Quaternary herbicides retention by the amendment of acid soils with a bentonite-based waste from wineries

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ABSTRACT

The agronomic utility of a solid waste, waste bentonite (WB), from wine companies was assessed. In this sense, the natural characteristics of the waste were measured, followed by the monitoring of its effects on the adsorption/desorption behaviour of three quaternary herbicides in acid soils after the addition of increasing levels of waste. This was done with the intention of studying the effect of the added organic matter on their adsorption. The high content in C ($294\,g\,kg^{-1}$), N ($28\,g\,kg^{-1}$), P ($584\,mg\,kg^{-1}$) and K ($108\,g\,kg^{-1}$) of WB turned it into an appropriate amendment to increase soil fertility, solving at the same time its disposal. WB also reduced the potential Cu phytotoxicity due to a change in Cu distribution towards less soluble fractions. The adsorption of the herbicides paraquat, diquat and difenzoquat by acid soils amended with different ratios of WB was measured. In all cases, Langmuir equation was fitted to the data. Paraquat (PQ) and diquat (DQ) were adsorbed and retained more strongly than difenzoquat (DFQ) in the acid soil studied. However, the lowest retention of DFQ in an acid soil can be increased by amendment with organic matter through a solid waste from wineries, and it is enough for duplicate retention a dosage rate of 10 t/ha. Anyway, detritivores ecology can still be affected. Detritivores are the organisms that consume organic material, and in doing so contribute to decomposition and the recycling of nutrients. The term can also be applied to certain bottom-feeders in wet environments, which play a crucial role in benthic ecosystems, forming essential food chains and participating in the nitrogen cycle.

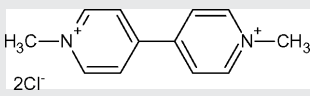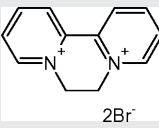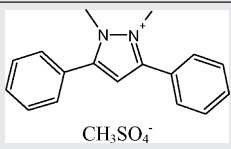© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Spain is the European country with larger surface devoted to vineyards and the third in wine production [1], and together with France and Italy accounts for the 50% of wine production in the world. These figures, indicate the economic relevance in Spain of wineries, are also a symptom of the high quantities of co-products and wastes generated, which were approaching 1.5 Mt in 2005 [1]. European legislation establish that part of the wineries wastes be devoted to alcohol distillation [2], but anyway many of the small wine merchants do not fulfil with the normative and do dispose the wastes in the environment. Moreover, the management of all these different materials is not easy; there are solid materials such as grape stalks, grape marcs and wine lees, but also liquids like vinasses.

There are many alternatives for reusing these waste materials [3]. Their direct application to soil is one of the most efficient for disposal or increasing in value [4,5], above all consider their contribution in organic matter and other nutritive elements to the soil–plant system [6]. Together with the potential use of these wastes for amending soils, they can also be used in the immobilization of heavy metals [7–9] and pesticides [10–12]. In these cases, their high-sorption capacity due to their high-organic matter contents can be joined to their low economic and environmental costs as regards to active carbon and peat.

Quaternary nitrogen herbicides (quats) were developed from the observation that quaternary ammonium germicides, like cetyl trimethylammonium bromide, desiccate the young plants [13,14]. Table 1 shows the chemical structure, chemical and common names, together with the physical–chemical properties of these ammonium quaternary herbicides. Paraquat (PQ) was first synthesized in 1882 and has been used as a redox indicator (under the name methyl viologen) in chemical laboratories since 1933. Its herbicidal properties were discovered in 1957, and since 1962

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Table 1
Characteristics of the quaternary herbicides studied

Common name	PQ	DQ	DFQ
Chemical structure	H$_3$C—N$^+$ ... N$^+$—CH$_3$ 2Cl$^-$	... 2Br$^-$	CH$_3$SO$_4^-$
Name	1,1′-Dimethyl-4,4′-bipyridinium	1,1′-Ethylene-2′2′-dipyridylium	CH$_3$SO$_4^-$ 1,2-dimethyl-3,5-diphenyl-4,5-dihydro-1H-pyrazol-2-ium methyl sulphate
CAS no.	1910-42-5	85-00-7	43,222-48-6
M_W[a]	257.2	344	362.4
S[b] (g/L)	620	677	740
log P_{ow}[c]	−4.5	−4.6	0.3
K_{oc}[d]	15–51	164–134	23–36
Soil half-life[e]	644	3450	6810

Data were obtained from Kenaga [52], Haag and Yao [53], and US-EPA [54].

[a] Molecular weight.
[b] Solubility in water 20 °C.
[c] Octanol/water partition coefficient at 20 °C.
[d] Partition coefficient normalized to organic carbon content (mL g_{oc}^{-1} or L Kg_{oc}^{-1}).
[e] Aerobic soil half-life (average, days).

paraquat has been marketed in over 130 countries as a highly effective contact herbicide. The bipiridinium herbicides diquat (DQ) and paraquat were introduced by Imperial Chemical Industries in 1958. They are very quick-acting herbicides that are absorbed by plants and translocated, thus causing desiccation of the foliage. DQ and PQ 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 [15]. Consequently, they may be present as residues in environmental, food and biological samples [16,17]. Diquat and paraquat are extremely toxic and are often encountered in cases of poisoning [18,19]. The pyrazolium monocation difenzoquat (DFQ) is also used throughout the world as a selective herbicide for post-emergence control of wild oats in barley and fall-seeded wheat. It is the active ingredient in registered trademarks of American Cyanamide Co. The predominant use is for the divalent cations PQ and DQ; the lowest presence of the monovalent DFQ is associated to their synergistic effects together with DQ [20,21].

Their strong retention to soil greatly limits any leaching or surface run-off [22], but also reduces their availability for microbial breakdown in the soil water, so they are very persistent in soil. However, findings of groundwater contamination with paraquat residues up to 18.9 μg L^{-1} [23] may be associated with a vertical transport through the soil profile promoted by dissolved colloids such as dissolved organic matter and dispersed colloidal clay [24]. Moreover, since vineyard soils have been identified as the most erodible agricultural soils [25], herbicides–organic amendment interactions provide the basis of attempts to reduce the hazardous distribution of the herbicides in the environment. The mobilization and transport of quats-enriched soil eroded particles may generate downslope and downstream environmental problems that mainly affect detritivore ecology [26]. Therefore, quats have the potential to become re-available in the soil environment and/or to move from the soil compartment to another environmental compartment.

Integrated with other herbicides and often used within conservation management regimes, paraquat has played an important role in improving agricultural production in many areas of the world. Paraquat has found widespread use to control weeds or to manipulate the ground cover so as to minimise competition with the crop.

A systematic approach to weed management based on paraquat is currently being developed for vines, olives and top fruit; this will help to maintain soil structural stability by avoiding cultivations and so minimise soil erosion in seasonally dry areas [27]. Agricultural practices including organic amendments will then have a beneficial effect in the control of leaching and sorption of these herbicides. Anyway, limitations on the role of organic matter in reducing leaching potential of contaminants such as pesticides should be taken into account [28], since dissolved organic matter can favour leaching not only by interactions with the pesticide (facilitated transport) but also by interactions with the soil surfaces (competitive sorption).

In this paper, the natural characteristics of the waste bentonite (WB) were measured for amending acid soils, followed by the monitoring of its effects on the properties of WB-amended acid soils to increase retention of quaternary herbicides such as paraquat, diquat and difenzoquat. The purpose of this work was to study the interactions between quats and WB, as part of a study that investigated the feasibility of employing WB as amendment for acid soils.

2. Material and methods

2.1. Soils

The soils used were obtained from Santa Cristina (Ribadavia, Ourense, Spain). They are samples from the C horizon layer that can be classified as Arenic Regosol (according to Ref. [29]) and is derived from 2-mica granite. The samples were dried to air and later passed through a 2-mm sieve. 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 Thermo-Finnigan 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$_4$Cl and determined by atomic absorption spectroscopy (Ca$_e$ and Mg$_e$) or flame emission spectrometry (Na$_e$ and K$_e$). Exchangeable aluminium was quantified by displacement with 1 M KCl, followed by atomic absorption spectrophotome-

Table 2
Main physical and chemical characteristics of soil and waste bentonite (WB) used (dry weight basis)

Parameter	Unit	Soil	B	WB
Sand	%	63	n.d.	n.d.
Silt	%	26	n.d.	n.d.
Clay	%	11	n.d.	n.d.
$pH_{(H_2O)}$		4.8	10.1	4.5
$pH_{(KCl)}$		3.8	10.1	4.7
C	$(g\,kg^{-1})$	5	3.1	294.0
N	$(g\,kg^{-1})$	1	<0.5	28
Protein	$(g\,kg^{-1})$	n.d.	<0.1	164
Tartrate	$(g\,kg^{-1})$	n.d.	<1	48
Electrical conductivity	$\mu S\,cm^{-1}$	n.d.	567	5100
$P_{(Bray)}$	$(mg\,kg^{-1})$	75	61	584
Na_e	$(cmol_{(+)}\,kg^{-1})$	0.24	33.6	0.8
K_e	$(cmol_{(+)}\,kg^{-1})$	0.03	0.8	118.0
Ca_e	$(cmol_{(+)}\,kg^{-1})$	0.30	7.5	3.4
Mg_e	$(cmol_{(+)}\,kg^{-1})$	0.27	1.9	1.5
Σ_{bases}	$(cmol_{(+)}\,kg^{-1})$	0.84	44	124
Al_e	$(cmol_{(+)}\,kg^{-1})$	0.80	0.1	0.1
CEC	$(cmol_{(+)}\,kg^{-1})$	1.64	44	124
Na_t	$(g\,kg^{-1})$	n.d.	17.0	2.0
K_t	$(g\,kg^{-1})$	n.d.	3.9	107.9
Ca_t	$(g\,kg^{-1})$	n.d.	16.5	2.3
Mg_t	$(g\,kg^{-1})$	n.d.	13.0	3.5
Cu_t	$(mg\,kg^{-1})$	21	20	1481
Zn_t	$(mg\,kg^{-1})$	70	147	37
Mn_t	$(mg\,kg^{-1})$	65	87	37

EC: electrical conductivity; n.d.: not determined; e: exchangeable; t: total.

try. 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.

2.2. Bentonite (B) and waste bentonite (WB)

Bentonite (B; 100% granulated montmorillonite, from Laffort) was used without any prior treatment to fine a white wine in a local winery (S.L. Bodegas Cunqueiro; Prado do Miño, Ourense, Spain). The resulting sludge (WB) was dried in air and passed through a 1-mm mesh sieve. Bentonite and waste bentonite properties were determined following the procedures described above for soil samples (Table 2). Protein was determined as per Lowry et al. [30] following extraction for 24 h with 0.5 M NaOH at 30 °C. Table 2 shows the comparison between the results of both materials. The presence of tartrate species in waste bentonite was measured as tartaric acid after acid extraction with 6 N HCl fort 12 h at 20 °C (solid/liquid ratio 1:150 g mL^{-1}). Tartaric acid quantification was done by HPLC using an ion-exclusion column for organic acids separations (Transgenomic, Inc., Omaha, NE).

2.3. Adsorption kinetics of PQ, DQ and DFQ

The kinetics of the sorption process were monitored by adding to soil subsamples a fixed concentration of quats in solution for different times to know the stirring time to reach equilibrium. A 1 g of soil was added to a propylene tube and suspended in 10 mL of herbicide solution containing CaCl$_2$ 0.01 M and 100 mg L^{-1} of PQ and DQ, and 40 mg L^{-1} of DFQ separately. Suspensions were shaken on a rotary shaker at 200 rpm at room temperature (20 ± 2 °C). Selected shaking times were 1, 6, 12, 24, 48 and 72 h. At the end of the process, the sample is centrifuged (4000 rpm, 10 min) to recover the supernatant. An aliquot of the supernatant was analysed by HPLC to calculate the sorbed concentration. All experiments were run in duplicate, together with a quat control without soil

Table 3
Sorbed concentration of herbicide in solution (mg g^{-1}) at different contact times between soil (amended or not) incubated with a herbicide solution of 100 mg L^{-1}

Time (h)	PQ (S, mmol$_{(+)}$ kg^{-1})		DQ (S, mmol$_{(+)}$ kg^{-1})		DFQ (S, mmol$_{(+)}$ kg^{-1})	
	Soil	30 t/ha	Soil	30 t/ha	Soil	30 t/ha
1	5.13	5.05	4.88	4.71	1.88	5.13
6	5.21	5.13	4.94	4.88	1.96	5.21
12	5.21	5.13	5.00	4.88	2.02	5.21
24	5.29	5.21	5.06	4.94	2.13	5.29
48	5.29	5.29	5.06	4.94	2.13	5.29
72	5.29	5.21	5.06	4.94	2.13	5.29

to check for degradation or adsorption of the quat standard during the experiment. Samples awaiting analysis were always kept in polypropylene tube protected from light and under refrigeration.

2.4. Adsorption isotherms of PQ, DQ and DFQ

The sorption isotherms were monitored by adding to soil sub-samples increasing concentration of quats in solution for 24 h to reach equilibrium (Table 3). Adsorption in a soil control without added WB was also performed. A 2-g sample of each soil was suspended in 20 mL of herbicide solution (5.0–400 mg L^{-1} for PQ and DQ at 11 different levels, and 1.0–100 mg L^{-1} for DFQ at 12 different levels, all containing 0.01 M CaCl$_2$). 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. An aliquot of the supernatant is analysed by HPLC to measure quat level, whereas another part is used to monitor solution pH. All experiments were run in duplicate, together with a quat control without soil to check for degradation or adsorption of the quat standard during the experiment. Samples awaiting analysis were always kept in polypropylene tube protected from light and under refrigeration.

Adsorption data were fitted with Langmuir equation (Table 4). Originally developed for describing the adsorption of gases to a surface [31], the Langmuir model is used extensively for describing solute and metal sorption to soils:

$$S = \frac{S_{max} K\,C}{1 + K\,C}$$

where S is the sorbed concentration (mmol$_{(+)}$ kg^{-1}), S_{max} is the maximum sorption capacity of the soil (mmol$_{(+)}$ kg^{-1}), K is the Langmuir binding-strength coefficient (L mmol$_{(+)}^{-1}$), and C is the equilibrium concentration (mmol$_{(+)}$ L^{-1}). Since the fitting of sorption data with linearized Langmuir equations potentially limits the ability to model sorption data accurately, we have used an accurate and easy-to-use Microsoft Excel spreadsheet capable of performing nonlinear regression (Table 4), which was proposed by Bolster and Hornberger [32].

Only one goodness-of-fit measure is calculated in the spreadsheet – the model efficiency (E) – because this statistic is considered by many to be the best overall indicator of model fit [33,34]. The model efficiency was calculated according to Nash and Sutcliffe [35]. An E equal to the unity indicates a perfect fit to the data, whereas $E < 0$ indicates that taking the average of all the measured values would give a better prediction than the model.

2.5. Quats determination in supernatants by HPLC–UV

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

Table 4
Langmuir isotherm coefficients for quats, with associated errors for model equations

Sample	C (%)	PQ			DQ			DFQ		
		K (L mmol$_{(+)}$$^{-1}$)	S_{max} (mmol$_{(+)}$ kg^{-1})	E	K (L mmol$_{(+)}$$^{-1}$)	S_{max} (mmol$_{(+)}$ kg^{-1})	E	K (L mmol$_{(+)}$$^{-1}$)	S_{max} (mmol$_{(+)}$ kg^{-1})	E
Soil	0.50	46.64	16.3	0.922	62.69	10.1	0.897	1369.70	1.1	0.989
1 t/ha	0.53	93.27	15.2	0.955	98.47	9.8	0.916	1549.68	1.1	0.995
10 t/ha	0.8	104.47	13.5	0.849	150.82	10.5	0.761	152.89	1.8	0.885
20 t/ha	1.1	105.04	16.8	0.929	153.13	8.9	0.714	277.43	2.3	0.874
30 t/ha	1.4	222.17	17.2	0.862	626.71	9.0	0.855	382.98	2.0	0.739

(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 amounts of PQ, DQ, and DFQ adsorbed were calculated as the differences between those initially present in solution and those remaining in the supernatant after centrifugation. All measurements were made in duplicate.

3. Results and discussion

3.1. Bentonite waste characteristics for soil amendment

The main physical and chemical characteristics of the soil used (in a dry weight basis) can be seen in Table 2. In general, soil is very acidic (pH$_{KCl}$ < 4.0), with a low content in total C and N, and a low cationic exchange capacity (<2 cmol$_c$ kg^{-1}), together with a texture characterized by the predominance of the sandy fraction (63%). All these characteristics are very common in soils developed from granite [36]. Must fining is responsible for the enrichment of bentonite in many different nutrients. The C contents increase from 3.1 to 294 g kg^{-1} (Table 2). In WB, there is also a significant increment in the level of N (28 g kg^{-1}). The protein levels in the waste, together with the practical absence of inorganic N (NO$_3$$^-$ y NH$_4$$^+$), makes clear that most of its N is of protein character. The C/N ratio in the WB (10.5) is considered as optimum (10–15) for composted materials [37].

Available P does also experiment an important increase in the waste from 61 to 584 mg kg^{-1} (Table 2). Some authors have also found very high levels of P in winery wastes (even reaching 11,000 mg kg^{-1}; [38]), explained by the addition of ammonium hydrogen phosphate to speed up the fermentation. This increment of available P is very important since acid soils are usually deficient in available P due to its immobilization by Fe and Al oxides [39]. In the other hand, the level of CEC in WB can increase three times with regards to B (Table 2). This is a consequence of the increase in cationic exchange sites in WB as a result of its enrichment in organic matter. The increase in CEC gives to soil a chance for longer fertility [40–42]. The CEC increase is also important for contaminants retention. WB passes from 0.8 to 118.0 cmol$_c$ kg^{-1} of exchangeable K (Table 2). High levels of K are usually found in wastes from wineries [43]. The addition of potassium tartrate in winemaking can contribute to the high levels of K in winery wastes [42].

It is also necessary to assess whether or not the WB pose any non-desirable effects as soil amendment. In such a sense, the water extract of the WB has a very large electrical conductivity (5 dS m^{-1}; Table 2). It is in the range of 1.6–6.1 dS m^{-1} as found in other studies with wastes obtained from winemaking [5,38]. The high level of rainfalls in NW Spain (800–1500 mm per year) would contribute to the leaching of salts, reducing the impact of the use of WB for amending crop soils. Consecutive application of wastes to soils can give place to the accumulation of heavy metals in soils. In WB, Cu is the most abundant metal with a concentration of 1481 mg kg^{-1} (Table 2). Cu levels in WB are likely due to use of copper-based fungicides in vineyards; these levels are of the same order than those found in wine lees (1187 mg kg^{-1}; [38]) or grape stalks (1342 mg kg^{-1}; [43]). However, organic matter forms very stable complexes with Cu [44], which reduce the potential phytotoxicity of WB even though it has a large Cu content. On the contrary, total Zn and Mn concentrations in WB (37 mg kg^{-1}; Table 2) are lower than for B, what is a clear indication that these elements are not incorporated from the most and there is a dilution effect due to the enrichment in organic matter. The concentration of other potentially toxic metals is similar or lower in WB than in other wastes applied to crop soils [45–47].

Due to the poor fertility of the acid soils devoted to vineyards, the direct application of WB to them could be an interesting tool for waste management because it provides C, N, P and K to soil [48]. Another management use for the wastes is based on its contribution to reduce the risk for erosion in hillside soils with large slopes [43].

3.2. Changes in quaternary herbicides adsorption after waste bentonite addition

Quats sorption kinetics were performed with the soil (0.5% C), but also with the soil amended with 30 t/ha (1.4% C). This was done with the intention of checking whether or not the organic matter content can influence the time to reach equilibrium between soil and solution. It was seen that there is not such an effect and that 24 h is the necessary time for equilibrium (Table 3). A more rapid sorption at the initial step indicated sorption occurred primarily on the external surface by electrostatic bonding. A decrease in sorption at a later stage of adsorption was explained by depletion of external surface sites and diffusion of quats into the internal surfaces [23].

Figs. 1–3 show the adsorption isotherms of quats to unamended soil and soil amended with 30 t/ha of WB. The three herbicides studied in this work exhibited strong adsorption in acid soils. The major factor governing the sorption of these pesticides is the solid-state organic fraction with the clay mineral content also making a significant contribution [49]. Anyway, what is clear from Langmuir isotherm coefficients (Table 4), it is the higher affinity of DFQ *vs.* DQ/PQ by the soil (Langmuir K = 1370 *vs.* 47–63 L mmol$_{(+)}$$^{-1}$). However, it was also found for the soil a much lower maximum adsorption for DFQ *vs.* DQ/PQ (Langmuir S_{max} = 1 *vs.* 10–16 mmol$_{(+)}$ kg^{-1}). This can be explained assuming that the soil has much less adsorption sites for DFQ than for DQ/PQ; therefore, DFQ is overall the least herbicide retained by the soil.

According to a previous paper published by us [22], these 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. Sorption to soil occurs onto both the organic matter and the clay fraction. The latter is especially important in giv-
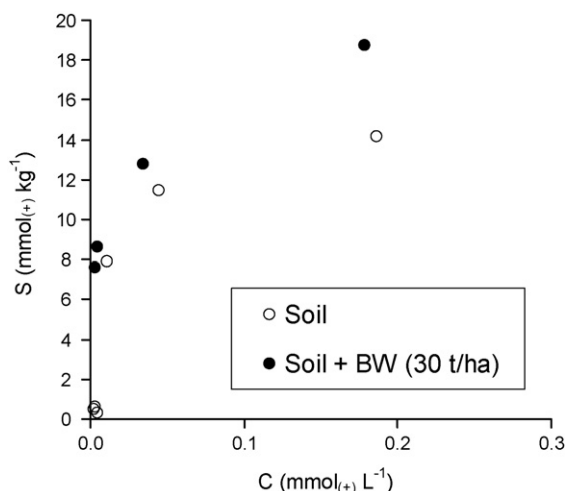
Fig. 1. Adsorption isotherms of paraquat to soil, and soil added with 30 t/ha of bentonite waste. *S*, sorbed concentration; *C*, equilibrium concentration.

ing strong long-term sorption, and depends on the type of clay present. Thus kaolinite, with a typical non-expanding lattice, sorbs in total about 2500–3000 mg kg^{-1} whereas montmorillonite with its expanding lattice sorbs about 75,000–85,000 mg kg^{-1}. 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 [27].

In the other side, the WB used is clearly a fine textured solid material with a very large specific surface. For all quats, adsorption isotherms to WB were non-linear. In order to compare the behaviour of the three herbicides, we obtained the equivalent linearized partition coefficient K_d^*, by using an isotherm linearization method 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. In some way, the divalent quats are more easily adsorbed. The lower affinity of DFQ *vs.* DQ/PQ by the WB gives as a consequence K_d^* of 111 *vs.* 871–661 L kg^{-1}, respectively. Therefore, the adsorbing sites were more reversible with respect to DFQ, or for DFQ the formation of bound residues is lower and it remains extractable at a higher degree. This suggests
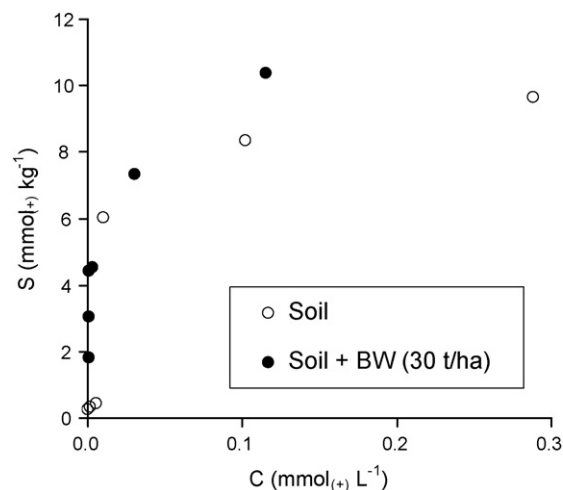

Fig. 2. Adsorption isotherms of diquat to soil, and soil added with 30 t/ha of bentonite waste. *S*, sorbed concentration; *C*, equilibrium concentration.
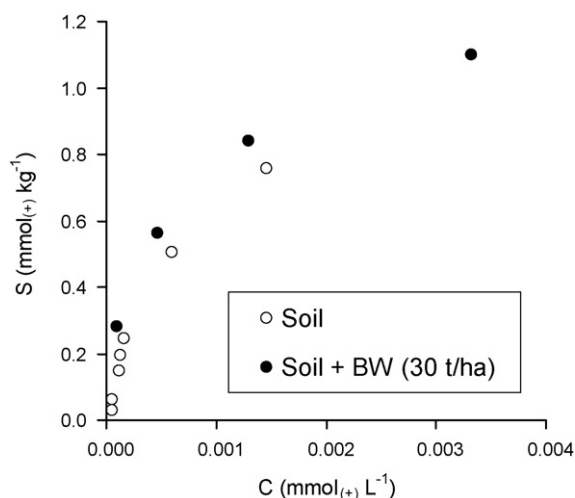

Fig. 3. Adsorption isotherms of difenzoquat to soil, and soil added with 30 t/ha of bentonite waste. *S*, sorbed concentration; *C*, equilibrium concentration.

that DFQ is more mobile and bound less strongly to the adsorption sites than did DQ and PQ.

By focusing our attention on the data about waste amendment at 10–30 t/ha, Langmuir *K* increased with the dose for divalent quats. Dose of 30 t/ha increased *K* 4.8 times for the PQ sorption while for DQ it increased 10 times; the most of the increase occurred when raise from 20 to 30 t/ha of WB added. DFQ behaviour was the opposite of divalent quats, because it had greater affinity to soil than PQ and DQ, as appointed above. Also, DFQ show less affinity for the WB than divalent quats. Thus, the observed effect of the WB addition is consistent with the expected from the *K* and K_d^* for soil and WB respectively.

Examining the effect of the amendment on the maximum sorption parameter, it seems that retention of DQ and PQ already in the acid soil reaches their maximum threshold and nothing changes with the addition to soil of WB. It was only found a moderate increment in the maximum adsorption of DFQ (*x*2), which can be attributed to the increase of sorption sites on the WB colloids. 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 [50]. 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, 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 addition of WB effectively increased the sorption sites for DFQ only.

Therefore, the lowest retention of DFQ in an acid soil can be increased by amendment with organic matter through a solid waste from wineries, and it is enough to double retention the dosage rate of 10 t/ha. This strong retention to organically amended soil greatly limits any leaching or surface run-off of these herbicides [22]. In practice the application of organic amendments for retarded movement of the herbicides is more effective in sandy soils because of their originally lower adsorptive surfaces [51].

4. Conclusions

The high content in C, N, P and K of WB turn it into an appropriate amendment to increase soil fertility, solving at the same time its disposal. The direct addition of WB to soil contributes to increase soil CEC, but can reduce the potential Cu phytotoxicity due to its

retention by the large content of organic matter in WB. In acid soils its use results in benefits from the agronomic point of view with no undesirable environmental side effects.

Herbicide pollution in crop soils is produced by their application inputs. The major factor governing the sorption of quats to soils was the solid-state organic fraction with the clay mineral content also making a significant contribution. Paraquat and diquat were adsorbed and retained more strongly (i.e., higher Langmuir K) than difenzoquat in the acid soil studied. It was also found that the lowest retention capacity (given by the Langmuir S_{max} parameter) of DFQ in an acid soil can be increased by amendment with organic matter through a solid waste from wineries, and that is enough for duplicate retention a dosage rate of 10 t/ha.

The results of this study reveal, in summary, the importance of assessing the effects of organic wastes on the fate of many of the compounds that are also applied to land in order to get a complete picture of the amendment practice effects. This type of studies will be useful in developing improved management practices in agrosystems to reduce water contamination by pesticides, or at least not to increase their levels in water.

Acknowledgements

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