

Factors Influencing Degradation of Pesticides in Soil

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Degradation and sorption of six acidic pesticides (2,4-D, dicamba, fluroxypyr, fluazifop-P, metsulfuron-methyl, and flupyrsulfuron-methyl) and four basic pesticides (metribuzin, terbutryn, pirimicarb, and fenpropimorph) were determined in nine temperate soils. Results were submitted to statistical analyses against a wide range of soil and pesticide properties to (i) identify any commonalities in factors influencing rate of degradation and (ii) determine whether there was any link between sorption and degradation processes for the compounds and soils studied. There were some marked differences between the soils in their ability to degrade the different pesticides. The parameters selected to explain variations in degradation rates depended on the soil–pesticide combination. The lack of consistent behavior renders a global approach to prediction of degradation unrealistic. The soil organic carbon content generally had a positive influence on degradation. The relationship between pH and degradation rates depended on the dominant mode of degradation for each pesticide. There were positive relationships between sorption and rate of degradation for metsulfuron-methyl, pirimicarb, and all acidic pesticides considered together (all $P < 0.001$) and for dicamba and all bases considered together ($P < 0.05$). No relationship between these processes was observed for the remaining seven individual pesticides.

KEYWORDS: Ionic pesticide; DT₅₀; half-life; sorption; persistence

INTRODUCTION

Alongside sorption, degradation is the second most important process used to predict the fate of pesticides in soils (1). Standard laboratory and field dissipation studies are performed to assess the rate of degradation (often expressed as a first-order half-life or DT₅₀, the time required for 50% of the initial dose to disappear). Rates of degradation are influenced by physico-chemical properties of the soil [such as pH and organic carbon (OC) content], biological properties (activity and distribution of microorganisms), and environmental conditions that control soil temperature and moisture content. Both route and rate of degradation also depend on properties of the chemical. Variability in degradation rate is expected, and numerous studies have provided evidence for field-to-field variation in the degradation rates of pesticides (2). Extrapolation from measurements on a set of soils to prediction for a different soil is a common problem in environmental assessment. A greater understanding of the factors that influence degradation rates is required to support this extrapolation and thus ensure the safe use of new and existing products.

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

processes (3). Although this group includes several important contaminants of 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 affects their reactivity in soils.

Many studies have demonstrated a positive influence of pH on total microbial biomass and activity, although microbial degradation seems to be restricted when pH becomes greater than 8–8.5. Consequently, degradation of many neutral compounds has been shown to be faster at high pH (4). In the case of ionizable compounds, the strength of sorption decreases and the availability for degradation generally increases with increasing pH. There are thus both biological and physical processes underpinning an increase in the rate of degradation with pH for ionizable compounds subject to microbial degradation. However, when abiotic degradation is dominant (e.g., for most sulfonylureas), the pH generally has a negative influence on rates of degradation (4).

Sorption processes may affect biodegradation mainly by modifying chemical bioavailability. A positive relationship between sorption coefficient (K_d) and half-life has been reported for many ionizable pesticides (4). However, several factors might counterbalance the influence of sorption on degradation, and the link between sorption and degradation is not always obvious (5–7). Conflicting results were sometimes observed for the same compounds, and no general trend is apparent at present. Even a weak correlation between sorption and degrada-

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Table 1. Main Properties of the Nine Arable Soils Studied

soil texture UK classification	vegetation when sampled	pH		%			OC ^a (g kg ⁻¹)	C/N ^b	CaCO ₃ (%)	CEC (cmol ⁺ kg ⁻¹)	-33 kPa water content (g water/100 g dry soil)	bioactivity ^c (mg TPF kg ⁻¹ soil)
		water	KCl	clay	silt	sand						
1 silty clay loam	set aside	8.20	8.02	38.5	48.7	12.8	17.7	9.6	76.40	6.96	32.2	202.3
2 sandy clay loam	wheat	7.81	7.54	25.7	24.8	49.5	32.4	9.1	36.30	16.60	28.0	381.4
3 sandy clay loam	cereals	8.08	7.41	27.5	21.0	51.5	10.8	9.4	0.49	12.90	17.7	91.7
4 sandy clay loam	grass/clover ley	7.91	7.29	34.5	21.5	44.0	20	10.1	0.70	18.10	26.9	136.0
5 sandy clay loam	cereals	6.85	6.27	19.9	26.5	53.6	23.8	10.4	0.09	11.60	26.3	113.8
6 sand	maize and weeds	7.07	6.46	5.6	4.6	89.8	7.65	12.4	0.21	3.41	9.7	15.2
7 loam	w.wheat	6.89	6.38	23.6	35.7	40.7	16.8	10.5	0.09	10.30	25.5	99.0
8 clay	set aside	5.96	4.87	41.5	33.0	25.5	32.3	11.5	0.09	22.30	35.5	32.1
9 sandy loam	set aside	5.28	4.40	13.5	20.1	66.4	15	11.4	0.09	6.62	20.1	52.2

^a OC, organic carbon content. ^b C/N, ratio of carbon and nitrogen content. ^c Bioactivity measured on soils sampled in July 2004 after 2 weeks of incubation.

tion greatly influences probabilistic analysis of leaching through soil and reduces the predicted extent of leaching (8). More experiments coupling measurement of sorption and degradation under differing conditions are required to better understand the extent and mechanisms of interactions between these processes.

In the current study, degradation and sorption parameters were determined for six acidic and four basic pesticides in nine contrasting arable soils. Results were submitted to statistical analyses against a wide range of soil and pesticide properties to (i) identify any commonalities in factors influencing rate of degradation and (ii) determine whether there was any link between sorption and degradation processes for the compounds and soils studied.

MATERIALS AND METHODS

The set of soils and pesticides used in this study was previously used in experiments aimed at predicting the sorption of ionizable pesticides in soils. More detailed descriptions of the soils, the pesticides, and the measurement of sorption can be found in ref 9.

Soils. Nine arable soils were sampled from the top 20 cm in several locations in southern England in July 2004 (2,4-D and dicamba degradation study and all sorption experiments), September 2004 (degradation of fluroxypyr, fluzifop-P, metsulfuron-methyl, and flupyr-sulfuron-methyl), and April 2005 (degradation of the four bases). 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 OC content (7.6–32.4 g kg⁻¹; **Table 1**). The soil water content for the incubation was determined with a pressure membrane system for samples of sieved soil loosely repacked into a ring of 1 cm height and 4 cm diameter (roughly 20 g of soil, three replicates). Samples were left in cells under a pressure of -33 kPa until there was no further change in weight. The moisture content was then determined by the difference in weight from oven-dried samples.

Pesticides. Ten ionizable pesticides were selected, comprising four carboxylic acids, two sulfonyleureas, two triazines, one carbamate, and one morpholine (**Table 2**). On the basis of pre-experiments (data not shown), it was assumed that no competition effects operate at low concentration. Pesticides were paired (2,4-D with dicamba, fluroxypyr with fluzifop-P, metsulfuron-methyl with flupyr-sulfuron-methyl, 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). Sorption of the weakly sorbed pesticides (2,4-D, dicamba, metsulfuron-methyl, and flupyr-sulfuron-methyl) was measured using radioisotopes (9). Considering the application rates in the field and incorporation in the upper 2.5 cm of the soil profile with a density of 1, degradation experiments for eight of the pesticides were carried out at 2 mg kg⁻¹. Sulfonyleurea herbicides are applied at very low rates in the field but were studied at a relatively high concentration (1 mg kg⁻¹) to facilitate analysis.

Table 2. Main Properties of the Pesticides (10)^a

Acidic Compounds					
	CAS RN	pK _a ^b	K _{oc} ^c (mL g ⁻¹)	DT ₅₀ ^d (days)	solubility (in water, g L ⁻¹)
carboxylic acids					
2,4-D	94-75-7	2.97	36–97	5–59	0.6
dicamba	1918-00-9	1.97	3–8	1.4–11	6.5
fluroxypyr	69377-81-7	2.94	50–136	5–68	0.091
fluzifop-P	83066-88-0	2.98	26–60	2–168	0.780
NHSO ₂ acids (sulfonyleureas)					
metsulfuron-methyl	74223-64-6	3.75	8–32	4–100	0.548 (pH 7); 213 (pH 9)
flupyr-sulfuron-methyl	144740-54-5	4.94	38–94	6–26	0.063 (pH 5); 0.600 (pH 6)
Basic Compounds					
	CAS RN	pK _a ^b	K _{oc} ^c (mL g ⁻¹)	DT ₅₀ ^d (days)	solubility (in water, g L ⁻¹)
triazines					
metribuzin	21087-64-9	1	9–76	6–377	1.05
terbutryn	886-50-0	4.3	66–3262	14–50	0.022
others					
pirimicarb	23103-98-2	4.54	212–4026	7–234	3 (pH 7.4)
fenpropimorph	67564-91-4	6.98	124–484	15–127	0.0043 (pH 7)

^a Molecular structures and additional properties can be found in Kah and Brown (9). ^b pK_a: dissociation constant ^c K_{oc}: distribution coefficient in soils normalized to the OC content, measured in Kah and Brown (9) ^d DT₅₀: half-life in soil, time required for 50% of the initial dose to be degraded.

Two-dimensional molecular properties were calculated for each pesticide using AdmeWorks ModelBuilder Version 2.1 (Fujitsu Kyushu System Engineering Ltd.). Estimates of degradation potential were included in the list of pesticide descriptors. Six estimates of aerobic biodegradability were determined using BIOWIN (11). The software calculates biodegradation probabilities based on the fragments of a molecule. The parameters Biowin1 and Biowin2 are calculated based upon the fragments derived from a data set of 187 chemicals, through linear and nonlinear regressions, respectively. Biowin5 and Biowin6 are calculated in a similar way, but regressions are based on another data set comprising 884 compounds. Biowin3 and Biowin4 are estimations of the time required for primary (transformation of the parent compound to an initial metabolite) and ultimate biodegradation (transformation to carbon dioxide and water), respectively. They are calculated based on a survey conducted by the U.S. Environment Protection Agency on 200 chemicals. As there is no consensus on the most appropriate estimation method for a particular compound, all six estimates were tested independently. Three DT₅₀ values from the literature were included as well for each pesticide (laboratory, field, and typical half-life reported in the Footprint database; 12).

Table 3. Details of Extraction and Analytical Procedures for the Acidic Pesticides^a

pesticide	purity (%)	extraction (soil: solvent ratio, 1:2, v:v)	HPLC analysis						retention time (min)	detection limit (mg L ⁻¹)	recovery (%)
			HPLC mobile phase	T (°C)	wavelength (nm)	flow rate (mL/min)	injection volume (μL)	column			
2,4-D	99.6	methanol acidified (0.25% H ₃ PO ₄)	ACN:water acidified (0.04% H ₃ PO ₄) (40:60, v:v)	30	202	1	20	Discovery C18, 4.6 mm × 150 mm, 5 μm	4.7	0.01	95–106
dicamba	97.1		ACN:water acidified (0.04% H ₃ PO ₄) (45:55, v:v)	30	200	1	20	Agilent eclipse XDB-C8, 4.6 mm × 150 mm, 5 μm	6.7	0.01	95–106
fluroxypyr	99.2	methanol acidified (1% H ₃ PO ₄)	ACN:water acidified (0.04% H ₃ PO ₄) (45:55, v:v)	30	200	1	20	Agilent eclipse XDB-C8, 4.6 mm × 150 mm, 5 μm	2.9	0.02	90–131
fluzifop-P	90–93		ACN:water acidified (0.04% H ₃ PO ₄) (45:55, v:v)	30	200	1	20	Agilent eclipse XDB-C8, 4.6 mm × 150 mm, 5 μm	8.8	0.02	97–112
metsulfuron-methyl	99.3	ACN:sodium acetate 0.1 M	ACN:water acidified (0.25% H ₃ PO ₄) (50:50, v:v)	25	225	0.5	20	Agilent eclipse XDB-C8, 4.6 mm × 150 mm, 5 μm	5.9	0.02	93–106
flupyr-sulfuron-methyl	99.0	pH 6.5 (75:25)	ACN:water acidified (0.25% H ₃ PO ₄) (50:50, v:v)	25	225	0.5	20	Agilent eclipse XDB-C8, 4.6 mm × 150 mm, 5 μm	12	0.17	59–120

^a Analysis of basic and radiolabeled compounds is described in Kah and Brown (9).

Incubation to Measure Degradation and Analysis. Samples of fresh soil were preincubated for 8 days prior to application of pesticide (moisture content just below -33 kPa, 15 °C, in the dark) to allow germination and removal of seeds and to establish equilibrium of microbial metabolism following the change from sampling or storage conditions to incubation conditions. The period between sampling and the beginning of incubation never exceeded 3 months to comply with OECD guidelines (13).

Technical grade pesticide solution in deionized water (5 mL) was applied dropwise to the equivalent of 200 g of dry soil (three replicates) to reach an initial concentration of 2 mg a.s. kg⁻¹ (1 mg a.s. kg⁻¹ for the two sulfonylureas). When the chemical properties did not allow dissolution in water (terbutryn and fenpropimorph), the pesticides were dissolved in acetone and 0.5 mL of pesticide solution was applied to the soil with a 0.5 mL syringe (Agilent Technology). Soil was thoroughly mixed, and the moisture content was adjusted by weight to exactly -33 kPa. The soil was then transferred to a 500 mL glass flask and incubated at 15 °C in the dark. During the incubation, the moisture content was maintained by weight twice a week and lids were not tightly closed to avoid anaerobic conditions being created. 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 chosen according to half-lives previously reported in the literature for each pair of pesticides. It ranged from 42 (2,4-D/dicamba) up to 119 days (metsulfuron-methyl/flupyr-sulfuron-methyl).

The soil bioactivity was evaluated by measuring the dehydrogenase activity after 2 and 6 weeks of incubation (triplicates). This enzyme is only active in living organisms and thus is an indicator for soil microbial activity (14). Soil samples (5 g) were incubated at 30 °C with 5 mL of colorless TTC solution (0.5% by weight, 2,3,5-triphenyl-2H-tetrazolium chloride, 98%, Avocado Research Chemicals Limited) in 0.1 M tris buffer adjusted to pH 7.6 with HCl [tris(hydroxymethyl)aminomethane, general purpose grade, Merck Science]. TTC is reduced by dehydrogenase enzymes to red water-insoluble TPF (triphenylformazane) and was extracted with 25 mL of acetone after 24 h of incubation. The samples were shaken for 1 h (end-over-end shaker, 22 rpm) and centrifuged at 2500g for 10 min. The intensity of the red color of the supernatant was measured by spectrophotometry at 485 nm (UV-160A, UV-visible recording spectrophotometer, Shimadzu) and converted to bioactivity (mg TPF kg⁻¹) based on a set of TPF standards (1,3,5-triphenylformazane, Sigma-Aldrich Co. Ltd.).

Extraction and quantification of pesticide remaining in soil were undertaken at the end of the respective incubation period. Degradation was measured through the relative decline of residues extracted with an appropriate organic solvent (soil to solution 1:2; see details in Table 3). After 1 h of end-over-end shaking (22 rpm), the samples were allowed to stand until the soil had settled (1 h), and the pesticide concentration in the clear supernatant was determined. Subsamples of supernatant containing metsulfuron-methyl and flupyr-sulfuron-methyl were concentrated two-fold by evaporation under nitrogen flow prior to analysis. Basic pesticides were extracted with acetone. Subsamples of supernatant were evaporated to dryness under nitrogen flow and redissolved in ethyl acetate. Analysis was by HPLC and GC-MS. Details

are provided in Table 3. Nonextractable residues were considered to be degraded, and the extraction efficiency was assumed to remain constant over the course of the experiment.

Three kinetic models were fitted to the degradation curves: a simple first-order equation, a first-order multicompartiment (Gustafson & Holden) model, and a first-order sequential (Hockey-Stick) model (15). Parameters were optimized according to recommendations by FOCUS (15) using the least-squares method with Microsoft Excel Solver. The simple first-order kinetic model always described the data adequately (and often better than the other two models). The first-order rate of degradation and the DT₅₀ (time required for 50% of the initial dose of pesticide to be degraded) of each compound in each soil were determined with the following equations: and

$$C_t = C_o \cdot e^{-rt}$$

$$DT_{50} = \frac{\ln 2}{r}$$

where C_t is the concentration of pesticide remaining in soil (mg kg⁻¹) after t (days), C_o is the initial concentration of pesticide (mg kg⁻¹), and r is the rate of degradation (day⁻¹).

Batch Experiments To Measure Sorption. Sorption coefficients (K_d , mL g⁻¹) were determined at one concentration (similar to the incubation experiment) and with four replicates using a standard batch equilibrium method (16). After a pre-equilibration period of 14 h, soil suspensions in 0.01 M CaCl₂ were spiked with a pesticide solution and returned to shaking for 72 h. The samples were then centrifuged at 5000g for 10 min, and the supernatant was analyzed to measure the concentration of pesticide remaining in solution after sorption. Samples were maintained in the dark at 4 °C throughout the procedure to minimize degradation. A detailed description of the procedure and results can be found in ref 9.

Statistical Analysis. The first objective was to identify the best combination of properties to describe the variation in rates of degradation. For screening purposes, the three best properties to include in the regression equations were selected with MobyDigs Version 1.0 (17), a program 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. A genetic algorithm is a search technique inspired by evolutionary biology that is used to find solutions to optimization and search problems. Essentially, the approach consists of generating populations of possible solutions (in the current case comprising combinations of variables to predict rate of degradation), testing the fitness of these solutions, and then recombining and/or mutating the fitter elements of the population into a successor generation. The process is then reiterated until either a specified number of generations or a predetermined level of fitness is attained. Each pesticide and soil were 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 for soil descriptors, pesticide descriptors, and finally all descriptors

Table 4. DT₅₀ (Days) of Six Acidic and Four Basic Pesticides Measured in Nine Arable Soils^a

soils	1	2	3	4	5	6	7	8	9
2,4-D	2.9 (0.26)	2.6 (0.37)	4.7 (0.52)	5.5 (0.38)	3.0 (0.36)	6.2 (0.56)	3.7 (0.22)	4.6 (0.12)	4.6 (0.36)
dicamba	15.1 (0.68)	7.6 (0.42)	24.2 (0.42)	11.3 (0.44)	9.1 (0.58)	46.1 (1.16)	9.1 (0.67)	8.2 (0.31)	15.0 (0.91)
fluroxypyr	8.6 (0.62)	8.6 (0.27)	13.4 (0.36)	9.9 (0.36)	7.4 (0.81)	21.3 (0.78)	9.2 (0.42)	9.3 (0.33)	6.6 (0.73)
fluzifop-P	6.0 (0.18)	6.1 (0.10)	10.3 (0.37)	6.3 (0.14)	11.3 (0.40)	16.6 (0.76)	7 (0.49)	10.6 (0.80)	13 (0.92)
metsulfuron-methyl	54.4 (0.97)	35.0 (1.11)	89.4 (2.16)	40.9 (1.22)	37.1 (1.05)	175.9 (22.95)	71.8 (3.04)	23.8 (1.30)	35.2 (1.30)
flupyrulfuron-methyl	7.8 (0.42)	7.9 (0.68)	16.1 (1.09)	10.5 (1.53)	21.3 (0.88)	12.2 (1.39)	21.7 (1.40)	7.5 (0.60)	21.5 (5.46)
metribuzin	9.3 (0.31)	10.6 (0.60)	23.3 (1.11)	15.6 (0.60)	16.6 (0.74)	49.4 (2.15)	15.7 (0.70)	21.4 (1.37)	19.5 (0.85)
pirimicarb	12.5 (0.38)	14.4 (0.61)	57.2 (1.77)	20.9 (0.54)	17.1 (0.46)	47.8 (2.05)	7.9 (0.46)	6.6 (0.62)	15.4 (0.55)
fenpropimorph	7.9 (0.27)	8.3 (0.58)	42.1 (3.81)	14.3 (0.75)	44.5 (4.82)	20.6 (2.63)	53.9 (3.34)	30.7 (3.12)	62 (6.33)
terbutryn	8.5 (0.11)	7.1 (0.11)	15.1 (0.55)	8.8 (0.29)	12 (0.35)	56.8 (1.37)	16.6 (0.53)	14.1 (0.47)	22.3 (0.62)

^a The value between parentheses is the standard error associated with the estimation of DT₅₀ with a first-order kinetic model (three replicates).

considered together. Correlation analysis was performed using Genstat for Windows, 7th edition, Rothamsted Research).

RESULTS AND DISCUSSION

There was no initial lag phase on any degradation curve. A lag phase is normally attributed to adaptation of the microbial population. First-order half-lives are reported in **Table 4**. There were some marked differences between soils in their ability to degrade different pesticides. DT₅₀ values for the acids were generally much larger in soil 6; this was probably related to the very weak bioactivity of this soil.

Multivariate Statistical Analysis. The MobyDigs package was used to select the best combination of parameters, among 26 soil and almost 200 pesticide properties, to explain the variability in degradation rate. Each pesticide and soil was considered individually before combining the data for acids, bases, and all the pesticides. Separate analyses were also undertaken with soil and pesticide descriptors and with both combined. When several pesticides were considered, rates of degradation were expressed as a percentage of the median. Main results from the analysis are given in **Table 5**.

Different combinations of soil properties were selected for the different pesticides. The level of microbial activity and the OC content of the soil are known to be essential parameters determining degradation rates. However, these properties were selected relatively infrequently. *R*² values decreased significantly when several pesticides were grouped, and this indicates that soil parameters driving degradation rates depend on the pesticide.

The same procedure was applied with pesticides properties and each soil to determine whether a particular behavior could be deduced from the characteristics of the pesticide (results partially shown in **Table 5**). The combinations of pesticide descriptors selected were different for the different soils. The descriptor ALLP (number of path in the structure) was selected for all soils except soil 6 and when all pesticides were considered together. The parameter describes the topological complexity in a molecule and might be useful to rank pesticides according to their intrinsic degradability. No other pesticide descriptor was common to several soils, and the large regression coefficients are probably due to the great number and variety of parameters available. Calculated biodegradability (BioWin6, BioWin1) and DT₅₀ reported in the literature (typical value, Footprint; 12) were selected as the best parameters to discriminate the pesticides in only three of the nine soils (soils 5, 7, and 9, respectively). This confirms that values from the literature must be used with care since degradation rates strongly depend on both the compound and the soil type.

An equation predicting the degradation of a range of compounds has not been proposed to date and is not supported

Table 5. Best Predictors for Variability in Rate of Degradation Selected by the MobyDigs Package and Regression Coefficients When Three Properties Are Considered^a

	soil properties	<i>r</i> ²
2,4-D	bioactivity, P ₂ O ₅ , Al	0.929
dicamba	pH, Log (OC), Al	0.971
fluroxypyr	Fe, K, Na	0.768
fluzifop-P	clay, Mg, K	0.979
metsulfuron-methyl	bioactivity, OC, Al	0.926
flupyrulfuron-methyl	CEC, Al, Na	0.936
all acids	C/N, P ₂ O ₅ , Mg	0.098
metribuzin	C/N, P ₂ O ₅ , Mn	0.968
pirimicarb	Si, Al, K	0.945
fenpropimorph	Mg, Al, K	0.914
terbutryn	Mg, K, Na	0.985
all bases	bioactivity, sand, P ₂ O ₅	0.463
all pesticides	C/N, P ₂ O ₅ , Mg	0.131
pesticide properties (all soils)		<i>r</i> ²
all acids	N3C, S0, V6P	0.742
all bases	NDB, EDMN	0.690
all pesticides	ALLP2, S6C, EDMX	0.635
all properties (all soils)		<i>r</i> ²
all acids	Log (OC), NATM, V6P	0.801
all bases	Log (OC), CaCO ₃ , ALLP4	0.496
all pesticides	loam, ALLP2, EDMX	0.670
ALLP2	ALLP 1/number of atoms in structure	
ALLP4	ALLP 3/number of atoms in structure	
EDMN	minimum electron density value	
EDMX	maximum electron density value	
N3C	third-order molecular connectivity number	
NATM	number of nonhydrogen atoms	
NDB	number of double bonds	
S6C	sixth order cluster molecular connectivity	
S0	zero-order molecular connectivity	
V6P	sixth order path molecular connectivity valence	

^a Rates were expressed as the percentage of the median when several compounds were considered together.

by results from the current study. The failure of such a global approach (quantitative structure–activity relationship type approach) could be expected considering the complexity of interactions between different processes that influence breakdown of organic compounds in soils. The routes and rates of degradation are influenced by chemical, biological, and physical properties of soils and also depend on the properties of the pesticide. Soil properties are interrelated and may influence these processes in opposite directions, thereby exhibiting a stimulating and restricting effect on the overall degradation process. The dominance of one process over another depends on the soil–pesticide combination and cannot therefore be generalized.

Table 6. Correlation Coefficients between Degradation Rates, Some Soil Properties, and Sorption Coefficients^a

	OC	bioactivity	pH KCl	clay	K_d
2,4-D	0.361	0.618***	0.379	0.280	-0.014
dicamba	0.902***	0.348	-0.210	0.534**	0.387*
fluroxypyr	0.479*	0.266	-0.289	0.205	0.287
fluzifop-P	0.380	0.758***	0.657***	0.606***	0.102
metsulfuron-methyl	0.830***	0.132	-0.500**	0.468*	0.824***
flupyrulfuron-methyl	0.552**	0.454*	0.312	0.621***	0.377
all acidic compounds	0.232**	0.229**	0.090	0.194*	0.295***
metribuzine	0.455*	0.808***	0.520**	0.518**	0.084
pirimicarb	0.600***	-0.028	-0.402*	0.508**	0.668***
fenpropimorph	0.241	0.749***	0.681***	0.295	-0.026
terbutryn	0.639***	0.864***	0.592**	0.639***	-0.019
all basic compounds	0.458***	0.537***	0.303**	0.458***	0.265*
all ionizable pesticides	0.259***	0.275***	0.128*	0.233***	-0.011

^a *, **, and *** indicate a significance at $p < 0.05$, 0.01 , and 0.001 levels, respectively.

Correlation Analysis. Correlations between rates of degradation and main soil parameters were investigated for each pesticide and are reported in **Table 6**. A positive correlation between OC content and degradation rates was observed for most of the pesticides, and a very strong correlation was obtained when all pesticides were considered together (**Table 6**). This relationship is generally seen as the reflection of an enhanced bioactivity in soils with a larger OC content (the OC content and bioactivity were strongly correlated for the set of soils studied here). Any inhibition of degradation due to stronger sorption and thus reduced bioavailability in soils with large OC content was insufficient to overcome the effect of OC on bioactivity. Moreover, sorption to humic substances could facilitate the abiotic transformation of the molecule, reinforcing the positive effect of OC on degradation rate. This effect has been previously shown for metribuzin and its metabolites (18), for azimsulfuron (19), and for triasulfuron (20).

A positive correlation between clay content and degradation rates was observed for most of the pesticides as well. This probably resulted from the very strong correlation between clay and OC contents ($r = 0.550^{***}$), highlighting the difficulty in determining the effect of a single soil parameter on degradation.

Several studies suggest that the determination of the type and activity of degrading microorganisms is necessary to describe the influence of microbial population on dissipation of pesticides (21, 22). Particularly slow degradation was observed in the soil exhibiting the weakest bioactivity (soil 6), and this parameter was strongly correlated with degradation rates for five of the pesticides studied, as well as when all pesticides were considered together. Numerous methods are available to characterize the microbial activity of soils, and the determination of dehydrogenase activity is one of the simplest techniques. Although it provided a good indicator for ranking the soils according to their biodegradation potential, more specific measurements would provide further information.

Many studies have demonstrated a positive influence of pH on total microbial biomass and activity (2, 23), and a very strong positive correlation was observed in the present study as well ($r = 0.619^{***}$). This probably explains the strong positive correlation between pH and degradation rates for fluzifop-P, metribuzin, fenpropimorph, and terbutryn (**Table 6**). A similar influence of pH was previously reported for metribuzin (24). Conversely, pH and degradation rates for metsulfuron-methyl and pirimicarb were negatively correlated. Degradation rates for these two compounds were not correlated to soil bioactivity, and this supports a dominance of abiotic hydrolysis over

biodegradation. The abiotic hydrolysis of sulfonylureas is generally more favored under acidic conditions, and a negative relationship between degradation and pH was reported for chlorsulfuron, prosulfuron, primisulfuron methyl, rimsulfuron, thifensulfuron methyl, and triasulfuron (4). Flupyrulfuron-methyl is a sulfonylurea herbicide as well. However, its hydrolysis was reported to be faster at alkaline pH (25). No significant influence of pH on its degradation was observed in the present study, and this confirms that common rules are difficult to apply, even for chemicals with similar structures.

Link between Sorption and Degradation Processes. There was no statistical relationship between sorption and degradation for most of the pesticides (**Table 6**). Significant correlations were only observed for dicamba, metsulfuron-methyl, and pirimicarb, with faster degradation in soils with stronger sorption. As discussed above, metsulfuron-methyl and pirimicarb seem particularly sensitive to chemical hydrolysis, and sorption onto humic acids might have catalyzed their degradation.

Acidic compounds are generally weakly sorbed in temperate soils, and their sorption might be too weak to counterbalance the effect of OC on degradation through an increase in bioactivity. Indeed, the OC content has a positive influence on both degradation and sorption processes and this might lead to mistaken inference of a positive relationship between sorption and degradation parameters.

Although the sorption of basic compounds was generally much stronger than that of acids, no relationship between sorption and degradation rates could be observed except for pirimicarb. Metribuzin, fenpropimorph, and terbutryn seem to be primarily degraded by microorganisms in this set of soils (strong correlation between degradation and soil bioactivity). The possibilities need thus to be considered as follows: (i) Microorganisms are generally more abundant at, or near, soil particle surfaces (26), and sorption may thus concentrate the pesticide in regions of greatest microbial activity; and (ii) biodegradation might not always be restricted to chemical in solution (27–30).

Beulke and Brown (8) suggested that the effect of sorption on degradation might be dominant if soils with a wide range of OC contents are compared. For instance, a strong positive relationship between K_d and DT_{50} was noticed for metazachlor when studied in 10 plots within the same field [$r = 0.9$, $1.5 < OC (\%) < 6.6$] while no clear relationship appeared when 18 soils were considered [$0.6 < OC (\%) < 2.4$; 31]. Significant relationships between sorption or degradation processes and soil properties are more likely when similar types of soils are compared because the range in other influences on degradation is somewhat restricted. The set of soils considered in the present study does not represent an extreme range in OC content (0.7–3.4%) but it presents large differences regarding texture and pH. These characteristics might not be favorable to emphasize a link between sorption and degradation processes.

Conclusion. There were some marked differences between the soils in their ability to degrade the different pesticides. The parameters selected to explain variations in degradation rates depended on the soil–pesticide combination. Degradation is the result of a complex interaction between different processes, and the lack of consistent behavior renders a global approach to prediction of degradation unrealistic.

On the other hand, a correlation analysis permitted us to identify distinct types of behavior. Metsulfuron-methyl and pirimicarb (and perhaps dicamba) seemed mainly degraded by abiotic acidic hydrolysis. The degradation rates of these three pesticides were positively influenced by soil OC content and

negatively influenced by soil pH. A positive relationship linked their sorption and degradation parameters, probably as a consequence of a catalyzed hydrolysis after sorption onto soil organic matter. In contrast, microbial degradation seemed to dominate the breakdown of 2,4-D, fluzifop-P, flupyr-sulfuron-methyl, metribuzin, fenpropimorph, and terbutryn. As a consequence, degradation rates of those pesticides were very sensitive to soil bioactivity level, positively influenced by soil pH, and not related to sorption. Finally, fluroxypyr had an intermediate behavior, and the influence of soil properties on its degradation was unclear. The dominance of one route of degradation over another strongly depends on the characteristic of the pesticide. Pesticides with similar structures may also behave differently as shown in the current study for the two sulfonylureas.

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