



## Competitive and non-competitive adsorption/desorption of paraquat, diquat and difenzoquat in vineyard-devoted soils

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### ABSTRACT

Mobility of agrochemicals in soils plays an important role in the fate and transport of contaminants in the environment. Competitive and non-competitive sorption experiments of three ammonium quaternary herbicides (paraquat, diquat and difenzoquat) onto eight vineyard soils was measured in batch experiments. Non-competitive experiments show that paraquat (PQ) is the most strongly adsorbed (70–97% of added PQ) followed by diquat (DQ) and difenzoquat (DFQ). The best fits were obtained with the Freundlich equation. In competitive experiments with variable mole ratios, it was found a large influence between the divalent cationic herbicides PQ and DQ, and between them and the monovalent herbicide DFQ, but DFQ did only show a scarce influence on PQ and DQ sorption. Desorption of herbicides into CaCl<sub>2</sub> showed very low values: around 11, 19 and 31% for, respectively, PQ, DQ and DFQ. In order to assess the ability of herbicides to displace others, desorption experiments were carried out by replacing CaCl<sub>2</sub> by any of the other two herbicides. In this case, the highest percentage of desorption was obtained when DFQ was desorbed with PQ (>72%) and DQ (>73%), but also when PQ was used to desorb DQ (100%) and vice versa (100%).

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### 1. Introduction

During the last decades, agricultural practices in vineyards have been changing to prevent low plant development and increase the yield and the quality of the grapes for winemaking. These changes contribute to introduce higher levels of herbicides in the agricultural ecosystem. The main drawback of these agricultural practices is the contamination of soils and waters, contributing to degrade the soil–water–plant system and bioaccumulate herbicide residues.

Quaternary ammonium herbicides paraquat (PQ), diquat (DQ) and difenzoquat (DFQ) are nonselective contact herbicides widely used at weed emergence to protect a wide range of crops [1]. PQ and DQ are divalent cations that are included in a priority list of herbicides of potential concern established for the Mediterranean countries by the European Union (EU), due to their widespread usage in this area [2]. DFQ occurs as monovalent cation and is also used through the world as a selective herbicide for post-emergence control of wild oats in barley and fall-seeded wheat. These herbicides are highly soluble in water and are

present as residues in environmental, food and biological samples [3,4].

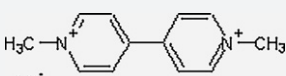
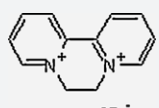
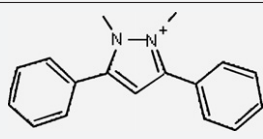
The adsorption of these herbicides, specifically paraquat and diquat, has been independently studied on various minerals and soils [5–8] and in adsorption–desorption processes where they are influenced by the presence of competing ions, as is the case of copper used as a fungicide in vineyard soils that interact with cationic herbicides for adsorption sites [9,10]. To the best of our knowledge little information is available about the competitive sorption of these herbicides for binding sites in colloids of agricultural soils and their potential mobility in the environment which play an important role in the fate and transport of these contaminants in soil.

Competitive sorption takes place at the water–solid interface when there are only limited sorption sites on the surface of soil. Therefore, in diluted systems, competitive sorption is characteristic of surface sorption rather than phase partitioning [11]. Moreover, competitive sorption is also the result of overlapping in the set of sites that can be occupied by the solutes [12]. Due to the diversity and complexity of organic compounds in the natural environment, competitive sorption may play an important role in the fate and transport of contaminants in soil.

This work is part of an ongoing research project intend to increase available knowledge about the specific factors affecting

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**Table 1**  
Characteristics of the quaternary herbicides studied.

Common name	Paraquat (PQ)	Diquat (DQ)	Difenzoquat (DFQ)
Chemical structure			
Name	1,1'-Dimethyl-4,4'-bipyridinium dichloride	1,1'-Ethylene-2,2'-dipyridylium dibromide	1,2-Dimethyl-3,5-diphenyl-1H-pyrazolium methyl sulphate
CAS no.	1910-42-5	85-00-7	43222-48-6
MW <sup>a</sup>	257.2	344	362.4
S <sup>b</sup> (g L <sup>-1</sup> )	620	677	740
log P <sub>ow</sub> <sup>c</sup>	-4.5	-4.6	0.3
Koc <sup>d</sup>	15–51	164–134	23–36
Soil half-life <sup>e</sup>	644	3450	6810

Data were obtained from Kenaga [30], Haag and Yao [31], and US-EPA [32].

<sup>a</sup> Molecular weight.

<sup>b</sup> Solubility in water at 20 °C.

<sup>c</sup> Octanol/water partition coefficient at 20 °C.

<sup>d</sup> Partition coefficient normalized to organic carbon content (mL g<sub>oc</sub><sup>-1</sup> or L kg<sub>oc</sub><sup>-1</sup>).

<sup>e</sup> Aerobic soil half-life (Avg, days).

adsorption–desorption processes, and hence pesticide mobility, in crop soils [13–15]. The aim of this work is to study competitive adsorption/desorption of three cationic quaternary ammonium herbicides (paraquat, diquat and difenzoquat) in eight untreated vineyard-devoted soils of Galicia (north-western Spain), which differ in organic matter and CEC content, via batch experiments to see if these herbicides show a competition in soils for adsorption sites.

## 2. Materials and methods

### 2.1. Chemicals

Paraquat dichloride (99.9%, CAS No. 1910-42-5), diquat dibromide (99.5%; CAS No. 85-00-7) and difenzoquat methyl-sulphate (99.9%; CAS No. 43222-48-6) were obtained from Sigma–Aldrich (Steinheim, Germany). Characteristics of the different chemicals are described in Table 1.

### 2.2. Soil samples

Eight samples of soil were obtained from the 0–5 cm depth layer of eight vineyard soils developed on granite and schist materials in Galicia (NW Spain). The soils differed in the organic matter and CEC content. 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.

The pH of 1:2.5 (solid/liquid) 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 pipette methods. Exchangeable cations were extracted with 0.2 M NH<sub>4</sub>Cl and determined by atomic absorption spectroscopy (Ca<sub>e</sub> and Mg<sub>e</sub>) or flame emission spectrometry (Na<sub>e</sub> and K<sub>e</sub>). Exchangeable aluminium 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<sub>e</sub>, K<sub>e</sub>, Ca<sub>e</sub> and Mg<sub>e</sub>) and exchangeable Al. Determination of the quats in the soils were carried out using the methodology described in Pateiro-Moure et al. [16].

### 2.3. Liquid chromatography determination

Liquid chromatography (LC) analyses were carried out on a Dionex Corporation liquid chromatograph (Sunnyvale, USA) equipped with a P680 quaternary pump, an ASI-100 autosampler, a TCC-100 thermostatted column compartment and a UVD170U detector. Chromatographic 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 mobile phases used were water containing 100 mM ammonium formate adjusted at pH 3 with formic acid and 15 mM HFBA (A), methanol (B) and isopropanol (C). The gradient was: 90% A and 10% B for 3 min, change to 10% A and 90% B in 2 min, hold 5 min, change to 10% A, 40% B and 50% C in 2 min and hold 4 min, change to 90% A and 10% B in 0.1 min and hold 10 min. The total analysis time was 26 min. The inject volume was 50 μL and the LC flow-rate 0.7 mL min<sup>-1</sup>. The wavelengths used for detection was 258 nm for PQ and DFQ, and 310 nm for DQ.

### 2.4. Adsorption experiments

A 1 g sample of each soil was suspended in 10 mL of herbicide solution (156–3110 μmol<sub>(+)</sub> L<sup>-1</sup> for PQ, 116–2326 μmol<sub>(+)</sub> L<sup>-1</sup> for DQ, 7–276 μmol<sub>(+)</sub> L<sup>-1</sup> for DFQ, all containing 0.01 M CaCl<sub>2</sub> as background electrolyte). The individual herbicide solutions were prepared from 3.888, 2.907 and 2.759 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 (previous experiments had shown that adsorption at times later than 24 h were negligible) and then centrifuged at 4000 rpm for 10 min. Solutions were added to pH 5.5. After equilibration between soil and adsorption solution, the solutions were still at such a pH (4.78 ± 0.46, for n = 644) measurements for many of the experiments with any of the quats). The resulting supernatant was analyzed by liquid chromatography according to the protocol described above. 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, together with a quat control without soil, but with soil solution, to check for any loss by degradation or adsorption of the quat standard during the experiment (24 h). Samples awaiting analysis were always kept in polypropylene tube protected from light and under refrigeration.

**Table 2**  
General properties of the studied soil.

Soil	Texture	%			pH		%		cmol <sub>(c)</sub> kg <sup>-1</sup>		mg kg <sup>-1</sup>		
		Sand	Silt	Clay	H <sub>2</sub> O	KCl	OC	CEC	PQ	DQ	DFQ		
1	Sandy loam	70	17	13	5.3	3.7	0.8	3.07	<0.02	n.d.	n.d.		
2	Sandy loam	64	21	14	5.3	4.0	1.9	3.96	<0.02	<0.02	<0.01		
3	Sandy loam	73	16	11	5.5	4.3	1.4	3.81	<0.02	<0.02	<0.01		
4	Loam	40	38	22	6.2	4.9	1.1	4.31	<0.02	<0.02	<0.01		
5	Loam	45	36	19	5.2	3.8	2.0	5.64	0.25	0.04	<0.01		
6	Loam	43	41	16	5.8	4.5	2.0	4.81	0.97	0.32	<0.01		
7	Sandy loam	69	17	14	5.6	4.9	3.7	19.52	<0.02	<0.02	<0.01		
8	Loam	51	32	17	5.6	5.0	5.0	12.30	<0.02	<0.02	<0.01		

The experimental adsorption data were fitted to the Freundlich (Eq. (1)), Langmuir (Eq. (2)) and Linear (Eq. (3)) equations, which are described by:

$$Q_e = K_F C_e^{1/n} \quad (1)$$

$$Q_e = \frac{K C_e Q_m}{1 + K C_e} \quad (2)$$

$$Q_e = b C_e + a \quad (3)$$

where  $Q_e$  is the concentration of sorbate sorbed at equilibrium ( $\mu\text{mol}_{(+)}\text{kg}^{-1}$ );  $C_e$  is the concentration of sorbate in the aqueous phase at equilibrium ( $\mu\text{mol}_{(+)}\text{L}^{-1}$ );  $K$  ( $\text{L}\mu\text{mol}^{-1}$ ) is a Langmuir constant related to the energy of adsorption, and  $Q_m$  ( $\mu\text{mol}\text{kg}^{-1}$ ) is the maximum adsorption capacity of the sample.  $K_F$  ( $\text{L}^n\text{kg}^{-1}\mu\text{mol}_{(+)^{(1-n)}}$ ) and  $1/n$  (dimensionless) are the Freundlich coefficients;  $K_F$  and  $n$  are constants characterizing the adsorption capacity and intensity, respectively. The optimal parameter values for the equations were determined by non-linear regression analysis. The goodness-of-fit for the isotherms was estimated by the coefficient of determination ( $R^2$ ) and the standard error (SD).

Competitive adsorption was assessed like non-competitive sorption. In this case, 1 g sample of each soil was suspended in 10 mL of herbicide solution containing two of the three quats. The concentration of one of the quat was fixed ( $778\mu\text{mol}_{(+)}\text{L}^{-1}$  for PQ,  $581\mu\text{mol}_{(+)}\text{L}^{-1}$  for DQ and  $55\mu\text{mol}_{(+)}\text{L}^{-1}$  for DFQ) while that of the other varied between  $109\text{--}3110\mu\text{mol}_{(+)}\text{L}^{-1}$  for PQ,  $111\text{--}2326\mu\text{mol}_{(+)}\text{L}^{-1}$  for DQ, and  $7\text{--}1104\mu\text{mol}_{(+)}\text{L}^{-1}$  for DFQ. Always one of these experiments was performed at a 1:1 mole ratio.

### 2.5. Desorption experiments

Immediately following adsorption of quats with initial concentrations of  $778\mu\text{mol}_{(+)}\text{L}^{-1}$  for PQ,  $581\mu\text{mol}_{(+)}\text{L}^{-1}$  for DQ and  $55\mu\text{mol}_{(+)}\text{L}^{-1}$  for DFQ, the centrifuged residues were weighed to determine the amount of occluded solution and were then resuspended in 10 mL of a 0.01 M  $\text{CaCl}_2$  solution without herbicide and left to equilibrate for 24 h. Afterwards, the samples were centrifuged at 4000 rpm to remove the supernatant. This procedure (suspension, equilibration and centrifugation) was repeated five times and the final volume was 50 mL.

In a second series the samples were desorbed in the following way: (i) PQ was desorbed with 276 and  $1104\mu\text{mol}_{(+)}\text{L}^{-1}$  of DFQ, (ii) PQ with 581 and  $2326\mu\text{mol}_{(+)}\text{L}^{-1}$  of DQ, (iii) DQ was desorbed with 276 and  $1104\mu\text{mol}_{(+)}\text{L}^{-1}$  of DFQ, (iv) DQ with 778 and  $3110\mu\text{mol}_{(+)}\text{L}^{-1}$  of PQ, (v) DFQ was desorbed with 581 and  $2326\mu\text{mol}_{(+)}\text{L}^{-1}$  of DQ and (vi) DFQ with 778 and  $3110\mu\text{mol}_{(+)}\text{L}^{-1}$  of PQ.

In all cases desorption data were given as percentages of the initial amounts adsorbed. All measurements were made in duplicate.

## 3. Results and discussion

This study presents an attempt to understand the competitive and non-competitive adsorption/desorption of paraquat, diquat and difenzoquat in vineyard-devoted soils by applying different sets of batch experiments. The stages of the work have involved characterization of the vineyard-devoted soils, followed by non-competitive adsorption of herbicides, competitive adsorption of herbicides and desorption of quats from soil samples.

### 3.1. General characteristics of samples

The characteristics of the soils are summarized in Table 2. The soils studied were acid ( $\text{pH}_{(\text{H}_2\text{O})}$  5.2–6.2); their textures were moving from loam to sandy loam; and their organic carbon contents ranged from 0.8 to 5.0%. Effective cation exchange capacities ranged from 3.07 to  $19.5\text{cmol}_{(c)}\text{kg}^{-1}$ , and were varying according to the organic carbon content.

The initial concentration of the three herbicides was measured in all soils. In the case of DFQ, their levels were below the quantification limit ( $10\mu\text{g}\text{kg}^{-1}$  for DFQ); for PQ and DQ, they were in most cases below quantification limits ( $20\mu\text{g}\text{kg}^{-1}$  for PQ and DQ), except for soil 5, but specially 6, which is one that was found to have 0.97 and  $0.32\text{mg}\text{kg}^{-1}$  for PQ and DQ, respectively.

### 3.2. Non-competitive adsorption of herbicides

Freundlich, Langmuir and Linear equations have been employed to describe the adsorption behaviour of quats. The best fits were obtained with the Freundlich equation, and these fittings were shown in Table 3.

PQ generally shows isotherms mainly of the L-type (Fig. 1a and b), for which according to Limousin et al. [17] the ratio between the concentration of the herbicides remaining in solution and adsorbed on the solid decrease when the solute concentration increase, providing a concave curve. It suggests a progressive saturation of the surfaces. The hydrophobic interactions between quats molecules and soils would be predominant, driving the adsorption, in the case of L-shape isotherms [18], whereas polar quats–solvent interactions would predominate in the soils if the case was an S-type shape, preventing adsorption at low concentration. The determination coefficients ( $R^2$ ) for Freundlich equation ranged between 0.88 and 0.99. Initially, the adsorption of paraquat onto the soil adsorbent is very high; this is then followed by a lower adsorption, and gradually approaches a plateau. Langmuir fittings, instead, were not satisfactory due to the large errors associated to the estimated parameters and low values of  $R^2$ , what is indicative of sorption increasing even at high PQ concentrations. Given the PQ curve shapes, linear fitting was obviously not necessary to be performed.

DQ behaviour was similar to that of PQ and gave satisfactory fittings with Freundlich equation ( $R^2$  between 0.90 and 0.99) (Fig. 1c and d). However, in this case, the fittings to Langmuir equation

**Table 3**  
Freundlich isotherm coefficients (average  $\pm$  standard deviations) for PQ, DQ and DF.

Soil	PQ			DQ			DF		
	$K_F$	$n$	$R^2$	$K_F$	$n$	$R^2$	$K_F$	$n$	$R^2$
1	4648 $\pm$ 1227	0.25 $\pm$ 0.04	0.942	1144 $\pm$ 55	0.21 $\pm$ 0.01	0.992	165 $\pm$ 19	0.68 $\pm$ 0.03	0.977
2	3431 $\pm$ 786	0.30 $\pm$ 0.04	0.964	906 $\pm$ 61	0.24 $\pm$ 0.02	0.985	103 $\pm$ 20	0.74 $\pm$ 0.05	0.993
3	3506 $\pm$ 684	0.31 $\pm$ 0.03	0.975	959 $\pm$ 102	0.19 $\pm$ 0.02	0.937	124 $\pm$ 17	0.72 $\pm$ 0.04	0.996
4	3990 $\pm$ 593	0.32 $\pm$ 0.03	0.984	959 $\pm$ 81	0.26 $\pm$ 0.02	0.978	29 $\pm$ 4	0.95 $\pm$ 0.03	0.999
5	6260 $\pm$ 3637	0.38 $\pm$ 0.13	0.879	7222 $\pm$ 1302	0.20 $\pm$ 0.04	0.896	664 $\pm$ 125	0.63 $\pm$ 0.09	0.930
6	1532 $\pm$ 373	0.38 $\pm$ 0.04	0.971	1469 $\pm$ 89	0.29 $\pm$ 0.01	0.996	39 $\pm$ 17	0.81 $\pm$ 0.10	0.979
7	1837 $\pm$ 590	0.36 $\pm$ 0.05	0.964	974 $\pm$ 275	0.38 $\pm$ 0.05	0.967	118 $\pm$ 10	0.65 $\pm$ 0.02	0.998
8	717 $\pm$ 98	0.51 $\pm$ 0.02	0.996	288 $\pm$ 113	0.58 $\pm$ 0.06	0.974	87 $\pm$ 11	0.68 $\pm$ 0.03	0.997

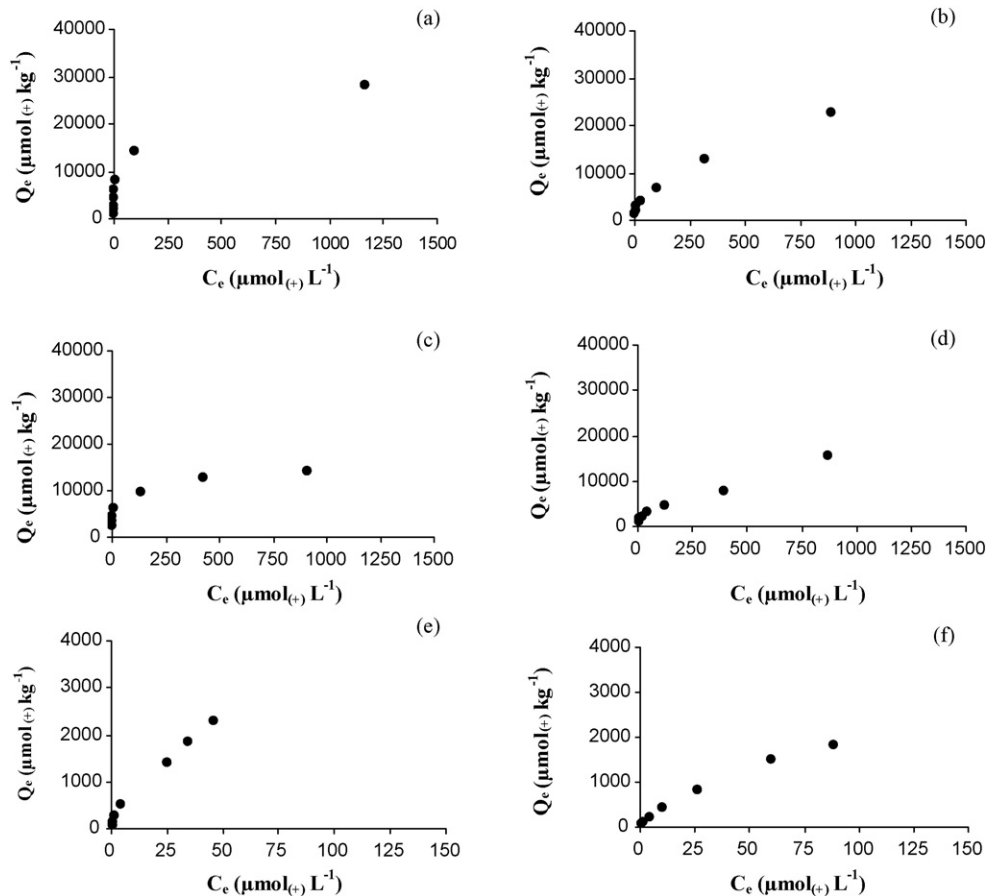
were also satisfactory ( $R^2$  between 0.90 and 0.95). As for PQ, linear equation fitting was not satisfactory.

DFQ sorption curves (Fig. 1e and f) were different and showed a trend to linearity. DFQ fittings were satisfactory for the two model equations: Freundlich ( $R^2$  between 0.93 and 0.99), and linear ( $R^2$  between 0.84 and 1.00). Fitting to Langmuir equation were also satisfactory ( $R^2$  between 0.98 and 0.99) but large uncertainties in parameters were found.

Although the Freundlich equation is an empirical function, it is in widespread use thanks to its usually accurate description of adsorption processes on heterogeneous solid surfaces such as those of soils [19]. Examination of the  $K_F$  parameters shows that for PQ ranged from 717 to 6260, whereas for DQ its values were between 288 and 7222, and for DFQ between 29 and 664. The values of the Freundlich coefficient  $n$  were lower and  $<1$  for the divalent herbicides PQ and DQ (which is typical of L-type isotherms), while for DFQ the values were close to unity ( $n$  between 0.63 and 0.95) indicating a near-linear behaviour.

In summary, paraquat was more strongly adsorbed. The maximum sorption reached for an input of 3110  $\mu\text{mol}_{(+)}\text{L}^{-1}$  of PQ was observed at 22,000–39,000  $\mu\text{mol}_{(+)}\text{kg}^{-1}$ , and 10,000–21,000  $\mu\text{mol}_{(+)}\text{kg}^{-1}$  for an input of 2326  $\mu\text{mol}_{(+)}\text{L}^{-1}$  of DQ, whereas for DFQ was 1800–2800  $\mu\text{mol}_{(+)}\text{kg}^{-1}$  for an input of 276  $\mu\text{mol}_{(+)}\text{L}^{-1}$ . These amounts adsorbed were lower than the CEC; therefore, the competition for the adsorption on the clay between monovalent and divalent organic cations should favour the divalent organic cations. In the same way, Rytwo et al. [5] indicate that, when the amounts adsorbed are larger than the CEC, the competition for adsorption on the clay should favour the monovalent organic cations.

This behaviour for DFQ can be because its steric impediment is higher for sorption to clays than for PQ and DQ. Both PQ and DQ have planar geometry and the pyridinium rings can rotate to form a layer of uniformly oriented molecules on clay surfaces [20]. Since the pyridinium rings of DFQ cannot rotate, the molecule is not planar; also, its molecular size is also greater than DQ and PQ. Therefore,



**Fig. 1.** Adsorption curves for PQ in soil 1 (a) and soil 8 (b), DQ for soil 1 (c) and soil 8 (d) and DFQ in soil 1 (e) and 8 (f).

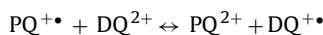
DFQ cannot access to the same sorption sites into the interlamellar spaces of the silicates as PQ and DQ, and the sorption may be limited by available sorption sites. That may explain why the sorption of DFQ is reduced in comparison with that of PQ and DQ. The process of sorption is essentially ion exchange, but greatly enhanced in expanding-lattice clay by the ability of the much more planar dication quat molecules (PQ/DQ) to become intercalated between the lattice layers and then be held by strong coulombic forces [21].

Electronic-structure calculations were reported for three oxidation states of paraquat [22]. The fully oxidized species,  $PQ^{2+}$ , is twisted about the inter-ring bond. One-electron reduction yields a radical cation,  $PQ^{1+}$ , which is predicted to be planar. Addition of a second electron enhances the propensity for planarity. A planar conformation is more stable in the reduced form than a twisted one, because the bond connecting the two pyridinium rings bears more double-bond character in the reduced form than in the oxidized form [23]. The diquat ion is, in the same way, not strictly planar [24]; the dihedral angle between the rings is  $-20^\circ$  [25]. Instead, DFQ has not planar structure. It should be also noted that as a whole the compounds which are apt to adopt more planar conformations give higher redox potentials [23]. It is also reasonable to consider that a bipyridinium salt whose torsion angle in the oxidized form is larger will experiment higher steric hindrance than the coplanar conformation in the corresponding reduced form [23].

### 3.3. Competitive adsorption of herbicides

We found low sorption decreases when DFQ was influencing the PQ and DQ sorption, with percentages ranging from 0–13% and 0.3–11%, respectively. When PQ is influenced by DFQ, significant correlations,  $r = 0.934$  ( $p < 0.01$ ) and  $r = 0.887$  ( $p < 0.01$ ), were obtained between the values of the decline in the percentages of adsorption for DFQ both with the percentage of total organic carbon and CEC (Fig. 2). This suggests that DFQ competes specially by adsorption sites with PQ when CEC and organic matter soil contents are high. This can also be related to different sorption mechanisms: DFQ (monovalent; not planar) can preferably be adsorbed to the organic matter while PQ (divalent; planar) can have preference in addition to the organic matter by other sorption sites related to clay fraction. In this sense, Rytwo et al. [5,26] highlights the strong adsorption of divalent quats in minerals like montmorillonite and sepiolite.

Diquat and paraquat behave as the relatively stronger acid and the relatively more powerful oxidizer, respectively. This difference can be rationalized by taking into account their reduction potentials and  $pK_a$  values. The recommended values of reduction potentials in water solutions are  $-358$  and  $-448$  mV for the diquat and paraquat dications, respectively [27]. A standard thermodynamic calculation [28] shows that the corresponding difference  $\Delta G^\circ$  for the redox equilibrium:



is  $-8.7$  kJ/mol. This means that diquat is a somewhat more powerful oxidizer than paraquat, but, compared with its acidity, paraquat is the more powerful oxidizer.

The ionization constants  $pK_a$  are unknown for these compounds. However, Palm [29] has suggested that these might be estimated via the concept of a structural analogy using 1,2-dinitroethane and nitromethane as models for diquat and paraquat, respectively. This analogy is based on the idea that a charged quaternary nitrogen atom and a nitro group are both strongly electronegative groups, with the first being somewhat stronger (leading to a difference in acidities of  $\approx 0.5$ – $1$   $pK_a$  unit). These values for nitro compounds are known or can be reliably estimated. In this way,  $pK_a$  values estimated by Palm are 5.5 and 9–9.5 for diquat and paraquat,

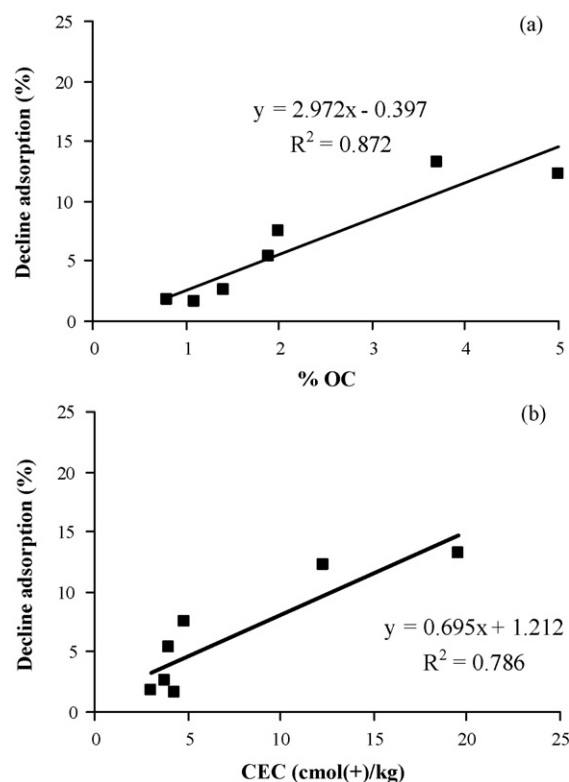
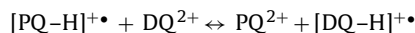


Fig. 2. Correlation between the values of the decline in the percentages of adsorption both with percentage of total organic carbon (a) and CEC (b) when PQ is influenced by DFQ.

respectively. Thus diquat is a far stronger acid than paraquat. For the acid–base equilibrium:



the  $\Delta G^\circ$  value calculated [28] using these  $pK_a$  values is  $-20.1$  kJ/mol. Thus the difference in acidity between diquat and paraquat is far more significant compared with the difference in reduction power. It is the relatively strong acidity that explains the acidic dissociation of the diquat dication, as compared with the ions formed by the competing reduction reactions. In the case of paraquat, the difference between acidity and reduction power is relatively lower. Compared with its acidity, paraquat is the more powerful oxidizer.

The strong influence of divalent cationic herbicides, PQ and DQ, on monovalent herbicide DFQ was also obtained (Fig. 3a and b). The influence of DQ on DFQ was higher than that of PQ on DFQ, which results in maxima decreases in the adsorption at 61% (Fig. 3a) and 55% (Fig. 3b), respectively. The difference in acidity and reduction power between diquat and paraquat can explain their differences in behaviour. In both cases soil 1 and soil 6 present a higher decline in the percentage of sorption. Sample 5 shows in all cases high adsorption percentages close to 100%; this can be due to presence of the montmorillonite in clay fraction, with high affinity for quats [26]. Declines in the percentages of adsorption are negatively correlated with total organic carbon percentage with values of  $r = -0.894$  ( $p < 0.01$ ) and  $r = -0.907$  ( $p < 0.01$ ) for the influence of DQ and PQ, respectively (Fig. 4). These correlations may mean the existence of different behaviour between divalent and monovalent herbicides and soil components. This could be related to the high charge density in divalents quats respect to monovalent quat.

Significant decreases in the adsorption were obtained by PQ competing with DQ, and DQ with PQ (Fig. 5). In the first case, the maximum percentage was 67%. The soils 1, 2 and 6 showed sim-

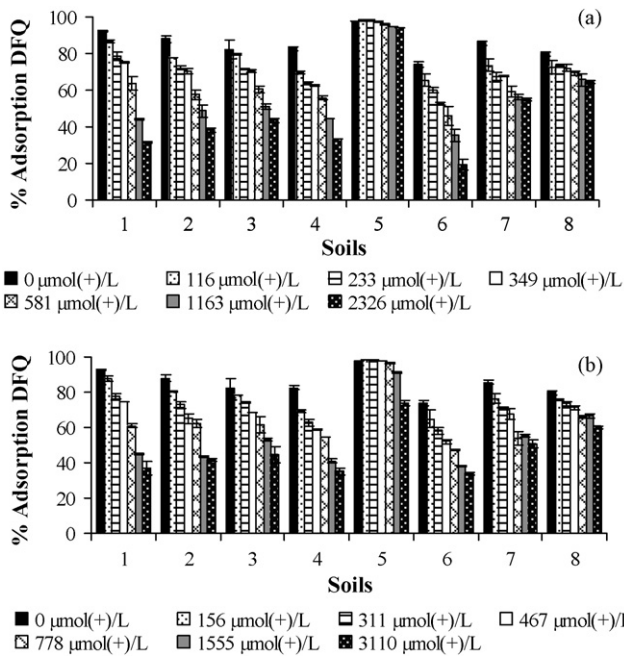


Fig. 3. Effect of DQ (a) and PQ (b) on adsorption DFQ.

ilar declines in the adsorption (around 65%). When DQ competed with the adsorption of PQ, the maximum percentage was 52%. All samples showed similar results except soils 5 and 7. As in all previous cases, sample 5 was the one that showed smaller decreases in the adsorption. No significant correlation was founded between decline of adsorption and soil variables.

### 3.4. Desorption of quats from samples

Desorption was performed in two samples, soils 2 and 6 (Fig. 6). Desorption into 0.01 M  $\text{CaCl}_2$  solution during non-competitive experiments showed low values for three herbicides (<35%). Paraquat was the one showing little amounts desorbed that ranged between 2% and 10% for soils 2 and 6, respectively (Fig. 6a), indicating its strong binding to the studied soils. The values of DQ ranged from 6% to 19% (Fig. 6b), whereas they ranged from 26% to 31% in the case of DFQ (Fig. 6c), for soils 2 and 6, respectively. The order of desorption was following the same trend than adsorption:  $\text{DFQ} > \text{DQ} > \text{PQ}$ .

Desorption increased when any of the herbicides was desorbed at two concentrations of the other two herbicides (Fig. 6). Higher percentages were obtained using concentrations of 3110  $\mu\text{mol}(+)/\text{L}^{-1}$  of PQ and 2326  $\mu\text{mol}(+)/\text{L}^{-1}$  of DQ to des-

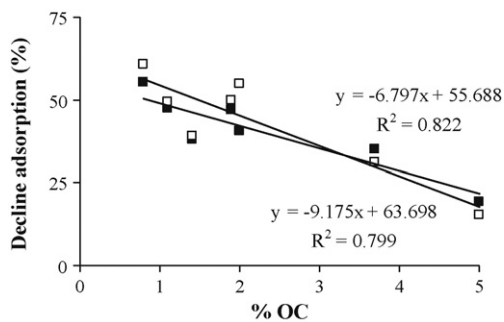


Fig. 4. Correlation between the values of the decline in the percentages of adsorption and the percentage of total organic carbon when PQ (■) and DQ (□) influence in the DFQ sorption.

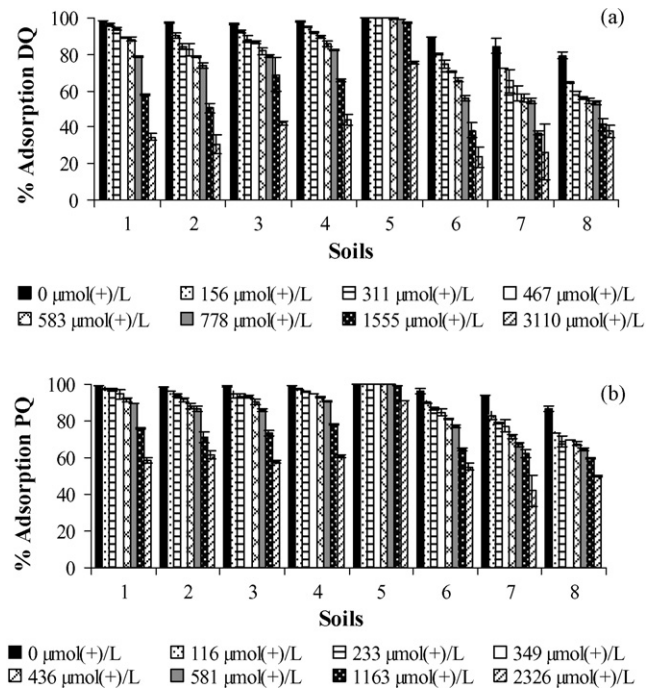


Fig. 5. Influence of PQ in the percentage of adsorption of DQ (a) and DQ in the percentage of adsorption of PQ (b).

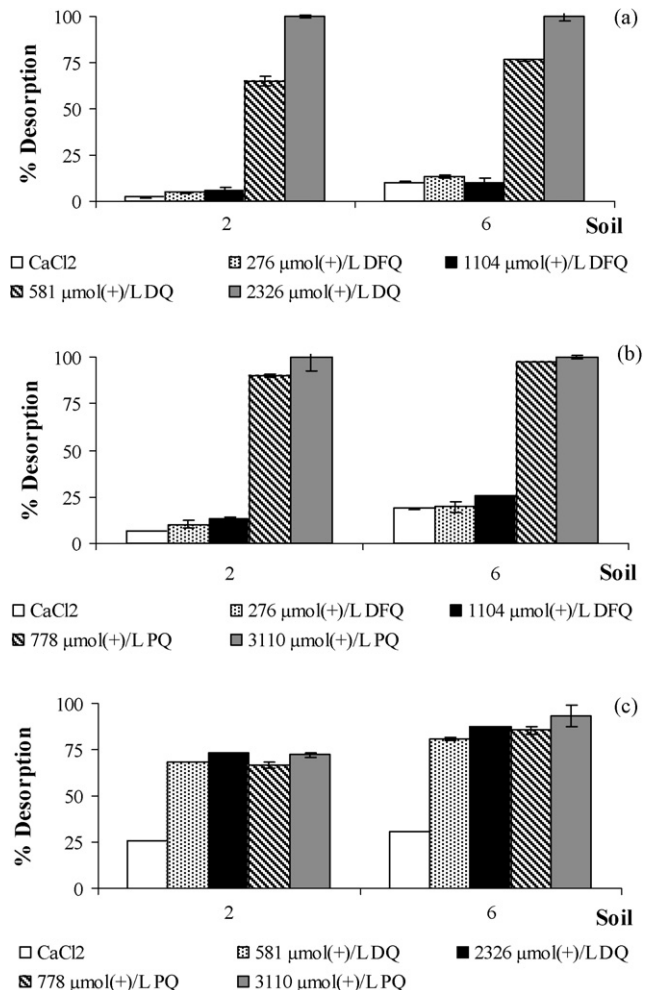


Fig. 6. Desorption of PQ (a), DQ (b) and DFQ (c) using 0.01 M  $\text{CaCl}_2$  solution and two concentrations of the other two herbicides.

orb DQ and DFQ, and PQ and DFQ, respectively. Furthermore, in the case of divalent herbicides, PQ and DQ, higher percentages of desorption were obtained when used to desorb each other. PQ desorption ranged in 64.8–76.3% and 99.0–100.0% at  $581 \mu\text{mol}_{(+)} \text{L}^{-1}$  and  $2326 \mu\text{mol}_{(+)} \text{L}^{-1}$  of DQ to soils 2 and 6, respectively (Fig. 6a). With regards to DQ desorption, values ranged in 90.3–97.7% and 99.0–100.0% at  $778 \mu\text{mol}_{(+)} \text{L}^{-1}$  and  $3110 \mu\text{mol}_{(+)} \text{L}^{-1}$  of PQ to soils 2 and 6, respectively (Fig. 6b). Percentages of DFQ desorption using PQ and DQ were slightly higher to those obtained in desorption into 0.01 M  $\text{CaCl}_2$  solution (Fig. 6c): these values ranged from 66.5–85.5% and 72.4–93.4% using  $778 \mu\text{mol}_{(+)} \text{L}^{-1}$  and  $3110 \mu\text{mol}_{(+)} \text{L}^{-1}$  of PQ to soils 2 and 6, respectively; and from 68.2–81.0% and 73.3–87.7% using  $581 \mu\text{mol}_{(+)} \text{L}^{-1}$  and  $2326 \mu\text{mol}_{(+)} \text{L}^{-1}$  of DQ to soils 2 and 6, respectively.

From a general overview of Fig. 6, it can be stated that:

- Desorption of PQ is not affected by DFQ, and is clearly affected by increasing concentrations of DQ (Fig. 6a).
- Desorption of DQ is also only affected by PQ, but it was not found a clear effect of PQ concentration on DQ desorption (Fig. 6b).
- Desorption of DFQ is already high with an electrolyte background solution (25%), and increase to a 75% with both dications PQ and DQ at the two concentrations used (Fig. 6c).

As in the case of competitive adsorption, in competitive desorption both PQ and DQ are somehow influenced by each other; DFQ is also influenced by PQ and DQ but they are not influenced by DFQ. This desorption behaviour can also be related to the adsorption competing mechanisms already described:

1. Diquat and paraquat behave as the relatively stronger acid and the relatively more powerful oxidizer, respectively, what governs the competition between them.
2. The increases in the percentages of DFQ desorption by the effect of PQ or DQ could be related to the high charge density in divalent quats respect to monovalent quat.
3. DFQ (monovalent; not planar) does not affect PQ/DQ desorption because it can preferably be adsorbed to the organic matter while PQ and DQ (divalent; planar) can have preference in addition to the organic matter by other sorption sites related to clay fraction.

#### 4. Conclusions

The changes in the agricultural practices in vineyards contribute to introduce high levels of herbicides resulting in herbicide pollution in crop soils. The three herbicides studied in this work exhibit a strong adsorption in all samples following the trend:  $\text{PQ} > \text{DQ} \gg \text{DFQ}$ . Hydrophobic interactions with polar contributions are responsible for such adsorption. The results of adsorption fit to Freundlich equation, nevertheless DFQ sorption curves shows a trend to linearity. The amounts adsorbed for the three herbicides are lower than the CEC; therefore the competition for the adsorption to the clay between divalent and monovalent organic cations should favour the divalent cations PQ and DQ.

The competitive adsorption experiments with the herbicides show the ability to displace each other from its adsorption sites: as the applied concentration of the herbicide competitor increased, the concentration adsorbed of PQ, DQ and DFQ decreased. These decreases in the adsorption are most significant when divalent cationic herbicides, PQ and DQ, influence each other and when they affect to DFQ. The importance of solution chemistry concepts such as acidity and reduction power was key to explain differences in the behaviour of PQ and DQ. Significant correlations are found between organic matter and CEC and percentages of decline adsorption of

PQ when is influenced by DFQ. This shows that DFQ only competes by adsorption sites when CEC and organic matter contents are low and is preferably adsorbed to the organic matter while PQ and DQ have preference in addition to the organic matter for other sorption sites related to clay fraction. Additionally, negative correlations were obtained between total organic carbon percentage and declines in percentages of adsorption when DQ and PQ influence on DFQ. This could be related to the high charge density in divalent quats respect to monovalent quat.

In the desorption process, higher percentages of PQ and DQ are obtained when they are desorbed with other divalent herbicides, while the percentages of DFQ desorption obtained using herbicide solutions are similar if they compare with desorption into 0.01 M  $\text{CaCl}_2$  solution.

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