

# SOIL ADSORPTION OF 2,4-D AS AFFECTED BY THE CLAY MINERALOGY

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The adsorption of 2,4-D has been studied obtaining adsorption isotherms on 22 soils by the batch equilibration technique. Fitting the adsorption data to the Freundlich equation three adsorption capacity were calculated at low ( $K_f$  or  $C_s1$ ), medium ( $C_s4.5$ ) and high ( $C_s30$ ) 2,4-D concentration. The adsorption capacity and intensity factors obtained in this study resulted in according with those reported by other authors. From the simple regression analysis between adsorption capacities and soil properties it was shown that organic matter and free iron contents of soils favoured the adsorption, whereas pH, surface area and clay content decreased the adsorption of 2,4-D. By dividing the soils according to their clay mineralogy it was shown that the soils properties determining the adsorption capacity were different for soils with phyllosilicates as essential clay components than for soils with iron oxides as major clay components.

**KEY WORDS:** Adsorption, Freundlich isotherm, pesticide, soil pollution, soil clay mineralogy.

## INTRODUCTION

The potential mobility of chemicals through soils and water is closely related to the sorption process at the solid/liquid interface. Mathematical models used to simulate pesticide fate in the environment include an adsorption parameter<sup>1-5</sup> which have to be experimentally calculated. Much work has been devoted to develop equations for predicting sorption coefficients of a chemical as a function of the soil or sediment properties and the adsorption of pesticides by soils has been generally related to organic matter content and sometimes to clay content. However, these soil fractions should not be considered as single variables but they represent a diversity of chemical surfaces that has been shown recently to be of great interest.<sup>6-10</sup> In previous studies<sup>10-13</sup> we showed that factors affecting soil sorption parameters of a nonionic and cationic pesticides depended upon the clay mineralogy of the soils considered and it seemed interesting to extend this study for an anionic chemical such as 2,4-D (2,4-dichlorophenoxyacetic acid) which has been extensively studied in other type of soils and because the weak acid herbicide is one of the most important type of pesticide for future developments.<sup>14</sup> The purpose of this work was to determine the physiochemical properties of soil related to the adsorption of 2,4-D in selected soil of South Spain, allowing for the clay mineralogy as an essential soil factor.

**Table 1** Selected properties of the soils

Soil	Depth cm	Soil number	Sand %	Silt %	Clay %	M.O. %	CEC meq/100 g	S <sub>BET</sub> m <sup>2</sup> /g	pH	Available Ca <sup>++</sup> meq/100 g
Chromoxerert	0-10	1	1.0	39.0	58.0	4.43	25.3	58.5	7.9	21.6
	10-20	2	2.3	26.0	72.0	2.41	22.6	63.5	7.8	19.6
	35-40	3	2.5	30.0	68.0	1.89	22.6	67.1	7.7	49.8
Pelloxerert	0-20	4	9.7	31.0	59.0	1.68	44.4	94.3	7.6	37.2
	20-40	5	10.7	29.8	59.0	1.03	40.7	99.5	7.6	39.6
	120-150	6	9.7	25.0	65.0	0.88	35.3	90.3	7.8	37.8
Pelloxerert	0-10	7	16.6	26.5	54.0	1.69	34.4	67.8	7.7	26.8
	90-100	8	15.9	23.6	59.3	1.45	36.5	67.9	8.3	30.0
Xerofluent	0-10	9	44.5	19.5	35.5	2.22	21.6	17.5	7.7	15.7
Xerofluent	0-10	10	70.0	13.2	14.0	1.22	15.7	7.9	7.2	9.0
	10-20	11	63.5	16.0	17.0	0.64	11.8	8.7	6.9	9.6
Xerofluent	0-20	12	52.4	20.3	20.3	4.70	21.6	33.2	6.3	9.6
Eutrochrepts	0-25	13	39.5	37.0	19.5	3.20	11.8	14.5	6.5	6.6
	50-100	14	37.5	43.0	14.5	1.17	12.7	29.0	6.8	6.7
Haploxeralf	0-10	15	29.8	40.5	26.0	4.15	24.3	22.9	6.5	15.9
	10-40	16	20.7	39.5	37.5	0.81	23.2	35.5	6.5	15.6
	70-100	17	26.2	63.3	29.0	0.48	26.2	37.2	6.5	13.8
Eutrochrepts	0-25	18	26.0	52.3	19.5	4.34	17.7	34.5	7.8	15.0
	50-85	19	20.3	41.8	35.5	0.84	17.3	43.0	7.7	10.8
Eutrochrepts	60-90	21	9.9	67.8	22.4	0.00	8.0	33.6	7.0	3.4
	90-120	22	9.8	65.3	24.4	0.00	5.2	27.5	6.7	3.5

## MATERIALS AND METHODS

The soils used in this study corresponded to surface and subsurface horizons of 10 soils of South Spain. These soils were selected for displaying a wide range of physicochemical and mineralogical properties which are shown in Tables 1 and 2. The methods for measuring these properties has been published elsewhere.<sup>10</sup> The adsorption isotherms were carried out with 9 initial 2,4-D concentrations from 0 (blank) to 45  $\mu\text{mol l}^{-1}$  in  $\text{CaCl}_2$  0.01 M solutions. The initial solutions were labelled with  $^{14}\text{C}$ -2,4-D at  $2 \times 10^{-5} \text{ mCi}(\text{mg } 2,4\text{-D})^{-1}$ . 2 g of air dried soil and 10 ml of labelled solutions in polyethylene centrifuge tubes were shaken for 24 h at  $22 \pm 2^\circ\text{C}$ . Previously it has been checked that equilibrium was reached before 12 h and 2,4-D was not adsorbed on polyethylene tubes. The suspensions were centrifuged at 14000 g for 15 min at  $22^\circ\text{C}$  and the supernatants were decanted to be analysed. All samples were run in duplicates. The initial and equilibrium solutions were counting using 2 ml of solutions and 12 ml of radioassay solution (Ready Safe, Beckman) on a Beckman LS 5000TD instrument, correcting for background, quenching and efficiency. The amounts of 2,4-D adsorbed were assumed to be equal to that calculated from the difference between initial and equilibrium solutions.

**Table 2** Mineralogical properties of the soils

Soil number	$Fe_f$ % $Fe_2O_3$	Mineral components of the clay fraction <sup>a</sup>											
		<i>M</i>	<i>I</i>	<i>C</i>	<i>V</i>	<i>Cl</i>	<i>T</i>	<i>Mi</i>	<i>Amph</i>	<i>G</i>	<i>Mg</i>	<i>H</i>	<i>L</i>
1	1.9	++	++++	++	—	+	—	—	—	—	—	—	—
2	2.2	+	++++	+	—	+	—	—	—	—	—	—	—
3	2.1	+	++++	++	—	+	—	—	—	—	—	—	—
4	1.5	+++	+++	++	—	+	—	—	—	—	—	—	—
5	1.5	+++	+++	++	—	+	—	—	—	—	—	—	—
6	1.3	+++	++	++	—	+	—	—	—	—	—	—	—
7	1.6	++++	++	+	—	+	—	—	—	—	—	—	—
8	1.5	++++	++	++	—	—	—	—	—	—	—	—	—
9	3.3	++	++++	++	—	—	—	—	—	—	—	—	—
10	3.4	+	++++	+++	+	+	—	—	—	—	—	—	—
11	3.3	+	++++	+++	—	—	—	—	—	—	—	—	—
12	16.2	—	+	++	+	—	—	—	—	++	+	+++	—
13	6.4	+	+++	++	++	—	—	—	—	++	—	+++	—
14	9.0	+	+++	+	+	—	—	—	—	++++	—	++	—
15	12.8	—	—	—	+	+	+++	—	—	+	—	++	+
16	14.2	—	—	—	+	+	+++	—	—	++	—	+	+
17	15.6	—	—	—	+	++	+++	—	—	+++	—	+	+
18	18.0	—	+	+	—	++	—	—	—	+	+++	++	—
19	21.4	—	+	+	—	+++	—	—	—	++++	—	+	+
20	32.0	—	—	—	+	+	+	+++	+	+	++++	++	++
21	38.0	—	—	—	+	++	++	++	+	+++	+++	++	++
22	38.5	—	—	—	+	+++	+	+	+	+++	+	+	++

<sup>a</sup>M=Montmorillonite, I=Illite, C=Kaolinite, V=Vermiculite, Cl=Chlorite, T=Talc, Mi=Mica, Amph=Amphibole, G=Goethite, Mg=Maghemite, H=Hematite, L=Lepidocrocite, ++++=very abundant, +++=abundant, ++=present and +=scarce.

The adsorption isotherm curves were obtained by plotting the amount of 2,4-D adsorbed ( $C_s$ ,  $\mu\text{mol Kg}^{-1}$ ) versus equilibrium concentration ( $C_e$ ,  $\mu\text{mol l}^{-1}$ ). These isotherms data ( $C_s$  and  $C_e$ ) were fitted to the logarithmic form of the Freundlich equation:

$$\log C_s = \log K_f + n_f \log C_e \quad (1)$$

and the capacity ( $K_f$ ) and intensity ( $n_f$ ) adsorption parameters were calculated.<sup>12</sup>

## RESULTS

The adsorption isotherms of 2,4-D on the soils studied were mostly of *L* type, although some of them displayed certain *S* character (soils No. 1 and 19) and also certain *C* character (soils No. 8 and 20) according to the isotherms classification of Giles *et al.*<sup>15</sup> Some of these isotherms are shown in Figure 1. Except some soils, as 3 and 6, most isotherms did not show to reach a "plateau" displaying a continuous increase of adsorption with solute concentration, in the range of concentration studied. Regardless of their diverse shapes all the adsorption isotherms fitted very well the logarithmic Freundlich equation (1). From this equations the parameters  $K_f$  and  $n_f$  were calculated. The values of  $K_f$  are the amount adsorbed at unity equilibrium concentration<sup>12</sup> which is considered as a measure of the relative adsorption capacity of soils and  $n_f$  is the intensity factor of the adsorption. These calculated parameters for 2,4-D adsorption on selected soils are summarized on Table 3. Using the regression of the Eq. 1 for each soils, other two adsorption capacity values were calculated at equilibrium concentration of  $4.5 \mu\text{mol l}^{-1}$  ( $C_{s4.5}$ ) and of  $30 \mu\text{mol l}^{-1}$  ( $C_{s30}$ ).  $C_{s4.5}$  was calculated in order to have a value being comparative with other authors' data, most of them were  $K_f$  for  $C_e = 1 \text{ ppm}$ <sup>16-19</sup> and  $C_{s30}$  as a measure of the adsorption capacity for high loading of 2,4-D. From the Freundlich  $K_f$  values, the adsorption capacity on the basis of soil organic matter,  $K_{om}$ , was also calculated. All the above parameters are summarized on Table 3 which also includes the correlation coefficients obtained for the Freundlich equation fitting.

The relationships between adsorption of 2,4-D and soil properties were determined by analysis the simple correlation between adsorption capacity parameters ( $K_f$  and  $C_{s30}$ ) and selected soil properties. The correlation coefficients found by this analysis are summarized on Table 4, considering the soils in three different groups: (1) All 22 soils together, (2) Soils of permanent charge with  $\text{Fef}$  (free iron oxides)  $< 5\%$  (soils No. 1-11) and (3) Soils of variable charge with  $\text{Fef} > 5\%$  (soils No. 12-22). The soils were thus considered according to their clay mineralogy (Table 2): Soils No. 1-11 had phyllosilicates (minerals of permanent negative charge) as essential clay components, whereas soils No. 12-22 had iron oxides (minerals of variable surface charge) as major clay components.

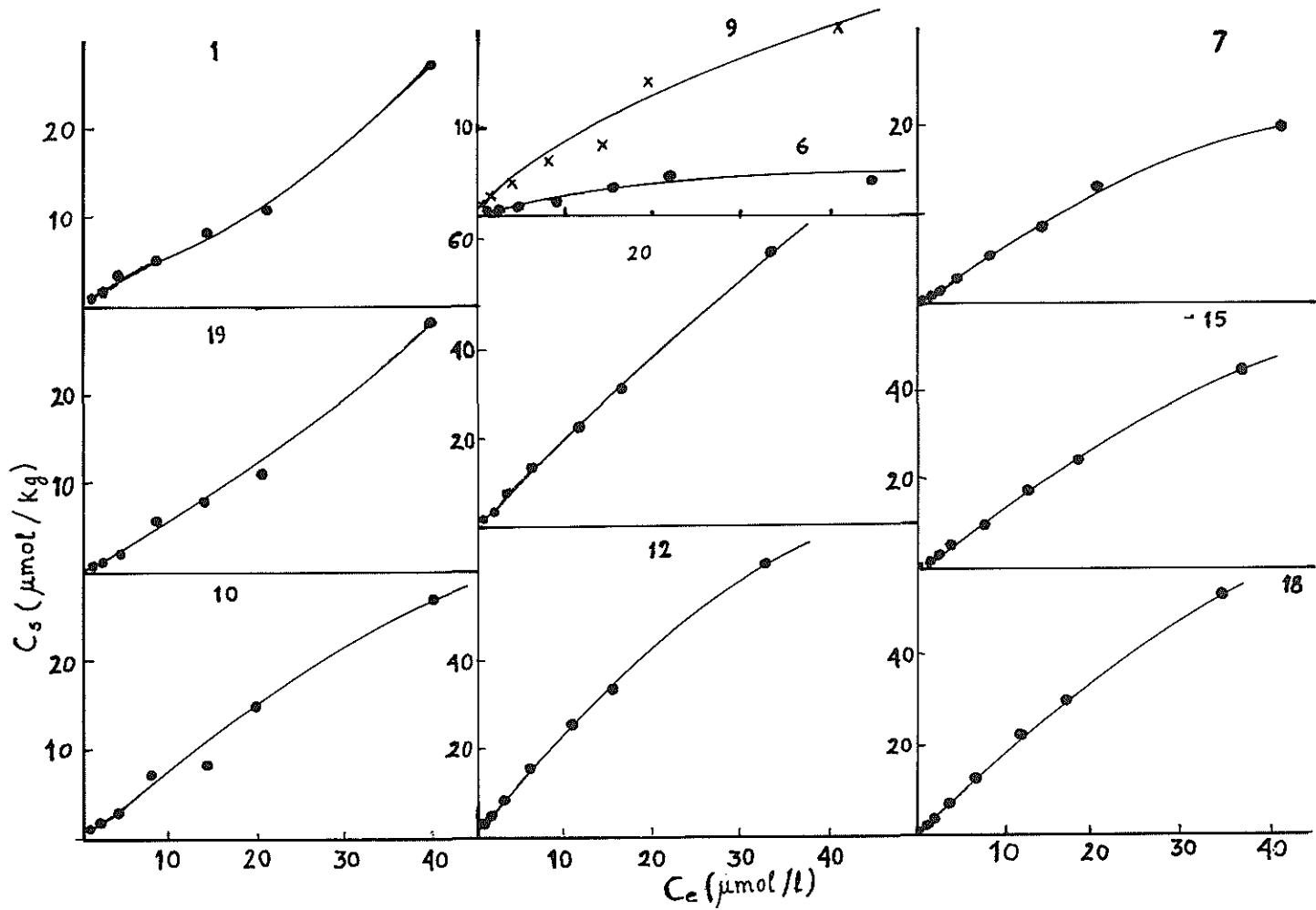


Figure 1 Adsorption isotherms of 2,4-D on some of selected soils.

**Table 3** Freundlich adsorption capacity (Kf, Cs4.5 and Cs30) and intensity (nf) parameters for 2,4-D adsorption on selected soils and the respective correlation coefficients

Soil number	Kf	Cs4.5	Cs30	Kom <sup>a</sup>	nf	r
	$\mu\text{mol Kg}^{-1}$					
1	0.82	3.24	18.24	18.51	0.91	0.992
2	0.37	1.42	7.83	15.35	0.99	0.990
3	0.16	0.91	8.18	8.46	1.16	0.943
4	0.62	0.38	13.27	36.90	0.90	0.990
5	0.53	1.97	10.19	51.40	0.87	0.992
6	0.18	0.74	4.47	20.45	0.95	0.980
7	0.77	2.99	16.58	45.56	0.90	0.993
8	0.30	1.42	9.88	20.68	1.02	0.970
9	0.77	3.25	19.25	34.68	0.96	0.993
10	0.93	3.62	20.01	76.23	0.90	0.996
11	0.78	3.34	20.92	221.82	0.97	0.999
12	3.08	11.64	62.19	65.53	0.88	0.999
13	1.43	5.55	30.60	44.68	0.90	0.998
14	1.14	4.70	28.06	97.43	0.94	0.998
15	1.64	0.39	38.70	39.51	0.93	0.999
16	0.43	1.82	11.36	53.08	0.96	0.998
17	0.41	1.41	6.73	85.41	0.82	0.966
18	2.20	8.82	50.75	647.05	0.92	0.998
19	0.68	2.87	17.71	80.95	0.96	0.996
20	2.23	9.28	55.99	67.78	0.95	0.999
21	0.99	4.13	24.84	—	0.95	0.999
22	2.06	4.92	34.09	—	1.02	0.999

<sup>a</sup>Kom = (Kf/%OM) × 100.

## DISCUSSION

The diverse shape of the isotherms obtained for 2,4-D on the soils considered were indicative that non unique mechanisms was operating in the sorption process, corresponding to a heterogeneous adsorbent as it is the soil surface. The relative adsorption capacity for low (Kf), medium (Cs4.5) and high (Cs30) 2,4-D concentration presented a wide range of variation, whereas the intensity factor, nf, resulted very homogeneous and close to the unity. The results of our study were generally consistent with previous results of other authors: our Cs4.5 (which ranked with the Kf values of other authors obtained at Ce = 1 ppm) were similar to those reported by Moreale and Van Bladel<sup>18</sup> on Belgium soils and Amonette and O'Connor<sup>17</sup> and lower than those of Lokke<sup>19</sup> for Danish soils. However, taking into account that our soils were two units of pH higher than those reported by the above authors, the adsorption of 2,4-D on our soils resulted higher than expected.

From a general comparison of the mineralogical properties (Table 2) and Kf, Cs4.5 and Cs30 values (Table 3) it was observed that soils with high content of iron oxides (Fef > 5%, No. 12–22) had higher adsorption capacity for 2,4-D, as expected from the adsorption studies on goethite.<sup>20,21</sup> However, this variable, Fef, as a measure of the iron minerals of soils has not been allowed for in previous

**Table 4** Correlations coefficients between the adsorption capacity (Kf or Cs30) and the selected soils properties

	<i>Sand</i>	<i>Silt</i>	<i>Clay</i>	<i>OM</i>	<i>CEC</i>	<i>S<sub>BET</sub></i>	<i>pH</i>	<i>Ca</i>	<i>Fef</i>
<i>Kf</i>									
All soils	0.387	0.241	-0.524 <sup>c</sup>	0.668 <sup>a</sup>	-0.333	-0.458 <sup>c</sup>	-0.471 <sup>c</sup>	-0.526 <sup>c</sup>	0.440 <sup>c</sup>
Soils of Fef < 5 %	0.616 <sup>c</sup>	-0.254	-0.732 <sup>c</sup>	0.203	-0.340	-0.594 <sup>d</sup>	-0.522 <sup>d</sup>	-0.732 <sup>c</sup>	0.562 <sup>d</sup>
Soils of Fef > 5 %	0.519	-0.281	-0.641 <sup>c</sup>	0.856 <sup>a</sup>	0.110	-0.250	-0.033	-0.062	-0.013
<i>Cs30</i>									
All soils	0.338	0.336	-0.702 <sup>a</sup>	0.605 <sup>b</sup>	-0.422 <sup>d</sup>	-0.509 <sup>c</sup>	-0.462 <sup>c</sup>	-0.565 <sup>b</sup>	0.541 <sup>b</sup>
Soils of Fef < 5 %	0.716 <sup>c</sup>	-0.360	-0.819 <sup>b</sup>	0.178	-0.518	-0.766 <sup>b</sup>	-0.547 <sup>d</sup>	-0.752 <sup>b</sup>	0.712 <sup>c</sup>
Soils of Fef > 5 %	0.348	-0.130	-0.695 <sup>c</sup>	0.787 <sup>b</sup>	-0.010	-0.278	0.038	-0.568 <sup>d</sup>	0.137

Kf=Amount adsorbed for Ce=1 μmol l<sup>-1</sup>.

Cs30=Amount adsorbed for Ce=30 μmol l<sup>-1</sup>.

<sup>a</sup>P < 0.001.

<sup>b</sup>0.001 < P < 0.01.

<sup>c</sup>0.01 < P < 0.05.

<sup>d</sup>0.05 < P < 0.1.

studies, of 2,4-D adsorption. On another hand, the  $K_{om}$  values were not independent of the soil considered, by the contrary they present a wide variability (Table 3) indicating that the organic matter of the soil was not the only factor controlling the retention of 2,4-D.

The results obtained from the simple regression analysis (Table 4) showed that the soils properties related to 2,4-D adsorption capacity changed with the groups of soils considered. For all 22 soils the adsorption capacity was favoured by organic matter and free iron content and was decreased by the pH, surface area and clay content. The levels of fitting of these relationships between 2,4-D adsorption and soil properties changed slightly from low to high 2,4-D concentrations. The direct relationship between adsorption capacity for 2,4-D and organic matter content of soils has been shown by other authors with different degree of fitness which in our case was similar to that reported by Moreale and Van Bladel.<sup>18</sup> The other soil properties related to 2,4-D adsorption had lower significative level ( $P > 0.05$ ) except at high 2,4-D concentration (Cs 30) where the maximum fitness correspond to the inverse relationship with clay content. This has not been reported previously.

If we considered the 22 soils divided into two groups according to their clay mineralogy, different relationships between soil properties and 2,4-D adsorption resulted as showed on Table 4. For soils with low iron minerals content and phyllosilicates as essential clay components (soils No. 1–11) organic matter content was not related to 2,4-D adsorption which was favoured by sand and free iron contents and low surface, clay and calcium contents. The fitting level of these relationships was much better for high concentration, indicating that for high loading of 2,4-D the iron minerals content of a soil or sediment play an important role on the sorption process. This fact has been mentioned by Artiola–Fortuny and Fuller<sup>22</sup> for nitrophenol adsorption on subsurface soils, but they did not report the amount of free iron content of their soils. For the other 11 soils of high iron content (soils of variable charge, No. 12–22) the only factor related to 2,4-D adsorption was the organic matter, although some negative influence of clay content at low 2,4-D concentration and of calcium at high 2,4-D concentration were observed.

From the above considerations, taking into account the soil properties related to the adsorption capacity for 2,4-D at the maximum significative level, that could be calculated as follows:

1) For all soils,

$$\text{—At low concentration: } K_f = 0.33 + 0.33 \text{ OM} \quad (2) \quad (r^2 = 0.45)$$

$$\text{—At high concentration: } C_s 30 = 43.83 + 0.55 \text{ CLAY} \quad (3) \quad (r^2 = 0.49)$$

2) For soils of permanent charge or with phyllosilicates as essential clay minerals,

a) Negatively related,

$$\text{—At low concentration: } K_f = 1.08 - 0.01 \text{ CLAY} \quad (4) \quad (r^2 = 0.53)$$

$$K_f = 0.97 - 0.01 \text{ Ca}^{++} \quad (5) \quad (r^2 = 0.53)$$

$$\text{—At high concentration: } C_s 30 = 25.80 - 0.42 \text{ CLAY} \quad (6) \quad (r^2 = 0.67)$$



2) Positively related,

—At low concentration:  $K_f = 0.41 + 0.01 \text{ SAND}$  (7) ( $r^2 = 0.38$ )

$K_f = 0.16 + 0.19 \text{ CLAY}$  (8) ( $r^2 = 0.31$ )

—At high concentration:  $Cs_{30} = 9.86 + 0.17 \text{ SAND}$  (9) ( $r^2 = 0.51$ )

$Cs_{30} = 2.65 + 5.10 \text{ Fef}$  (10) ( $r^2 = 0.50$ )

c) For soils of variable charge or with iron oxides as major clay components,

—At low concentration:  $K_f = 0.58 + 0.39 \text{ OM}$  (11) ( $r^2 = 0.73$ )

—At high concentration:  $Cs_{30} = 2.65 + 5.10 \text{ OM}$  (12) ( $r^2 = 0.62$ )

The negative influence of pH and calcium observed in all cases, except for soils of variable charge, was indicative that 2,4-D adsorption should occur preferentially as molecular form whereas the anionic form, which is favoured at high pH and calcium content, had less affinity for the soil surfaces specially in soils with high content of phyllosilicates where the negatively charged surfaces are predominant. For that very reason a negative correlation coefficient was found between  $K_f$  or  $Cs_{30}$  and the clay content (Table 4). It is interesting to note that the soil factors determining 2,4-D adsorption resulted very different than those previously reported for a cationic and a non ionic pesticides by these same soils.<sup>10-13</sup>

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