

# Adsorption and degradation of four acidic herbicides in soils from southern Spain

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**BACKGROUND:** Pesticide degradation and adsorption in soils are key processes determining whether pesticide use will have any impact on environmental quality. Pesticide degradation in soil generally results in a reduction in toxicity, but some pesticides have breakdown products that are more toxic than the parent compound. Adsorption to soil particles ensures that herbicide is retained in the place where its biological activity is expressed and also determines potential for transportation away from the site of action. Degradation and adsorption are complex processes, and shortcomings in understanding them still restrict the ability to predict the fate and behaviour of ionisable pesticides. This paper reports the sorption and degradation behaviour of four acidic pesticides in five soils from southern Spain. Results are used to investigate the influence of soil and pesticide properties on adsorption and degradation as well as the potential link between the two processes.

**RESULTS:** Adsorption and degradation of four acidic pesticides were measured in four soils from Spain characterised by small organic matter (OM) contents (0.3–1.0%) and varying clay contents (3–66%). In general, sorption increased in the order dicamba < metsulfuron-methyl < 2,4-D < flupyrsulfuron-methyl-sodium. Both OM and clay content were found to be important in determining adsorption, but relative differences in clay content between soils were much larger than those in OM content, and therefore clay content was the main property determining the extent of herbicide adsorption for these soils. pH was negatively correlated with adsorption for all compounds apart from metsulfuron-methyl. A clear positive correlation was observed for degradation rate with clay and OM content ( $P < 0.01$ ), and a negative correlation was observed with pH ( $P < 0.01$ ). The exception was metsulfuron-methyl, for which degradation was found to be significantly correlated only with soil bioactivity ( $P < 0.05$ ).

**CONCLUSIONS:** Both OM and clay content were found to be important in determining adsorption, but relative differences in clay content between soils were much larger than those in OM content, and therefore clay content was the main property determining the extent of herbicide adsorption for soils of this type. pH was negatively correlated with adsorption for all compounds apart from metsulfuron-methyl. The contrasting behaviour shown for these four acidic pesticides indicates that chemical degradation in soil is more difficult to predict than adsorption. Most of the variables measured were interrelated, and different behaviours were observed even for compounds from the same chemical class and with similar structures.

**Keywords:** carboxylic acids; sulfonylureas; clay; correlation; adsorption; organic matter

## 1 INTRODUCTION

Pesticide degradation and adsorption in soils are key processes determining whether pesticide use will have any impact on environmental quality. Ideally, a pesticide remains in the treated area long enough to produce the desired effect and then degrades into inactive materials via biological, chemical and/or photochemical breakdown. Pesticide degradation in soil generally results in a reduction in toxicity, but some pesticides have breakdown products that are more toxic than the parent compound. Adsorption

to soil particles ensures that herbicide is retained in the place where its biological activity is expressed and also determines potential for transportation away from the site of action. For most pesticides, organic matter (OM) and clay content are the most important soil properties controlling the extent of adsorption.

The processes of adsorption and degradation have often been found to be correlated. Evidence that degradation can be restricted to the soil solution and that sorbed molecules may be protected from microbial attack has been provided by several studies

for a broad range of chemicals, including pesticides<sup>1,2</sup> and other organic contaminants.<sup>3–5</sup> On the other hand, a positive relationship has also been reported for the pesticides triclopyr,<sup>6</sup> mesotrione<sup>7</sup> and 2,4-D.<sup>6,8</sup>

Adsorption and degradation of ionisable pesticides are often related through pH. Changes in pH of the soil solution can lead to differences in adsorption, as the molecular form is more hydrophobic and does not suffer repulsion by the negatively charged surfaces of soil particles.<sup>9</sup> Dubus *et al.*<sup>10</sup> did not find a clear relationship between adsorption and pH for 2,4-D. Degradation tends to proceed faster at high pH for compounds mainly degraded by microorganisms because biological activity is often greater in weakly alkaline media.<sup>11</sup> However, chemical hydrolysis is favoured in acidic media for sulfonylureas.

Thus, degradation and adsorption are complex processes, and shortcomings in understanding still restrict the ability to predict the fate and behaviour of ionisable pesticides. This paper reports the sorption and degradation behaviour of four acidic pesticides in five soils from southern Spain. Results are used to investigate the influence of soil and pesticide properties on adsorption and degradation, as well as the potential link between the two processes.

## 2 MATERIALS AND METHODS

### 2.1 Soils

Five agricultural soils were sampled in August 2006 from the top 20 cm at several locations in southern Spain. Soils were selected to give a gradient in pH (pH in 1 M KCl from 6.3 to 8.4) and to have a range in texture (clay content from 2.5 to 65.9%) (Table 1). The soils all had small OM content (from 2.96 to 10.21 g kg<sup>-1</sup>), and ratios of clay to OM ranged between 5 and 37. The moisture content of each soil was adjusted by weight to exactly –33 kPa.

Soil bioactivity was evaluated by measuring dehydrogenase activity after 2 weeks of incubation (triplicates). This enzyme is only active in living organisms and thus is an indicator for soil microbial activity. Soil samples (5 g) were incubated at 30 °C with 5 mL of colourless TTC solution (0.5% by weight, 2,3,5-triphenyl-2*H*-tetrazolium chloride, 98%, Avocado Research Chemicals Limited) in 0.1 M Tris buffer [tris(hydroxymethyl)aminomethane, general-purpose grade, Merck Science] adjusted to pH 7.6

with hydrochloric acid. TTC is reduced by dehydrogenase enzymes to red water-insoluble TPF (1,3,5-triphenylformazan), and the latter was extracted with 25 mL acetone after 24 h incubation. The samples were shaken for 1 h (end-over-end shaker, 22 rev min<sup>-1</sup>) and centrifuged at 5000 *g* for 12 min. The intensity of the red colour of the supernatant was measured by spectrophotometry at 485 nm (UV-160A, UV-visible recording spectrophotometer, Shimadzu) and converted to bioactivity (mg TPF kg<sup>-1</sup> soil) based on a set of TPF standards (Sigma-Aldrich Company Ltd).

### 2.2 Pesticides, other chemicals and analytical techniques

Four acidic pesticides were selected, comprising two carboxylic acids (dicamba and 2,4-D) and two sulfonylureas [metsulfuron-methyl (MSM) and flupyrsulfuron-methyl-sodium (FSM)] (Table 2). Radiolabelled 2,4-D was purchased from American Radiolabelled Chemicals Inc. (St Louis, MO) and dicamba from Izotop Institute of Isotopes Co., Ltd (Budapest, Hungary), and MSM and FSM were supplied by EI DuPont de Nemours (Wilmington, DE). Pre-experiments demonstrated that no competition effects operated at low concentrations, so pesticides were paired (2,4-D with dicamba, and FSM with MSM) and studied together. Lipophilicity profiles (log *D*) represent the shift in octanol/water partition coefficient with pH as a consequence of dissociation. They were determined for each acid using the pH metric method (GLpKa; Sirius Analytical Instruments Ltd).<sup>9</sup>

Pesticide concentrations in the degradation experiments were measured on an Agilent 1100 series HPLC equipped with a photodiode array detector and a Discovery C-18 column, 4.6 × 150 mm, 5 μm (Supelco, Bellefonte, PA), with the following conditions: for dicamba and 2,4-D, mobile phase acetonitrile + water acidified with 0.4 g L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> (40 + 60 by volume), wavelength 202 nm; for FSM and MSM, acetonitrile + water acidified with 2.5 g L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> (50 + 50 by volume), wavelength 225 nm; flowrate 1 mL min<sup>-1</sup>. The detection limit was below 0.03 mg L<sup>-1</sup>, and the recoveries ranged between 85 and 115%.

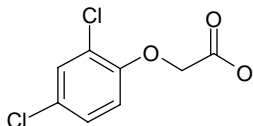
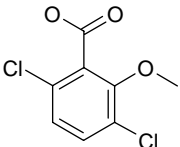
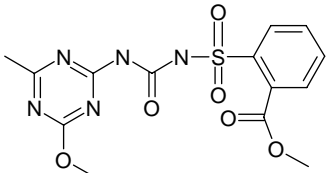
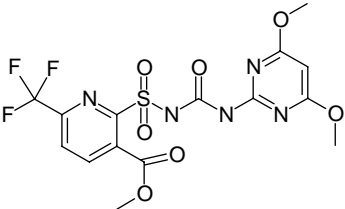
All sorption experiments were undertaken using radioisotopes, and pesticide concentrations were measured on a liquid scintillation counter (LS 6500; Beckman Coulter Inc., Fullerton, CA). The solution

**Table 1.** Mean properties for soils selected

Soils	Textural classification <sup>a</sup>	pH (1 M KCl)	OC (g kg <sup>-1</sup> )	CO <sub>3</sub> <sup>2-</sup> (g kg <sup>-1</sup> )	Water content for incubation (g 100 g <sup>-1</sup> dry soil)	Sand (%)	Silt (%)	Clay (%)	Bioactivity
A	Loam	6.3	7.60	218.1	17.2	28.5	45.8	25.7	0.78
B	Sandy	8.4	2.96	0.0	10.9	92.8	4.4	2.5	0.14
C	Sandy loam	8.3	7.31	182.2	9.2	74.6	12.1	13.2	0.69
D	Sandy clay loam	7.9	8.00	0.0	10.2	75.6	2.2	22.1	0.82
E	Clay	7.5	10.21	241.0	25.4	2.7	31.5	65.9	0.95

<sup>a</sup> Textural classification FAO/UNESCO/ISRIC.

**Table 2.** Molecular structures, uses and properties of the pesticides<sup>35</sup>

Pesticide name [CAS RN]	Structural formula	Use and application rate (g ha <sup>-1</sup> )	pKa <sup>a</sup>	K <sub>oc</sub> <sup>b</sup> (mL g <sup>-1</sup> )	DT <sub>50</sub> <sup>c</sup> (days)	Solubility (in water, g L <sup>-1</sup> )
2,4-D [94-75-7] (2,4-Dichlorophen- oxy)acetic acid		Selective systemic post-emergence control of annual and perennial broad-leaved weeds in cereals, maize, sorghum, grassland, orchards, sugar cane, rice and non-crop lands (280–2300)	2.97	5–212	5–59	0.6
Dicamba [1918-00-9] 3,6-Dichloro-2- methoxybenzoic acid		Selective systemic herbicide to control annual and perennial broad-leaved weeds and brush species in cereals, maize, sorghum, sugar cane, asparagus, turf, pastures and non-crop lands (100–11 200)	1.97	3.5–21	1.4–11	6.5
Metsulfuron-methyl [74223-64-6] Methyl 2-(4- methoxy-6- methyl-1,3,5- triazin-2- ylcarbamoyl- sulfamoyl) benzoate		Selective systemic herbicide pre- or post-emergence application to control a wide range of annual and perennial broad leaved weeds in wheat, barley, rice and oats (4–7.5)	3.75	4–60	4–100	0.548 (pH 7) 213 (pH 9)
Flupyr-sulfuron- methyl-sodium		Selective, post-emergence control of black grass and other weeds in cereals  (10)	4.94	15-47	6-26	0.063 (pH 5)  0.600 (pH 6)
[144740-54-5] Methyl 2-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-6-trifluoromethylnicotinate monosodium salt						

to be analysed (2 mL) was added to 10 mL of Ecoscint A scintillation cocktail (National Diagnostics, Hesse, UK). The detection limit was 1.5 Bq per 2 mL sample. The counting efficiency was 95%. Samples were counted 3 times for 5 min and were corrected for background using blank controls. Counting efficiency and colour quenching were corrected by the external standard ratio method.

Based on the application rates in the field and incorporation in the upper 2.5 cm of the soil profile, all degradation experiments were carried out at 2 mg AI kg<sup>-1</sup>. Sulfonylurea herbicides are applied at very low rates in the field, but were studied at a relatively

high concentration (1 mg AI kg<sup>-1</sup>) to facilitate analysis in the degradation experiment.

### 2.3 Batch experiments

Sorption coefficients ( $K_d$ , mL g<sup>-1</sup>) were determined at one concentration, similar to that used in the incubation experiments (Section 2.4), with four replicates, using a standard batch equilibrium method.<sup>12</sup> After a pre-equilibration period of 14 h, the soil suspensions were spiked with a pesticide solution in 0.01 M CaCl<sub>2</sub> (mixture of labelled and unlabelled) and returned to shaking until pseudoequilibrium was reached (72 h). Samples were maintained in the

dark at 4 °C throughout the procedure to minimise degradation. Afterwards, samples were centrifuged at 5000 *g* for 15 min, and the supernatant was analysed to measure the concentration of pesticide remaining in solution after adsorption ( $C_e$ , mg L<sup>-1</sup>). Triplicates without soil were used as reference for the initial concentration ( $C_i$ , mg L<sup>-1</sup>). Assuming that all pesticide removed from the solution was sorbed by the soil, the concentration of pesticide adsorbed in the solid phase ( $C_s$ , mg g<sup>-1</sup>) was calculated as

$$C_s = V(C_i - C_e)/m_s$$

where  $V$  (mL) is the volume of solution in the suspension and  $m_s$  is the mass of soil (g). The soil sorption coefficients  $K_d$  (mL g<sup>-1</sup>) and  $K_{oc}$  were then calculated as

$$K_d = C_s/C_e \quad \text{and} \quad K_{oc} = K_d \times 1000/OC$$

where OC is the organic carbon content of the soil (g kg<sup>-1</sup>).

## 2.4 Degradation experiments

Samples of fresh soil were preincubated for a week prior to application of pesticide to allow germination and removal of seeds and establish equilibrium of microbial metabolism following the change from sampling or storage conditions to incubation conditions.

Pesticide solution in deionised water (5 mL) was applied dropwise to the equivalent of 200 g of dry soil (three replicates) to give an initial concentration of 2 mg AI kg<sup>-1</sup> (1 mg AI kg<sup>-1</sup> for the two sulfonylureas). Soil was thoroughly mixed, then transferred to a 500 mL glass flask and incubated at 15 °C in the dark. During the incubation, moisture content (w/w) was maintained twice a week and lids were not tightly closed to avoid the creation of anaerobic conditions. At appropriate time intervals, samples of 20 g of soil were weighed into 125 mL amber glass jars and immediately frozen. Nine samples were taken during the incubation period. The duration of incubation was 80 days for 2,4-D and dicamba and 110 days for MSM and FSM.

Extraction and quantification of pesticide remaining in soil from the nine samples (each in triplicate) were undertaken at the end of the respective incubation period to minimise errors between sampling intervals. Degradation was measured through the relative decline of residues extracted with an appropriate organic solvent (soil to solution 1:2): acidified methanol (0.25% H<sub>3</sub>PO<sub>4</sub>) for dicamba and 2,4-D, and acetonitrile + 0.1 M sodium acetate (pH 6.5) (75 + 25 by volume) for FSM and MSM. After 2 h of platform shaking (250 rpm), the samples were allowed to stand until the soil had settled (1 h), and the pesticide concentration in the clear supernatant was determined.

Degradation curves were fitted to three kinetic models: a simple first-order equation, a first-order

multicompartment (Gustafson and Holden) model<sup>13</sup> and a first-order sequential (hockey-stick)<sup>13</sup> model. Parameters were optimised according to recommendations by FOCUS<sup>13</sup> using the least-squares method with Microsoft Excel Solver. Simple first-order kinetics was found to be the best descriptor for the experimental data. The rate of degradation and the DT<sub>50</sub> (time in days required for 50% of the initial dose of pesticide to be degraded) of each compound in each soil were determined with the following equations:

$$C_t = C_0 e^{-kt} \quad \text{and} \quad DT_{50} = \ln 2/k$$

where  $C_t$  is the concentration of pesticide remaining in soil (mg kg<sup>-1</sup>) at time  $t$  (days),  $C_0$  is the initial concentration of pesticide (mg kg<sup>-1</sup>) and  $k$  is the rate of degradation (day<sup>-1</sup>).

## 2.5 Statistical analysis

Relationships between adsorption coefficients and properties of soils and pesticides were investigated using the statistical analysis program SPSS for windows v. 11.5. The soil properties given in Table 1 were evaluated as predictors for adsorption and degradation processes.

## 3 RESULTS AND DISCUSSION

### 3.1 Batch adsorption experiments

The strength of sorption for the four acidic herbicides under study increased in the order dicamba < MSM < 2,4-D < FSM. The adsorption coefficients ( $K_d$ ) for the different soils are shown in Table 3. The largest  $K_d$  values were obtained for soils A and E, and the smallest values for soil B. In general, a relationship was found for  $K_d$  with both OM and clay content. The adsorption coefficient normalised to organic carbon content ( $K_{oc}$ ) can be used as a measure of the influence of hydrophobic bonds on the adsorption of non-polar hydrophobic pesticides on OM. However, even when hydrophobic bonds dominate adsorption, the use of  $K_{oc}$  may result in deviation from reality because the sorption capacity of a natural particle is highly dependent on the nature and amount of surface exposed, which in turn is determined by the degree of interassociation of the individual constituents.  $K_{oc}$  values are not usually used to compare the behaviour of ionisable pesticides; while OM has been broadly reported as one of the

**Table 3.** Sorption coefficients ( $K_d$ , mL g<sup>-1</sup>) (± SD) measured for the four herbicides

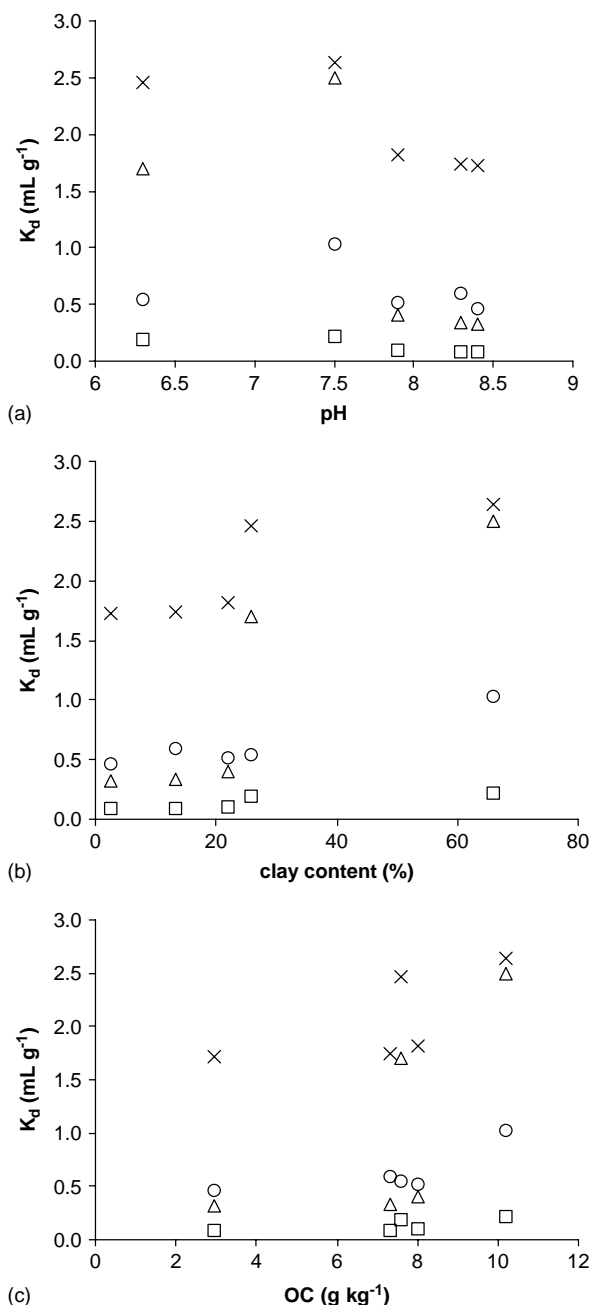
Soil	Dicamba	2,4-D	MSM	FSM
A	0.19 (±0.02)	1.70 (±0.39)	0.54 (±0.02)	2.46 (±0.11)
B	0.09 (±0.02)	0.32 (±0.00)	0.46 (±0.14)	1.72 (±0.15)
C	0.09 (±0.04)	0.34 (±0.16)	0.59 (±0.03)	1.74 (±0.07)
D	0.10 (±0.09)	0.40 (±0.04)	0.51 (±0.03)	1.82 (±0.05)
E	0.22 (±0.09)	2.49 (±0.62)	1.03 (±0.04)	2.64 (±0.11)

main soil properties determining adsorption for this type of pesticide, other soil characteristics have to be taken into account, including the clay fraction, pH, ionic strength and cation exchange capacity.<sup>14–16</sup> When a wide range of  $K_{oc}$  values is observed, the role of hydrophobic interactions in adsorption is probably not dominant and more investigations are necessary to determine what other processes are acting.<sup>17</sup> In the present case, significant differences between  $K_{oc}$  values were observed for all pesticides (a factor of 2–5 between the largest and smallest values), suggesting that soil properties other than OM should be investigated.

Based on the hypothesis of mineral blockage by OM, clay mineral contribution is expected to be at a maximum when the ratio of clay mineral to OC fractions is more than 30, regardless of the mineral content; a very large ratio could be observed for some of the soils investigated in this paper (33 and 64 for soils A and E) (Table 1). Barriuso *et al.*<sup>18</sup> concluded that the contribution of clay constituents to pesticide retention can be dominant in low-OM soils. For instance, Harper<sup>19</sup> studied the behaviour of metribuzin down a silty clay loam profile, and found that clay content was the single best predictor of adsorption. On the other hand, the determination of the effect of a single soil variable on adsorption is always difficult because soil properties are often correlated with each other.

It is likely that ionic interactions may contribute to some degree to anionic pesticide sorption under some conditions. This is more apparent in soils with small OC content and large clay content, as in the present research. Sorption coefficients ( $K_d$ ) were plotted against OC, pH and clay content of the soils under study (Fig. 1). pH values were measured in 1 M KCl, as this is a measure of surface acidity ( $K^+$  extracts  $H^+$  and  $Al^{3+}$  ions present at the surface of soil particles), and this provides an image of the total potential acidity of a soil. Figure 1a shows that sorption was generally greater at lower pH values, but that sorption was stronger than would be expected from pH alone for soil E (pH = 7.5). This soil had the largest clay content, and clay content had a greater influence on adsorption in this soil. Figure 1b shows a linear and strong relationship between  $K_d$  and clay content. Nevertheless, there is significant sorption even in soil B which has only 2.5% clay, indicating that both OM and clay are important in determining sorption. Figure 1c shows the relationship between organic carbon content and  $K_d$ , where no clear correlation is observed. Table 4 shows correlations between different soil properties where organic carbon content is itself strongly correlated with clay content ( $P < 0.001$ ).

Table 5 gives statistical correlations between selected soil properties and  $K_d$ . Significant correlations were found for all of the characteristics plotted, with the only exceptions being for pH and log  $D$  for MSM. Correlations were positive between  $K_d$  and



**Figure 1.** Plot of adsorption coefficient ( $K_d$ ) against soil properties: (a) pH, (b) clay content, (c) organic carbon content. x, FSM; O, MSM;  $\Delta$ , 2,4-D;  $\square$ , dicamba.

organic carbon content, clay content, carbonate content and log  $D$ . Sorption was negatively correlated with pH. Stronger correlations with  $K_d$  were found for clay ( $P < 0.01$ ) than OC content ( $P < 0.05$ ). Strong correlations have sometimes been found between clay content and adsorption of certain acidic pesticides, especially for some sulfonylureas.<sup>20,21</sup> Lack of correlation with pH for MSM has been observed previously by Madsen *et al.*,<sup>22</sup> who studied sorption of seven pesticides in ten Danish aquifer sediments with a very low OM ( $< 1 \text{ g kg}^{-1}$ ); it was concluded that MSM sorbed only at  $\text{pH} < 5$ . In the present work, the pH of the soils ranged from 6.3 to 8.4.

**Table 4.** Correlation matrix between soil properties<sup>a</sup>

Clay	1.000					
Log D	0.397	1.000				
CO <sub>3</sub> <sup>2-</sup>	0.637*	0.573	1.000			
Bioactivity	0.759**	0.499	0.599	1.000		
OC	0.845***	0.435	0.655**	0.980***	1.000	
PH	-0.400	-1.000***	0.573*	-0.500	-0.440	1.000
	Clay	Log D	CO <sub>3</sub> <sup>2-</sup>	Bioactivity	OC	pH

<sup>a</sup> Correlation significant at: \*  $P < 0.05$ ; \*\*  $P < 0.01$ ; \*\*\*  $P < 0.001$ .

**Table 5.** Statistical correlations between  $K_d$  and selected soil properties plus log  $D$ <sup>a</sup>

Pesticide	OC	pH	Clay	CO <sub>3</sub> <sup>2-</sup>	Log $D$
Dicamba	0.653*	-0.753**	0.839**	0.763**	0.753**
2,4-D	0.675*	-0.634*	0.900***	0.743**	0.634*
MSM	0.704**	-0.117	0.905***	0.654*	0.177
FSM	0.624*	-0.759**	0.821**	0.724**	0.759**

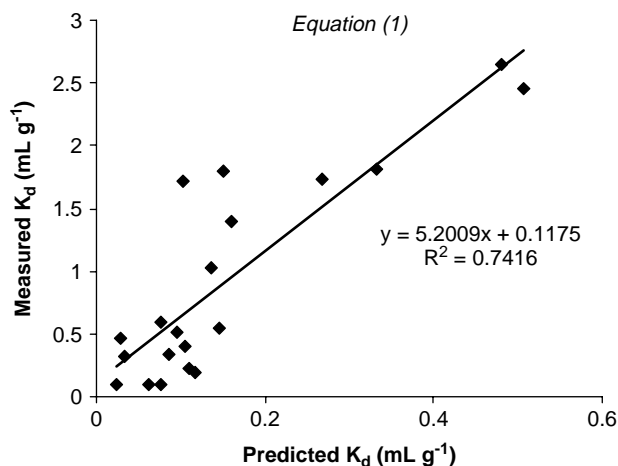
<sup>a</sup> Correlation significant at: \*  $P < 0.05$ ; \*\*  $P < 0.01$ ; \*\*\*  $P < 0.001$ .

Statistical correlations were also found for other selected properties in this work. Content of CO<sub>3</sub><sup>2-</sup> in soil has previously been reported as fundamental for 2,4-D sorption in soil with a very large content of calcium carbonate. Rodriguez-Rubio *et al.*<sup>23</sup> found a dramatic decrease in 2,4-D adsorption in the absence of carbonates (they were previously extracted) and suggested that the herbicide was also adsorbed on soil carbonates. The parameter log  $D$  describes two sources of variability in adsorption. When log  $D$  is selected for a single compound, it describes the shift in concentrations of the neutral and ionic forms and the difference in their strength of sorption. The correlation between  $K_d$  and log  $D$  is thus positive for acids. The neutral and ionic forms of ionisable compounds have different polarities. Since their ratio varies with pH, the lipophilicity of ionisable pesticides is pH dependent. For acids, log  $D$  decreases with increasing pH as the proportion of anionic species increases. In the current case, strong positive correlations were found, except in the case of MSM, where correlation was not significant ( $P > 0.05$ ).

In a previous work<sup>11</sup> the influence of pH and OC on adsorption was confirmed for ten ionisable pesticides in nine arable soils from southern England. In general, these soils had a larger organic carbon content (average 20 g kg<sup>-1</sup>) than those in the present study (average 7 mg kg<sup>-1</sup>). Kah and Brown<sup>11</sup> proposed two different equations to describe the experimental results obtained for the acidic pesticides:

$$\log K_d = 0.13 \log D + 1.02 \log OC - 1.51 \quad (1)$$

Figure 2 shows the application of equation (1) to the current dataset. While there appears to be a relationship between measured and predicted values ( $r^2 = 0.74$ ), measured  $K_d$  values were underpredicted

**Figure 2.** Independent evaluation of the equation proposed by Kah and Brown<sup>11</sup> against  $K_d$  values measured for the Spanish soils.

by a factor of 10; this underestimation arises because OM content in the Spanish soils is so small.

The clay fraction is not considered in either equation, since OM content was much larger in the soils studied by Kah and Brown.<sup>11</sup> In the present work, arid soils with a very small OM content from southern Spain were investigated, and relative differences in clay content between soils were much larger than relative differences in OC content.

### 3.2 Degradation experiments

Values for degradation rate and half-lives are shown in Table 6. In general, the rate of degradation decreased in the order dicamba > FSM > 2,4-D > MSM.

Table 7 gives correlation coefficients between degradation rates and soil properties and adsorption coefficients for each pesticide. Overall, a clear positive correlation was observed for degradation rate with clay and OM content, and a negative correlation was observed with pH. The exception was MSM, for which only bioactivity was found to be significantly correlated with degradation rate.

A negative relationship between pH and rate of degradation can be expected for the two sulfonylurea herbicides because abiotic hydrolysis can be a significant contributor to total degradation and is generally favoured under acidic conditions for this class of compound.<sup>24,25</sup> The result is more surprising for dicamba and 2,4-D, as microbial

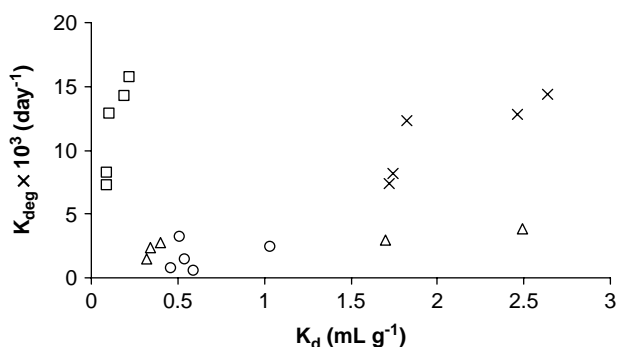
**Table 6.** Degradation rate ( $K_{\text{deg}}$ ,  $\text{day}^{-1}$ ) ( $\pm$  SD) and half-life ( $T_{1/2}$ , days) for the four herbicides

Soil	Dicamba		2,4-D		MSM		FSM	
	$K_{\text{deg}} \times 10^3$	$T_{1/2}$	$K_{\text{deg}} \times 10^3$	$T_{1/2}$	$K_{\text{deg}} \times 10^3$	$T_{1/2}$	$K_{\text{deg}} \times 10^3$	$T_{1/2}$
A	14.3 ( $\pm 0.32$ )	4.8	3.0 ( $\pm 0.02$ )	23.4	1.5 ( $\pm 0.02$ )	45.2	12.8 ( $\pm 0.45$ )	5.4
B	7.3 ( $\pm 0.12$ )	9.5	1.5 ( $\pm 0.01$ )	47.3	0.8 ( $\pm 0.02$ )	86.6	7.4 ( $\pm 0.17$ )	9.4
C	8.2 ( $\pm 0.14$ )	8.4	2.4 ( $\pm 0.07$ )	28.5	0.6 ( $\pm 0.03$ )	104.0	8.1 ( $\pm 0.15$ )	8.5
D	12.9 ( $\pm 0.16$ )	5.4	2.8 ( $\pm 0.02$ )	24.5	3.3 ( $\pm 0.16$ )	20.6	12.3 ( $\pm 0.43$ )	5.6
E	15.8 ( $\pm 0.02$ )	4.4	3.8 ( $\pm 0.06$ )	18.4	2.5 ( $\pm 0.15$ )	27.4	14.4 ( $\pm 0.56$ )	4.8

**Table 7.** Statistical correlations between  $K_{\text{deg}}$  and selected soil properties plus  $K_{\text{d}}^{\text{a}}$ 

Pesticide	$K_{\text{d}}$	OC	pH	Clay	$\text{CO}_3^{2-}$	Bioactivity
Dicamba	0.843**	0.821**	-0.738**	0.842**	0.615*	0.827**
2,4-D	0.801**	0.968***	-0.752**	0.914***	0.675*	0.762**
MSM	0.009	0.153	-0.123	0.116	-0.078	0.589*
FSM	0.796**	0.825**	-0.713**	0.838**	0.660*	0.825**

<sup>a</sup> Correlation significant at: \*  $P < 0.05$ ; \*\*  $P < 0.01$ ; \*\*\*  $P < 0.001$ .

**Figure 3.** Plot of adsorption coefficient ( $K_{\text{d}}$ ) against rate of degradation ( $K_{\text{deg}}$ ).  $\times$ , FSM;  $\text{O}$ , MSM;  $\Delta$ , 2,4-D;  $\square$ , dicamba.

degradation is expected to dominate, and both microbial biomass and activity have been shown to be greater at higher pH.<sup>26,27</sup> In addition, sorption was negatively correlated with pH (Table 5), and it is frequently assumed that degradation is promoted by having a greater proportion of the chemical available in solution. In fact, strength of sorption and rate of degradation were positively related for all four compounds (Fig. 3). Picton and Farenhorst<sup>28</sup> concluded that mineralisation rates were greater in soils that sorbed more 2,4-D per unit OC, and that those soils had larger nitrogen contents. Park *et al.*<sup>8</sup> developed a kinetic formulation, termed ‘enhanced bioavailability model’, where the degradation rate of 2,4-D was studied in silica–slurry systems to evaluate the bioavailability of sorbed-phase contaminant; the results provided evidence that desorption to the bulk solution is not a prerequisite for degradation and that sorbed substrate may be available for degradation. A relationship between  $K_{\text{d}}$ , OC and bioactivity has been previously reported, based on the fact that the pesticide would be sorbed onto OM and microorganism activity would be highest close to that, since a higher microorganism concentration could be found there.<sup>28–31</sup> Moreover, adsorption onto OM

can facilitate abiotic transformations of a molecule, as shown for metribuzin and its metabolites using infrared spectroscopy<sup>20</sup> as well as for the sulfonylureas, azimsulfuron<sup>32</sup> and triasulfuron.<sup>24</sup> Degradation of MSM was only found to be positively correlated with the microbial activity. Many authors have concluded that soil bioactivity is the main factor influencing degradation of this sulfonylurea. Studies of the influence of soil properties on degradation have shown that largest effects on degradation were observed in response to soil sterilisation.<sup>33,34</sup>

## 4 CONCLUSIONS

Adsorption and degradation of four acidic pesticides were measured in four soils from Spain with very small organic carbon contents and varying clay contents. In general, sorption increased in the order dicamba < metsulfuron-methyl < 2,4-D < flupysulfuron-methyl. Both OM and clay content were found to be important in determining adsorption, but relative differences in clay content between the soils were much larger than those in OM content, and therefore clay content was the main property determining the extent of herbicide adsorption for this type of soil. pH was negatively correlated with adsorption for all compounds apart from metsulfuron-methyl.

Degradation was also investigated. Results were analysed (i) to identify any commonalities in factors influencing the rate of degradation and (ii) to test for any link between sorption and degradation. A clear positive correlation was observed for degradation rate with clay and OM content, and a negative correlation was observed with pH. The exception was MSM, for which degradation was found to be significantly correlated only with soil bioactivity. The contrasting behaviour shown for the selected acidic pesticides indicates that chemical degradation in soil is more difficult to predict than adsorption. Most of the

variables measured were interrelated, and different behaviours were observed even for compounds from the same chemical class and with similar structures.

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