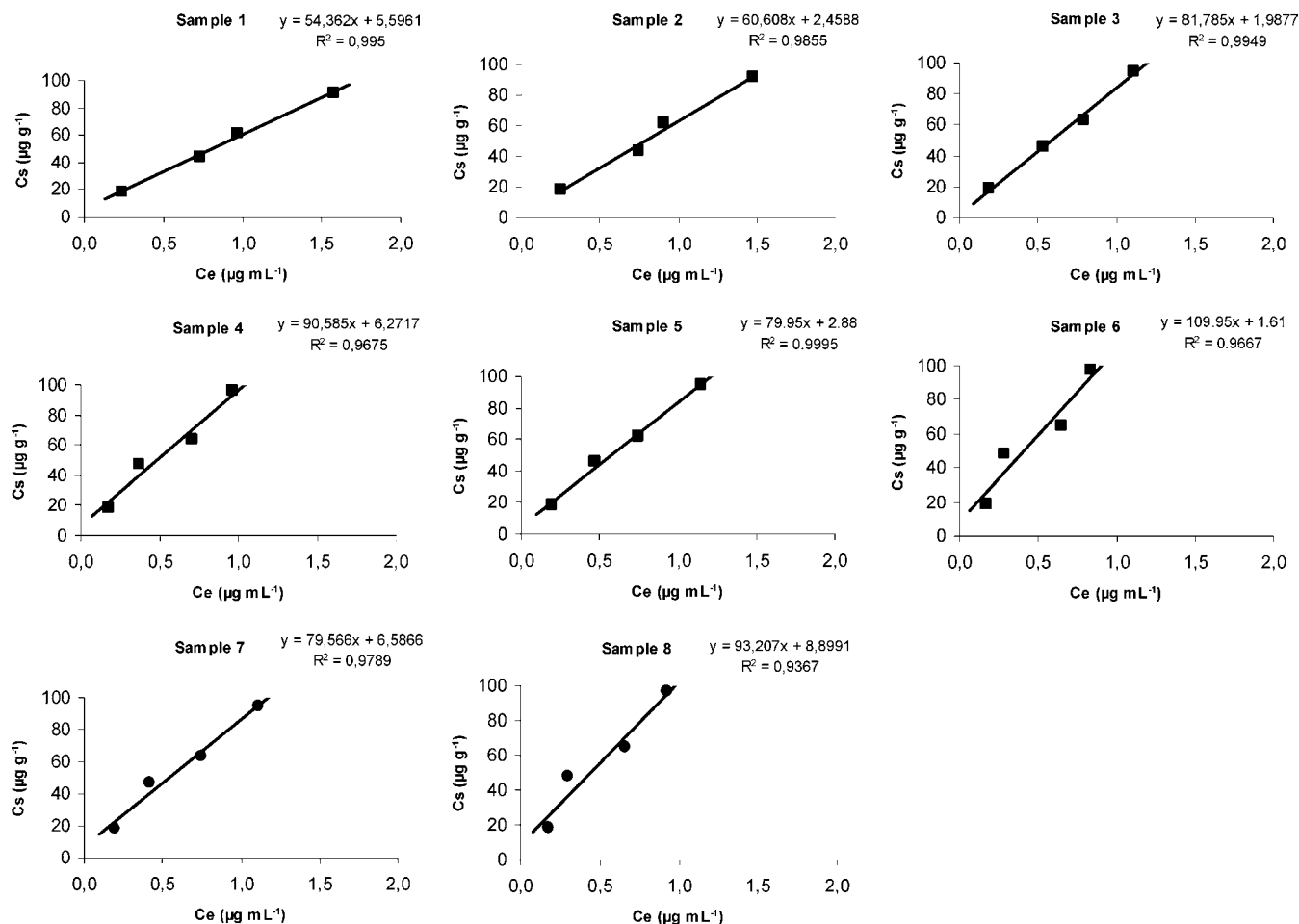


Figure 2. Adsorption isotherms for cyprodinil.

Although this relationship might suggest that soil 6's being the only soil for which cyprodinil had a higher K_d than did fludioxonil was due to its also being the soil with the highest carbon content, the partition coefficient normalized with respect to C content, K_{OC} , exhibited the same pattern as K_d , being greater for fludioxonil than for cyprodinil in all soils except soil 6 (Table 4). However, normalizing with respect to C content did reduce the relative standard deviation (RSD) of the partition coefficient for cyprodinil (from 22% for K_d to 14% for K_{OC}), suggesting that organic matter did play a role in the adsorption of cyprodinil. In contrast, the RSD of fludioxonil was the same for K_{OC} as for K_d , 37%. In this respect, Jerzy et al. (9) found that cyprodinil interacted with soil organic matter through two different mechanisms: first, sequestration by humin; and, second, covalent bonding to humic acids, the abundance and low mobility of which endow them with great capacity to immobilize pesticides in the soil (10, 11). This suggests that to prevent cyprodinil from percolating to underground waters it is necessary to keep humic acid content high enough to ensure its continued immobilization, particularly for soils under crops that substantially reduce soil organic matter.

For both fungicides, adsorption was reduced if the other fungicide was also present in solution, leaving a higher concentration C_e in solution after 24 h of equilibration (Figure 4); proportionally, the presence of cyprodinil affected the residual concentration of fludioxonil much more than vice versa. This behavior suggests competition for adsorption sites, although in the field, where the soil/solution ratio is much higher than in the batch laboratory experiment, competition for adsorption sites may not be a significant effect.

Table 5. Desorption of Cyprodinil (Cyp) and Fludioxonil (Flu) in Each of Three 24-h Desorption Steps (Percentages of Amounts Originally Adsorbed) and Total Desorption after 72 h

soil	24 h		48 h		72 h		total	
	Cyp	Flu	Cyp	Flu	Cyp	Flu	Cyp	Flu
1	8.0	1.6	6.8	1.7	6.4	2.0	21.2	5.3
2	7.8	1.1	6.8	1.7	5.4	1.6	20.0	4.4
3	5.2	1.2	4.9	1.8	4.5	1.7	14.6	4.7
4	4.4	0.7	5.7	1.6	6.7	1.6	16.8	3.9
5	4.7	1.6	6.6	1.8	7.3	1.6	18.6	5.0
6	3.8	1.6	5.5	1.3	7.0	1.5	16.3	4.4
7	4.8	2.3	6.4	1.7	7.0	1.7	18.2	5.7
8	4.3	2.2	4.2	1.5	4.1	1.5	12.6	5.2

Desorption. The extent of desorption of the fungicides was determined following adsorption from solutions with initial cyprodinil/fludioxonil ratios of 1.5:1, their ratio in the commercial formulation Switch. In keeping with its generally lower and less dispersed K_d values, cyprodinil was desorbed to a greater extent than fludioxonil (13–21% in contrast to 4–6%; see Table 5) and with less variation among soils (RSD = 13 versus 17%). Cyprodinil nonetheless showed considerable reluctance to desorb, possibly due to the covalent bond formation mentioned in the preceding section. The even greater reluctance of fludioxonil to desorb is probably attributable to its desorption being limited by its low solubility; as is supported by the fact that at the end of each of the three desorption steps, and in all eight soils, the equilibrium fludioxonil concentration was virtually the same, ranging only from 0.06 to 0.10 mg L^{-1} .

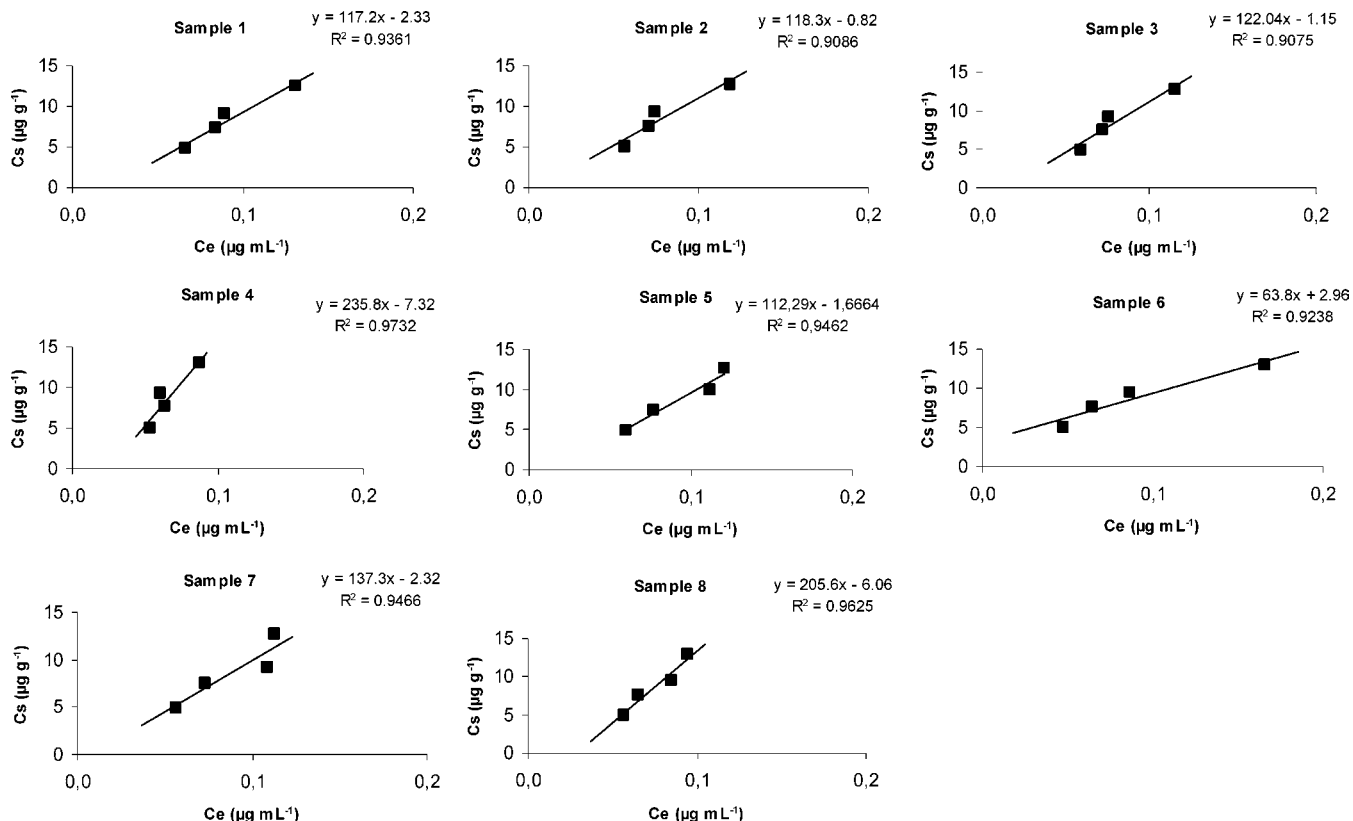


Figure 3. Adsorption isotherms for fludioxonil.

For fludioxonil there was no clear-cut relationship between desorption and any of the soil variables studied, which is again probably attributable to the desorption of fludioxonil being limited by its low solubility rather than by soil characteristics.

For cyprodinil, the soil variable most strongly influencing desorption was, as in the case of its adsorption, C content, total desorption after 72 h decreasing linearly with increasing C ($r = -0.666$, $p < 0.05$). The parallelism with the behavior of adsorption is highlighted by the good correlation ($r = -0.907$, $p < 0.01$) between percentage desorption and K_d (Figure 5a). No such relationship was observed for fludioxonil, for which desorption values varied very little among soils (Figure 5b); this is in keeping with the hypothesis that its desorption is

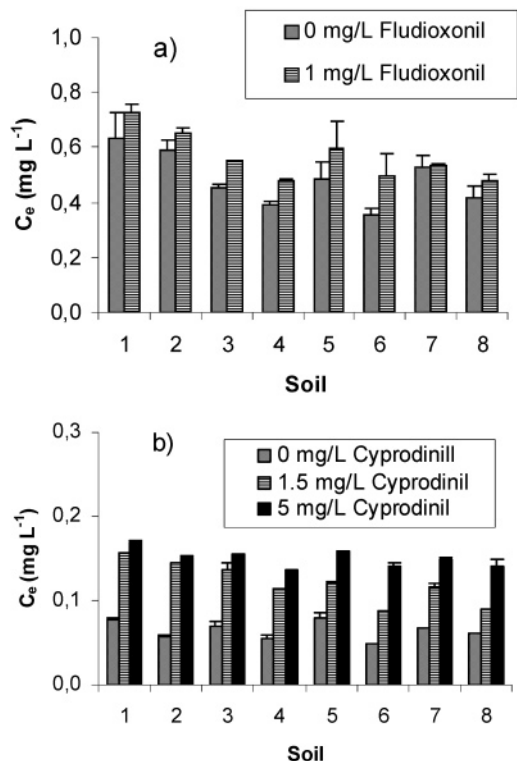


Figure 4. Influence of the presence of fludioxonil on the equilibrium concentration, C_e , of cyprodinil (a) and of the presence of cyprodinil on the equilibrium constant of fludioxonil (b).

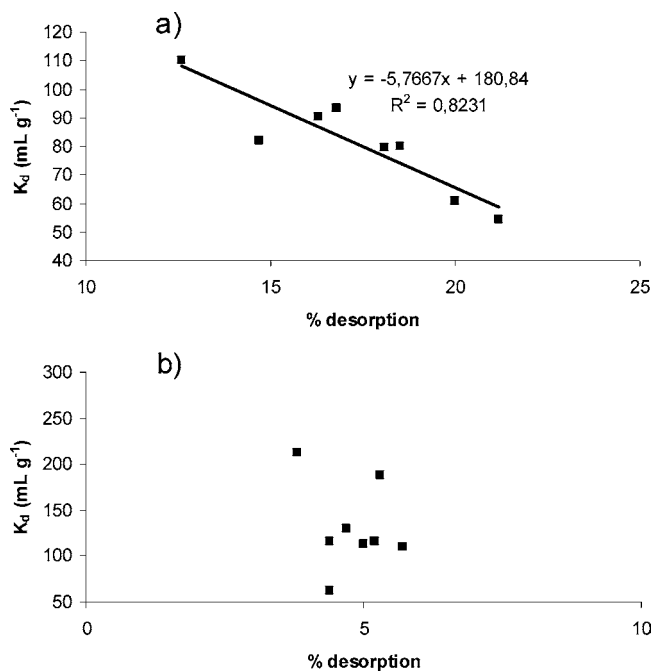


Figure 5. Relationship between the partition coefficient, K_d , and the extent of desorption (percent) of cyprodinil (a) and fludioxonil (b).

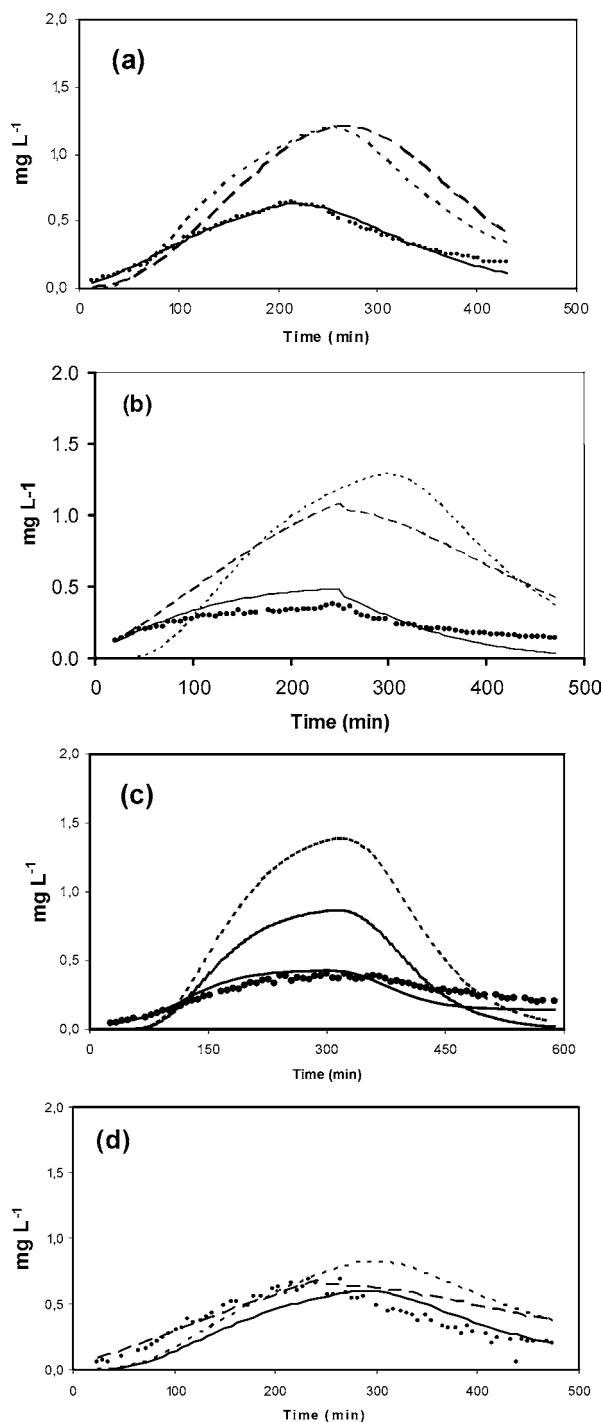


Figure 6. Results of the column experiments and fitted models: (a, b) cyprodinil; (c, d) fludioxonil; (a, c) soil 3; (b, d) soil 7. Single points represent experimental data, short dashes (---) the results of the LE model, long dashes (---) the results of the NLE model, and the continuous curve (—) the results of the IRR model.

governed mainly by its solubility rather than by adsorption-desorption mechanisms.

Column Experiments and Transport Modeling. The results of the column experiments are shown in **Figure 6** (large dots), and the values of the transport model parameters obtained directly or indirectly by measurement are listed in the top panel of **Table 6**. It was not possible to fit any of the models reliably when the Péclet number, P , was included among the parameters to be optimized, because the “optimized” value of this parameter depended heavily on the value used to initiate the optimization.

Table 6. Parameters of the Transport Models, with Goodness of Fit (r^2)

parameter	soil 3		soil 7	
	cyprodinil	fludioxonil	cyprodinil	fludioxonil
L	1.8	1.8	1.8	1.8
v	2.5	1.2	3.5	2.2
θ	0.37	0.50	0.21	0.33
R	236	291	357	303
$P^a (D)$	9 (0.5)	4.3 (0.5)	12.6 (0.5)	7.9 (0.5)
$\omega^b (\alpha)$	5.3(0.10)	5.4(0.04)	3.8(0.07)	9.7(0.12)
$\mu^b (\mu_s)$	0.79 (0.015)	0.66 (0.005)	2.40 (0.042)	0.71 (0.009)
r^2 (IRR)	0.975	0.980	0.742	0.940
r^2 (LE)	0.265	0.184	0.123	0.393
r^2 (NLE)	0.306	0.345	0.500	0.547

^a Value calculated by assuming that $D = 0.5 \text{ cm}^2/\text{min}$ (see Results and Discussion). ^b Dimensionless parameters fitted by CXTFIT using the IRR model, with the corresponding dimensional parameters in parentheses.

We therefore imposed values of this parameter corresponding to the value $D = 0.5 \text{ cm}^2/\text{min}$, approximately the mean of the values obtained in an earlier study of bromide transport through columns of similar size. Even then it was not possible to fit the NLE model, but the IRR model was successfully fitted, affording the values of ω , α , μ , and μ_s that are listed in the middle panel of **Table 6**. The bottom panel of this table lists values of the determination coefficient r^2 corresponding to this fit of IRR, together with those characterizing the fit of LE and NLE models calculated using $D = 0.5 \text{ cm}^2/\text{min}$ and, for NLE, the value of ω obtained in fitting IRR.

The total amounts of fungicide eluted from the columns were considerably less than the amounts injected at the column heads, showing that fungicide was being retained in the column by adsorption processes that were irreversible on the time scale of these experiments. This is reflected in **Figure 6** in the difference between the areas under the curves corresponding to the LE and NLE models, which assume totally reversible adsorption, and the areas under the curves corresponding to the experimental data and IRR model. Note also that the LE model underestimated elution during the early phase of the experiment, a clear sign that the assumption of equilibrium was untenable.

The optimized values of μ_s , the rate constant for irreversible adsorption, were quite similar in the three columns, the data from which were fitted by the IRR model with r^2 values >0.9 . In all three cases, the rate constant for reversible adsorption, α , was ~ 10 times greater. The fact that the experimental data worst fit by the IRR model were those for cyprodinil in soil 7 may be related to this breakthrough curve having a heavier tail (in comparison with the rest of the curve) than any of the others (**Figure 6b**): heavy tails reflect slow desorption, and in the IRR model only the full reversible process and a totally irreversible process are considered. That cyprodinil desorbed more slowly from soil 7 than from soil 3 in the column experiments is in keeping with its behavior in these soils in the desorption experiments.

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