

## Influence of pH and Soil Copper on Adsorption of Metalaxyl and Penconazole by the Surface Layer of Vineyard Soils

M. ARIAS,<sup>†</sup> M. PARADELO,<sup>†</sup> E. LÓPEZ,<sup>†</sup> AND J. SIMAL-GÁNDARA<sup>\*,§</sup>

Soil and Agricultural Science Group, Plant Biology and Soil Science Department, and Nutrition and Bromatology Group, Analytical and Food Chemistry Department, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E-32004 Ourense, Spain

The upper horizons of old vineyard soils have substantial copper contents due to the traditional use of copper-based fungicides. Total copper levels in eight vineyard soils in the Rías Baixas area of Galicia (northwestern Spain) ranged from 60 to 560 mg kg<sup>-1</sup> (mean ± SD = 206 ± 170 mg kg<sup>-1</sup>). The adsorption of the fungicides metalaxyl (pK<sub>a</sub> = 1.41) and penconazole (pK<sub>a</sub> = 2.83) by these soils was determined using fungicide solutions of pH 2.5 and 5.5, and desorption of fungicide adsorbed at pH 5.5 was also determined. In all cases, Freundlich equations were fitted to the data with  $R^2 > 0.96$ . Penconazole was adsorbed and retained more strongly than metalaxyl, with  $K_F$  values more than an order of magnitude greater. In the desorption experiments, both fungicides exhibited hysteresis. Soil copper content hardly affected the adsorption of metalaxyl, but  $K_F$  values for adsorption of penconazole increased at a rate of about 0.1 mL<sup>n</sup> (μg of penconazole)<sup>(1-n)</sup> (μg of Cu)<sup>-1</sup>, which is attributed to the formation of Cu<sup>2+</sup>–penconazole complexes with greater affinity for soil colloids than penconazole itself. Because the dependence of  $K_F$  for penconazole adsorption on copper content was the same at both pH values, complex formation appears not to have been affected by the solubilization of 6–17% of soil copper at pH 2.5. A similar copper dependence, or lack of dependence, was observed when 100–1000 mg kg<sup>-1</sup> of copper was added as Cu(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O to the solutions from which the fungicides were adsorbed.

**KEYWORDS:** Soil contamination; metalaxyl; penconazole; adsorption–desorption; copper

### INTRODUCTION

In Galicia (northwestern Spain), an increasing area of land is being devoted to the production of quality wines with the Designation of Origin Monterrei, Rías Baixas, Ribeira Sacra, Ribeiro, or Valdeorras. Production is threatened by fungal grapevine diseases favored by the high relative humidity and abundant spring rains of this region. Among the fungicides currently used most widely to fight these diseases are metalaxyl [methyl *N*-(2,6-dimethylphenyl)-*N*-methoxyacetyl-DL-alaninate] and penconazole [1-[2-(2,4-dichlorophenyl)pentyl]-1*H*-1,2,4-triazole]. Both of these systemic fungicides are sprayed on foliage, and a proportion of the dose applied inevitably enters the soil, either at spraying time or in wash-off from treated foliage or in fallen plant debris. Metalaxyl is also applied directly to the soil as a soil fungicide (1).

Two of the key processes determining the environmental fate of pesticides in the soil are adsorption on and desorption from soil particles (2). Adsorption prevents the pesticide from polluting surface or ground waters, but hinders volatilization

(3) and biodegradation (4), whereas, on the contrary, desorption into the soil solution allows runoff and leaching into water bodies (5–8), but makes the pesticide available to soil microorganisms (9, 10).

Metalaxyl appears to be adsorbed mainly by soil organic matter (11), but it is also adsorbed by soil clay minerals (12, 13), especially in soils with low organic matter contents (11). However, it is relatively soluble in water and has been detected at levels >100 ng L<sup>-1</sup> in agricultural drainage water (14). Laboratory studies using thin soil layer chromatography (11) and soil columns (13) have confirmed that its mobility increases as the Freundlich constant  $K_F$  for its adsorption falls.

Adsorption–desorption studies of hexaconazole, triadimefon, and penconazole have found that penconazole was adsorbed more and desorbed less than the other two triazole fungicides (15, 16). Its strong adsorption and poor mobility have been confirmed for a large variety of vineyard soils (17), and its poor mobility has been confirmed in the field (18).

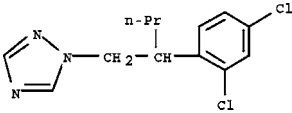
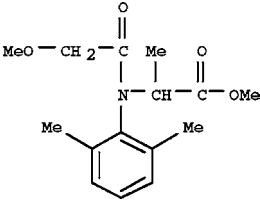
The upper horizons of old vineyard soils have substantial copper contents due to long use of the traditional copper-based fungicide known as Bordeaux mixture (22, 23). As far as we know, the possibility that these copper contents might influence the mobility of organic fungicides has previously only been

\* Corresponding author (e-mail jsimal@uvigo.es).

<sup>†</sup> Soil and Agricultural Science Group.

<sup>§</sup> Nutrition and Bromatology Group.

**Table 1.** Characteristics of the Fungicides Studied

chemical family	fungicide	structure	solubility in H <sub>2</sub> O <sup>a</sup> (22 °C; g/L)	log K <sub>ow</sub> <sup>a</sup>	pK <sub>a</sub> <sup>b</sup>
triazole	penconazole		0.073	3.72	2.83 ± 0.12
phenylamide	metalaxyl		7.1	1.65	1.41 ± 0.50

<sup>a</sup> From ref 33. <sup>b</sup> From SciFinder Scholar (2004 version, by American Chemical Society).

**Table 2.** Soil Characteristics<sup>a</sup>

soil	pH (H <sub>2</sub> O)	pH (KCl)	C (%)	CEC (cmol <sub>(c)</sub> kg <sup>-1</sup> )	sand (%)	silt (%)	clay (%)	Cu <sub>e</sub> (mg kg <sup>-1</sup> )	Cu <sub>p</sub> (mg kg <sup>-1</sup> )	Cu <sub>o</sub> (mg kg <sup>-1</sup> )	Cu <sub>ao</sub> (mg kg <sup>-1</sup> )	Cu <sub>t</sub> (mg kg <sup>-1</sup> )	Cu <sub>E</sub> (%)	Cu <sub>OM</sub> (%)	Cu <sub>IA</sub> (%)	Cu <sub>C</sub> (%)	Cu <sub>R</sub> (%)
1	6.9	5.8	2.7	19.2	70	16	14	2.5	54	60	64	83	3	62	7	4	24
2	7.4	6.6	3.6	33.2	46	35	19	5.0	31	40	44	60	8	43	15	7	27
3	7.0	5.4	3.1	12.8	67	15	18	6.5	62	88	98	107	6	52	24	10	8
4	6.5	6.1	4.4	17.2	59	23	18	9.0	348	429	503	560	2	60	15	13	10
5	5.6	4.9	3.7	19.5	69	17	14	3.5	99	123	124	149	2	65	16	1	16
6	5.6	5.0	4.9	12.3	51	32	17	8.0	205	248	267	315	3	62	14	6	15
7	5.3	4.6	3.1	8.6	53	30	17	6.5	72	83	93	96	7	68	22	10	3
8	5.5	5.0	4.1	24.7	65	19	16	8.0	185	243	249	274	3	65	21	2	9

<sup>a</sup> C, total organic carbon; CEC, cation exchange capacity; Cu<sub>e</sub>, exchangeable Cu; Cu<sub>p</sub>, pyrophosphate-extractable Cu; Cu<sub>o</sub>, oxalic-oxalate-extractable Cu; Cu<sub>ao</sub>, ascorbic-oxalic-oxalate-extractable Cu; Cu<sub>t</sub>, total Cu content; Cu<sub>E</sub>, exchangeable Cu (% of Cu<sub>t</sub>); Cu<sub>OM</sub>, Cu associated with organic matter (% of Cu<sub>t</sub>); Cu<sub>IA</sub>, Cu associated with amorphous inorganic forms (% of Cu<sub>t</sub>); Cu<sub>C</sub>, Cu associated with crystalline oxides (% of Cu<sub>t</sub>); Cu<sub>R</sub>, residual copper (% of Cu<sub>t</sub>).

studied in the case of glyphosate (19–21). In this study we investigated the influence of soil copper content on the sorption of metalaxyl and penconazole by the surface layers of eight Rías Baixas vineyard soils with copper contents ranging from 60 to 560 mg kg<sup>-1</sup> (cf. contents of 12–83 mg kg<sup>-1</sup> in local soils that have never borne vineyards).

## MATERIALS AND METHODS

**Fungicides.** Metalaxyl and penconazole were obtained from Riedel-Häen (Seelze, Germany) with a purity of >99%. Some of their relevant characteristics are listed in **Table 1**.

**Soil Samples.** In April 2004, composite samples of the top 0–20 cm of the soil were obtained from each of eight Rías Baixas vineyards in the Galician province of Pontevedra (northwestern Spain). Each of these composite samples was made up of five initial samples that were collected within 0.5 m of each other using an Edelman auger; these five initial samples 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 at 4 °C until they were analyzed.

**Analytical Methods.** Current and potential soil acidities were determined by measuring the pH of 1:2.5 (soil/liquid) suspensions in water and in 0.1 M KCl, respectively; measurements were taken using 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 NH<sub>4</sub>Cl (24) and determined by atomic absorption spectroscopy (Ca<sub>e</sub> and Mg<sub>e</sub>) or flame emission spectrophotometry (Na<sub>e</sub> and K<sub>e</sub>). Exchangeable Al was quantified by displacement with 1 M KCl, followed by atomic absorption spectrophotometry. Finally, cation exchange

capacity (CEC) was calculated as the sum of bases (Na, K, Ca, and Mg) and exchangeable Al.

Soil copper fractions were determined by selective extraction followed by measurement of copper in the extracts by atomic absorption spectrophotometry using a Thermo Solar M series spectrometer. Extractions were performed as follows.

(1) *Cu<sub>e</sub> (exchangeable Cu)*: Five grams of soil was shaken for 5 min in 30 mL of 0.2 M NH<sub>4</sub>Cl. This extraction step was repeated five times, and the pooled extracts were brought up to 250 mL for spectrophotometry (25).

(2) *Cu<sub>p</sub> (pyrophosphate-extractable Cu)*: One gram of soil was shaken for 16 h in 100 mL of 0.1 M sodium pyrophosphate at pH 10.1 (26).

(3) *Cu<sub>o</sub> (oxalic-oxalate-extractable Cu)*: One gram of soil was shaken in darkness for 4 h in 50 mL of 0.2 M oxalic acid–ammonium oxalate buffer (27).

(4) *Cu<sub>ao</sub> (ascorbic-oxalic-oxalate-extractable Cu)*: One gram of soil was shaken for 30 min at 96 °C in 50 mL of 0.1 M oxalic acid–ammonium oxalate–ascorbic acid buffer (28).

(5) *Cu<sub>t</sub> (total Cu content)*: Half a gram of soil was digested in a microwave oven at 100 psi with 5 mL of HNO<sub>3</sub>, 4 mL of HF, and 1 mL of HCl.

Copper may be associated with various soil components that differ in their ability to retain it. In terms of the Cu fractions described above, the following association-based fractions were defined as percentages of Cu<sub>t</sub> (23):

$$\text{Cu}_E = 100 \times \text{Cu}_e / \text{Cu}_t \text{ (exchangeable Cu)}$$

$$\text{Cu}_{OM} = 100 \times (\text{Cu}_p - \text{Cu}_e) / \text{Cu}_t \text{ (Cu associated with organic matter)}$$

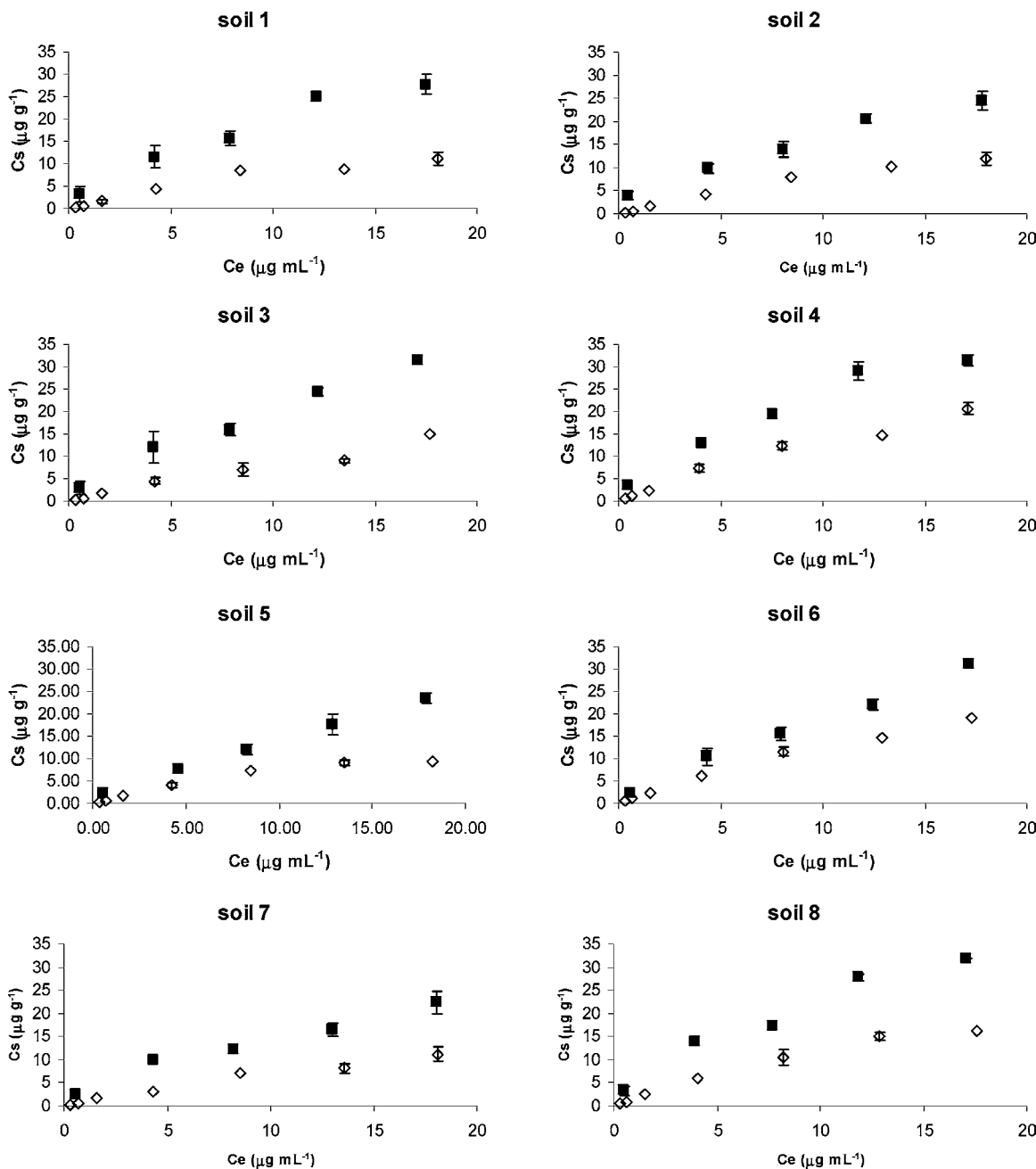


Figure 1. Adsorption isotherms for metalaxyl: (■) pH 2.5; (◇) pH 5.5.

$$Cu_{IA} = 100 \times (Cu_o - Cu_p)/Cu_t$$

(Cu associated with amorphous inorganic components)

$$Cu_C = 100 \times (Cu_{ao} - Cu_o)/Cu_t$$

(Cu associated with crystalline oxides)

$$Cu_R = 100 \times (Cu_t - Cu_{ao})/Cu_t \text{ (residual Cu)}$$

Prior to adsorption studies, the pre-existing metalaxyl and penconazole contents of the soils were determined according to a method with analyte recoveries of about 100% (29), 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 at 200 rpm in an orbital mixer for 45 min. After spending 10 min at 4 °C to reduce between-phase foam, the aqueous and organic phases were separated by centrifugation at 1500 rpm for 20 min. A 7 mL sample of the organic phase was concentrated to dryness in a rotary evaporator at 40 °C and 240 mbar, and the resulting residue was dissolved in 0.5

mL of a 4 mg L<sup>-1</sup> solution of the internal standard (lindane) in ethyl acetate. This final 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.

**Statistical Analyses.** The statistical significance of differences between means was estimated by two-tailed *t* tests or by analyses of variance followed by multiple-range tests based on least significant differences (LSD). Pearson correlation coefficients between variables were also estimated. All statistical analyses were performed using SPSS v. 12.0 for Windows.

**Adsorption and Desorption Assays.** *Adsorption, pH 5.5.* Aqueous solutions of metalaxyl (0.5–20 mg L<sup>-1</sup>; seven concentrations) or penconazole (2.0–40 mg L<sup>-1</sup>; seven concentrations) were made up by adding the appropriate volume of stock solutions of the fungicides (1 g L<sup>-1</sup> in methanol) to 0.01 M CaCl<sub>2</sub> (pH 5.5), after which the methanol was removed by passage of a stream of nitrogen. In each assay, a 5 g sample of soil was suspended in 50 mL of the fungicide/CaCl<sub>2</sub> solution, and these suspensions were shaken end-over-end at 200 rpm for 24 h

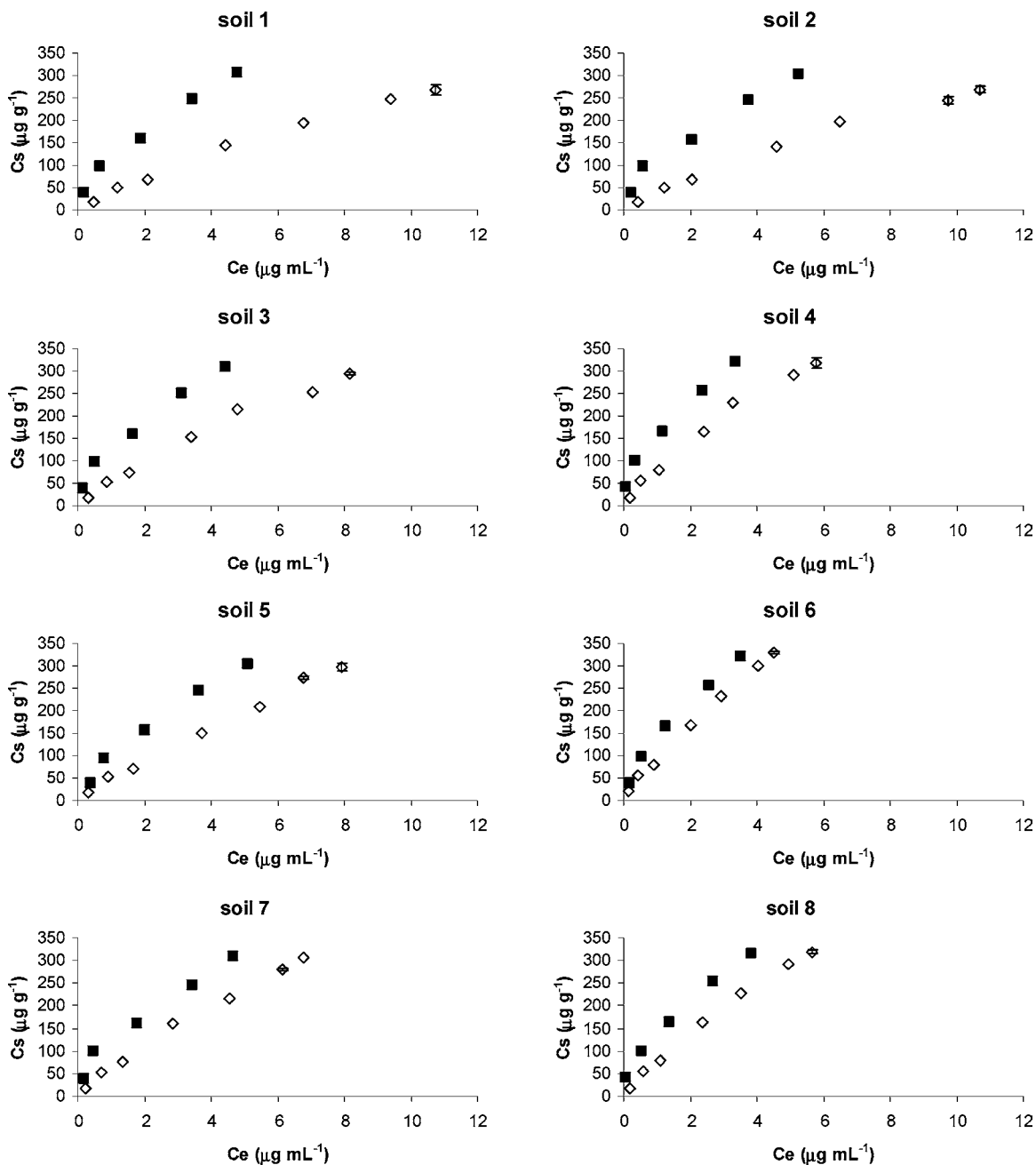


Figure 2. Adsorption isotherms for penconazole: (■) pH 2.5; (◇) pH 5.5.

at  $25 \pm 1$  °C, after which they were centrifuged for 30 min at 2000 rpm in a rotor approximately 12 cm in diameter. Preliminary experiments had indicated that 24 h of contact was long enough for equilibrium to be reached and that with lower fungicide concentrations no fungicide was detectable in solution after this time (it may also be worth pointing out that the fungicide concentrations employed are not totally unrealistic: they amounted to fungicide/soil ratios of 5–200 mg kg<sup>-1</sup> for metalaxyl and 20–400 mg kg<sup>-1</sup> for penconazole, the lower ends of which ranges are not unusual in soil samples collected in late September, at the end of the wine-growing season). No buffers were used [buffers can interfere with sorption (30)], but the pH of the supernatant was measured following centrifugation. The supernatants were analyzed by isocratic HPLC on an octadecylsilica column with 50:50 and 70:30 acetonitrile/water as mobile phases for metalaxyl and penconazole, respectively; the HPLC apparatus was from Fisons Instruments, and ultraviolet detection at 200 nm was employed. The amounts of metalaxyl or penconazole adsorbed by the soil were calculated as the differences between the amounts in the initial solution and those remaining in solution after centrifugation. All analyses were

performed in triplicate; control assays were performed in the same conditions but without the presence of soil.

**Adsorption, pH 2.5.** Adsorption from fungicide solution that had been acidified to pH 2.5 by the addition of hydrochloric acid was determined in the same way as above. Acidification will have modified soil variable charge (especially that of iron and aluminum oxides and organic matter) and the proportion of pesticide bearing positive charge and will have solubilized some of the copper content of the soil.

**Adsorption, with Addition of Copper.** Adsorption of fungicide from solutions of pH 5.5 to which Cu(NO<sub>3</sub>)<sub>2</sub> had been added (10, 50, or 100 mg L<sup>-1</sup>) was also measured. In these experiments the fungicide concentrations were 5 mg L<sup>-1</sup> for metalaxyl and 15 mg L<sup>-1</sup> for penconazole. All analyses were performed in triplicate.

**Desorption.** Desorption experiments were carried out with soil samples on which fungicide had been adsorbed from 15 mg L<sup>-1</sup> metalaxyl or 30 mg L<sup>-1</sup> penconazole solutions of pH 5.5 as described above. Following equilibration and centrifugation of the adsorption mixture, 40 mL of the supernatant was replaced with the same volume of fungicide-free 0.01 M CaCl<sub>2</sub> solution (pH 5.5), and this mixture

**Table 3.** Freundlich Adsorption Parameters  $n$  (Dimensionless) and  $K_F$  ( $\mu\text{g}^{(1-n)} \text{ mL}^n \text{ g}^{-1}$ ) for Metalaxyl and Penconazole at pH 5.5 (A) and 2.5 (B)<sup>a</sup>

soil	metalaxyl			penconazole		
	$K_F$	$n$	$R^2$	$K_F$	$n$	$R^2$
(A) pH 5.5						
1	1.7 ± 0.4	0.67 ± 0.09	0.966	41.8 ± 3.1	0.79 ± 0.03	0.996
2	1.5 ± 0.2	0.73 ± 0.06	0.990	41.7 ± 3.9	0.78 ± 0.04	0.994
3	1.0 ± 0.3	0.91 ± 0.12	0.971	59.5 ± 5.7	0.76 ± 0.05	0.991
4	2.3 ± 0.4	0.76 ± 0.07	0.986	85.9 ± 6.1	0.75 ± 0.05	0.992
5	1.6 ± 0.4	0.64 ± 0.09	0.962	47.4 ± 3.8	0.89 ± 0.04	0.996
6	2.0 ± 0.3	0.79 ± 0.05	0.993	94.5 ± 3.3	0.83 ± 0.03	0.998
7	1.1 ± 0.2	0.79 ± 0.08	0.985	65.2 ± 3.0	0.81 ± 0.03	0.998
8	2.2 ± 0.4	0.73 ± 0.07	0.986	79.5 ± 3.4	0.81 ± 0.03	0.998
(B) pH 2.5						
1	4.7 ± 0.9	0.63 ± 0.08	0.979	112.5 ± 5.47	0.63 ± 0.04	0.996
2	4.2 ± 0.8	0.61 ± 0.07	0.981	110.2 ± 8.6	0.60 ± 0.06	0.988
3	3.8 ± 0.6	0.74 ± 0.06	0.991	126.3 ± 6.2	0.60 ± 0.04	0.994
4	6.0 ± 1.2	0.60 ± 0.08	0.978	159.8 ± 6.7	0.56 ± 0.04	0.993
5	2.2 ± 0.3	0.85 ± 0.05	0.995	97.6 ± 6.8	0.70 ± 0.05	0.992
6	2.9 ± 0.4	0.82 ± 0.06	0.994	137.5 ± 2.7	0.67 ± 0.19	0.999
7	3.5 ± 0.6	0.62 ± 0.07	0.982	120.5 ± 9.5	0.59 ± 0.06	0.986
8	5.4 ± 1.1	0.63 ± 0.08	0.980	140.1 ± 3.8	0.60 ± 0.02	0.998

<sup>a</sup> Values listed are means ± asymptotic standard deviations as obtained using GraFit 2.0.

**Table 4.** Freundlich Desorption Parameters  $n$  (Dimensionless) and  $K_F$  ( $\mu\text{g}^{(1-n)} \text{ mL}^n \text{ g}^{-1}$ ) for Metalaxyl and Penconazole at pH 5.5<sup>a</sup>

soil	metalaxyl			penconazole		
	$K_F$	$n$	$R^2$	$K_F$	$n$	$R^2$
1	7.1 ± 0.5	0.16 ± 0.03	0.919	87.4 ± 2.5	0.42 ± 0.02	0.994
2	5.9 ± 0.3	0.22 ± 0.02	0.979	100.4 ± 2.8	0.35 ± 0.02	0.992
3	3.9 ± 0.3	0.32 ± 0.04	0.977	127.0 ± 4.1	0.35 ± 0.03	0.981
4	4.9 ± 0.4	0.44 ± 0.04	0.990	161.2 ± 5.2	0.27 ± 0.03	0.956
5	3.6 ± 0.7	0.37 ± 0.08	0.938	120.2 ± 3.7	0.35 ± 0.02	0.985
6	7.0 ± 0.7	0.32 ± 0.05	0.962	188.9 ± 1.7	0.20 ± 0.01	0.962
7	5.2 ± 0.4	0.21 ± 0.03	0.952	139.5 ± 3.0	0.32 ± 0.02	0.989
8	6.0 ± 0.6	0.36 ± 0.04	0.978	146.2 ± 3.8	0.33 ± 0.03	0.982

<sup>a</sup> Values listed are means ± asymptotic standard deviations as obtained using GraFit 2.0.

was shaken for 24 h and centrifuged as in the adsorption experiments. The concentration of fungicide in the supernatant was determined by HPLC, and the percentage of adsorbed fungicide that had undergone desorption was calculated accordingly. For each sample, this procedure (replacement of supernatant, equilibration, and centrifugation) was repeated three times (for metalaxyl) or four times (for penconazole).

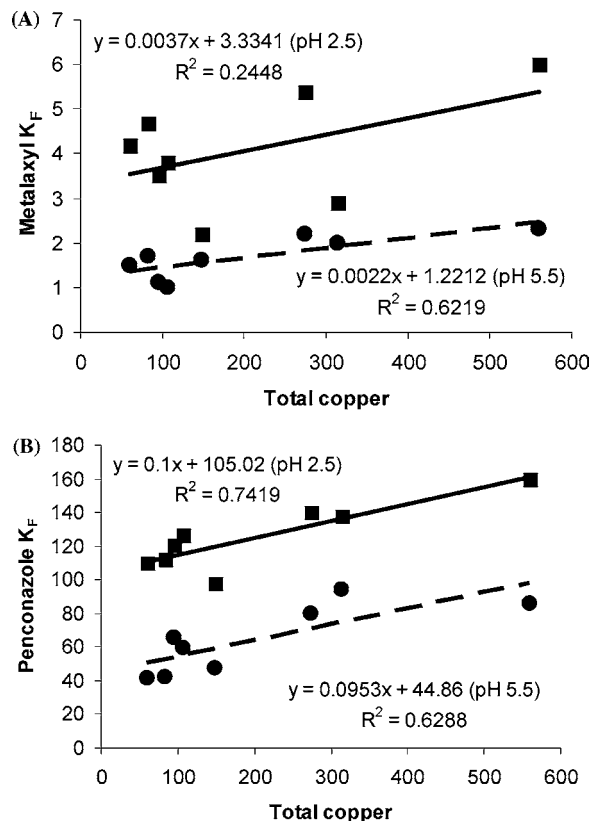
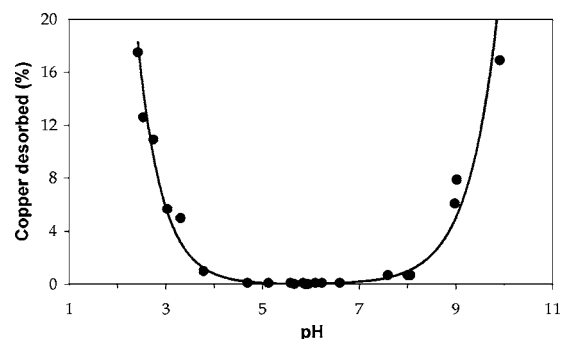
Both adsorption and desorption data were fitted with Freundlich equations

$$C_s = K_F C_e^n$$

where  $C_s$  is the mass of adsorbed fungicide per unit mass of dry soil at equilibrium ( $\mu\text{g g}^{-1}$ ),  $C_e$  is the concentration of fungicide in solution at equilibrium ( $\mu\text{g mL}^{-1}$ ), and  $K_F$  and  $n$  are adjustable constants. Curve fitting was performed using the nonlinear Levenberg–Marquardt least-squares algorithm as implemented in GraFit 2.0 (from Eritachus Ltd.).

## RESULTS AND DISCUSSION

The soils studied had C contents ranging from 2.7 to 4.9%, sandy loam textures, and  $\text{pH}_{\text{KCl}}$  values of 4.6–6.6 (Table 2). The higher pH values are attributable to liming with mussel shells; amelioration of pH is usual in this region, the natural soils having mostly developed over acid geological materials. Metalaxyl was detected in four soils, at levels close to the detection limit ( $10 \mu\text{g kg}^{-1}$ ) in two cases and close to the

**Figure 3.** Effect of soil copper content on  $K_F$  for adsorption of metalaxyl (A) and penconazole (B) at pH 2.5 (■) and pH 5.5 (●).**Figure 4.** Effect of pH on desorption of copper from soil 4.

quantification limit ( $25 \mu\text{g kg}^{-1}$ ) in the others. Penconazole was detected in three soils: in one at the detection limit ( $20 \mu\text{g kg}^{-1}$ ) and in two at the quantification limit ( $50 \mu\text{g kg}^{-1}$ ). These residual levels were taken into consideration in the experiments. To avoid higher residual levels, samples were collected in April, at the beginning of the growing season; at the end of the season, in late September, levels can be 100 times higher. Total copper contents were high but varied widely (Table 2), which is attributable to varying usage of copper-based fungicides.

Exchangeable copper ( $\text{Cu}_E$ ) was in all soils <10% of total copper, indicating that most Cu in vineyard soils is bound relatively irreversibly. The largest copper fraction was associated with organic matter [ $\text{Cu}_{\text{OM}} = 60 \pm 8\%$  (mean ± standard deviation), range = 43–68%]. In addition, significant proportions of copper were associated with amorphous inorganic colloids ( $\text{Cu}_{\text{IA}} = 17 \pm 5\%$ , range = 7–24%) and with crystalline oxides ( $\text{Cu}_C = 7 \pm 4\%$ , range = 1–13%). The residual copper fraction  $\text{Cu}_R$ , which generally accounts for >50% of copper in natural soils, was only  $14 \pm 8\%$  (range =

3–27%), reflecting the anthropogenic origin of most of the copper present.

**Effect of pH and Soil Copper Content on Fungicide Adsorption.** In the adsorption experiments, postequilibration supernatants were of pH  $5.1 \pm 0.7$  when fungicide had been adsorbed from solutions of initial pH 5.5 and of pH  $3.0 \pm 0.4$  when the initial pH had been 2.5. In no case was there any significant difference in pH between supernatants containing metalaxyl and supernatants with penconazole ( $p > 0.05$ ).

In all series of adsorption and desorption experiments, smooth L-type adsorption isotherms were recorded (Figures 1 and 2) that were satisfactorily fitted by Freundlich equations (31) ( $r^2 > 0.96$  for adsorption,  $r^2 > 0.91$  for desorption; see Tables 3 and 4). All values of the Freundlich exponent  $n$ , which reflects the influence of adsorbed sorbate on further adsorption, were less than unity, as expected for an adsorbate that creates no new adsorption sites. Penconazole was the more strongly adsorbed compound, with  $K_F$  values more than an order of magnitude greater than those for metalaxyl; this may be due to the greater hydrophobicity of penconazole ( $K_{ow} = 3.72$  versus 1.65 for metalaxyl; 24).

Lowering the pH substantially increased the adsorption of both fungicides, increasing the value of  $K_F$  by a factor of 2–3 (Figures 1–3). At the lower pH a significant proportion of the fungicide is positively charged (especially in the case of penconazole) and is therefore attracted to the negative charge of soil colloids. The same effect of pH on adsorption onto soil has been reported for pesticides such as diuron (30). However, the values of the Freundlich exponent  $n$  for penconazole were 20–30% lower at pH 2.5 than at pH 5.5; that is, for penconazole the increase in adsorption induced by the lowering of pH was greater at lower concentrations.

Soil copper content had little influence on the adsorption of metalaxyl at pH 5.5 and no statistically significant influence at pH 2.5 (Figure 3A). In contrast, the value of  $K_F$  for the adsorption of penconazole increased with copper content at a rate of about  $0.1 \text{ mL}^n (\mu\text{g of penconazole})^{(1-n)} (\mu\text{g of Cu})^{-1}$ , regardless of pH (Figure 3B). This suggests the formation of  $\text{Cu}^{2+}$ –penconazole complexes with greater affinity for soil colloids than penconazole itself. Because lowering the pH from 5.5 to 2.5 did not affect this behavior, complex formation appears not to have been affected by the fact that 6–17% of soil copper was solubilized at pH 2.5 (as was determined in experiments in which fungicide-free soil samples were equilibrated with buffers of pH ranging from 2.5 to 10; see Figure 4 for the results for soil 4). Other authors have reported a similar influence of copper on the adsorption of glyphosate (19–21). It seems likely that the side chains borne by the nitrogen atom of metalaxyl prevent coordination of this atom to copper, and it appears that any complexation via its carbonyl groups fails to influence its affinity for soil colloids. Experiments in which copper was added to a metalaxyl solution in the absence of soil showed that copper did not lead to any decomposition of metalaxyl.

In desorption experiments, both fungicides exhibited hysteresis, the fitted Freundlich equations having larger  $K_F$  values and smaller  $n$  values than those fitted to the corresponding adsorption data (Tables 3 and 4). Adsorption thus appears to be partially irreversible. For metalaxyl, this finding agrees with those of other authors (32). Metalaxyl was desorbed to a greater extent than penconazole (48–77 versus 20–43%,  $p < 0.05$ ; see Table 5), which is again attributable to its greater solubility in water. For penconazole, desorption  $K_F$  correlated significantly both with organic matter and with all of the extractant-defined soil copper

**Table 5.** Desorption of Metalaxyl (A) and Penconazole (B) in Each of the 24-h Desorption Steps (Percentages of Amounts Originally Adsorbed) and Total Desorption

soil	desorption step				total desorption
	1	2	3	4	
(A) Metalaxyl					
1	26	18	4		48
2	38	17	5		60
3	39	27	3		69
4	50	20	6		76
5	30	44	3		77
6	43	17	4		64
7	33	19	3		55
8	45	23	4		72
(B) Penconazole					
1	17	10	9	7	43
2	16	9	8	7	40
3	12	8	6	6	32
4	8	7	5	5	25
5	12	8	7	7	34
6	7	5	4	4	20
7	10	7	6	6	29
8	9	7	5	5	26

**Table 6.** Linear Correlation Coefficients between Desorption  $K_F$  ( $\mu\text{g}^{(1-n)} \text{ mL}^n \text{ g}^{-1}$ ) and Soil Properties<sup>a</sup>

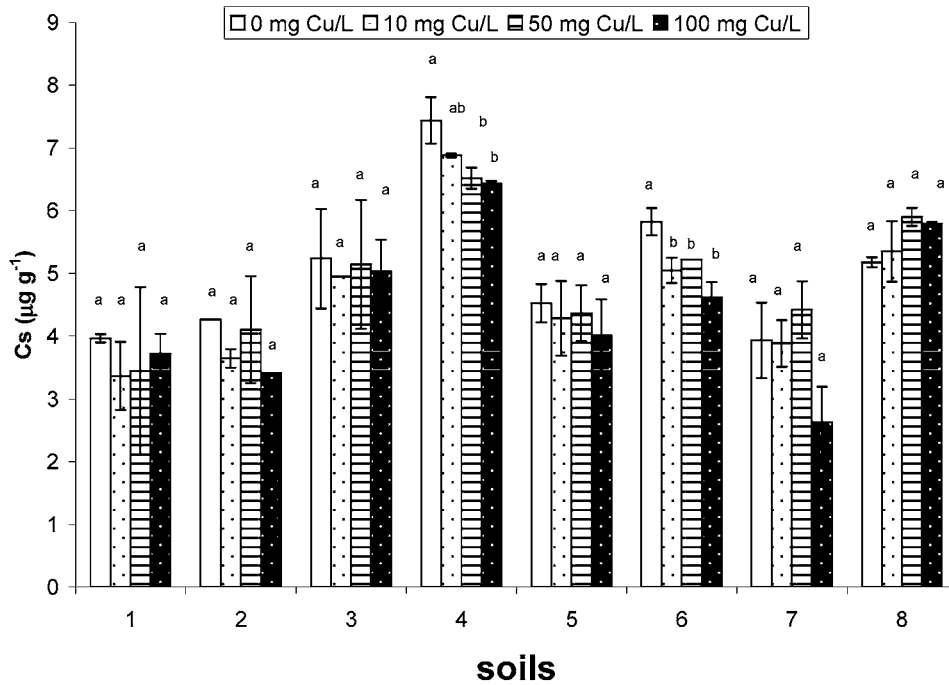
	metalaxyl	penconazole <sup>b</sup>
C (%)	0.161	0.833*
$\text{Cu}_e$ ( $\text{mg kg}^{-1}$ )	0.002	0.850**
$\text{Cu}_p$ ( $\text{mg kg}^{-1}$ )	0.035	0.740*
$\text{Cu}_o$ ( $\text{mg kg}^{-1}$ )	0.012	0.738*
$\text{Cu}_{ao}$ ( $\text{mg kg}^{-1}$ )	−0.004	0.717*
$\text{Cu}_t$ ( $\text{mg kg}^{-1}$ )	0.019	0.717*

<sup>a</sup> C, total organic carbon;  $\text{Cu}_e$ , exchangeable Cu;  $\text{Cu}_p$ , pyrophosphate-extractable Cu;  $\text{Cu}_o$ , oxalic–oxalate-extractable Cu;  $\text{Cu}_{ao}$ , ascorbic–oxalic–oxalate-extractable Cu;  $\text{Cu}_t$ , total Cu content. <sup>b</sup> \*,  $p < 0.05$ ; \*\*,  $p < 0.01$ .

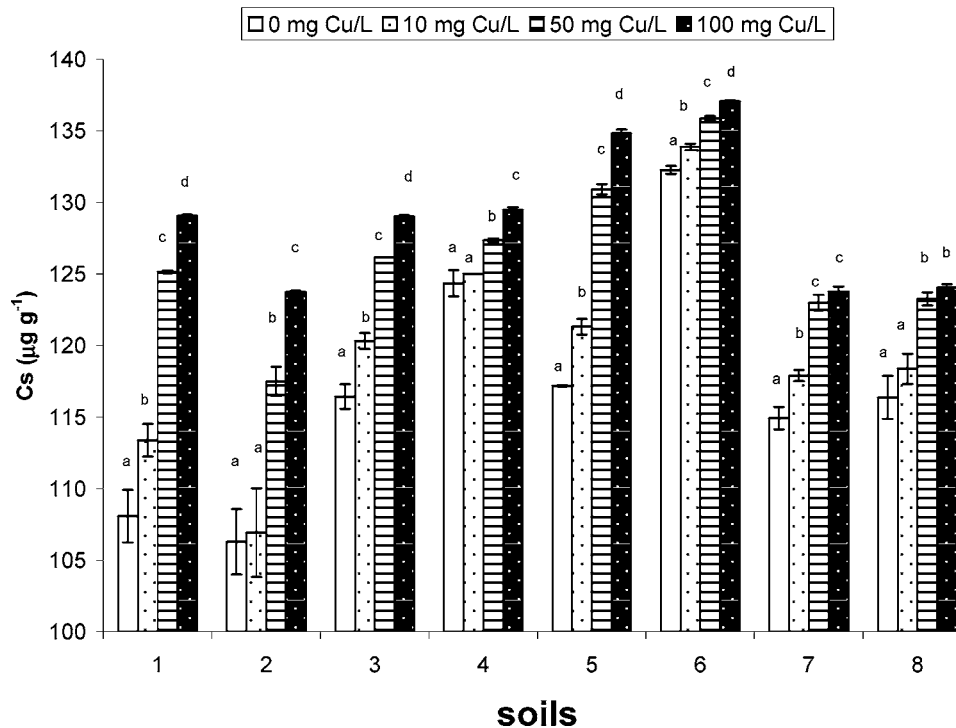
fractions, especially with  $\text{Cu}_e$ , the fraction most easily desorbed into solution (Table 6). This could be due to penconazole–copper complexes being bound to soil colloids by weaker bonds than free penconazole.

**Effect of Added Copper on Fungicide Adsorption.** In general, the addition of copper did not significantly affect metalaxyl adsorption, except for a slight reduction in adsorption onto soils 4 and 6 ( $p < 0.05$ ), the soils that had the largest organic matter contents and that adsorbed the most metalaxyl (Figure 5). It is possible that in these two soils the added copper competed with metalaxyl for some adsorption sites. For penconazole, added copper had the same effect as pre-existing copper, significantly increasing adsorption in most soils when added at a concentration of  $10 \text{ mg L}^{-1}$  and in all soils when added at  $50 \text{ mg L}^{-1}$  (Figure 6), plausibly as the result of the formation of  $\text{Cu}^{2+}$ –penconazole complexes in which the copper cation increases the affinity for soil colloids. The affinity of the soil for copper, free or complexed with penconazole, is reflected by the fact that only 10–20% of the added copper remained in solution in these experiments. Again, as in the case of pre-existing copper, the same effect has been reported for the adsorption of glyphosate (19–21).

In summary, penconazole was more strongly adsorbed in the surface layer of Rías Baixas vineyard soils than was metalaxyl, with  $K_F$  values more than an order of magnitude greater. For both fungicides, adsorption  $K_F$  was 2–3 times greater when they were adsorbed from a solution of pH 2.5 than when the solution pH was 5.5. Soil copper content hardly affected the adsorption



**Figure 5.** Adsorption of metalaxyl ( $C_s$ ,  $\mu\text{g g}^{-1}$ ) from  $5 \text{ mg L}^{-1}$  solutions containing 0, 10, 50, or  $100 \text{ mg L}^{-1}$  of  $\text{Cu}^{2+}$ . For each soil, the adsorptions indicated by columns labeled with different letters were significantly different at the 95% confidence level according to least significant difference tests.



**Figure 6.** Adsorption of penconazole ( $C_s$ ,  $\mu\text{g g}^{-1}$ ) from  $15 \text{ mg L}^{-1}$  solutions containing 0, 10, 50, or  $100 \text{ mg L}^{-1}$  of  $\text{Cu}^{2+}$ . For each soil, the adsorptions indicated by columns labeled with different letters were significantly different at the 95% confidence level according to least significant difference tests.

of metalaxyl, but for penconazole  $K_F$  increased with copper content at a rate of about  $0.1 \text{ mL}^n (\mu\text{g of penconazole})^{(1-n)} (\mu\text{g of Cu})^{-1}$  regardless of solution pH. The addition of copper to the fungicide solution also increased the adsorption of penconazole but not that of metalaxyl. The behavior of penconazole is attributed to the formation of penconazole- $\text{Cu}^{2+}$  complexes with more affinity for soil colloids than penconazole itself.

These findings imply that metalaxyl is more mobile than penconazole in Rías Baixas vineyard soils and that the risk of its reaching water bodies is greater than that for penconazole.

The greater retention of penconazole in these soils appears to be favored by its greater hydrophobicity and by the high soil copper contents that have resulted from long-established use of copper-based fungicides.

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