

## Prediction of the Adsorption of Ionizable Pesticides in Soils

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Adsorption of six acidic and four basic pesticides was measured in nine temperate soils. In general, sorption of acids was weak as compared to bases and followed the order dicamba < metsulfuron-methyl < fluazifop-P < metribuzin < 2,4-D < flupyrsulfuron-methyl < fluroxypyr < terbutryn < pirimicarb < fenpropimorph. Adsorption was negatively correlated with soil pH and positively correlated with organic carbon content. Statistical analysis against a wide range of soil and pesticide descriptors was used to identify the best combination of properties that describes the variation in adsorption. A regression equation including Log *D* (lipophilicity corrected for pH), the soil organic carbon content, and a pesticide descriptor (related to the van der Waals volume) was selected to predict the adsorption of acids ( $r^2 = 72.1\%$  on an independent dataset). The behavior of bases was more complex, and approaches specific to each compound seem to be required.

**KEYWORDS:** Ionic; sorption; Log *D*; herbicide; lipophilicity; hydrophobicity; organic carbon

### INTRODUCTION

Understanding the fate of a pesticide in soil is fundamental to the accurate assessment of its environmental behavior and vital in ensuring the safe use of new and existing products. Sorption is one of the key processes affecting the fate of pesticides in soil and determines their distribution in the soil/water environment. A greater understanding of the factors that influence adsorption of a pesticide underpins the use of existing chemicals as well as allowing predictions for situations where experimental data are not available.

Ionizable pesticides comprise a significant and increasing proportion of the active substances used in Europe, and the formation of acidic metabolites is common during degradation in soil (1). Although this group includes some of the contaminants that occur most frequently in surface and groundwater, approaches to predict their behavior in soils are poorly developed. Ionizable pesticides possess either a basic or an acidic functional group. They can be partially ionized within the range of natural soil pH, and this strongly influences their reactivity in soils. It is essential that this specific behavior is recognized within risk assessment procedures to obtain a robust analysis of likely behavior.

The adsorption of ionizable compounds in soils is strongly influenced by pH, and this effect depends on soil composition and the characteristics of the compound (2). This pH dependence derives mainly from the different proportions of ionic and neutral forms of the pesticide present at each pH level and from differences in their strength of sorption. The influence of varying pH on the charge at the surface of soil particles also plays a role in some cases (2). A decrease in adsorption with increasing pH is often observed. However, bell-shaped curves, increases

in adsorption, and pH-independent behaviors have also been reported (2–7).

Several authors developed equations to predict the sorption of ionizable compounds in soils or sediments (3–7). Different assumptions were made regarding the relationship between the pH and the adsorption of the neutral and ionic forms and the pH-dependent changes to consider in the surface charges or soil components. Unfortunately, the applicability of these models to other systems was rarely demonstrated. Approaches specific to a particular class of pesticide and/or soil type might be necessary to describe the complexity of interactions among ionizable molecules. Experiments in which the pH of a soil is adjusted artificially are useful with respect to experimental design and control, but experiments dealing with a natural pH range will give more realistic results. The two methods have generated conflicting results because the influence of some experimental factors and/or soil properties has superposed and often masked the influence of pH. The standardization of experimental settings (e.g., ionic strength, soil to solution ratio, and method to modify pH) would allow an easier determination of that part of the variance truly attributable to the influence of pH.

The aim of this study was to better understand how soil and pesticide properties influence the adsorption of ionizable pesticides in soils. One of the main concerns was the identification of any particular behavior linked with a pesticide or soil type that would allow a better understanding and a better prediction of the variability in adsorption. First, adsorption coefficients of six acidic and four basic pesticides were measured in nine contrasting arable soils. Results were then submitted to statistical analyses against a wide range of soil and pesticide properties to identify the best combination of properties that describe the variation in adsorption. Finally, approaches to

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**Table 1.** Main Properties of the Nine Arable Soils Studied

	soil texture	vegetation when sampled	pH		clay (%)	silt (%)	sand (%)	OC (g kg <sup>-1</sup> )	C/N	CaCO <sub>3</sub> (%)	CEC (cmol <sup>+</sup> kg <sup>-1</sup> )	Mg (cmol <sup>+</sup> kg <sup>-1</sup> )	P <sub>2</sub> O <sub>5</sub> (g kg <sup>-1</sup> )
			water	1 M KCl									
1	silty clay loam	set aside	8.20	8.02	38.5	48.7	12.8	17.7	9.6	76.40	6.96	0.517	0.043
2	sandy clay loam	wheat	7.81	7.54	25.7	24.8	49.5	32.4	9.1	36.30	16.60	0.613	0.091
3	sandy clay loam	cereals	8.08	7.41	27.5	21.0	51.5	10.8	9.4	0.49	12.90	3.27	0.683
4	sandy clay loam	grass/clover ley	7.91	7.29	34.5	21.5	44.0	20	10.1	0.70	18.10	0.924	0.27
5	sandy clay loam	cereals	6.85	6.27	19.9	26.5	53.6	23.8	10.4	0.09	11.60	1.72	0.243
6	sandy	maize and weeds	7.07	6.46	5.6	4.6	89.8	7.65	12.4	0.21	3.41	0.187	0.242
7	loam	w.wheat	6.89	6.38	23.6	35.7	40.7	16.8	10.5	0.09	10.30	0.492	0.225
8	clay	set aside	5.96	4.87	41.5	33.0	25.5	32.3	11.5	0.09	22.30	6.12	0.214
9	sandy loam	set aside	5.28	4.40	13.5	20.1	66.4	15	11.4	0.09	6.62	0.918	0.264

predict adsorption coefficients were proposed and tested on an independent data set.

## MATERIALS AND METHODS

**Soils.** Nine arable soils were sampled from the top 20 cm in several locations in southern England in July 2004. Soils were selected to give a gradient in pH (pH in 1 M KCl from 4.4 to 8.0) and to have a range in texture (clay content from 5.6 to 41.5%) and organic carbon content (7.6–32.4 g kg<sup>-1</sup>). Soils were sieved to 3 mm, air-dried, and analyzed by the Laboratoire d'analyses des sols (INRA Arras, France) (**Table 1**). The properties were determined as follows: clay (<2 μm), silt (2–50 μm), and sand (50–2000 μm) content; organic carbon and nitrogen content (ISO 10694; ISO 13878); pH in water, 0.01 M CaCl<sub>2</sub> and 1 M KCl (ISO 10390); CaCO<sub>3</sub> content (ISO 10693); P<sub>2</sub>O<sub>5</sub> content (dye method, NF X 31-160); cationic exchange capacity (CEC, Metson method, NF X 31-130); exchangeable Ca, Mg, K (NF X 31-108), and Mn (NF X 31-120); Si, Al, and Fe contents (Tamm method, 8); Al and Fe contents (Merha–Jackson method, 9); total Al and Fe contents (ISO 11885); and total Na content (NF X 31-108). Only those properties shown to have an influence on adsorption of ionizable pesticides are shown in **Table 1**. Subsamples (triplicates of roughly 30 g) were dried overnight at 110 °C to determine soil moisture content of air-dried soils.

**Pesticides and Other Chemicals.** Ten ionizable pesticides were selected, comprising four carboxylic acids, two sulfonylureas, two triazines, one carbamate, and one morpholine (**Table 2**). Pestanal analytical grade standards of 2,4-D, dicamba, fluroxypyr, metsulfuron-methyl, metribuzin, pirimicarb, fenpropimorph, and terbutryn were purchased from Sigma-Aldrich (Seelze, Germany), fluzifop-P was supplied by Syngenta (Bracknell, United Kingdom), and flupyr-sulfuron-methyl was supplied by E.I. DuPont de Nemours (Wilmington, DE). Fluroxypyr is applied in the field as fluroxypyr-meptyl, which is rapidly hydrolyzed to the parent acid (half-life in soil–water slurries = 2–5 h at pH 6–7 and 22–24 °C, 10), so fluroxypyr was directly applied to the soils in this study. Similarly, the first metabolite of fluzifop-P-butyl (fluzifop-P) was used because the DT<sub>50</sub> of the former was less than 24 h in soils (10). On the basis of pre-experiments (data not shown), it was assumed that no competition effects operate at low concentration. Pesticides were paired (fluroxypyr with fluzifop-P, metribuzin with pirimicarb, and fenpropimorph with terbutryn) and studied together by high-pressure liquid chromatography (HPLC) and gas chromatography with mass spectrum detection (GC-MS). Details are provided in **Table 3**. Radiolabeled 2,4-D was purchased from American Radiolabeled Chemicals Inc. (St. Louis, MO), dicamba was from Izotop Institute of Isotopes Co., Ltd. (Budapest, Hungary), and metsulfuron-methyl and flupyr-sulfuron-methyl were supplied by E.I. DuPont de Nemours. All organic solvents were HPLC grade (Fisher Scientific, United Kingdom).

More than 700 two-dimensional properties were calculated for each pesticide using Dragon Web Version 3.0 (Talete srl, Milan, Italy). The neutral and ionic forms of ionizable compounds have different polarities. Because their ratio varies with pH, the lipophilicity of ionizable pesticides is pH-dependent. Lipophilicity profiles (Log *D*) represented the shift in the octanol/water partition coefficient with pH as a consequence of dissociation. The decrease in Log *D* with pH was

measured for each acid using the pH metric method (GLpKa, Sirius Analytical Instruments Ltd.; 11). The method consists of determining the dissociation constant (p*K*<sub>a</sub>) by titration before and after the addition of octanol. The partitioning of the compound between water and octanol shifts the apparent p*K*<sub>a</sub>. The shift is then interpreted to calculate Log *D* at each pH.

**Measurement of Sorption.** Sorption coefficients were determined at one concentration on nine different soils and with four replicates using a standard batch equilibrium method (12). Considering the application rates in the field and incorporation in the upper 2.5 cm of the soil profile, all experiments were carried out at 2 mg 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 kg<sup>-1</sup>) to ensure consistency with a parallel degradation study (13). Soil suspensions in 0.01 M CaCl<sub>2</sub> were prepared in 50 mL PTFE centrifuge tubes (Oak Ridge centrifugation tube, FEP by Nalgene Nunc International). Soil to solution ratios were chosen according to the strength of sorption reported in the literature. A ratio of 1:25 (w:w) was used for terbutryn and fenpropimorph, while the other pesticides were studied at a ratio of 1:2 (w:w). After a pre-equilibration period of 14 h on a side-to-side shaker (300 oscillations min<sup>-1</sup>), the soil suspensions were spiked with a minimal amount of pesticide solution in 0.01 M CaCl<sub>2</sub> (0.2–0.5 mL, mixture of labeled and unlabeled when radiolabeled compounds were used) and returned to shaking until pseudo-equilibrium was reached. A 72 h equilibration period was chosen based on a pre-experiment measuring adsorption between 12 and 120 h in soils 2 and 8 (results not shown). Samples were maintained in the dark at 4 °C throughout the procedure to minimize degradation. The samples were then centrifuged at 5000g for 10 min, and the supernatant was analyzed to measure *C*<sub>e</sub> (mg L<sup>-1</sup>), the concentration of pesticide remaining in solution after adsorption. Triplicates without soil were used as reference for *C*<sub>i</sub>, the initial concentration (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*<sub>s</sub> (mg kg<sup>-1</sup>), can be calculated as:

$$C_s = \frac{V(C_i - C_e)}{m_s}$$

where *V* (mL) is the volume of solution in the suspension and *m*<sub>s</sub> is the mass of soil (g). The soil sorption coefficients *K*<sub>d</sub> (mL g<sup>-1</sup>) and *K*<sub>oc</sub> (mL g<sup>-1</sup>) were then calculated as:

$$K_d = \frac{C_s}{C_e}$$

and

$$K_{oc} = \frac{K_d \times 1000}{OC}$$

where OC is the organic carbon content of the soil (g kg<sup>-1</sup>). The pH of the suspension was also measured on blanks without pesticide.

Table 2. Molecular Structures, Uses, and Properties of the Pesticides (Ref 10; www.inra.fr/agritox)

Pesticide name [CAS RN]	Formula	Use and application rate (g ha <sup>-1</sup> )	pK <sub>a</sub> <sup>a</sup>	K <sub>oc</sub> <sup>b</sup> (mL g <sup>-1</sup> )	DTS <sub>50</sub> <sup>c</sup> (d)	Solubility (in water, g L <sup>-1</sup> )	Log P <sup>d</sup>
<b>Acidic compounds</b>							
<b>Carboxylic acids</b>							
2,4-D [94-75-7] (2,4-dichlorophenoxy)acetic acid		Selective systemic post-emergence control of annual and perennial broad-leaved weeds in cereals, maize, sorghum, grassland, orchards, sugar cane, rice, non crop lands (280-2300)	2.97	5-212	5-59	0.6	2.7
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 (100-11200)	1.97	3.5-21	1.4-11	6.5	2.3
fluroxypyr [69377-81-7] [(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy]acetic acid		Post emergence herbicide to control a range of broad leaved weeds in all small grain crops and pasture (200)	2.94	51-81	5-68	0.091	2.2
fluazifop P [83066-88-0] (2 <i>R</i> )-2-[4-[[5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]-propanoic acid		Post-emergence control of wild oats, volunteer cereals and annual and perennial grass weeds in oilseeds rape, sugar beet, potatoes, vegetables, fruits, vines, citrus ornamentals and other broad-leaved crops (125)	2.98	39-84	2-168	0.780	3.1
<b>NHSO<sub>2</sub> acids (Sulfonylureas)</b>							
met sulfuron-methyl [74223-64-6] 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]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 (pH7); 213 (pH9)	1.2
flupysulfuron-methyl [144740-54-5] methyl 2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-6-(trifluoromethyl)-3-pyridinecarboxylate monosodium salt		Selective, post-emergence control of black grass and other weeds in cereals (10)	4.94	15-47	6-26	0.063 (pH5) 0.600 (pH 6)	4.3
<b>Basic compounds</b>							
<b>Triazines</b>							
metribuzin [21087-64-9] 4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4 <i>H</i> )-one		Selective systemic herbicide, predominantly absorbed by roots, for pre- or post-emergence control of many grasses and broad-leaved weeds in soya beans, potatoes, sugar cane, maize and cereals (350-700)	1	9-95	6-377	1.05	1.6 (pH 5.6)
terbutryn [886-50-0] <i>N</i> -(1,1-dimethylethyl)- <i>N'</i> -ethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine		Selective herbicide, used pre-emergence in winter cereals to control blackgrass and annual meadow grass. Also used post-emergence in cereals, sugar cane and maize (1000-2000)	4.3	2000	14-50	0.022	3.65
<b>Others</b>							
pirimicarb [23103-98-2] 2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyl dimethylcarbamate		Selective systemic insecticide used in cereals, fruit, ornamentals, strawberries, potatoes, sugar beet, tobacco and glasshouse crops (70-140)	4.54	290	7-234	3 (pH7.4)	1.7
fenpropimorph [67564-91-4] <i>rel</i> -(2 <i>R</i> ,6 <i>S</i> )-4-[3-(4-(1,1-dimethylethyl)phenyl)-2-methylpropyl]-2,6-dimethylmorpholine		Systemic foliar fungicide with protective and curative action used on cereals (750)	6.98	2772-5943	15-127	0.0043 (pH7)	4.4 (pH 9)

<sup>a</sup> pK<sub>a</sub>, dissociation constant. <sup>b</sup> K<sub>oc</sub>, adsorption coefficient in soils normalized by the organic carbon content. <sup>c</sup> DT<sub>50</sub>, half-life in soil, time required for 50% of the initial dose to be degraded. <sup>d</sup> Log P, octanol-water partition coefficient; indicates the lipophilicity of the compound. Log P was measured for the six acids, whereas data for bases are from the literature.

**Table 3.** Details of Analytical Procedures for the 10 Ionizable Pesticides

HPLC Analysis <sup>a</sup>										
pesticide	purity (%)	HPLC mobile phase	T (°C)	wavelength (nm)	flow rate (mL min <sup>-1</sup> )	injection volume (μL)	column	retention time (min)	detection limit (mg L <sup>-1</sup> )	recovery (%)
fluroxypyr	99.2	ACN:water acidified (0.04% H <sub>3</sub> PO <sub>4</sub> ) (45:55, v:v)	30	200	1	20	Agilent eclipse XDB-C8	2.9	0.02	90–131
fluazifop P	90–93		4.6 × 150 mm, 5 μm	8.8	0.02	97–112				
GC-MS Analysis <sup>b</sup>										
pesticide	purity (%)	T (°C)	helium flow rate (mL min <sup>-1</sup> )	injection volume (μL)	column	mass to charge ratio (m/z)	retention time (min)	detection limit (mg L <sup>-1</sup> )	recovery (%)	
metribuzin	99.3	injector, 250 °C detector, 300 °C	0.7	1	J&W HP5-MS,	198	12.5	0.0092	71–92	
pirimicarb	99.4				30 m × 0.25 mm	166	11.8	0.0036		
fenpropimorph	93.6				i.d., 0.25 μm film	128	13.9	0.0019		
terbutryn	98.7				thickness	226	13.3	0.0053		
LSC Analysis <sup>c</sup>										
pesticide	<sup>14</sup> C position	specific activity (MBq mmol <sup>-1</sup> )	procedure	counting efficiency (%)	detection limit (Bq)					
2,4-D	ring- <sup>14</sup> C	2960.0	the solution to analyse was diluted in 10 mL of ecoscint A scintillation cocktail (National Diagnostics, Hesse, UK)	94–95	1.5					
dicamba	carboxyl- <sup>14</sup> C	693.0								
metsulfuron-methyl	triazine-2- <sup>14</sup> C	703.8								
flupyr-sulfuron methyl	pyrimidine-2- <sup>14</sup> C	739.9								

<sup>a</sup> Agilent 1100 MWD multiwavelength detector. <sup>b</sup> GC, Agilent 6890N; MS detector, HP 5973. <sup>c</sup> Liquid scintillation counter LS 6500, Beckman Coulter Inc., Fullerton, United States. Samples were counted three times for 5 min and were corrected for background using blank controls. Counting efficiency and color quenching were corrected with the external standard ratio method.

**Table 4.** Adsorption Coefficients ( $K_d$ , mL g<sup>-1</sup>) Obtained Using the Batch Technique for Six Acidic and Four Basic Pesticides in Nine Agricultural Soils<sup>a</sup>

soil	2,4-D	dicamba	fluroxypyr	fluazifop-P	metsulfuron-methyl	flupyr-sulfuron-methyl	metribuzin	pirimicarb	fenpropimorph	terbutryn
1	0.77 (0.03)	0.09 (0.02)	0.89 (0.04)	0.48(0.04)	0.15 (0.00)	0.78(0.05)	0.29 (0.02)	2.34 (0.08)	19.75 (2.73)	2.20 (0.79)
2	1.57 (0.14)	0.14 (0.02)	1.89 (0.07)	1.20(0.05)	0.34 (0.05)	1.23(0.11)	1.25 (0.07)	2.37 (0.15)	23.72 (3.23)	5.92 (0.72)
3	0.38 (0.04)	0.08 (0.06)	0.59 (0.02)	0.28(0.02)	0.13 (0.01)	1.02(0.02)	0.33 (0.04)	4.42 (0.41)	43.48 (5.26)	1.70 (0.51)
4	1.19 (0.09)	0.09 (0.04)	1.66 (0.04)	0.76(0.07)	0.28 (0.08)	1.13(0.08)	1.14 (0.19)	3.68 (0.20)	12.93 (2.05)	2.93 (0.37)
5	1.04 (0.09)	0.09 (0.08)	1.42 (0.06)	0.64(0.01)	0.27 (0.00)	1.11(0.03)	0.75 (0.06)	8.19 (1.09)	23.34 (7.96)	5.75 (1.40)
6	0.36 (0.03)	0.07 (0.05)	0.58 (0.02)	0.27(0.02)	0.06 (0.01)	0.39(0.02)	0.07 (0.05)	0.51 (0.03)	4.86 (1.55)	2.76 (0.43)
7	0.66 (0.08)	0.13 (0.14)	0.95 (0.05)	0.51(0.02)	0.23 (0.02)	0.78(0.04)	0.52 (0.04)	2.42 (0.34)	6.67 (0.57)	5.46 (0.58)
8	3.08 (0.14)	0.14 (0.04)	4.39 (0.19)	1.57(0.04)	0.81 (0.03)	3.02(0.21)	2.47 (0.48)	105.35 (7.16)	33.99 (1.89)	15.62 (1.57)
9	1.46 (0.06)	0.04 (0.05)	1.73 (0.16)	0.89(0.12)	0.47 (0.09)	1.40(0.10)	0.58 (0.09)	8.92 (0.57)	3.18 (0.30)	5.08 (0.63)

<sup>a</sup> The value between parentheses is the standard deviation for four replicates.

For basic pesticides, a liquid–liquid extraction of the CaCl<sub>2</sub> supernatant was performed with ethyl acetate (ratio 1:1). After 1 h of shaking (200 oscillation min<sup>-1</sup>), the samples were allowed to stand, and pesticide concentrations in the ethyl acetate supernatant were analyzed by GC-MS.

**Statistical Analysis.** Relationships between adsorption coefficients and soil/pesticide descriptors were investigated using two software packages. The aim was to identify the best combination of properties to describe the variation in adsorption. The three best properties to include in the regression equations were selected with (i) a forward stepwise search with Genstat (starting with no terms in the model, variables are added or dropped according to the residual mean square; Genstat for Windows, seventh edition, organization Rothamsted Research, United Kingdom) and (ii) MobyDigs (software designed to identify an optimal regression model where a large number of potential parameters are available, using a genetic algorithm approach coupled with ordinary least-squares regression; MobyDigs Version 1.0, Talete srl.; 14). Each pesticide and soil was first considered individually. The data for the acids and bases were then integrated, and the software was run again. Finally, the whole data set was considered. The same approach was followed for the descriptors with separate analysis with

soil descriptors, pesticide descriptors, and finally all descriptors considered together.

## RESULTS AND DISCUSSION

**Adsorption Coefficients ( $K_d$ ).** In general, sorption of the acids was weak as compared to the bases, broadly following the order dicamba < metsulfuron-methyl < fluazifop-P < metribuzin < 2,4-D < flupyr-sulfuron-methyl < fluroxypyr < terbutryn < pirimicarb < fenpropimorph (**Table 4**). The adsorption coefficient normalized to the organic carbon content of the soil ( $K_{oc}$ ) is usually much less variable than  $K_d$  for a given hydrophobic molecule (15), and this parameter is widely used for comparing pesticide binding in soil. The normalization of adsorption coefficients to the clay content ( $K_{clay}$ ) has also been proposed for polar and ionic pesticides (16). In this study,  $K_{oc}$  and  $K_{clay}$  values varied significantly between soils ( $p < 0.001$ ). This confirms that the  $K_{oc}$  or  $K_{clay}$  approaches are not suitable for ionizable compounds.

Adsorption coefficients were plotted against the pH in KCl and organic carbon content (OC) of the soils (**Figures 1** and



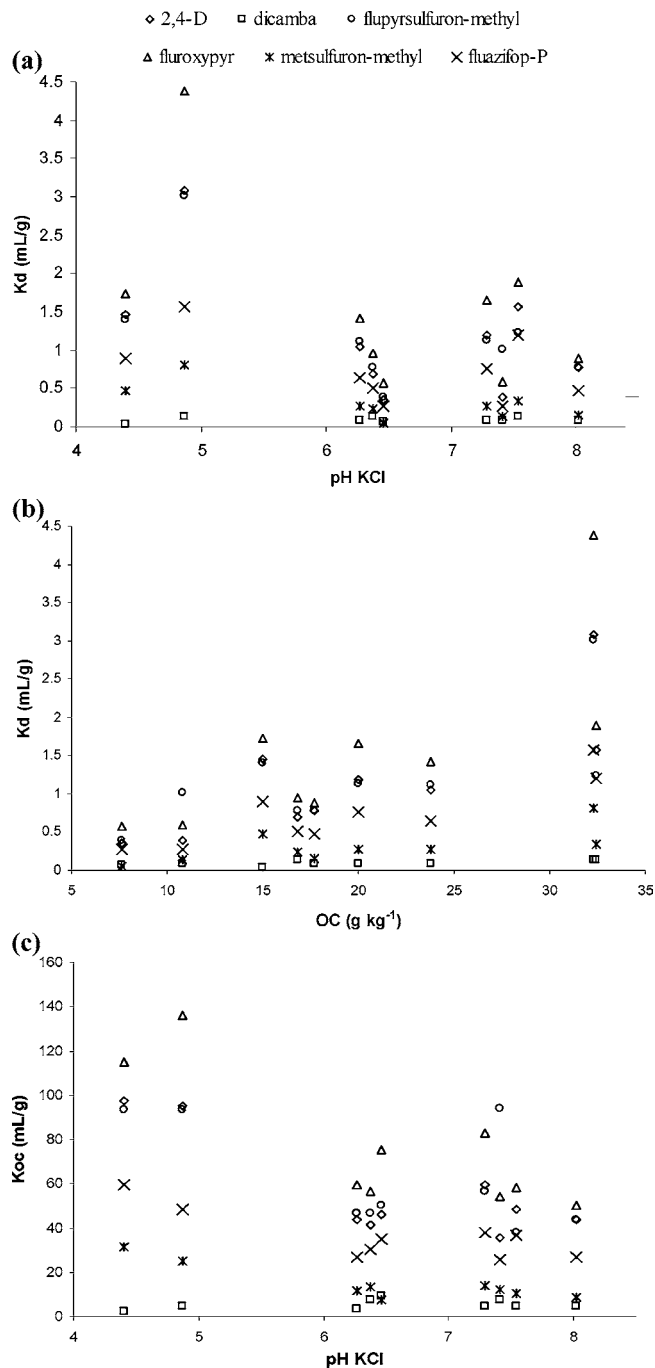
2). Those are the two soils properties expected to have the greatest influence on the fate of ionizable compounds in soils (2). Adsorption was generally stronger in soils with lower pH and containing more organic carbon. There were weak but significant correlations between  $K_d$  values and pH KCl ( $r = -0.385$ ,  $p < 0.001$  for the six acids;  $r = -0.219$ ,  $p < 0.01$  for the four bases) and between  $K_d$  and OC ( $r = 0.513$ ,  $p < 0.001$  for the acids;  $r = 0.329$ ,  $p < 0.001$  for the base).

Four measurements of soil pH were initially considered (i.e., pH determined in 0.01 M  $\text{CaCl}_2$ , in 1 M KCl, in water, and in the soil suspension just before centrifugation). pH KCl provided the widest range and was the most strongly correlated with  $K_d$ . This is probably because pH KCl is a measure of surface acidity ( $\text{K}^+$  extracts  $\text{H}^+$  ions present at the surface of soil particles) and provides a measure of the total potential acidity of a soil (active and exchangeable pools of acidity, 17). This measure seems to be a better indicator for the dissociation of ionizable compounds in soil than an apparent acidity measurement (e.g., pH of a soil suspension). Therefore, only pH KCl was selected for further analysis.

A negative effect of pH on the sorption of ionizable pesticides has frequently been reported, and plots of  $K_d$  against pH resembling dissociation curves have been observed in experiments in which the pH of a soil was adjusted artificially (18–21). The comparison of soils representing a range of native pH is expected to provide more realistic information on the behavior of a compound. However, variations in other soil properties, such as OC, counterbalance the effect of pH and make the interpretation of the results more difficult. Soil 8 has a large organic carbon content (Table 1) resulting in strong adsorption for all pesticides (Table 4). This explains why a peak in adsorption appears at pH 4.87 on the plot of  $K_d$  vs pH (Figure 1a). The plot of  $K_{oc}$  (instead of  $K_d$ ) against pH eliminates a major part of the influence of organic matter and thus distinguishes the part of variation attributable to other factors such as pH.

For each acid,  $K_{oc}$  was stronger in soils with low pH (Figure 1c). The plots do not perfectly fit the shape of a dissociation curve, probably because the organic matter in each soil type has different characteristics and/or because adsorption depends on other soil parameters. Sorption of some acids at  $\text{pH} > \text{pK}_a + 2$  is not negligible although 99% of the pesticide should be in the anionic form. This suggests that (i) some anions might adsorb even though they are generally repulsed by negatively charged soil surfaces and/or that (ii) neutral species still exist at  $\text{pH} > \text{pK}_a + 2$ , presumably because some surfaces or microenvironments of the soil matrix have lower pH than the bulk solution (2). The anionic form of acidic pesticides can strongly interact with the positively charged surface of oxides. However, no influence of oxides contents (Al and Fe extracted with the Merha–Jackson method) on the adsorption of acids could be observed. This is probably because the soils studied were formed in a temperate area where the relatively high concentration of organic compounds prevents the formation of oxides in soils.

The influence of pH and OC on the adsorption of basic compounds is less apparent than for the acids (Figure 2a,b). The adsorption of fenpropimorph seems independent from these two parameters, and correlations between its sorption and OC or pH are not significant. Fenpropimorph has a very different molecular structure and a much higher volatility than the other basic compounds studied, and this might result in a particular behavior and/or experimental artifacts, respectively. Although no clear influence of pH on  $K_{oc}$  can be noticed for metribuzin,



**Figure 1.** Plots of  $K_d$  ( $\text{mL g}^{-1}$ ) against pH KCl (a), OC ( $\text{g kg}^{-1}$ ) (b), and  $K_{oc}$  ( $\text{mL g}^{-1}$ ) against soil pH KCl (c) for the six acids.

pirimicarb, or fenpropimorph, a peak in adsorption is observed for terbutryn. This type of pH influence is sometimes observed for basic compounds and was previously reported for terbutryn in experiments in which the pH was modified artificially (18, 22).

Basic compounds are known to interact with the soil clay fraction, and significant correlations were observed between  $K_d$  and clay content for the four bases. Correlations with clay content were nevertheless weaker than with OC content (except for fenpropimorph), and plotting  $K_d$  against the clay content gives evidence that this soil parameter is not the primary factor controlling adsorption in this set of soils.

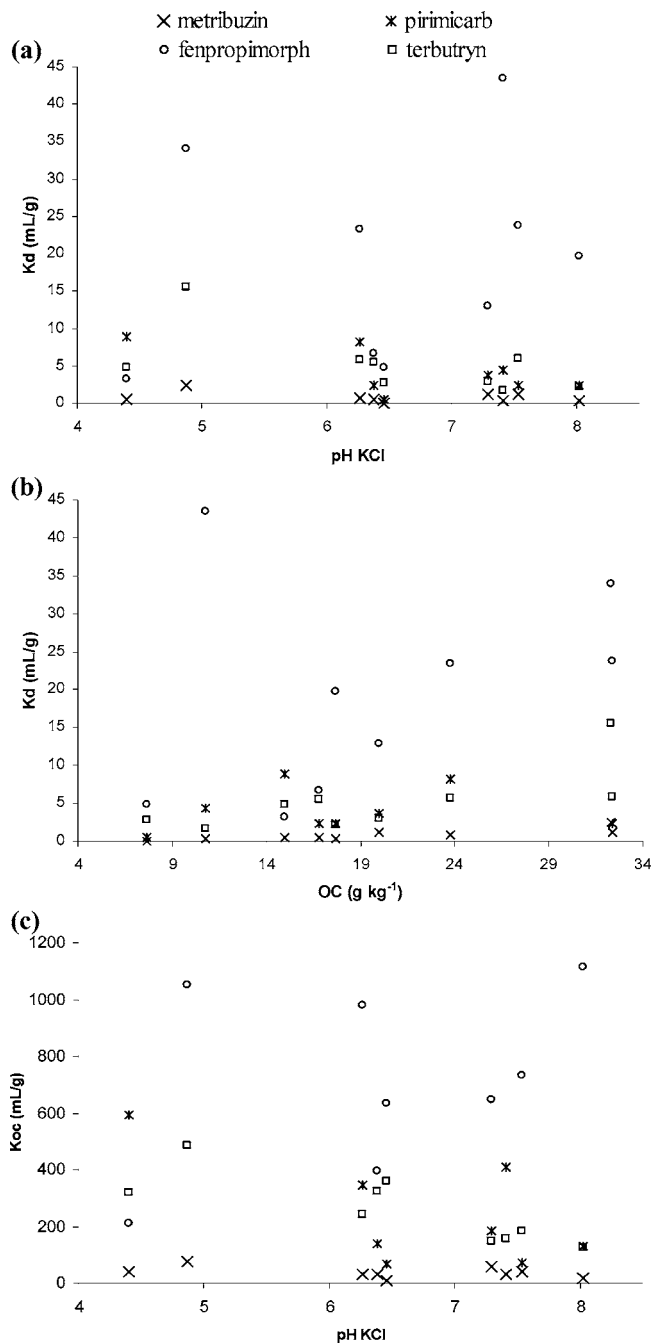
A first analysis of the results confirmed the influence of OC and pH on the adsorption of ionizable compounds. It also

suggested that other parameters are needed to predict the variability in adsorption between soils and pesticides.

**Multivariate Analysis.** Two software packages were used to select the best combination of parameters, among 26 soil and 762 pesticide properties, to explain the variability in adsorption. Each pesticide and soil was considered individually before combining the data for acids, bases, and for all the pesticides. Separate analyses were also undertaken with soil and pesticide descriptors and with both combined. The main results from the analysis are given in **Table 5**. Regression coefficients are generally large even when only soil properties are considered. The low level of adsorption of dicamba makes the determination of adsorption difficult and prone to error, and this probably explains the low regression coefficients obtained for this compound. Results obtained with the Genstat package were generally similar to those obtained with MobyDigs (results not shown). Differences in the parameters selected and the generally lower regression coefficients obtained with the Genstat package can be attributed to the sequential nature of the stepwise approach. Indeed, the selection of new variables is conditioned on the variables already selected. The number of models examined is thus restricted as compared to the genetic algorithm approach that examines all possible models. Better predictions were generally obtained for  $\text{Log } K_d$  than for  $K_d$  probably because  $\text{Log } K_d$  gives a narrower range of values.

Different combinations of soil properties were generally selected for the different pesticides, but some trends can be identified. The lipophilicity of each compound corrected for soil pH ( $\text{Log } D$ ) was selected for four of the six acids studied, one basic compound, and when all acids, all bases and all pesticides were considered together. It seems therefore to be the major determinant of the variability in adsorption. Soil OC content and CEC give a measure of the quantity of sorption sites of each soil, and one of these two properties was selected for almost all pesticides. Metsulfuron-methyl and flupyr-sulfuron-methyl are sulfonylurea herbicides. The soil parameters selected to predict their adsorption (phosphorus content, exchangeable magnesium, and sodium content) differ from those for the four carboxylic acids. A link between phosphorus content ( $\text{P}_2\text{O}_5$ ) and sorption of ionizable pesticide has not been reported previously, and the reason why this soil property has been selected for almost all pesticides is unclear. Nevertheless,  $\text{Log } D$  appeared within the ten strongest predictors selected by the software. The content of exchangeable magnesium (Mg) was selected for the two sulfonylureas and for the basic compounds as an important parameter influencing adsorption. This is probably because sorption was particularly strong in soil 8 due to a high OC content combined with a low pH. This soil also has much more exchangeable magnesium than the other soils (6.12 as compared to an average of  $1.64 \text{ cmol}^+ \text{ kg}^{-1}$ ). Exchangeable magnesium is unlikely to have a direct effect on adsorption.

Regression coefficients decreased significantly when several pesticides were grouped so the same procedure was then applied with pesticide properties and each soil to determine whether a particular behavior could be deduced from the characteristics of the pesticide (results not shown). The pesticide properties were too numerous to be included in the Genstat package, and only MobyDigs was used for this purpose. The pesticide properties selected were different for each soil and did not generate any mechanistic explanation. Regression coefficients were generally large, but this was probably attributable to the great number and variety of molecular descriptors available. Finally, all descriptors were included in the analysis and the data set was split between acids and bases.



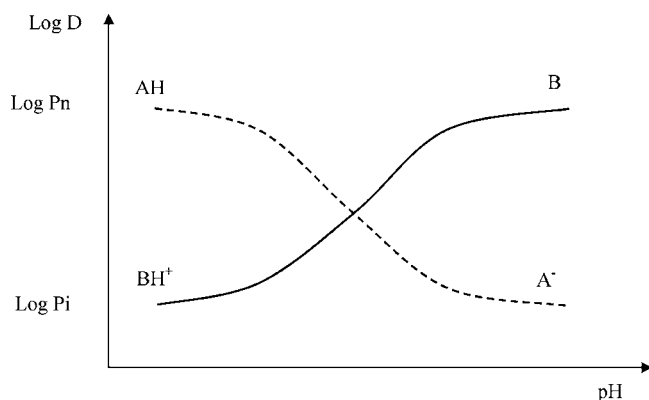
**Figure 2.** Plots of  $K_d$  ( $\text{mL g}^{-1}$ ) against pH KCl (a), OC ( $\text{g kg}^{-1}$ ) (b), and  $K_{oc}$  ( $\text{mL g}^{-1}$ ) against soil pH KCl (c) for the four basic compounds. Outliers for pirimicarb:  $K_d = 105$  ( $\text{mL g}^{-1}$ ),  $K_{oc} = 3262$  ( $\text{mL g}^{-1}$ ) in soil 8 (pH 4.87, OC = 32.3). Outliers for fenpropimorph:  $K_{oc} = 4026$  ( $\text{mL g}^{-1}$ ) in soil 2 (pH 7.41, OC = 10.8).

**Equation to Predict the Adsorption of Acids.** When all descriptors were considered together,  $\text{Log } D$  and OC were selected as the best predictors for the adsorption of acids (**Table 5**). Better predictions were obtained for  $\text{Log } K_d$  than for  $K_d$ , and to be consistent with linear free energy relationships, the OC content was transformed to logarithmic values as well. Several authors previously used the partition coefficient between octanol and water to predict hydrophobic partitioning of neutral compounds (23, 24) as well as ionizable compounds such as dichlorprop (25) and 2,4-D (26). The neutral and ionic forms of ionizable compounds have different polarities. Because their ratio varies with pH, the lipophilicity of ionizable pesticides is pH-dependent. For acids,  $\text{Log } D$  decreases with increasing pH

**Table 5.** Best Predictors for Sorption Variability (Expressed as  $K_d$  and Log  $K_d$ ) Selected by the MobyDigs Package<sup>a</sup>

	soil properties selected for $K_d$	$r^2$	soil properties selected for Log $K_d$	$r^2$
2,4-D	Log $D$ , CaCO <sub>3</sub> , CEC	0.961	P <sub>2</sub> O <sub>5</sub> , CEC, Al	0.953
dicamba	Log $D$ , OC	0.161	CaCO <sub>3</sub> , CEC, Al	0.418
fluroxypyr	Log $D$ , CEC, K	0.946	pH, CEC, Al	0.969
fluzifopP	Log $D$ , OC, Ca	0.952	P <sub>2</sub> O <sub>5</sub> , CEC, Al	0.957
metsulfuron-methyl	P <sub>2</sub> O <sub>5</sub> , Mg, Na	0.911	sand, pH, Ca	0.953
flupyrsulfuron-methyl	P <sub>2</sub> O <sub>5</sub> , Mg, Na	0.961	CaCO <sub>3</sub> , CEC, K	0.939
all acids	Log $D$ , Ca	0.119	Log $D$ , OC	0.397
metribuzin	pH, CEC, K	0.931	clay, OC, Na	0.922
pirimicarb	C/N, P <sub>2</sub> O <sub>5</sub> , Mg	0.979	Log $D$ , Al, Fe	0.972
fenpropimorph	pH, C/N, Mg	0.791	C/N, Mg, Na	0.862
terbutryn	CaCO <sub>3</sub> , P <sub>2</sub> O <sub>5</sub> , Mg	0.912	OC, CaCO <sub>3</sub> , Si	0.919
all bases	Mg, K	0.303	Log $D$ , OC, K	0.412
all pesticides	Log $D$ , CEC	0.159	Log $D$ , OC, Al	0.554
	all properties for $K_d$	$r^2$	all properties for Log $K_d$	$r^2$
all acids	Log $D$ , OC, nCs	0.710	Log $D$ , OC, GATS7v	0.906
all bases	CaCO <sub>3</sub> , Mg, BELp1	0.458	OC, Mg, BELv3	0.821
all pesticides	Mg, ATS1 m, ATS8e	0.360	OC, CIC2, JGI3	0.838

<sup>a</sup> ATS1m, Broto–Moreau autocorrelation of a topological structure – lag 1/weighted by atomic masses; ATS8e, Broto–Moreau autocorrelation of a topological structure – lag 8/weighted by atomic Sanderson electronegativities; BELp1, lowest eigenvalue 1 of Burden matrix/weighted by atomic polarizabilities; BELv3, lowest eigenvalue 3 of Burden matrix/weighted by atomic van der Waals volumes; CIC2, complementary information content (neighborhood symmetry of two-order); GATS7v, Geary autocorrelation – lag 7/weighted by atomic van der Waals volumes; JGI3, mean topological charge index of order three; and nCs, number of total secondary C (sp<sup>3</sup>).

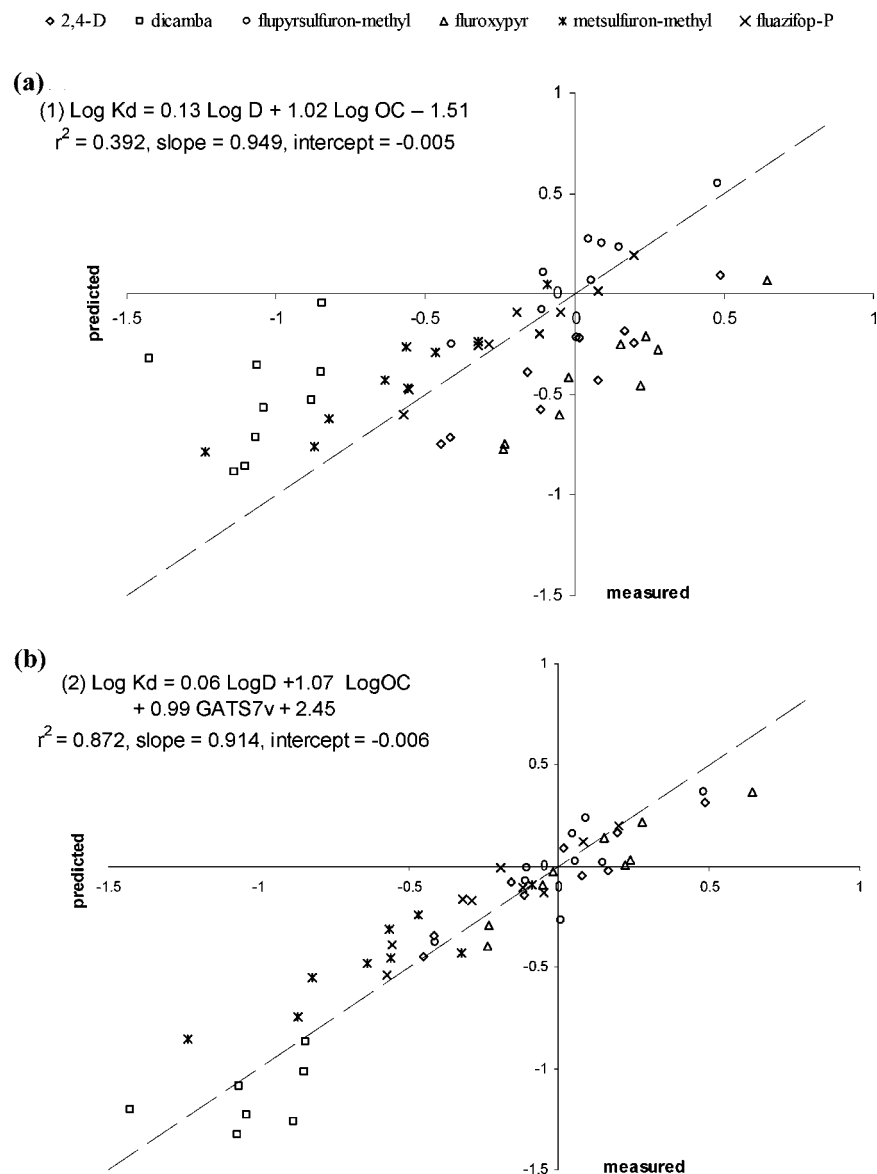


**Figure 3.** Variation in lipophilicity (Log  $D$ ) with pH for acids (dashed line) and basic compounds (plain line). Log  $P_n$  and Log  $P_i$  are the lipophilicities of the neutral and ionic form, respectively. [AH] and [BH<sup>+</sup>] are the protonated forms and [A<sup>-</sup>] and [B] are the dissociated forms of the acidic and basic compounds, respectively. For acids: Log  $D = \text{Log} [10^{(\text{Log } P_n + 10^{-(\text{Log } P_i + \text{pH} - \text{p}K_a)})} - \text{Log} [1 + 10^{(\text{pH} - \text{p}K_a)}]$ .

as the proportion of anionic species increases. For bases, Log  $D$  increases with pH since the dominant form at pH > pK<sub>a</sub> is neutral (**Figure 3**). 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 and negative for bases (for which the cation adsorbs more strongly than the neutral form). When several pesticides are considered together, Log  $D$  also allows ranking of pesticides according to their intrinsic tendency for hydrophobic partitioning. In this case, the relationship between  $K_d$  and Log  $D$  is always positive. Log  $D$  can thus be used to predict the adsorption of acids that mainly occurs through hydrophobic partitioning, but it is unsuitable for bases.

Finally, two regression equations are proposed to predict the adsorption of acids in soils. When tested on our set of data, eq 1 that includes Log  $D$  and Log OC described a large part of the variation in adsorption (**Figure 4a**). The inclusion of the pesticide parameter GATS7v (Geary autocorrelation – lag 7/weighted by atomic van der Waals volumes) significantly improved the description (eq 2, **Figure 4b**). In combination with other pesticide descriptors, van der Waals volume has been used previously to predict the  $K_{oc}$  of 14 carbamates and 12 triazines (27, 28) and to distinguish compounds that are found in groundwater from those that are not (29). Adsorption on hydrophobic constituents of OM can be explained either in terms of solute partition between water and organic matter (solvent-motivated sorption, described by Log  $D$ ) or in terms of solute adsorption (sorber-motivated, physical adsorption by van der Waals interactions, 2). Although it is not fully understood, the GATS7v parameter might describe the propensity of an organic compound to adsorb to OM by van der Waals interaction and thus explain the part of sorption that is not explained by Log  $D$ .

The two equations were then tested on an independent data set of adsorption coefficients comprising seven acidic pesticides (three common to both data sets: 2,4-D, metsulfuron-methyl, and dicamba; and four independent phenoxy acids: MCPA, 2,4,5-T, dichlorprop, and mecoprop-P) and 36 temperate soils sampled in France and the United Kingdom [ $2.13 < \text{OC} (\text{g kg}^{-1}) < 47.9$  and  $3.43 < \text{pH KCl} < 8.02$ ; 30; **Figure 5**]. Log  $D$  for MCPA, 2,4,5-T, dichlorprop, and mecoprop-P was calculated based on the lipophilicity of the neutral form ( $K_{ow}$ ) estimated by KowWin v.1.67 (31) and using the equation: Log  $D = \text{Log } P_n - \text{Log} [1 + 10^{(\text{pH} - \text{p}K_a)}]$  (with Log  $P_n$ , the lipophilicity of the neutral form). Better predictions were again observed with eq 2 that includes the pesticide parameter related to van der Waals volumes (eq 1,  $r^2 = 0.451$ ; eq 2,  $r^2 = 0.721$ ). Although it requires further validation, this descriptor seems to be a useful indicator for the behavior of organic compounds in soil.



**Figure 4.** Adsorption coefficients measured for the acids ( $\text{Log } K_d$ ) are plotted against the values predicted with two regression equations including the lipophilicity of the compound corrected for soil pH ( $\text{Log } D$ ), the soil organic carbon ( $\text{Log } OC$ ), and the pesticide descriptor GATS7v (Geary autocorrelation – lag 7/weighted by atomic van der Waals volumes). The dashed line is the 1:1 line.

**Equation to Predict the Adsorption of Bases.** When the four bases were considered together, the MobyDigs package selected the parameters OC, exchangeable magnesium, and BELv3 to predict adsorption (Table 5 and Figure 6). Nevertheless, as previously noted, the influence of magnesium content is probably due to the set of soils studied (very high content in soil 8), and because this property is rarely reported in the literature, its relevance is difficult to test on external data sets.

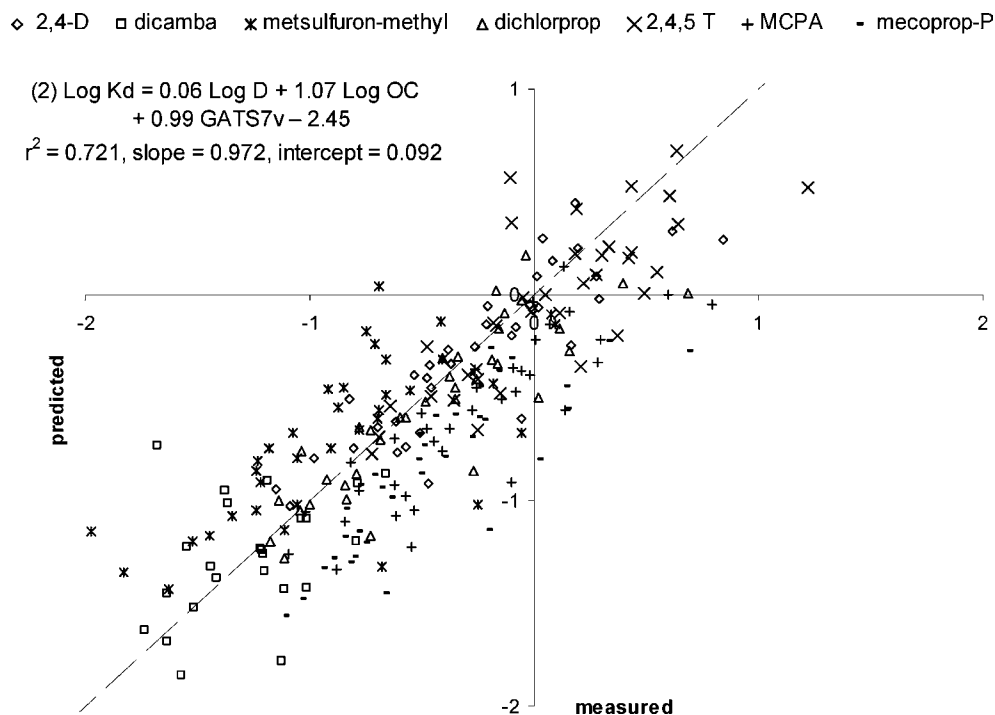
Fenpropimorph had a different behavior relative to the other bases (no significant influence of pH or OC). When this compound was excluded from the data set, the best properties selected for the three bases remaining were then pH, CEC, and BELm8 (lowest eigenvalue 8 of Burden matrix/weighted by atomic masses). The equation that only included the soil properties pH and CEC gave a good match to adsorption data for terbuthryn reported by Barriuso and Calvet (22) but failed to predict sorption of metribuzin (32; Figure 7). In the latter study, clay content was the single best predictor of the adsorption of metribuzin. In contrast to results for the acids, the inclusion of

the pesticide parameter (BELm8) did not improve the match to independent data sets for the bases.

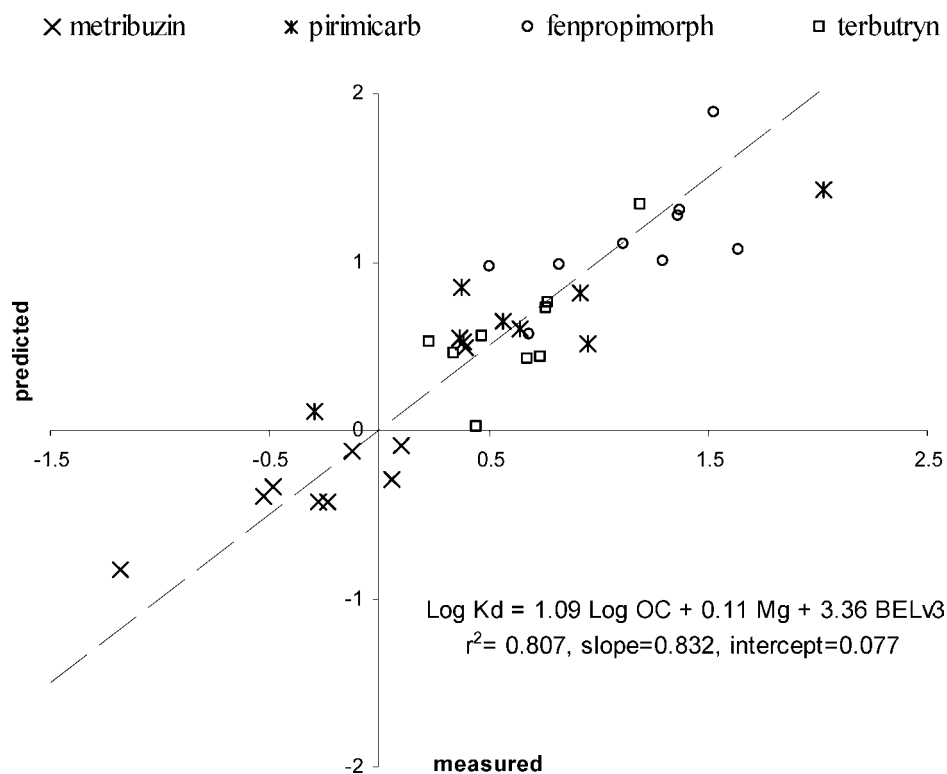
Several authors previously observed high correlations between the adsorption of basic compounds and the soil pH, OC, and clay content (2). However, an equation applicable to a range of basic compounds has not been proposed to date and is not supported by results from the current study. Basic compounds can bind to soil organic and clay fractions through many different mechanisms. The relative importance of one mechanism over another depends on the soil constituents, the molecule, and the chemical environment of the soil. Relatively little experimental evidence is available, and the balance between these processes is not fully understood (2). Equations specific to a particular compound are thus preferred at present.

On the basis of numerous literature data, Weber et al. (33) proposed regression equations to predict the adsorption of several basic compounds. The equation for metribuzin ( $\text{p}K_a = 0.99$ ) included pH, OC, and clay content, whereas the equation for terbuthryn ( $\text{p}K_a = 4.3$ ) only included OC. No equation was





**Figure 5.** External validation of the regression equation including three parameters: lipophilicity of the compound corrected for soil pH (Log *D*), soil organic carbon content (Log *OC*), and pesticide descriptor (GATS7v). The data set comprises adsorption coefficients (Log *K<sub>d</sub>*) measured for seven acids in 36 temperate soils. The dashed line is the 1:1 line.

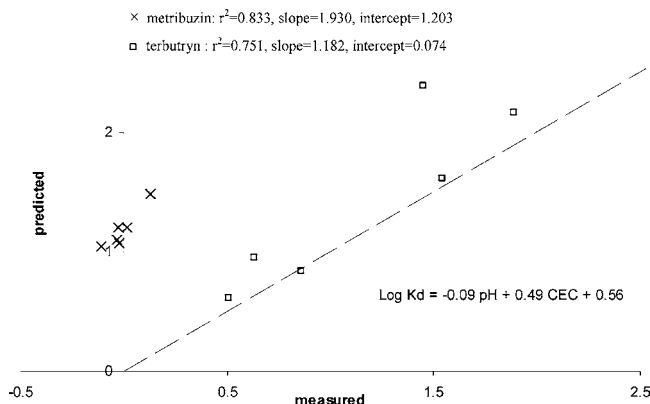


**Figure 6.** Prediction of the adsorption coefficient of four basic compounds using three parameters: the soil organic carbon content ( $\text{g kg}^{-1}$ ), the magnesium content ( $\text{cmol}^+ \text{ kg}^{-1}$ ), and a pesticide descriptors (BELv3). The dashed line is the 1:1 line.

proposed for fenpropimorph or pirimicarb, probably because too few data were available. When applied to our data set, the equations proposed by Weber et al. (33) provided a good match to data for metribuzin ( $r^2 = 0.863$ ,  $p < 0.001$ ) but consistently underestimated sorption for terbutryn ( $r^2 = 0.452$ ,  $p = 0.028$ ) (Figure 8). More experimental data are needed to achieve a greater level of accuracy and to provide equations for other basic compounds.

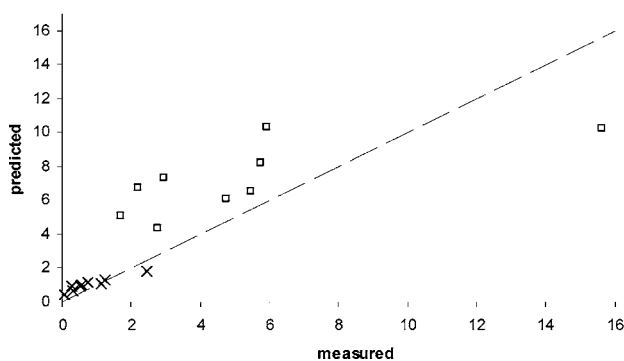
Adsorption of ionizable pesticides tends to be stronger in soils with lower pH and containing more organic carbon. The influence of these two parameters was less apparent for basic compounds than for acids, and results indicate that different approaches are required to predict adsorption for acids and bases.

For the acids, the two strongest descriptors of the variability in adsorption were (i) the lipophilicity of the compound corrected for soil pH (Log *D*) and (ii) the soil organic carbon



**Figure 7.** Prediction of the adsorption coefficient measured for metribuzin (27) and terbutryn (17) with the regression equation including two parameters: soil pH and CEC. The dashed line is the 1:1 line.

$\times$  metribuzin:  $K_d = -0.12 \text{ pH} + 0.18 \text{ OM} (\%) + 0.01 \text{ clay} (\%) + 0.9$ ,  $r^2=0.863$ , slope=0.502, intercept=0.623  
 $\square$  terbutryn:  $K_d = 1.39 \text{ OM} (\%) + 2.5$ ,  $r^2=0.452$  slope=0.355, intercept=5.354



**Figure 8.** Prediction of the adsorption of two bases measured in the current study with the equations proposed by Weber et al. (28). The dashed line is the 1:1 line.

content (OC). A regression equation including these two parameters described a large part of the variability in sorption of the acids ( $r^2 = 0.454$ ). The inclusion of a pesticide descriptor related to the van der Waals volume of the molecule (GATS7v) significantly improved the prediction ( $r^2 = 0.721$ ) but requires further validation. Reliable determination of the lipophilicity of ionizable compounds is still a problem (34), and the value used in any regression equation needs to be either measured or selected from the literature with great care.

The behavior of basic pesticides is more complex than that of acids. This is probably due to the variety of mechanisms likely to retain basic compounds on soil particles. A large part of the variation in adsorption for individual compounds could be explained by variation in the soil CEC and pH. Nevertheless, differences in behavior between bases could not be deduced from molecular properties of the compounds. Approaches specific to each basic compound are required.

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