Influence of Copper on the Adsorption and Desorption of Paraquat, Diquat, and Difenzoquat in Vineyard Acid Soils

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Retention of the cationic herbicides paraquat (PQ), diquat (DQ), and difenzoquat (DFQ) in two vineyard soils with a different management history and retention capacity was examined. The influence of copper on the ability of the soils to retain the herbicides was determined by comparing the results of adsorption and desorption tests on untreated and Cu-enriched soil samples, and also on soils that were previously treated with EDTA to extract native copper. The three herbicides were strongly adsorbed by both soils. Soil 1 exhibited linear adsorption isotherms for PQ and DFQ with partition coefficients, K_D, of 1.28×10^3 and 1.37×10^3 L kg^{-1}, respectively, and a Freundlich-type isotherm for DQ with a linearized partition coefficient, K_D^*, of 1.01×10^3 L kg^{-1}. On the other hand, soil 2 exhibited curved isotherms and smaller K_D^* values (*viz.* 106, 418, and 28 L kg^{-1} for PQ, DQ, and DFQ, respectively). Using EDTA to extract copper from the soils released new sites for the herbicides to bind. The three herbicides exhibited strong hysteresis in the adsorption–desorption process. Extracting copper decreased the percent desorption of PQ and DQ; on the other hand, it decreased the affinity of DFQ for the resulting vacant adsorption sites. Similarly, competitive adsorption tests with copper and the herbicides revealed that the metal was only capable of displacing DFQ from adsorption sites. The behavior of this herbicide in the soils was consistent with a specific adsorption model. The disparate behavior of the two soils toward the herbicides was a result of the adsorption sites in soil 1 being less extensively occupied than those of soil 2 in the adsorption tests. The effect of copper on the adsorption of DFQ in the two soils was acceptably reproduced by an adsorption model involving Coulombic and specific sorption with competition from the metal.

KEYWORDS: Paraquat, diquat, difenzoquat, copper effect, adsorption–desorption, vineyard acid soils

INTRODUCTION

Diquat (1,1′-ethylene-2,2′-bipyridinium, DQ), paraquat (1,1′-dimethyl-4,4′-bipyridinium, PQ), and difenzoquat (1,2-dimethyl-3,5-diphenyl-1H-pyrazolium, DFQ) are three nonselective contact herbicides widely used at weed emergence to protect a wide range of crops (see selected properties in **Table 1**) (*1−3*). In aqueous solutions, PQ and DQ occur as divalent cations, and DFQ occurs as a monovalent cation. PQ has been used as an agricultural herbicide for more than 40 years (*4*), whereas DQ was issued by EPA in 1986 and DFQ was registered in 1988.

The adsorption and desorption of these compounds in heterogeneous soils govern their fate. Soil adsorption of bipyridinium herbicides (largely PQ and DQ) has been studied since the 1960s and 1970s. Tests have revealed that both are strongly adsorbed by soils and soil clays (*5−8*). Also, according to Calderbank (*9*), some clays in soil dramatically reduce the herbicidal power of both compounds. More recent studies have shown that these herbicides have a high affinity for clay surfaces in relation to soil organic matter, especially as compared with inorganic cations (*10−14*). Their interactions with clay particles depend on the particular type of clay. Thus, Weber and Scott (*15*) found PQ to bind to interlayer spacings in montmorillonites via Coulombic and van der Waals forces, and also to kaolinite via Coulombic forces alone.

Adsorption–desorption processes can additionally be influenced by the presence of competing ions. In vineyard soils, cationic herbicides interact with inorganic cations such as the copper used in fungicides or from the application of swine manure (*16*). Elucidating interactions between dipyridilium- and pyrazolium-based organic cations and copper can be very useful

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Table 1. Characteristics of the Bipyridinium Salts Studied[a]

	PQ	DQ	DFQ
chemical structure			
chemical name	1,1′-dimethyl-4,4′-bipyridinium	1,1′-ethylene-2′,2-dipyridylium	1,2-dimethyl-3,5-diphenyl-4,5-dihydro-1H-pyrazol-2-ium methyl sulphate
CAS no.	1910-42-5	85-00-7	43222-48-6
molecular wt	257.2	344	362.4
solubility in water at 20 °C (g/L)	620	677	740
octanol/water partition coefficient (log P_{ow}) at 20 °C	−4.5	−4.6	0.3
partition coefficient normalized to organic carbon content, K_{oc} (mL g_{oc}^{-1} or L kg_{oc}^{-1})	15–51	164–134	23–36
aerobic soil half-life (avg days)	644	3450	6810

[a] Data were obtained from Kenaga (1980), Haag and Yao (1992), and US-EPA (1994).

Table 2. General Properties of the Studied Soils

soil	texture	% sand	% silt	% clay	pH_{H_2O}	pH_{KCl}	% C	CEC (cmol$_c$ kg^{-1})	SA[a] (m^2 g^{-1})
1	loam	45	36	19	5.2	3.8	2.0	5.64	78
2	loam	43	41	16	5.8	4.5	2.0	4.81	66

[a] SA = surface area.

Table 3. Herbicide Recoveries (% ± Relative Standard Deviations %) at 200 μg kg^{-1} and LOQs (μg kg^{-1}) Obtained

herbicide	LOQ	% (RSD)
PQ	20	98 (10)
DQ	20	102 (14)
DFQ	10	100 (5)

with a view to predicting the fate and environmental impact of these herbicides, which can easily compete with binding sites in soil colloids.

This work is part of an ongoing research project intended to increase available knowledge about the specific factors affecting adsorption−desorption processes, and hence pesticide mobility, in crop soils (*17*−*19*). In this work, we studied the adsorption and desorption of three cationic herbicides in two vineyard soils essentially differing in cultivation history and retention capacity. Also, we examined the influence of "aged" copper present in the soils or added in the laboratory, as we did in previous work with metalaxyl and penconaloze (*20*). To this end, we developed a new method for extracting and measuring the herbicides in soil, which are made more difficult by the increased complexity of the studied matrix relative to water (*21*).

MATERIALS AND METHODS

Soils. Two samples of soil were obtained from the 0−5 cm deep layer of two vineyard soils developed on granite materials in Galicia (NW Spain). The soils differed in the length of time they had been used for vine growing (more than 100 years for soil 1 and only 7 for soil 2). Five replicates of each soil were collected within 0.5 m of each other and pooled. Once in the laboratory, the soils were dried at room temperature, passed through a 2 mm mesh sieve, homogenized, and stored until analysis.

Analytical Methods. The pH of 1:2.5 suspensions of soil in water or 0.1 M KCl was measured with a combined glass electrode. The organic carbon content was determined by elemental analysis on a ThermoFinnigan 1112 Series NC instrument. The proportions of sand (2−0.05 mm), silt (0.05−0.002 mm), and clay (<0.002 mm) were determined by using the wet sieving and pipet methods. Exchangeable cations were extracted with 0.2 M NH$_4$Cl and determined by atomic absorption spectroscopy (Ca$_e$ and Mg$_e$) or flame emission spectrometry (Na$_e$ and K$_e$). Exchangeable aluminum was quantified by displacement with 1 M KCl, followed by atomic absorption spectrophotometry. Finally, the cation exchange capacity, CEC, was determined as the combination of bases (Na$_e$, K$_e$, Ca$_e$, and Mg$_e$) and exchangeable Al. The characteristics of the soils are summarized in **Table 2**.

PQ, DQ, and DFQ in the soils were extracted by a method developed by us for this work with analyte recoveries of about 100% (**Table 3**).

A sample of 5 g of soil was extracted for 3 h with 30 mL of a 70:30 mixture of MeOH/5% EDTA, which was previously acidified with the addition of 2% (v/v) formic acid. The resulting extract was concentrated to 4 mL following pH adjustment to 9−10 with 3 N NaOH and cleaned up by passage through silica cartridges and elution with 10 mL of 70:30 MeOH/6.5 M HCl (*22*). Finally, the extract was evaporated to dryness and filled up to a volume of 1 mL with a mixture of 100 mM ammonium formate and formic acid, which was added to bring the solution to pH 3, with the addition of 15 mM heptafluorobutyric acid (HFBA) before analysis by liquid chromatography.

Liquid chromatography runs were performed on a Thermo Fisons system including a P200 binary pump, an AS 1000 autosampler, a TSP SCM 1000 vacuum membrane degasser, and a UV 2000 detector. Separations were done on a Luna C18 column (150 mm long × 4.60 mm i.d., 5 μm particle size) obtained from Phenomenex (Madrid, Spain) and a guard column (4 mm long × 2 mm i.d., 5 μm particle size) packed with the same material. The temperature of the HPLC column was kept at 40 °C throughout the tests.

The mobile phases used were (A) water containing 100 mM ammonium formate/formic acid to bring the solution to pH 3/15 mM HFBA and (B) methanol. The gradient was as follows: 90% A for 3 min, change to 90% B 10% A in 3 min, hold 5 min, change to 90% A and 10% B in 0.1 min, and hold 9 min. The total analysis time was 20 min. The injected volume was 50 μL, and the LC flow-rate was 0.7 mL/min. The wavelengths used for detection were 258 nm for PQ and DFQ, and 310 nm for DQ.

The primary copper fractions in the soils were selectively extracted as follows:

(1) Cu$_e$ (exchangeable Cu) by shaking 10 g of soil in 50 mL of 1 M ammonium acetate at pH 7 for 1 h (*23*).

(2) Cu$_p$ (pyrophosphate-extractable Cu; Cu ascribed to organic matter) by shaking 1 g of soil in 100 mL of 0.1 M sodium pyrophosphate at pH 10.1 for 16 h (*24*).

(3) Cu$_o$ (oxalic/oxalate-extractable Cu; Cu ascribed to amorphous materials) by shaking 1 g of soil in 50 mL of 0.2 M oxalic acid/ammonium oxalate for 4 h (*25*).

(4) Cu$_{ao}$ [ascorbic/oxalic/oxalate-extractable Cu; Cu ascribed to soil colloids (amorphous materials and crystalline oxides included)] by shaking 1 g of soil in 50 mL of 0.1 M oxalic acid/ammonium oxalate/ascorbic acid at 96 °C for 30 min (*26*).

(5) Cu$_t$ (total Cu) by digesting 0.5 g of soil with 5 mL of HNO$_3$, 4 mL of HF, and 1 mL of HCl in a microwave oven at 100 psi.

Paraquat, Diquat, and Difenzoquat in Vineyard Acid Soils

J. Agric. Food Chem., Vol. 55, No. 15, 2007   **6221**

(6) Cu_{EDTA} (potentially available Cu) by shaking 5 g of soil in 50 mL of a solution containing 0.5 M NH_4OAc and 0.02 M EDTA at pH 4.65 for 1 h (27).

Adsorption of Copper. A soil sample of 1 g at room temperature (22 ± 2) °C was equilibrated with a volume of 10 mL of $CuCl_2\cdot2H_2O$ solutions of variable concentration in the range 0.150−3.150 mmol L^{-1} in the presence of 0.01 M $CaCl_2$ as background electrolyte for 24 h. The resulting supernatant was separated by centrifugation at 4000 rpm for 10 min and filtered in order to measure copper by atomic absorption spectrophotometry. The amount of Cu adsorbed in the soil was calculated as the difference between that initially added and that remaining in solution after equilibration. All measurements were made in duplicate.

Adsorption of PQ, DQ, and DFQ. A 1 g sample of each soil was suspended in 10 mL of herbicide solution adjusted to a pH of 5.0 (0.020−0.390 mmol L^{-1} for PQ, 0.015−0.290 mmol L^{-1} for DQ, and 0.03−0.056 mmol L^{-1} for DFQ, all containing 0.01 M $CaCl_2$). The individual herbicide solutions were prepared from 4.650, 3.462, and 1.140 mM stock solutions of PQ, DQ, and DFQ, respectively. Suspensions were shaken on a rotary shaker at 200 rpm at room temperature (20 ± 2 °C) for 24 h and then centrifuged at 4000 rpm for 10 min. The resulting supernatant was treated as described above for analysis on a Fisons Instruments LC/UV−vis system. The amounts of PQ, DQ, and DFQ adsorbed were calculated as the differences between those initially present in solution and those remaining after centrifugation. All measurements were made in duplicate.

Influence of Copper in the Soils on PQ, DQ, and DFQ Adsorption. The previous adsorption tests were repeated following extraction of copper with EDTA, even though this treatment may cause side-effects, especially in the aggregation of the soil particles. To this end, amounts of 30 g of soil were treated with 300 mL of an EDTA/NH_4-OAc mixture. Subsequently, the soils were washed with 0.01 M $CaCl_2$ and allowed to dry prior to subjection to the adsorption tests.

Desorption of PQ, DQ, and DFQ. Once the adsorption process was finished after 24 h, a volume of 7 mL of the liquid phase in each centrifuge tube (three-fourths) was replaced with an identical volume of a 0.01 M $CaCl_2$ solution containing no herbicide and the solution was processed as described in the previous section, with the procedure being repeated five times (six steps in all). The PQ, DQ, and DFQ concentrations used in the tests were 0.230, 0.170, and 0.014 mM, respectively. Desorption data are given as percentages of the initial amounts adsorbed. All measurements were made in duplicate. The desorption tests were repeated following treatment of the soils with EDTA as described in the previous section.

Additional tests involving desorption with 0.01 M $CuCl_2$ were conducted with a view to confirming the ability of copper to release the studied herbicides from the soils.

Influence of Added Copper on the Adsorption of PQ, DQ, and DFQ. Determinations included adsorption of the herbicides from solutions at pH 5.5 to which $CuCl_2\cdot2H_2O$ was added at concentrations of 0, 0.16, 0.80, 1.6, or 3.2 mmol Cu L^{-1}. The herbicide concentrations used in these tests were 0.389, 0.291, and 0.056 mmol L^{-1} for PQ, DQ, and DFQ, respectively. All measurements were made in duplicate.

RESULTS AND DISCUSSION

Table 2 summarizes the characteristics of the surface soils studied. Both soils were acidic; thus, their pH values in water were 5.2 and 5.8, respectively. Also, both had a loam texture and an organic carbon content of 2%. However, their surface areas were somewhat different (78 m^2 g^{-1} for soil 1 and 66 m^2 g^{-1} for soil 2).

Soil 2 was found to contain increased amounts of DQ and PQ relative to soil 1 (see **Table 4**). This was so even though soil 1 had been used to grow vines for longer; in fact, soil 2 started to be cropped only 7 years ago, but the needs for herbicides were higher to remove abundant weeds from previous use as woodland. In soil 1, instead, weeds had traditionally been removed mechanically rather than by applying herbicides. The concentration of total copper in soil 1 was very high (583 mg

Table 4. Concentrations of the Three Herbicides, Total Copper (Cu_t), and Various Copper Forms, All in mg kg^{-1}, in the Studied Soils[a]

soil	PQ	DQ	DF	Cu_e	Cu_p	Cu_o	Cu_{ao}	Cu_{EDTA}	Cu_t
1	0.25	0.04	<0.01	23	375	408	530	213	583
2	0.97	0.32	<0.01	<1	14	19	29	6	42

[a] Cu_e, ammonium acetate-extractable copper; Cu_p, sodium pyrophosphate-extractable copper; Cu_o, oxalic acid/ammonium oxalate-extractable copper; Cu_{ao}, oxalic acid/ammonium oxalate/ascorbic acid-extractable copper; Cu_{EDTA}, ammonium acetate/EDTA-extractable copper.
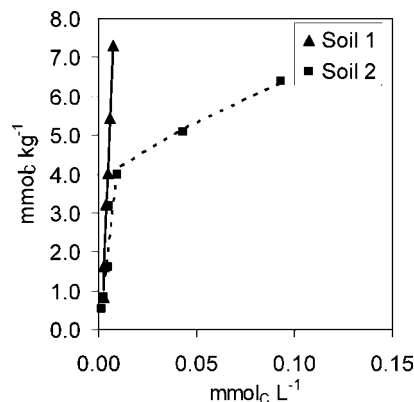

Figure 1. Adsorption isotherm for PQ in both soils. Symbols represent experimental data points and lines their best fits: a linear isotherm (solid line) for soil 1 and two consecutive linear isotherms (dashed lines) for soil 2. Standard deviations: lower than 3%.

kg^{-1}) relative to soil 2 (41 mg kg^{-1}, **Table 4**). This was a result of the metal accumulating in the former through repeated application of copper-based fungicides over a long time. Cu% bound to organic matter (($Cu_p − Cu_e$) × 100/Cu_t) is 60 and 33%, respectively, for soils 1 and 2. Cu% bound to inorganic amorphous material (($Cu_o − Cu_p$) × 100/Cu_t) is 6 and 12%, respectively, for soils 1 and 2. Cu% bound to crystalline oxides (($Cu_{ao} − Cu_o$) × 100/Cu_t) is 21 and 14%, respectively, for soils 1 and 2. Residual Cu% (($C_t − Cu_{ao}$) × 100/Cu_t) is 9 and 31%, respectively, for soils 1 and 2. In noncontaminated soils, copper is mainly found as a part of the mineral structure, whereas, in highly contaminated soils, copper is associated with soil colloids, mainly organic colloids (28−29), as is the case for soil 1. The higher level of residual Cu% for soil 2 (31%) than for soil 1 (9%) is typical of noncontaminated/low-contaminated soils.

Adsorption and Desorption of PQ, DQ, and DFQ. The pH of the herbicide solutions used in the adsorption tests decreased from its initial value, 5.0, on contact with the soil suspensions. Thus, after 24 h, PQ caused the pH to decrease to 4.5 ± 0.1 in soil 1 and 4.8 ± 0.1 in soil 2 (n = 20); DQ decreased it to 4.4 ± 0.1 and 4.7 ± 0.1 (n = 20), respectively; and DFQ lowered it to 4.4 ± 0.1 and 4.8 ± 0.1 (n = 14), respectively. The previous pH data represent average values for the numbers of soil samples given in parentheses.

As can be seen from **Figures 1−3**, soil 1 exhibited a high affinity for the three herbicides throughout the adsorbed concentration range. Thus, the isotherms obtained from the herbicide concentrations of PQ and DFQ in millimoles of charge ($mmol_c$) were linear and provided the K_D values 12.8 × 10^3 and 1.37 × 10^3 L kg^{-1}, respectively (**Table 5**). On the other hand, the data for DQ fitted the Freundlich equation, which suggests that its partition coefficient changed with the extent of occupation of adsorption sites in the soils. In order to compare the behavior of the three herbicides, we obtained the equivalent K_D values, K_D^*, by using an isotherm linearization method

6222   *J. Agric. Food Chem.,* Vol. 55, No. 15, 2007
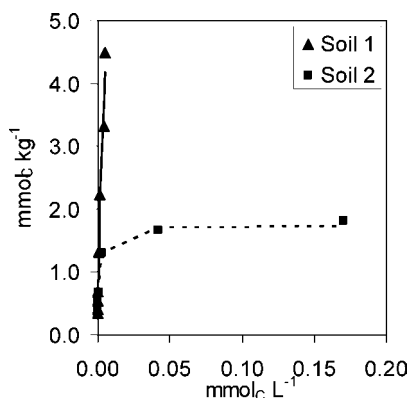
Pateiro-Moure et al.

Figure 2. Adsorption isotherm for DQ in both soils. Symbols represent data points and lines their best fits: a linear isotherm (solid line) for soil 1 and a Langmuir-type isotherm (dashed line) for soil 2. Standard deviations: lower than 3%.
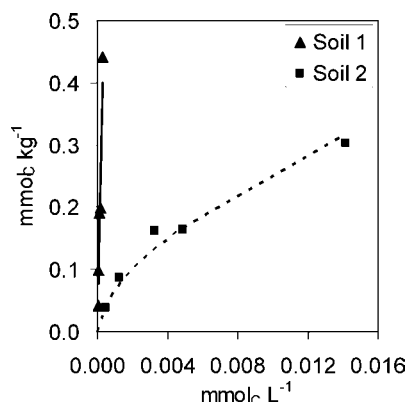

Figure 3. Adsorption isotherm for DFQ in both soils. Symbols represent data points and lines their best fits: a linear isotherm (solid line) for soil 1 and a Freundlich-type isotherm (dashed line) for soil 2. Standard deviations: lower than 3%.

involving equalling the area under a nonlinear isotherm to that under a linear one and solving for K_D over the concentration range used to obtain the isotherms. This yielded a K_D* value of 1.01×10^3 L kg^{-1} for PQ over the studied concentration range. In the first third of the concentration range, the isotherm fitted a linear isotherm with $K_D = 1.60 \times 10^3$ L kg^{-1} and $R^2 = 0.998$. Therefore, the partition constants were similar for the three herbicides.

Soil 2 exhibited a change in the slopes of the three isotherms beyond a given concentration of adsorbed herbicide. The equations fitting the isotherms for soil 2 differed from those for soil 1. The sharp decreasing slope of PQ to soil 2 below 4 mmol$_c$ kg^{-1} in **Figure 1** suggests that retention sites with the highest affinity were saturated at such a sorbed concentration. The best fit for the PQ isotherm was obtained by splitting it into two linear segments, according to affinity, namely: one with $K_D = 429$, corresponding to the sites capable of adsorbing up to 4 mmol$_c$ PQ kg^{-1}, and the other with $K_D = 24$ L kg^{-1}, corresponding to those adsorbing more than 4 mmol$_c$ PQ kg^{-1}. The slope of the adsorption isotherm for DQ (**Figure 2**) decreased abruptly at concentrations above 1.5 mmol$_c$ kg^{-1}. The optimum fit of the isotherm to the Langmuir equation provided a maximum adsorption capacity $Q_{max} = 1.75$ mmol$_c$ kg^{-1} and a coefficient $K_L = 1.68 \times 10^3$ L mmol$_c^{-1}$ ($K_D* = 418$). These results suggest that soil 2 has a lower DQ retention capacity than soil 1, but after comparing the slopes of both isotherms at very low concentrations (*viz.* <1 mmol$_c$ kg^{-1}), it exhibits as high an affinity for the herbicide at low concentrations as the

latter. This in turn suggests that soil 2 has fewer retention sites for DQ, even though the sites in both soils have a similar binding affinity for this compound.

The isotherm for DFQ in soil 2 was not linear (**Figure 3**); rather, it fitted the Freundlich equation. The decreased linearized partition coefficient obtained, $K_D* = 28$, reveals that the affinity of soil 2 for this herbicide is lower than that for the other two.

The soil samples were treated with EDTA in order to examine the effect of extracting copper from the soils on the adsorption of the three herbicides. The treatment removed 37 and 14% of total copper in soil 1 and 2, respectively. Copper extraction led to an increase in the adsorption of the three herbicides by soils, i.e., a decrease in the equilibrium concentrations measured during the adsorption experiments (**Table 6**). Thus, the supernatant from soil 1 contained undetectable amounts of PQ (<0.19 $\times 10^{-3}$ mmol L^{-1}) and DQ (<10^{-5} mmol L^{-1}), and that from soil 2 had concentrations roughly 1 order of magnitude lower than before extraction with EDTA. The DFQ concentration exhibited a substantial decrease in soil 1 (from 1.4×10^{-3} to 5 $\times 10^{-4}$ mmol L^{-1}) but remained virtually constant in soil 2, where it decreased from 0.014 to 0.013 mM. The decrease was especially marked in soil 1, where EDTA extracted more copper. These results suggest that extracting copper increases the proportion of new sites available for binding to the herbicides.

A comparison of the adsorption data obtained after the EDTA treatment reveals an increase in the herbicide concentrations retained amounting to 1.7, 0.3, and 1.6% for PQ, DQ, and DFQ, respectively, in soil 1 and to 2.8, 1.6, and 3.1%, respectively, in soil 2. If one assumes that the released sites were previously occupied by Cu^{2+} ions, the effect of the EDTA treatment can be quantified as 6.6 mmol$_c$ kg^{-1} for soil 1 and 0.19 mmol$_c$ kg^{-1} for soil 2. The increase in PQ, DQ, and DFQ retention was equivalent to the replacement of 6.4, 2.6, and 1.9% of the charges theoretically released by Cu^{2+} in soil 1 and to 1.6–1.8% of those released in soil 2. Therefore, the degree of copper release was not stoichiometrically related to the increase in herbicide retention. Most of the EDTA-extracted Cu was not occupying places available for a future adsorption of the herbicides, with this behavior being more remarkable in the case of soil 2.

Table 7 shows the results of the sequential desorption tests. Soil 1 exhibited less than 1% desorption of the three herbicides. Soil 2 exhibited higher proportions which, however, were still very low. Thus, PQ was desorbed in proportions from 1% in the first step to 0.2% in the sixth; DQ exhibited slightly higher proportions which never exceeded 4% and tended to decrease as the desorption sequence progressed; and DFQ was the herbicide desorbed to the greatest extent (5–8%). The three herbicides exhibited strong hysteresis in the adsorption–desorption process (especially PQ and DQ as a result of their strong binding to adsorbing surfaces).

As can be seen from **Table 7**, PQ and DQ desorption decreased upon extraction with EDTA, and the opposite was true in general with DFQ. In fact, DFQ was adsorbed and desorbed to a greater extent following extraction of the soil with EDTA. This suggests that DFQ bound less strongly to the new sites released by EDTA than did DQ and PQ.

We also conducted desorption tests on soil samples incubated with the three herbicides but subjected to no EDTA extraction. In these tests, CaCl$_2$ was replaced with CuCl$_2$ in order to assess the ability of copper to displace the three herbicides. In soil 1, copper exhibited a PQ and DQ displacement capacity similar to that of calcium; however, it resulted in significantly increased desorption of DFQ (**Figure 4**). In soil 2, copper resulted in

Paraquat, Diquat, and Difenzoquat in Vineyard Acid Soils

J. Agric. Food Chem., Vol. 55, No. 15, 2007 **6223**

Table 5. Figures of Merit of the Isotherm Equations[a] Fitted to the Adsorption Data for the Three Herbicides and Copper

	soil 1		soil 2	
adsorbate	type of isotherm	R^2	type of isotherm	R^2
PQ	(a) $K_D = 1.28 \times 10^3$	0.996	(a) two regions: for $q \leq 4$, $K_D = 429$; for $q > 4$, $K_D = 24$ ($K_D^* = 106$)	0.961
DQ	(b) $K_F = 91.3$, $n = 0.587$ ($K_D^* = 1.01 \times 10^3$)	0.973	(c) $Q_{max} = 1.75$, $K_L = 1.68 \times 10^3$ ($K_D^* = 418$)	0.974
DFQ	(a) $K_D = 1.37 \times 10^3$	0.970	(b) $K_F = 3.9$, $n = 0.59$ ($K_D^* = 28$)	0.996
copper	(b) $K_F = 7.9$, $n = 0.63$	0.959	(b) $K_F = 10.0$, $n = 0.3$	0.937

[a] Isotherm equations. (a) Linear: $q = K_D c$. (b) Freundlich: $q = c K_F{}^n$. (c) Langmuir: $q = K_L c Q_{max}/(1 + c K_L)$. q is the amount adsorbed expressed in electrical charge (mmol$_c$ kg^{-1} of soil); c is the concentration in solution, expressed in charge units (mmol$_c$ L^{-1}); K_D is the linear coefficient of distribution; K_F and n are the Freundlich coefficient and exponent, respectively; K_L and Q_{max} are the coefficients and the maximum adsorption capacity for the soil in the Langmuir isotherm; and K_D^* is the apparent coefficient of distribution obtained by linearizing the isotherms

Table 6. Comparison of the PQ, DQ, and DFQ Equilibrium Concentrations Found in EDTA-Treated (EDTA-1 and EDTA-2) and Untreated Soil Samples (1 and 2), All in mmol L^{-1}, in the Adsorption Tests[a]

	equilibrium concentration		
soil sample	PQ	DQ	DFQ
1	1.5×10^{-3}	0.2×10^{-3}	1.4×10^{-3}
EDTA-1	$<0.19 \times 10^{-3}$	$<0.01 \times 10^{-3}$	0.50×10^{-3}
2	2.4×10^{-3}	1.3×10^{-3}	14.0×10^{-3}
EDTA-2	0.3×10^{-3}	0.40×10^{-3}	12.7×10^{-3}

[a] Initial concentrations: 0.078 mM PQ, 0.058 mM DQ, and 0.056 mM DFQ. Standard deviations: lower than 3%.
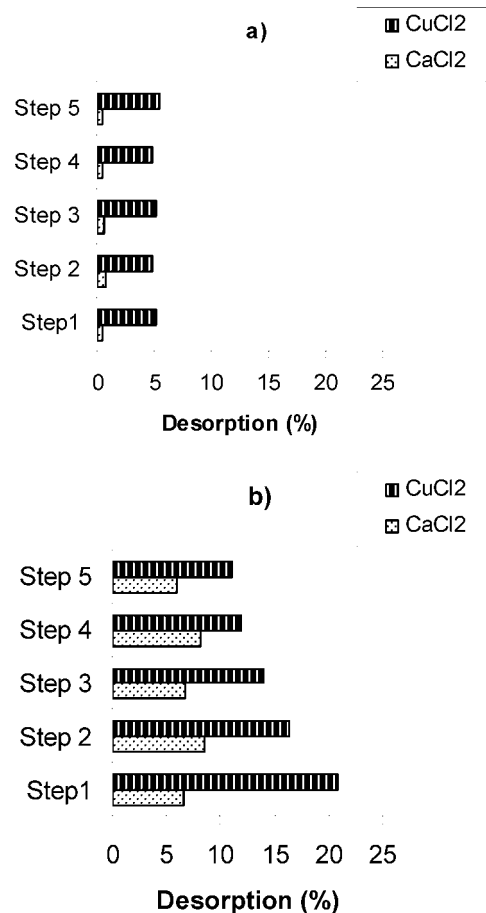
Table 7. Percent Desorption of PQ, DQ, and DFQ at an Added Concentration of 230, 170, and 16 μmol L^{-1}, Respectively, as Calculated from the Initial Adsorbed Concentrations in EDTA-Treated (EDTA-1 and EDTA-2) and Untreated Soil Samples (1 and 2)[a]

soil sample		desorption (%)					
		step1	step 2	step 3	step 4	step 5	step 6
1	PQ	1.0	0.4	0.3	0.2	<0.08	<0.08
	DQ	0.5	0.5	0.3	0.3	0.2	<0.01
	DFQ	0.5	0.7	0.6	0.4	0.5	0.5
EDTA-1	PQ	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08
	DQ	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	DFQ	1.5	1.9	0.5	0.5	0.3	0.3
2	PQ	1.5	0.9	0.7	0.7	0.5	0.2
	DQ	3.2	3.2	3.6	3.3	3.2	2.1
	DFQ	6.6	8.5	6.7	8.2	6.0	4.8
EDTA-2	PQ	0.3	0.2	0.4	0.4	0.3	0.2
	DQ	1.9	1.5	0.5	1.4	1.1	0.5
	DFQ	11.0	9.0	7.4	5.9	5.1	5.0

[a] Standard deviations: lower than 3%.

Figure 4. Variation of DFQ desorption in successive extractions with CaCl$_2$ and CuCl$_2$ of soils 1 (**a**) and 2 (**b**) with CaCl$_2$ and CuCl$_2$. Standard deviations: lower than 3%.

slightly increased desorption of PQ (from <1% to 1.4−2.1%) but in virtually no differences in DQ desorption and in more marked changes in DFQ desorption (**Figure 4**). Based on the assumption that the disparate behavior of the soils was a result of the different extents of occupation of adsorption sites, copper was more efficient in displacing the herbicides from soil 2, which was that containing the greater proportion of occupied sites. This is consistent with the differences between the two soils. In fact, soil 2 released increased amounts of herbicides by effect of the presence of calcium and copper.

Copper−herbicide competition tests were conducted at a constant initial concentration of herbicide and variable concentrations of copper. The addition of copper at concentrations from 0 to 3.15 mM resulted in no significant increase in the PQ and DQ concentrations in solution. PQ added at an initial concentra-

tion of 0.344 mM to soil 1 was not detected in solution at any concentration of added copper and was detected only in proportions of 4−7% of the initial level in soil 2; also, its concentration exhibited no change with the copper concentration added. DQ behaved similarly to PQ; thus, it was not detected in the solution from soil 1 and was detected in proportions of only 4−8% in soil 2. On the other hand, DFQ was slightly affected by the presence of copper, with its concentration increasing as that of the metal was raised (**Figure 5**). Therefore, the presence of copper has a significant effect on the adsorption of DFQ, but not on that of DQ or PQ.

The presence of the herbicides raised the copper concentration in solution, especially at low concentrations of added copper (**Table 8**). Consequently, the herbicides exhibit a higher affinity
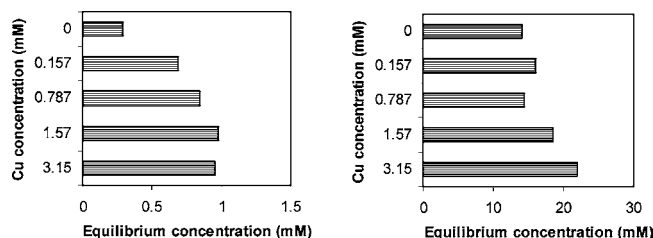
6224 *J. Agric. Food Chem.,* Vol. 55, No. 15, 2007

Pateiro-Moure et al.

Figure 5. Influence of the initial concentration of copper on the equilibrium concentration of DFQ in soils 1 (left) and 2 (right). Standard deviations: lower than 3%.

Table 8. Influence of the Herbicides at Concentrations of 0.389 (PQ), 0.291 (DQ), and 0.056 mmol L^{-1} (DFQ) on the Concentration of Dissolved Copper[a]

| soil	initial [Cu] (mM)	equilibrium [Cu] (mM)			
		Cu	Cu + PQ	Cu + DQ	Cu + DFQ
1	0.16	0.056 (35)	0.091 (57)	0.084 (53)	0.080 (50)
	0.80	0.310 (39)	0.425 (53)	0.412 (52)	0.395 (49)
	1.6	0.785 (49)	0.932 (58)	0.944 (59)	0.862 (54)
	3.2	1.782 (57)	1.755 (56)	2.077 (66)	1.857 (59)
2	0.16	0.006 (4)	0.015 (9)	0.014 (9)	0.010 (6)
	0.80	0.122 (15)	0.290 (36)	ND	0.258 (32)
	1.6	0.441 (28)	0.763 (48)	0.783 (49)	0.641 (40)
	3.2	1.759 (56)	ND	1.668 (53)	1.857 (59)

[a] The percent of copper in solution relative to the amount initially added is given in parentheses. ND = not determined. Standard deviations: lower than 3%.

for adsorbing surfaces than does copper in the studied concentration range.

Modeling DFQ Adsorption. We checked the adsorption data for DFQ against the model of Nir (*30*) for univalent cations. This model uses the Gouy–Chapman theory for planar geometries with an electric double layer and specific binding via electrostatic interactions between negatively charged surfaces in soil and an organic cation.

Because the amounts of DFQ added to the soils were smaller than their CEC, we excluded non-Coulombic binding, which was used by Nir to model herbicide binding at adsorbed concentrations above the CEC.

The binding of a univalent cation X^+ to a negatively charged site P^- with a low tendency to form a neutral complex at a soil surface can be described as
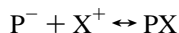
$$P^- + X^+ \leftrightarrow PX$$

The binding coefficient for a univalent cation, K^1, is given by

$$K^1 = [PX]/\{[P^-][X(0)^+]\}$$

where $[X(0)^+]$ is the concentration of univalent cation at the adsorbing surface, which was calculated in the light of the electrical double layer model, using the relation $X_i = [X_i]Y_0^z$, with $[X_i]$ being the molal concentration of cation in the equilibrium solution, $Y_0 = \exp(-e\Psi(0)/kT)$, z the valence of the ion, e the amount of electric charge, $\Psi(0)$ the surface potential, k the Boltzmann constant, and T the absolute temperature.

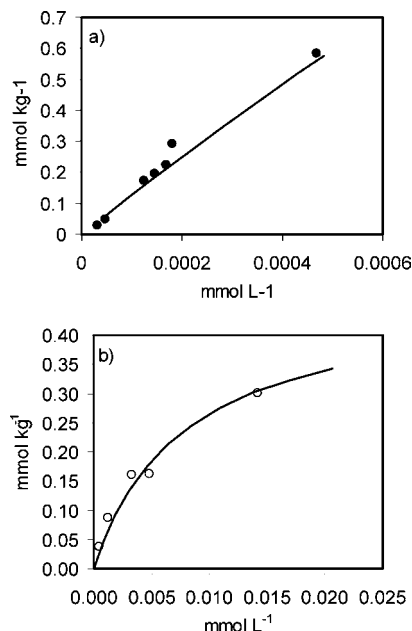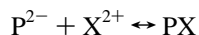Divalent sites are defined as $P^{2-} = P^-/2$, and their binding to divalent cations is defined as

$$P^{2-} + X^{2+} \leftrightarrow PX$$

Figure 6. DFQ adsorption isotherms. Symbols represent experimental data points and lines their fits to the Nir model: (**a**) soil 1; (**b**) soil 2. Standard deviations: lower than 3%.

Their binding coefficient is therefore given by

$$K^2 = [PX]/\{[P^{2-}][X(0)^{2+}]\}$$

Organic cations are assumed to bind to surfaces by forming inner sphere complexes which alter the surface potential.

The calculations involved in applying this model were performed by using the software Visual MINTEQ, version 2.32 (*31*), with the intrinsic binding coefficients as inputs for its databases. MINTEQ allowed us to calculate the distribution of adsorbed and dissolved species in competition with copper and protons, and also the charge balance in the double layer, the surface potential, and the adsorption equilibria involved.

The DFQ adsorption model was calibrated by optimizing the binding coefficient and the number of adsorption sites in the soils in order to reproduce the DFQ adsorption isotherms and the observed effect of the addition of copper on the herbicide concentration in the adsorption equilibrium with the soil. The uncertainty derived from the joint estimation of these two parameters was reduced by assuming the binding constant to be identical for both soils. Therefore, the two soils were assumed to exhibit identical types of binding but a different number of adsorption sites.

Figure 6 shows the adsorption isotherms provided by the calibrated model. The optimum value of the binding constant for the two soils was $K^1 = 63.6$. The concentration of binding sites was 0.21 cmol kg^{-1} for soil 1 and 0.04 cmol kg^{-1} for soil 2. Based on these results, the disparate adsorption of DFQ can be ascribed to soil 1 possessing five times as many adsorption sites as soil 2.

The model also reproduces the effect of the addition of copper on both soils with a copper binding constant of 100. The DFQ concentrations in solution thus calculated were 0.41, 0.5, 0.6, 0.71, and 0.82 mmol L^{-1} in soil 1 and 13.6, 14.4, 15.1, 15.9, and 16.5 mmol L^{-1} in soil 2. This suggests that implementing the Nir model in MINTEQ provides results consistent with the experimental findings. The binding constants are smaller than that obtained by Rytwo et al. (*13*) for the adsorption of DFQ in montmorillonite.

Paraquat, Diquat, and Difenzoquat in Vineyard Acid Soils

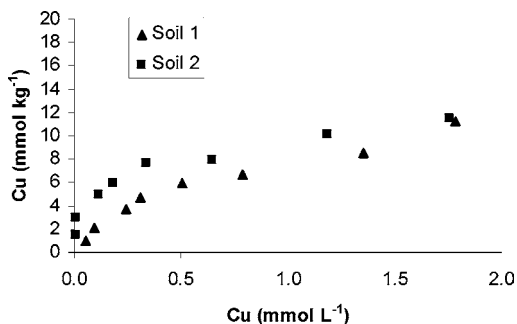*J. Agric. Food Chem.*, Vol. 55, No. 15, 2007 **6225**

Figure 7. Copper adsorption isotherms for the two soils. Standard deviations: lower than 3%.

To sum up, the three herbicides studied in this work exhibited strong adsorption in both types of soils, but especially in soil 1, which may have been a result of the residual contents of PQ and DQ of soil 1 being lower by 1 order of magnitude. By contrast (**Figure 7**), copper was more strongly adsorbed in soil 2; in fact, this soil exhibited a lower content in residual copper (both total and bound to organic and inorganic colloids). Extracting copper in soil with EDTA released new sites for binding of the herbicides, with the effect being more marked in soil 1, which contained more EDTA-extractable copper. The extent of desorption of the herbicides from both soils was very small and was somewhat greater in soil 2, which was initially more markedly saturated with PQ and DQ. PQ and DQ desorption was further decreased by the EDTA treatment, and the opposite held for DFQ. Therefore, the adsorbing sites released by EDTA were more reversible with respect to DFQ. Copper−herbicide competitive adsorption tests showed copper to have a modest ability to displace DFQ from its adsorption sites; however, copper adsorption was influenced (reduced) by the presence of the herbicides. Based on our experimental results and the DFQ adsorption model used, retention of the three studied herbicides is influenced by the degree of occupation of the soil adsorption sites. The adsorption equilibrium coefficient for DFQ was identical in both soils. The herbicides exhibited differences as regards affinity of the soil surfaces; thus, PQ and DQ were retained by sites of a higher affinity than was DFQ.

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