Adsorption of Ionisable Pesticides in Soils

M. Kah and C.D. Brown

Contents

I. Introduction

Pesticides are intensively used in agriculture, and much effort is expended to manage and reduce possible deleterious effects on the environment. The soil compartment has a major influence on the fate and behaviour of pesticides applied to crops preemergence or early postemergence or chemicals subject to washoff from crop surfaces. Once in the soil, pesticide molecules partition between the aqueous and solid phases, which affects many other aspects of their behaviour: sorption can be rate limiting to volatilization, bioavailability (and thus efficacy and biodegradation rate), and subsurface transport. Understanding the fate of a pesticide in soil is fundamental to the accurate assessment of its environmental behaviour and vital in ensuring the safe use of new and existing products. It is also necessary to develop and validate computer simulation models for use as predictive tools in future environmental fate assessments.

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It is estimated that ionisable compounds comprise 25% of the existing active substances currently undergoing review for reregistration by the European Union (EU 2002). Also, a significant and increasing proportion of new actives proposed for registration are ionisable, including most sulfonylureas, and the formation of acidic metabolites is common during degradation processes (EU 2002). Ionisable herbicides (e.g., phenoxy acids, triazines, sulfonylureas, imidazolinones) are particularly common and represent the largest major group of soil-applied herbicides (Harper 1994). This group includes chemicals that are frequently found in groundwater and surface waters worldwide. Among the 15 main molecules quantified in surface and groundwater in France in 2002, 8 were ionisable compounds (IFEN 2002). This category represented up to half of the pesticides detected in surface and drinking water samples in Hungary (Győrfi et al. 1998).

Among the 9 pesticides most frequently exceeding $0.1\,\mu g/L$ in surface fresh waters in the UK between 1998 and 2003, 6 were ionisable (mecoprop, MCPA, 2,4-D, dichlorprop, simazine, and atrazine). Similarly, 7 of the 10 pesticides exceeding threshold concentrations in UK groundwater in 2003 were ionisable (Environment Agency 2003). Atrazine and simazine were among the three most frequently detected pesticides in groundwater collected from wells of agricultural areas in the US (USEPA 1990) and Portugal (Cerejeira et al. 2003).

Ionisable compounds possess either weak acidic and/or basic functional group(s). As a consequence, they may be partially ionised within the range of normal soil pH, which strongly affects their soil reactivity. The adsorption of neutral organic compounds in soils occurs mainly by hydrophobic partitioning, whereas a number of additional mechanisms are postulated for the adsorption of ionisable pesticides. It is essential that this specific behaviour is recognised within risk assessment procedures to obtain a robust analysis of likely behaviour.

Several reviews are available on the adsorption of organic chemicals in soils (Calvet 1989; Harper 1994; Von Oepen et al. 1991; Wauchope et al. 2002). These reviews mainly covered the behaviour of hydrophobic compounds in soils, which is now relatively well understood. Relatively less information was available concerning ionisable pesticides. Although similar levels of information are available concerning the sorption of ionisable pesticides, there is still much debate regarding the underlying mechanisms and the approaches to describe and predict variation in sorption with properties of the pesticide and of the soil. Numerous articles reported results of adsorption of ionisable pesticides in soils in the past 15 years. The purpose of this review is to present the state of knowledge on the particular behaviour of ionisable pesticides in soils.

The review first introduces the issues concerning adsorption and the characteristics of this particular kind of pesticide. The mechanisms postulated for their adsorption are described. Subsequently, it focuses on the

influence of soil properties on adsorption and on the potential to predict the behaviour of ionisable pesticides in soils. We concentrate particularly here on those soil factors that do not particularly influence the adsorption of neutral compounds but which often have a great importance for the sorption of ionisable pesticides (soil pH, clay and oxide contents). Finally, it briefly reviews degradation of ionisable compounds in soil and evidence for its dependence on the adsorption process.

II. Background

A. Ionisation

A weakly acidic compound dissociates in water to produce protons. Thus, it exists in both anionic and neutral forms in aqueous solutions. The relative amounts of each form are determined by the acid equilibrium constant, K_a, and the pH of the aqueous solution. Assuming activity coefficients to be near unity, this equilibrium may be represented as:

$$[HA] + [H_2O] \rightleftharpoons [A^-] + [H_3O^+] \quad \text{with } K_a = [H_3O^+] \cdot [A^-]/[HA]$$
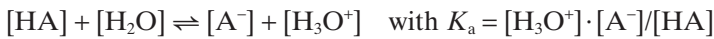
where $[H_3O^+]$, $[A^-]$, and $[HA]$ are defined as the aqueous concentration of hydronium ion (or proton), anionic species, and neutral species, respectively (all in mole L^{-1}).

In addition,

$$pK_a = -\log_{10} K_a \quad \text{and} \quad pH = -\log_{10} [H_3O^+]$$

which gives

$$[HA]/[A^-] = 10^{(pK_a - pH)}$$

This gives the ratio of the neutral species to the anion as a function of pH and shows the increasing dominance of the anion at higher pHs (Fig. 1).

A weakly basic compound dissociates in water to produce OH^- or is a compound that can accept a proton (Brønsted definition). Thus, it exists both in cationic and neutral form in solution. As for acidic compounds, a basic equilibrium constant, K_b, can be defined:

$$[B] + [H_2O] \rightleftharpoons [BH^+] + [OH^-] \quad \text{with } K_b = [OH^-] \cdot [BH^+]/[B]$$
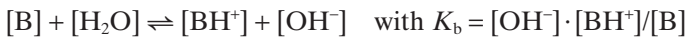
where $[OH^-]$, $[BH^+]$, and $[B]$ are defined as the aqueous concentration of the hydroxide ions and positive and neutral species, respectively (all in mole L^{-1}). The ratio of cationic to neutral species in solution can also be calculated according to the pH of the solution. However, it is now more usual to describe the strength of bases also in terms of K_a and pK_a, thereby establishing a single continuous scale for both acids and bases. To make this possible, our reference reaction for bases becomes the equilibrium:
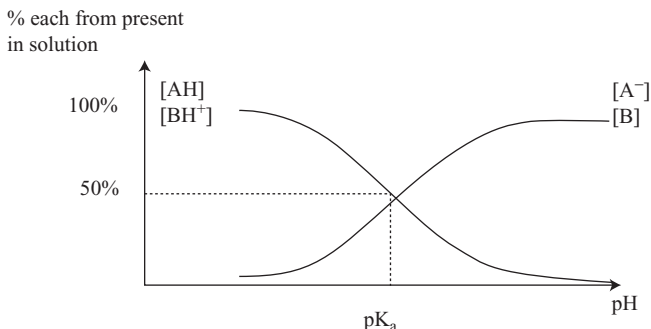
% each from present
in solution

Fig. 1. Dominance of neutral or ionic form in solution according to the pH, assuming that the activity coefficient is near unity. [AH] and [BH$^+$] are the protonated form, [A$^-$] and [B] the dissociated form, of the acidic and basic compounds, respectively. With [AH] the concentration of the protonated form of an acid and pK_a, its dissociation constant: $[AH] = \dfrac{1}{1+10^{pH-pK_A}}$.

$$[BH^+] + [H_2O] \rightleftharpoons [B] + [H_3O^+] \quad \text{with } K_a = [B] \cdot [H_3O^+]/[BH^+]$$
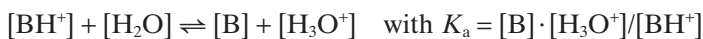
Here, K_a is a measure of the acid strength of the conjugate acid BH$^+$ of the base B. The stronger BH$^+$ is as an acid, the weaker B will be as a base (pK_a + pK_b = 14).

A zwitterion is an ion that has a positive and negative charge on the same group of atoms. Zwitterions can be formed from compounds that contain both acidic and basic groups in their molecules. For example, imazethapyr is an ampholytic compound due to the presence of both carboxyl (pK_a = 3.9) and basic quinoline groups (pK_a = 2.1). As pH decreases, the imazethapyr molecule will be alternatively negatively charged (COO$^-$; N), neutral (COOH; N), and then positive (COOH; NH$^+$). As for acidic and basic compounds, it is possible to determine the ratio of each form at a given pH. See Table 1 for examples of ionisable pesticides and their main characteristics.

It is important to notice that compounds with a very low/high pK_a dissociate at pH not relevant to the soil environment. Therefore, only one type of species is present in the soil solution for the range of natural soil pH. The behaviour of this kind of ionisable compound is unlikely to be sensitive to soil pH. Ionic pesticides (e.g., diquat, paraquat) whose charge is not dependent on pH shifts are not considered in this review.

B. Measurement of Soil pH

Soil pH values are usually determined in 1:5 soil:liquid suspension (in water, 0.01 M CaCl$_2$ or 1 M KCl according to ISO 10390; 1994), but it is known that the pH at soil surfaces may be lower than in the bulk solution.

Indeed, according to electrical double-layer theory, the net negative charge at soil surfaces is compensated by cations held in a diffuse layer close to the surface. Some of the excess of cations in the diffuse layer over those in bulk solution will be hydrogen ions, and so pH close to soil surfaces is lower than that in bulk solution (Talibudeen 1981).

Hayes (1970) assumed that the pH at the surface of humic substances might be 0.5 to 2 units lower than that of the liquid phase, or that localised areas of low pH could exist within soil organic matter (OM). Bailey et al. (1968) reported that the pH at a montmorillonite surface appears to be 3 to 4 units lower than the pH of the bulk solution. Moreover, decreasing water content increases the conversion of NH_3 to NH_4^+ on the surface of clay minerals (Raman and Mortland 1969); this is caused by the enhanced ionization of water molecules in the solvation spheres of adsorbed inorganic cations at lower water contents (greater Brønsted acidity). Therefore, Che et al. (1992) proposed that the protonation of imazaquin and imazethapyr by clay mineral surfaces would also be greatly enhanced at lower water content, which implies that dissociation could occur in the field at higher pH than in batch conditions and that pH effects could thus be stronger under field conditions. Thus, significant surface protonation of a basic or acidic molecule may occur even though the measured pH is greater than the pK_a of the compound.

This phenomenon complicates the examination of pH effects on the retention of ionisable compounds on soil surfaces. A consequence is that although sorption versus pH curves for ionisable pesticides resemble the sigmoidal shape of acid dissociation curves, they are often positioned about 1.8 pH units more alkaline than the pK_a curve (Nicholls and Evans 1991a). Another way to interpret this phenomenon has been given by Feldkamp and White (1979), who concluded that ionization of weak bases such as triazines can be modified by an adsorbent phase, or as a consequence of adsorption. The equilibrium is displaced toward the formation of BH^+, and thus the amount adsorbed is greater than the amount deduced from the pK_a value. This explanation was also proposed for adsorption of atrazine and simazine on clay by Celis et al. (1997a) (cf. III. C).

The difference in pH between soil particle surfaces and soil solution is mediated by soil characteristics such as the charge of soil particles and the type and quantity of cations present in solution. There is thus no general rule on the relative difference. For instance, Regitano et al. (1997) obtained a reasonable agreement between a model and measured sorption data, and concluded that the pH measured in the bulk soil solution was representative of the pH encountered by the herbicide imazaquin at the sorbent surface. Current techniques for measuring pH do not allow the observation of these specific phenomena at sorbent surfaces. Thus, further research is needed to better understand and determine the pH at soil interfaces.

Table 1. Molecular Structures, Uses, and Properties for Examples of Ionisable Pesticides (Source: Tomlin 1997; www.inra.fr/agritox).
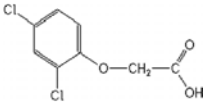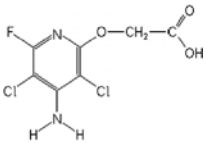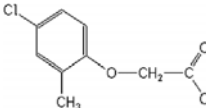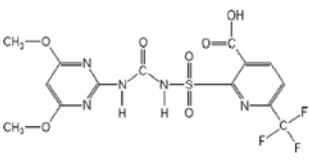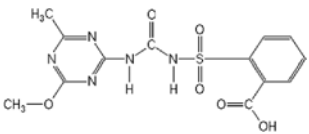
Pesticide name [CAS RN]	Formula	Use and application rate (g ha^{-1})
Acidic compounds **Carboxylic acids** 2.4-D [94-75-7]		Herbicide on cereals, maize, sorghum, grassland, orchards, sugar cane, rice, noncrop lands (280–2300)
Fluroxypyr [69377-81-7]		Control of a range of broad-leaved weeds in all small grain crops and pasture (200)
Mecoprop [7085-19-0]		Hormone-type herbicide for the control of broad-leaved weeds in wheat, barley, oats, grassland, and pasture (1200–1500)
MCPA [94-74-6]		Hormone-type herbicide for the control of broad-leaved weeds in cereals, rice, peas, potatoes, grassland, turf, roadside, and embankments (3000)
NHSO$_2$ acids Flupysulfuron-methyl-sodium [144740-54-5]		Selective control of black grass and other weeds in cereals (10)
Metsulfuron-methyl [74223-64-6]		Control of a wide range of annual and perennial broad-leaved weeds in wheat, barley, rice, and oats (4–7.5)

Table 1. *Continued*

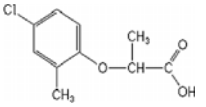| pK_a	K_{oc} (mL g^{-1})	DT$_{50}$ (d)	Solubility (in water, g L^{-1})	Log P
2.97	5–212	5–59	0.6	−1 (pH9) 2.7 (pH1)
2.94	51–81	5–68	0.091	156 (pH4) 0.23 (pH10)
3.11	5–43	7–13	>250	−0.19
3.73	10–157	7–79	294	2.7 (pH1) −1.07 (pH9)
4.94	15–47	6–26	0.063 (pH5) 0.600 (pH6)	0.06 (pH6)
3.75	4–60	4–100	0.548 (pH7); 213 (pH9)	−1.7 (pH7)

Table 1. *Continued*

Pesticide name [CAS RN]	Formula	Use and application rate ($g\,ha^{-1}$)
Flumetsulam [98967-40-9]		Control of broad-leaved weeds and grasses in soya beans, field peas, and maize (10–20)
Other acids Mesotrione [104206-82-8]		Control of broad-leaved and some grass weeds in maize (70–225)
Basic compounds **Triazines** *Chlorotriazines* Atrazine [1912-24-9]		Control of annual broad-leaved weeds and annual grasses in maize, sorghum, sugar cane, grassland, conifers, industrial weed control (750–1000)
Simazine [122-34-9]		Control of most germinating annual grasses and broad-leaved weeds in pome fruit, stone fruit, bush and cane fruit, citrus fruit, vines, strawberries, nuts, olives, pineapples, cocoa, coffee (1500 in EU to 3000 in tropics and subtropics)
Methylthiotriazines Prometryn [7287-19-6]		Selective systemic herbicide on cotton, sunflowers, peanuts, potatoes, carrots, peas, and beans (800–2500)

Table 1. *Continued*

pK_a	K_{oc} (mLg^{-1})	DT$_{50}$ (d)	Solubility (in water, gL^{-1})	Log P
4.6	5–182	30–60	0.049 (pH2.5)	−0.68
3.12	19–387	4–31.5	2.2 (pH5) 22 (pH9)	0.9 (pH5) −1 (pH7)
1.7	39–173	166–77	0.033 (pH7)	2.5
1.62	103–277	27–102	0.062 (pH7)	2.1 (unionised)
4.1	185–575	14–150	0.033	3.1 (unionised)

Table 1. *Continued*
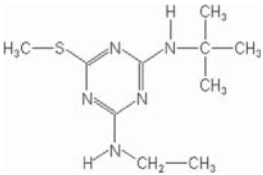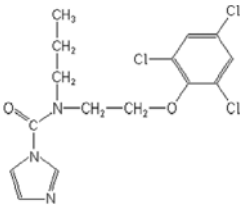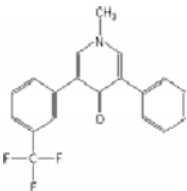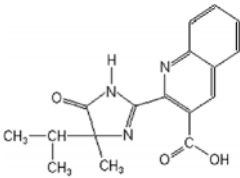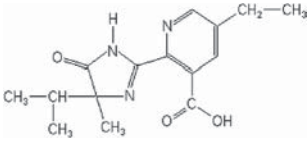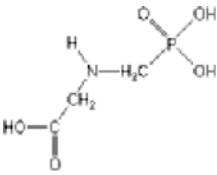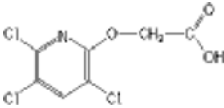
Pesticide name [CAS RN]	Formula	Use and application rate (g ha^{-1})
Terbutryn [886-50-0]		Control of black grass and annual meadow grass in winter cereals; also in mixture on sugar cane, sunflower, beans, peas potatoes, cotton, and peanut (200–2000)
Other basic compounds		
Prochloraz [67747-09-5]		Protectant and eradicant fungicide effective against a wide range of diseases affecting field crops, fruit, turf, and vegetables (400–600)
Fluridone [59756-60-4]		Aquatic herbicide for control of most submerged and emerged aquatic plants in ponds, reservoirs, irrigation ditches (10^{-6}–10^{-3} g L^{-1})
Amphoteric compounds **Imidazolinones**		
Imazaquin [81335-37-7]		Preplanting or preemergence control of broad-leaved weeds in soya beans (70–140)
Imazapyr [81334-34-1]		Control of annual and perennial grasses, sedges, and broad-leaved weeds in noncrop areas, forestry management, and plantation of rubber trees and oil palms (100–1700)

Table 1. *Continued*

pK_a	K_{oc} (mL g^{-1})	DT$_{50}$ (d)	Solubility (in water, g L^{-1})	Log P
4.3	2000	14–50	0.022	3.65 (unionised)
3.8	1222–5818	5–37	0.034	4.12 (unionised)
1.7	350–1100	>343	0.012 (pH7)	1.87 (pH7)
3.8	13–40	60	0.060–0.120	0.34
1.9 3.6 11	4–170	30–150	9.74	0.11

Table 1. *Continued*

Pesticide name [CAS RN]	Formula	Use and application rate (g ha^{-1})
Imazethapyr [81335-77-5]		Control of many major annual and perennial grass and broad-leaved weeds in soya and other leguminous crops (70–200)
Others		
Glyphosate [1071-83-6]		Control of annual and broad-leaved weeds in cereals, peas, beans, oilseed rape, vines, olives, orchards, pasture, forestry and industrial weed control; inactivated on contact with soils (1500–4300)
Triclopyr [55335-06-3]		Control of woody plants and many broad-leaved weeds in grassland, uncultivated land, industrial areas, coniferous forest, rice field, and plantation crops (100–8000)

pK_a, dissociation constant; K_{oc}, distribution coefficient in soils normalised by the organic carbon content; DT$_{50}$, half-life in soil, time required for 50% of the initial dose to be degraded; log P, hydrophobicity of the compound.

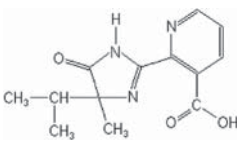# III. Adsorption of Ionisable Compounds

A. Measurement of Sorption

Adsorption refers to the attraction and accumulation of molecules at the soil–water or soil–air interface, resulting in molecular layers on the surface of soil particles (Harper 1994). Soil sorption is characterized by a partition constant K, conventionally written with a subscript d ("distribution"), defined as the ratio of the quantity of molecules adsorbed to the quantity of molecules in solution at equilibrium. For direct measurement of the distribution coefficient (K_d), the batch slurry method is generally used (OECD 1997). However, the soil–solution ratios required to reach equilibrium

Table 1. *Continued*

pK_a	K_{oc} (mL g^{-1})	DT$_{50}$ (d)	Solubility (in water, g L^{-1})	Log P
2.1 3.9	75–173	30–90	1.4	1.04 (pH 5) 1.49 (pH 7) 1.2 (pH 9)
2.3 5.7 10.2	1,000–59,000	3–174	11.6	−3.2 (pH 2–5)
2.7 3.97	41–59	8–156	7.9 (pH 5) 8.22 (pH 9)	0.42 (pH 5) −0.45 (pH 7) −0.96 (pH 9)

(from 1:1 to 1:100) are atypical of field soil moisture conditions, and the results may not adequately reflect sorption processes in field-moist or unsaturated soil.

Recovery of soil solution from field-moist soil provides a more realistic representation of field situations because the soil is wetted to field capacity and is not reduced to slurry as in a batch equilibrium experiment. However, Wehtje et al. (1987) found good agreement in sorption of both sulfometuron and imazapyr as determined by batch equilibrium and solution recovery protocols. Goetz et al. (1986) pointed out that differences in sorption across soils were much more apparent with the soil solution recovery than with the batch technique.

Walker and Jurado-Exposito (1998) compared the adsorption data obtained from standard batch measurements and those obtained using a

centrifugation technique for isoproturon, diuron and metsulfuron-methyl. Although the results were not fully consistent, they generally indicate lower K_d, less adsorption, and lower n values (greater curvature) of the isotherms than in the standard batch system, implying that batch experiments might overestimate K_d in some cases.

Johnson and Sims (1998) compared soil thin-layer chromatograpy (TLC) and batch equilibrium results for the sorption of atrazine and dicamba on six soils. Agreement between the two methods was good for some horizons but differed significantly for others. It was suggested that the soil TLC gives results under nonequilibrium conditions whereas the batch procedure, by definition, measures quasiequilibrium. The authors concluded that the soil TLC procedure could provide additional information relevant to pesticide partitioning in the field environment.

Gel filtration chromatography was found useful for the study of ionic as well as nonionic pesticides (Madhun et al. 1986) but only gives a relative evaluation of the strength of sorption. Another procedure to measure sorption is to estimate sorption based on retardation of the solute during its transport through a column of soil (Heistermann et al. 2003; Shaw and Burns 1998b; Tuxen et al. 2000). This method has the advantage of maintaining soil structure during measurements and thus incorporating the importance of water flow through soil pores and the accessibility of soil particles within aggregates at a realistic soil to solution ratio. The use of intact soil cores provides the greatest similarity to natural soil. However, this method is more complex than those already described, and degradation also becomes a factor in reducing the accuracy of the results (Harper 1994).

Berglöf et al. (2003) proposed the use of low-density supercritical fluid extraction ($0.3\,g\,mL^{-1}$) to remove metsulfuron-methyl from the soil water phase of three soils at 11% water content. The authors were able to predict K_d values obtained using the batch slurry technique with a combination of the results, the pK_a value, and the pH of the soil. Although this could provide an easy method to predict sorption in soil at different pH levels, it still must be validated with other compounds.

Finally, the partition coefficient (K_d) could be calculated indirectly from regression with other partition coefficients (solubility, K_{ow}, HPLC capacity factor) or estimated using quantitative structure–activity relationships (QSAR). However, no satisfactory model has yet been proposed for ionisable pesticides.

B. Factors Influencing Adsorption of Ionisable Compounds in Soils

Soil Properties.   Once the organic molecule reaches the soil, its partition between the solid and liquid phase depends to a large extent on soil properties. Nonpolar compounds mainly adsorb by hydrophobic partitioning, so OM content is generally the dominant soil parameter determining their

adsorption. Ionic compounds also sorb on organic matter, but also can bind to clay and Fe/Al (hydr)oxides. These two components seem to play a significant role in certain cases. Last, in contrast to hydrophobic compounds, ionisable pesticide adsorption is highly sensitive to pH variation. The importance of pH influence depends on the molecule and on the other soil properties. The influence of soil properties on sorption is considered in detail in Section III.D.

Climatic Factors: Temperature, Water Content.   The main climatic factors that influence adsorption of organic compounds in soils are the temperature and moisture content of the soil. It is often assumed that adsorption is an exothermic process, whereby an increase in temperature leads to decreased adsorption and increased desorption rates (Calvet 1989; Harper 1994). However, thermodynamic studies have shown a highly variable relationship to temperature due to the complexicity of the soil environment (Harper 1994) and a variable influence of temperature on the different binding mechanisms (Hayes 1970). Di Vicenzo and Sparks (2001) explore the differences in the sorption mechanisms of the protonated and ionized forms of pentachlorophenol (PCP) by measuring their sorption coefficients at different temperatures (4°, 25°, and 55°C). Although no apparent trend was observed for the neutral form, a clear decrease in K_d with increasing temperature was observed for the ionised form (suggesting more-specific adsorption processes). Similarly, Thirunarayanan et al. (1985) observed an increase in K_d values for chlorsulfuron with a decrease in temperature from 30° to 8°C. Temperature affected the amount adsorbed with the smallest effect at the lowest pH, where the neutral form dominates. The same inverse relationship was observed with glyphosate (Eberbach 1998) and atrazine on clays (Fruhstorfer et al. 1993). In practice, temperature seems to have only a minor effect on sorption. Ukrainczyk and Ajwa (1996) found no significant effect of temperature, between 10° and 35°C, on primisulfuron adsorption to 23 soils, and a study carried out in three Norwegian reference soils indicated that the effect of a colder climate on the soil formation does not affect sorption of bentazone, dichlorprop, and MCPA (Thorstensen et al. 2001).

It has often been reported that adsorption coefficients increase as water content decreases. This effect can be attributed to reduced competition by water for sorption sites and an influence of solubility as the herbicide solution becomes more concentrated (Harper 1994). Indeed, Goetz et al. (1986) observed that temporarily drying and returning to field capacity generally increased sorption of imazaquin; this was attributed to a reduction in thickness of the water film coating the soil minerals, which serves to concentrate the imazaquin near the sorption surface or facilitate precipitation. Wehtje et al. (1987) confirmed that desiccation apparently concentrates sulfometuron and imazethapyr near the sorptive surface. Roy et al. (2000) have

shown that weakly basic compounds such as prochloraz may partition rapidly into the liquid-like interior of humus at low soil moisture contents. However, increased diffusion at high soil moisture content may cause additional sorption by ion exchange at colloid surfaces. Stronger basic compounds (e.g., fenpropimorph, $pK_a = 6.98$) may essentially adsorb due to ionic interactions, and their sorption is enhanced at high soil moisture content due to diffusion. Increased sorption with increased water content has been observed with atrazine (Koskinen and Rochette 1996; Rochette and Koskinen 1996) and metsulfuron methyl (Berglöf et al. 2003). Thus, effects of moisture content on sorption seem to be more complex when compounds are likely to be protonated in soil.

Pesticide Properties.   Several chemical characteristics have been correlated successfully to sorption of neutral compounds onto soil. However, broad-spectrum applicability to include ionisable compounds has not been achieved (Harper 1994). For hydrophobic compounds, sorption to soil OM can be described predominantly as a partitioning process between a polar aqueous phase and a nonpolar organic phase (soil OM). Significant correlations have been published between the sorption coefficient (K_d) and water solubility or K_{ow} (octanol–water partition coefficient evaluating the hydrophobicity of the compound) (Karickhoff et al. 1979; Karickhoff 1981; Gerstl 1990; Nicholls and Evans 1991a; Schwarzenbach and Westall 1981; Von Oepen et al. 1991). For hydrophobic ionisable compounds, the solvophobic mechanism alone is not sufficient for estimating soil–water distribution coefficients as the sorption mechanism depends on the degree of dissociation, which is itself a function of the dissociation constant and the pH of the soil solution. Riise and Salbu (1992) showed that K_{ow} for dichlorprop was inversely related to pH and that the relationship was similar to that between K_{oc} (K_d normalised by the organic carbon content) and pH. In the pH range 4–7, the K_{ow} value changes from 114 to 0.6. Thus, the relationship between K_{oc} and K_{ow} for dichlorprop corresponds to that previously reported for neutral organic chemicals.

Experimental Factor: Importance Of Ionic Strength.   Different salt solutions, including $CaCl_2$ or KCl, NH_4Cl, HCl, NaCl, $Ca(H_2PO_4)_2$, $Na_4P_2O_7$, and KH_2PO_4 have been used to assess the influence of ionic strength and ionic composition of the soil solution on pesticide sorption. Solution concentration varied usually between 0 and 1 M, although the strength of natural soil solution rarely exceeds 10^{-3} M. Results demonstrate that this variation can strongly influence the sorption of ionic molecules, either positively or negatively, according to the electrolyte composition and concentration and characteristics of the pesticide and sorbent. Uncharged molecules seem to be much less sensitive to variation in ionic strength (Alva and Singh 1991; Clausen et al. 2001; de Jonge and de Jonge 1999).

A positive influence of ionic strength on adsorption is often observed. For instance, Clausen et al. (2001) observed increasing adsorption of meco-prop and 2,4-D on kaolinite with increasing $CaCl_2$ concentration and increasing mecoprop adsorption on quartz. Increased sorption of PCP (Lee et al. 1990), imazaquin (Regitano et al. 1997), 2,4,5-T (Koskinen and Cheng 1983), silvex and DNOC (Jafvert 1990), 2,4-DNP, DNOC, dinoseb, and dinoterb (Martins and Mermoud 1998), and glyphosate (de Jonge and de Jonge 1999) were also observed with increasing ionic strength. The positive influence of ionic strength on sorption results in part from a replacement of protons from the soil surface as ionic strength increases, causing a slight decrease in pH and shifting acidic compounds toward neutral forms that are more strongly sorbed than the anionic forms (de Jonge and de Jonge 1999; Regitano et al. 1997). Complexation of the pesticide molecule with surface-exchanged multivalent cations could also contribute to stronger sorption at higher ionic strengths, as the diffuse double layer is compressed and Ca^{2+} becomes more strongly attached to the clay surfaces (Clausen et al. 2001; de Jonge and de Jonge 1999). Ion pairing between the anionic form of the pesticide and cations in the solution could occur, and sorption of neutral ion pairs would be possible. This process depends on the avail-ability of the "complementary cations" in solution, either due to high salt concentrations or near negatively charged colloid surfaces (Spadotto and Hornsby 2003). Colloidal stability may influence sorption processes as fine colloids and dissolved OM coagulate at higher ionic strength; this would lead to an increase in the measured K_f value (de Jonge and de Jonge 1999). Lower solubility of 2,4-D in 1 M NaCl compared to 0.01 and 0.1 M NaCl, could explain the increasing sorption of 2,4-D on goethite with increasing ionic strength observed by Watson et al. (1973). The salting-out effect can vary directly or inversely with salt concentration, depending on the salt of interest, but an increase in sorption with increasing salt concen-trations occurs for most common salts (e.g., NaCl, $CaCl_2$, and KCl) (Lee et al. 1990).

A negative relationship between adsorption and ionic strength has been reported as well, especially for variably charged sorbents. For instance, Hyun and Lee (2004) observed a fivefold decrease in prosulfuron sorption as the solution changed from 0.0015 to 1.5 M $CaCl_2$ in a variably charged soil with a high contribution of hydrophilic processes (high anionic-exchange capacity, AEC). In contrast, no difference was observed for a soil with an AEC approaching zero. Clausen et al. (2001) noted that the adsorp-tion of ionic pesticides on calcite and alpha-alumina decreases with increas-ing $CaCl_2$ concentration. The authors proposed several effects that might oppose that resulting from an increasing positive charge at the surface with increasing ionic strength: (i) enhanced competition with the chloride anion that is known to adsorb on iron oxides (owing to its relative larger size and lower concentration, the anionic pesticide is not able to compete effectively for anion exchange sites); (ii) possible complexation between the anionic

pesticides and Ca^{2+}, which results in nonsorbing solution complexes; or (iii) a decrease in the activity of the charged ions caused by the increasing electrolyte concentration. The addition of $Ca(H_2PO_4)_2$ and KH_2PO_4 resulted in significantly less adsorption of imazaquin and glyphosate, respectively (de Jonge and de Jonge 1999; Regitano et al. 1997), probably because of competition effects. This result suggests that the application of large amounts of phosporus and lime to agricultural fields could reduce pesticide sorption and enhance pesticide concentration in solution, especially in weathered soils.

Finally, variation in sorption does not necessarily vary linearly with ionic strength. For instance, in batch experiments involving 2,4-D, mecoprop, bentazone, and iron oxides, Clausen and Fabricius (2001) observed that the addition of $CaCl_2$ at concentrations between 0 and 0.01 M caused adsorption capacity to diminish, with the greatest effect between 0 and 0.0025 M. The effect seemed to arise from the type of binding mechanism, with outer-sphere complexation being more strongly affected by the electrolyte concentration than inner-sphere complexation. Similarly, sorption values for picolinic acid measured in distilled water by Nicholls and Evans (1991b) were almost the same as those measured in 0.01 M $CaCl_2$, but strength of sorption decreased about fivefold when $CaCl_2$ increased from 0.01 to 1 M, probably because the protonated form of picolinic acid was displaced by calcium ions.

Ionic composition has been shown to play a role in ionic pesticide sorption, but there is some conflict in results, and further research is needed to better understand the complex interaction of mechanisms involved. The ionic strength of natural soil solution does not normally exceed 10^{-3} M, so that effects of ionic strength on sorption can usually be neglected (Lee et al. 1990). Nevertheless, the choice to use 0.01 M $CaCl_2$ in standardized soil sorption experiments (OECD 1997) will affect the sorption coefficients of ionisable pesticides, and this places a constraint on the use of results from these standardized tests to predict sorption behaviour of ionisable compounds in the field.

C. Adsorption Mechanisms

Adsorption–desorption is a dynamic process in which molecules are continually transferred between the bulk liquid and solid surface. A number of mechanisms have been postulated to be involved in the retention of pesticides. However, it is difficult to isolate a definitive mechanism because most retention arises from an interaction of a variety of forces and factors. In addition, direct experimental evidence for a particular mechanism is quite rare, and one is often confined to propose a hypothesis (Calvet 1989). Only kinetic, thermodynamic, and spectroscopic studies can truly lead to mechanistic interpretations (Di Vincenzo and Sparks 2001), and spectroscopic

studies are often impractical because of the heterogeneous nature of soil. Several reviews are available on the retention mechanisms of pesticides in soils (Calvet et al. 1980a,b; Calvet 1989; Harper 1994; Koskinen and Harper 1990; Senesi 1992; Von Oepen et al. 1991), and we concentrate here on the current state of knowledge for ionic compounds.

Most organic compounds of interest as environmental contaminants are hydrophobic. Thus, they have low polarity and solubilities in the mg L^{-1} (ppm) range or less. The driving force for their adsorption consists mainly of entropy changes (solvent-motivated adsorption: hydrophobic interaction) and relatively weak enthalpic forces (sorbent-motivated adsorption: van der Waals and hydrogen bonding). The combined effect of these two mechanisms is often referred to as hydrophobic sorption (Hamaker and Thomson 1972; Pignatello 1989). Other sorption mechanisms can occur for more polar solutes, including ionic exchange, charge transfer, ligand exchange, and cation or water bridging. Furthermore, decreased extractability of organic chemicals with increased incubation time may be due to the formation of covalent bonds or the physical trapping of the chemical in the soil matrix (Koskinen and Harper 1990). Advanced techniques such as Fourier transform infrared (FT-IR), X-ray diffraction, or electron spin resonance (ESR) spectroscopy have been applied in some studies to prove or disprove the existence of some retention mechanisms in soils. The results are summarized in Table 2. Seven mechanisms have been identified of which hydrogen bonding is the most frequently inferred. Evidence is usually cited to support the operation of one or more mechanisms. It is rare to find studies that have demonstrated that any particular mechanism is not operating.

Hydrophobic Sorption.   Hydrophobic adsorption is proposed as the main mechanism for the retention of nonpolar pesticides by hydrophobic active sites of humic substances (HS) or clay. The hydrophobic solute is expelled from the water (solvent-motivated adsorption), and this mechanism can also be regarded as a partitioning between a solvent and a non-specific surface. These sites include aliphatic side chains or lipid portions and lignin-derived moieties with high carbon content of the HS macromolecules (Senesi 1992). Hydrophobic adsorption to soil has been suggested as an important mechanism for some ionisable pesticides in their molecular form, including some weakly basic sterol fungicides (Roy et al. 2000), prometryn (Khan 1982), 2,4-D and triclopyr (Johnson et al. 1995), PCP (Lee et al. 1990), primisulfuron (Ukrainczyk and Ajwa 1996), imazaquin (Ferreira et al. 2002), and atrazine and simazine (Herwig et al. 2001). Celis et al. (1997a) suggested that *s*-triazine sorption on montmorillonite, as the protonated species (cationic form), must be preceded by sorption as the molecular species on hydrophobic microsites of the clay. However, cation exchange would also be operative if the pH of the bulk solution were close to the pK_a of the herbicide. The authors demonstrated that the protonation of atrazine

Table 2. Experimental Evidence of Adsorption Mechanisms.

Pesticide	Sorbent	Hydrophobic	van der Waals	H-bonding	Ionic exchange
Acidic pesticides					
Mecoprop, 2,4-D; bentazone	Iron oxides				x
2,4-D	Organoclays			x	
Acifluorfen	Cu (II)				
Fluazifop-butyl	Homoionic clays			x	
Fluazifop-butyl, fluazifop	Smectites				
Pentachlorophenol	Variable charge soils	x			x
Azimsulfuron	Iron oxides				
Primisulfuron	Oxides and soils	x		x	x
Ethametsulfuron-methyl	Acidic soil			x	
Basic pesticides					
Atrazine	HA			x	x
Atrazine	HA			x	
Atrazine	HA	x		x	
Hydroxyatrazine	HA	x		x	
Atrazine	OM			x	
Zwitterionic pesticides					
Imazaquin	Soils, HA	x		x	x
Imazethapyr	Soils, HA		x	x	x
Glyphosate	Clays and oxides			x	x
Glyphosate	Goethite				

FT-IR, Fourier transform infrared spectroscopy; ESR, electron spin resonance spectroscopy; TLC, thin-layer chromatography; EPR, electron paramagnetic resonance; NMR, nuclear magnetic resonance.

and simazine at clay interfaces would involve a movement from hydrophobic to hydrophilic sites on the clay surface, so new hydrophobic sites would become available for the molecular species in solution.

Hydrophobic partitioning is usually regarded as a pH-independent mechanism. However, the dissociation of some humic acid (HA) functional groups at low pH might reduce the potential of OM for hydrophobic adsorption. Conversely, Ferreira et al. (2001) propose that consequent conformation changes might create water protected sites at pH < 5 and thus create some very hydrophobic adsorption sites at low pH.

van der Waals Interactions. Particular adsorption on hydrophobic constituents of OM can be explained either in terms of solute partition between water and organic matter (solvent-motivated sorption, entropy-driven) or

Table 2. *Continued*

Charge transfer	Ligand exchange	Cation bridging	Methods	Reference
	x		Interpretation of isothems	Clausen and Fabricius 2001
		x	FT-IR, X-ray diffraction	Hermosin and Comejo 1993
	x		Polarographic techniques, X-ray diffraction	Kozlowski et al. 1990
x			IR and X-ray diffraction	Gessa et al. 1987
x	x	x	IR spectroscopy, X-ray diffraction, and TLC	Fusi et al. 1988
			Interpretation of isotherms	Hyun et al. 2003
	x	x	IR	Pinna et al. 2004
			Interpretation of isotherms	Ukrainczyk and Ajwa 1996
			FT-IR	Si et al. 2005
x			FT-IR and ESR	Senesi et al. 1995
no			UV-visible, FT-IR and ESR	Martin-Neto et al. 1994
no			UV-visible, FT-IR and ESR	Martin-Neto et al. 2001
x			UV-visible, FT-IR and ESR	Martin-Neto et al. 2001
			NMR spectroscopy	Welhouse and Bleam 1993a,b
no		x	FT-IR and EPR	Ferreira et al. 2002
x			FT-IR and EPR	Senesi et al. 1997
		x	IR and X-ray diffraction	McConnell and Hossner 1989
	x		FT-IR	Sheals et al. 2002

in terms of solute adsorption (sorbent-motivated, enthalpy-driven). Physical adsorption on OM by van der Waals interactions is probably the more satisfactory explanation, according to Calvet (1989). Such interactions are usually weak ($2–4\,kJ\,mol^{-1}$), constituting short-range dipolar or induced-dipolar attractions, but may be magnified by the hydrophobic effect. Because these forces are additive, their contribution increases with an increasing area of contact. Bonding by van der Waals forces has not been proved or disproved (Koskinen and Harper 1990) because scarce experimental evidence is available. However, Barriuso et al. (1994) suggested that atrazine is primarily retained on surfaces of smectites with low surface charge density through relatively weak van der Waals forces or H bonds. This mechanism was also proposed as contributing to sorption of imazethapyr (Senesi et al. 1997) and fluridone (Weber et al. 1986).

H-Bonding.   H-bonding is an intra- or intermolecular dipole–dipole inter-
action that is stronger than van der Waals bonds. The energy of this binding
amounts to about 2–40 kJ mole^{-1}. It is caused by the electron-withdrawing
properties of an electronegative atom (F, N, O) on the electropositive
hydrogen nucleus of functional groups such as —OH and —NH. The pres-
ence of numerous oxygen and hydroxyl-containing functional groups on HS
renders the formation of H-bonding highly probable for pesticides con-
taining suitable complementary groups, although a strong competition with
water molecules may be expected for such sites (Senesi 1992). Martin-Neto
et al. (1994) applied UV-visible, FT-IR, and ESR spectroscopy to HA
samples reacted with atrazine and found evidence for weak adsorption
involving H-bonding. Moreover, Welhouse and Bleam (1993b) observed the
formation of weak to moderately strong complexes between atrazine and
amine, and hydroxyl and carbonyl functional groups. The strong complex-
ation observed with carboxylic acid and amide functional groups was the
result of cooperative interactions (multifunctional H-bonds) in which both
partners in the complex donate and accept hydrogen bonds (Welhouse and
Bleam 1993b). H-bonding has also been proposed as a binding mechanism
for primisulfuron (Ukrainczyk and Ajwa 1996), metribuzin (Ladlie et al.
1976c), and 2,4-D and triclopyr (Johnson et al. 1995) on soils. It has been
implicated in the adsorption of fluazifop-butyl on homoionic clays (Gessa
et al. 1987), atrazine on smectite (Barriuso et al. 1994), and atrazine (Senesi
et al. 1995; Piccolo et al. 1998), imazethapyr (Senesi et al. 1997), ethamet-
sulfuron-methyl (Si et al. 2006), and imazaquin (Ferreira et al. 2002) on
soil OM.

Ionic Exchange.   Ionic exchange is a nonspecific electrostatic interaction
(>20 kcal mole^{-1}) that can involve either anionic or cationic pesticide forms.
    Anion exchange is the attraction of an anion to a positively charged site
on the soil surface and involves the exchange of one anion for another at
the binding site. Adsorption of organic anions by soils via anion exchange
is not likely in temperate climates as clays and organic matter are gener-
ally either noncharged or negatively charged. Moreover, direct sorption
involving the few positive charges at the edge of sheets in clays or proto-
nated amine groups within the organic matter is an insignificant mechanism
for weak acids (Stevenson 1972). Anion exchange is more likely to occur in
tropical soils that contain significant quantities of positively charged
adsorption surfaces in the form of aluminium and iron (hydr)oxides. For
instance, pentachlorophenol was readily desorbed on addition of phosphate
with no apparent hysteresis, suggesting that pentachlorophenol sorption on
variably charged soils is primarily through nonspecific ion-exchange reac-
tions (Hyun et al. 2003). Hyun and Lee (2004) demonstrated that anion
exchange of prosulfuron accounted for up to 82% of overall sorption in the
pH range 3–7, and that its relative importance was positively correlated to
the ratio of anion and cation exchange capacities of the 10 variably charged

soils studied. Similarly, anion exchange was implicated in the adsorption of the dissociated form of chlorsulfuron (Shea 1986), 2,4-D (Celis et al. 1999; Watson et al. 1973), mecoprop and bentazone (Clausen and Fabricius 2001), and clofenset, salicylic acid, and 2,4-D (Dubus et al. 2001). However, Ukrainczyk and Ajwa (1996) did not observe any correlation between the anionic-exchange capacity (AEC) of minerals and primisulfuron adsorption and concluded that anion exchange is not an important mechanism for primisulfuron sorption on mineral surfaces. Because anion exchange is affected by the presence of other anions, Hyun et al. (2003) suggest that sorption of acidic pesticides could be better predicted by considering the electrolyte composition.

Cation exchange is relevant to those pesticides that are in the cationic form in solution or can accept a proton and become cationic (e.g., basic compounds at pH < pK_a). For these pesticides, it is among the most prevalent sorption mechanism due to the large proportion of negatively charged sites associated with clay and organic matter in soils (Harper 1994). For instance, there is abundant evidence for cation exchange involving triazines (Herwig et al. 2001; Ladlie et al. 1976a; Piccolo et al. 1998; Roy et al. 2000), even though their pK_a (1.7 < pK_a < 4.3) is lower than the pH of most common soils. Cation exchange can occur at negatively charged sites on clay mineral surfaces occupied by a metal cation. According to Sannimo et al. (1999), simazine arrived at a montmorillonite interface mostly as the molecular species, where the compound was protonated by the microenvironmental pH (lower than the bulk solution pH), and eventually adsorbed by cation exchange. Cation exchange can also occur between the protonated triazines or the positively charged bipyridylium compounds (e.g., diquat or paraquat) and the negatively charged sites of HS (carboxylate, phenolate groups) (Senesi et al. 1995). However, not all negative sites on OM seem to be positionally available to bind large organic cations, probably because of steric hindrance. For instance, the higher reactivity of simazine relative to atrazine and prometryn may be related to the smaller steric hindrance of the reactive N–H group of the former herbicide (Senesi 1992).

Charge Transfer.   The presence in humic substances of both electron-deficient structures, such as quinones, and electron-rich moieties, such as diphenols, suggests the possible formation of charge-transfer complexes via electron donor-acceptor mechanisms (π–π reaction). Pesticides can act as electron donors (amine and/or heterocyclic nitrogen atoms of the s-triazines, pyridines, imidazolinones) or electron acceptors (e.g., deactivated bypyridilium ring of atrazine) (Senesi 1992). Charge transfer involves the overlapping of the respective molecular orbitals and a partial exchange of electron density (Von Oepen et al. 1991).

The interaction between atrazine and soil OM has been widely studied, but the mechanisms are still a topic of considerable controversy. Martin-Neto et al. (1994) concluded, in agreement with theoretical studies by

Welhouse and Bleam (1993a,b), that the electron-donating capability of atrazine was usually not sufficient to allow an electron-transfer complexation with HA. In contrast, the results of Piccolo et al. (1992) indicate that atrazine is mainly adsorbed through a charge-transfer mechanism. FT-IR and ESR spectroscopic results suggested charge-transfer bonds between the electron-donor triazine ring or the electron-acceptor deactivated bipyridylium ring and complementary electron-donor or -acceptor structural moieties of HA (Senesi et al. 1995). Nevertheless, Martin-Neto et al. (2001) confirmed their previous results indicating that atrazine does not readily undergo electron-transfer reactions with humic substances. However, they demonstrated that hydroxyatrazine reacts through an electron-transfer mechanism with HA and FA.

This behaviour is similar to other *s*-triazine herbicides, such as prometon, which has a significant basicity ($pK_a = 4.28$) that renders it highly effective in engaging electron-transfer mechanisms to complex HA (Senesi and Testini 1982). Atrazine readily converts to hydroxyatrazine, even in laboratory samples at low water content, and this may explain some of the electron-transfer product detected in studies of atrazine–HA interactions (Celis et al. 1997a). Senesi et al. (1997) suggest a charge transfer between the electron-donating pyridine ring and/or imidazolinone ring of imazethapyr and the electron-acceptor structural units of HA (e.g., the quinone groups). In contrast, Ferreira et al. (2002) observed no change in the semiquinone-type free radical contents between HA and HA–imazaquin complexes; this indicated that imazaquin did not undergo charge-transfer reactions with HA.

Although charge transfer seems to be most likely for sorption to humic acids (Pignatello 1989), some authors also infer this mechanism for interactions between acidic pesticides and clays. Indeed, the polarizing power of a cation determines the degree of acidity of the coordinated water molecules and therefore the tendency to protonate an organic molecule according to the strength of its basic character. Fusi et al. (1988) have shown that fluazifop-butyl could apparently adsorb to Al- and Fe-homoionic clays by protonation of the pyridine nitrogen, but this was not the case with other exchangeable cations. Similar results were obtained for fluazifop-butyl (Gessa et al. 1987) and azimsulfuron (Pinna et al. 2004).

Ligand Exchange.   Adsorption by a ligand-exchange mechanism involves the replacement, by suitable adsorbent molecules such as *s*-triazines and anionic pesticides, of hydration water or other weak ligands that partially hold polyvalent cations associated to soil OM or hydrous oxide surface (Senesi 1992). Ainsworth et al. (1993) proposed a two-step reaction: the first reaction represents the rapid formation of an ion-pair complex on the protonated surface site (outer-sphere complex; 4–16 kJ mol^{-1}); the second reaction, much slower and thus rate limiting, involves the breaking and forming of bonds and results in the formation of an inner-sphere complex (>20 kJ mol^{-1}) that may be bidentate or binuclear. A study involving several dif-

ferent iron oxides suggested that mecoprop adsorbs by outer- and inner-sphere complexes, whereas 2,4-D and bentazone are only weakly adsorbed through outer-sphere complexes (Clausen et al. 2001).

The ligand-exchange mechanism is implicated in the retention of many organic acids to oxide surfaces: an organic functional group, such as carboxylate or hydroxyl, displaces a surface coordinated —OH or water molecule of a metal ion (Fe, Al) at the surface of a soil mineral. For instance, sorption of clofenset and salicylic acid onto oxide surfaces is achieved predominantly through ligand exchange (Dubus et al. 2001). Moreover, salicylic acid and clofenset have both —COOH and —OH groups close to one another, making possible the formation of surface bidendate complexes with metals. The chemical structure of 2,4-D does not seem to allow the formation of these complexes with metals (Dubus et al. 2001). IR spectra of azimsulfuron sorbed to iron oxide indicate a Fe^{3+} coordination to the azimsulfuron sulfonylurea group acting as a bidentate bridging ligand through sulfonyl and carbonyl oxygen atoms (Pinna et al. 2004). This binding mode, giving rise to a six-membered chelated ring, explains the unusual IR spectra of the azimsulfron–iron oxide complex. Similarly, Nicholls and Evans (1991b) explained the difference in sorption between the two weak bases methyl-nicotinate and methyl-picolinate by the capacity of the latter to form a weak bidentate ligand to an acceptor atom.

Ligand exchange has also been proposed as a mechanism of retention for zwitterionic compounds such as imazaquin on highly weathered tropical soils (Regitano et al. 2000) and glyphosate on goethite (Sheals et al. 2002). While the phosphonate group of glyphosate binds directly to goethite by formation of inner-sphere complexes, predominantly as a monodentate complex, the carboxylate group remains relatively free from complexation, leaving it subject to degradation and/or complexation with metal ions present in the environment (Sheals et al. 2002).

Cation (or Water) Bridging.   Cation bridging arises from the formation of an inner-sphere complex between an exchangeable cation, at a clay or OM surface, and an anionic or polar functional group on a pesticide. Because cations are normally surrounded by hydrating water molecules, the organic functional group must be able to either displace the water or it must react in the presence of a dry surface to form an inner-sphere complex. Water bridging occurs when the organic functional group is unable to displace the solvating water molecule: it is an outer-sphere interaction between a proton in a hydrating water molecule of an exchangeable cation and an organic functional group (Koskinen and Harper 1990). Water molecules participate in H-bonding if they are involved in bonds between organic molecules and cations.

Water bridging is more likely to occur with the larger, higher-valency cations such as Fe^{3+}, Al^{3+}, and Mg^{2+} because they have large negative enthalpy of hydration so that water molecules are more difficult to displace

(Harper 1994). A measurable adsorption of mecoprop and 2,4-D on kaolinite, which exhibits a negative surface charge, was only found when $CaCl_2$ was added as an electrolyte; this probably resulted from the formation of Ca–pesticide–surface complexes (Clausen et al. 2001). Complexation with surface-exchanged multivalent cations has been suggested as a possible sorption mechanism for glyphosate, clofenset, and salicylic acid onto oxide surfaces (de Jonge and de Jonge 1999; Dubus et al. 2001; McDonnell and Hossner 1985, 1989; Sheals et al. 2002). Fusi et al. (1988) concluded that fluazifop-butyl and fluazifop are adsorbed to homoionic smectites through both a water bridge and a direct coordination between their C=O group and an exchangeable cation. The extent and strength of this coordination depended on the nature of the cation that saturated the clays.

Bound Residues.   For most pesticides, it is often assumed that a rapid and reversible equilibrium is established between the chemical in solution and the chemical adsorbed onto the soil surface. However, once adsorbed, many organic chemicals react further to become covalently and irreversibly bound while others may become physically trapped in the soil matrix (Koskinen and Harper 1990). These mechanisms lead to stable, mostly irreversible incorporation of the molecule, mainly into humic substances (Harper 1984; Scribner et al. 1992; Senesi 1992).

Bound residues are common for pesticides and for their intermediates and degradation products (Koskinen and Harper 1990). For instance, 9 yr after application of atrazine to a soil under field condition, the soil contained about 50% [14]C residues in the bound (nonextractable) form, distributed among the various soil humic fractions (Capriel et al. 1985). Trapping of molecules by humic materials acting as a molecular sieve form has been hypothesized as a retention mechanism for prometryn (Khan 1982) and simazine (Scribner et al. 1992). Moreover, X-ray diffraction has shown that prometon (Weber et al. 1965), fluridone (Weber et al. 1986), and fluazifop (Fusi et al. 1988; Gessa et al. 1987) can penetrate into interlamellar spaces of smectites.

The proportion and distribution of bound residues depends on properties of the herbicide and the soil (Barriuso et al. 1997; Hang et al. 2003; Weber et al. 1993; Yutai et al. 1999). Von Oepen et al. (1991) showed that the higher the lipophilicity of a substance, the lower its tendency to form nonextractable residues. This mechanism occurs because polar compounds, those that contain OH^- or NH_2 groups, similar to those in humic substances, are more easily incorporated into humic substances. Thus, the formation of nonextractable residues may require particular attention when assessing the behaviour and mobility of polar compounds in soil.

Conclusion.   Soil constituents have a complex chemistry, and a multitude of functional groups have the potential to react with polar organic xenobiotics. Many retention mechanisms have been postulated to be responsible

for the adsorption of ionisable pesticides in soils, even if relatively little experimental evidence is available. The relative importance of one mechanism over another depends on the soil constituents, the molecule, and the chemical environment of the soil (Table 3), and several mechanisms are often found to be operating in combination. Nearly 15 years after the original assertion of Von Oepen et al. (1991), we are still unable to determine the quantitative contribution of each sorption mechanism in a particular situation.

Johnson et al. (1995) observed that the amount of 2,4-D and triclopyr desorbed increased with initial concentration, suggesting that specific binding sites became saturated at higher concentrations and that weaker sites were then responsible for retaining excess herbicide. Moreover, the capacity to form specific bonds, for instance, the formation of a bidentate complex with metal by the ligand-exchange mechanism, depends on the molecular structure of the pesticide and might explain the different sorption behaviour of some compounds having similar pK_a (Dubus et al. 2001).

Phosphate is applied as a fertilizer to agricultural soils and adsorbs mainly by ligand exchange. Several recent articles reported a likely reduction in the adsorption of some ionisable pesticides with increasing phosphate application (de Jonge and de Jonge 1999; de Jonge et al. 2001; Regitano et al. 1997). This phenomenon depends on the adsorbent (Gimsing and Borggaard 2002) and seems more likely on mineral surface sites such as Fe and Al (hydr)oxides (Nearpass 1976).

Our understanding of soil constituent chemistry, particularly that of humic substances and their modes of interaction with pesticides, deserves further research with a more extended application of advanced techniques such as NMR, ESR, FT-IR, and fluorescence spectroscopies. Finally, the formation of bound residues seems more likely for polar than for neutral compounds and also needs to be taken into account.

D. Prediction of the Adsorption Behaviour of Ionisable Pesticides in Soils

Influence of Soil pH.   Soil pH has been shown to influence the sorption of many ionisable pesticides. Several strategies can be followed to obtain a range of pH and study its influence on pesticide behaviour, but each has some disadvantages.

Artificial Modification.   Experiments in which the pH of a soil is adjusted artificially are useful with respect to experimental design and control. In some experiments, only the pH of the soil suspension is modified before the K_d measurement (Barriusso et al. 1992; Weber et al. 1986; Berglöf et al. 2002). In others, the pH of the soil has been modified and equilibrates for a long period (de Jonge et al. 2001; Loux and Reese 1992), or soil samples taken from different depths or with different pretreatment histories (tillage, crop) are compared (Barriusso et al. 1992; Harper 1988; Reddy et al. 1995;

Table 3. Potential Mechanisms for the Adsorption of Ionisable Compounds and How These are Influenced by Properties of the Compound and the Soil.

	pH dependent?	Type	Energy
Hydrophobic partition	To some extent	Partitioning	Low
van der Waals	No	Short-range induced dipolar attractions	2–4 kJ mol^{-1} (Koskinen and Harper 1990)
H-bonding	To some extent	Dipole–dipole interaction	2–110 kJ mol^{-1} (Haberhauer et al. 2001; Koskinen and Harper, 1990)
Anion exchange	Yes	Nonspecific electrostatic interaction	>80 kJ mol^{-1}
Cation exchange	Yes	Nonspecific electrostatic interaction	>80 kJ mol^{-1}
Charge transfer	Yes	Electron donor-acceptor mechanisms (π–π reaction)	12 kJ mol^{-1} (Haberhauer et al. 2001)
Ligand exchange	Yes	Inner-sphere complex, may be multidentate or multinuclear	>20 kJ mol^{-1}
Water bridging	Yes	Outer-sphere complex	4–16 kJ mol^{-1}
Cation bridging	Yes	Inner-sphere complex	150–330 kJ mol^{-1} on clays 140 kJ mol^{-1} on OM (Haberhauer et al. 2001)

OM, organic matter.

Table 3. *Continued*

Compound		Soil	
Positive influence	Negative influence	Positive influence	Negative influence
Hydrophobicity (high K_{ow})		High OM (with high carbon content) and/or clay content, low pH: creation of water protected site at pH < 5 by (Ferreira et al. 2001)	low pH: OM dissociation
		OM and clay content	
Nonionic but polar molecule capable of cooperative (or multifunctional) interactions		OM and clay content	Competition with water molecules
Anion low pK_a	Steric hindrance	Aluminium and iron (oxi)hydroxides	OM (coating), ionic strength (competition)
Cation high pK_a	Steric hindrance	High OM (functional acidity) and/or clay content	Ionic strength (competition)
Basicity of compound (ability to give electrons⁻) or acidity (ability to accept electrons⁻)	Very low or high pK_a	OM: capacity to give or accept electron (aromaticity) Clay: type of exchangeable cation (different acidity of water molecule surrounding)	
Chemical structure allowing the formation of multidentate/nuclear complexes.		High aluminium and iron (oxi)hydroxides and/or clay content (but less hydroxyl group at the edges than oxides)	OM (coating the oxides)
Anionic or polar functional group		Large, high-valency exchangeable cations such as Fe^{3+}, Al^{3+}, and Mg^{2+}	
Anionic or polar functional group able to displace the water surrounding the cation		Small, low-valency exchangeable cations	

Walker et al. 1989). However, such experiments have been deemed unsatisfactory because changes in soil characteristics other than pH can occur during pH adjustments. For instance, liming causes an increase in concentrations of amorphous aluminium and iron (hydr)oxides and a reduction in concentrations of Olsen-P (de Jonge et al. 2001). These factors might have opposing effects on the sorption or degradation characteristics of the pesticide, and this may obstruct interpretation of the results (Koskinen and Harper 1990; Singh et al. 1989; Walker and Thomson 1977).

Range of Native pH.   The comparison of soils representing a range of native pH is expected to provide more realistic information on the behaviour of a compound but also gives results with multiple, often conflicting influences. Furthermore, relationships between sorption and pH that have been demonstrated in a soil adjusted to different pH level are often not confirmed by regression analyses involving different soils. For instance, Weber et al. (1986) did not observe a significant correlation between pH and the adsorption of fluridone in 18 soils studied at their native pH (4.4–8.1; $r^2 = 0.10$). However, fluridone adsorption increased by between 38% and 42% when solution pH was decreased artificially from 6.4 to 3.5. Fontaine et al. (1991) obtained similar results with fluridone, which can partly be attributed to the generally narrower range and higher level of native pH values compared to those considered in adjusted soils. Moreover, surface acidity (exchangeable acidity) is probably the real operative, and it may not be appropriate to compare apparent acidity (pH of a soil suspension) for a wide range of soil types (see section on pH measurements).

   The determination of the effect of a single soil variable on sorption is always difficult because soil properties are often correlated with each other. Nevertheless, experiments dealing with a natural pH range or soil equilibrated for a long period are preferred because they are more prone to give realistic results.

Theory.   The effect of pH on the adsorption of ionisable pesticides has been investigated in many studies and depends on soil composition and the characteristics of the compound. The pH dependence of sorption 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. As described above, these effects are already relevant at pH above the pK_a. Studies into the effects of pH on adsorption are complicated by the influence of varying pH on the electrostatic charge of soil colloids (OM and (hydr)oxides). Indeed, as organic colloids have strongly pH-dependent charge, the solution pH also governs the degree of ionisation of humic acid groups. At neutral pH, the phenolic and alcoholic groups with pK_a of about 8 are assumed to be nonionised, whereas uncharged and ionized forms of carboxylic groups with pK_a of about 5.2 are assumed to coexist (Moreau-Kervevan and Mouvet 1998; Stevenson 1972).

The dissociation constant descibes the sensitivity of ionisable pesticides to soil pH (Table 4), and four types of pH influence have been recorded (Fig. 2). These are discussed in turn next.

Curve A.   The most common case when sorption is negatively related to pH is represented by curve A. A greater change in sorption coefficient is generally observed at lower pH (because pK_a are generally low). Weak acids (e.g., carboxylic acids, sulfonylureas, phenols) exist predominantly in the anionic form at pH values greater than their pK_a. With decreasing pH, the proportion of the protonated fraction increases. This neutral form is much more strongly sorbed in soils than the anion for several reasons.
    Some are direct consequences of the molecular dissociation:

  i. The neutral molecule does not undergo repulsion by the negatively charged surfaces of soil particles.
 ii. The hydrophobicity of the neutral form is greater than that of the ionic form (Hyun et al. 2003; Lee et al. 1990; Ukrainczyk and Ajwa 1996). For instance, Hyun et al. (2003) showed that hydrophobic sorption of neutral PCP is two orders of magnitude greater than that of the anion.
iii. The solubility in water of the anionic form is greater than that of the neutral form. For instance, Mersie and Foy (1985) showed that solubility of chlorsulfuron is higher at pH 7 than in acidic solutions. However, this should not have a significant effect in the field as pesticide concentrations in soil solution rarely approach the solubility limit (Nicholls 1988), except perhaps immediately after application.

Others are consequences of pH-dependent characteristics of the soil:

 iv. In variable-charge soils (mainly tropical and subtropical soils with significant quantities of iron and aluminium (hydr)oxides), the anionic-exchange capacity increases at lower pH values (or the surface charge becomes more positive as pH decreases). Thus, while pH decreases, sorption of the anion increases by ionic interactions (Hyun et al. 2003).
  v. Conformational changes due to OM dissociation could further account for the low adsorption under alkaline pH (Martin-Neto et al. 2001; Spadotto and Hornsby 2003). Indeed, some molecular environments, including protected sites of significant hydrophobicity, could disappear at high pH because of conformational changes induced by acidic functional group deprotonation (Ferreira et al. 2001; Martin-Neto et al. 2001).
 vi. With increasing pH, more hydroxyl ions are present to outcompete other anions for any remaining positively charged sites (Hyun et al. 2003).

A decrease of adsorption with increasing pH is also observed with some basic pesticides. This time, the explanation lies simply in the effect of pH on protonation of the molecule. Weak bases (e.g., triazines) are mainly

Table 4. Changes with pH in Form, Behaviour, and Adsorption Mechanism Operating for Acidic and Basic Compounds.

pH ⟶

Acidic compounds:			
pK_a	pK_a > 10	3 < pK_a < 10	pK_a < 3
Dominant form	AH	Ratio A⁻/AH	A⁻
General behaviour	Like neutral compounds, except under extremely alkaline conditions	Mobility, solubility, and volatility sensitive to pH	Highly mobile in soils unless chemical complexes are formed
			Temperate soils
Adsorption mechanisms		hydrophobic interactions (OM, clay) van der Waals (OM, clay) H-bonding (OM, clay)	Anion repulsion by negatively charged adsorbents Cation (or water) bridging (OM, clay) H-bonding Charge transfer (OM) van der Waals (OM)
			Soil with pH-dependent charge
			Anion exchange (Al, Fe (hydr)oxides) Ligand exchange (protonated (oxi)hydroxides, OM) Cation bridging (through ligand exchange: H₂O–metal)

Basic compounds:			
pK_a	pK_a > 10 (pK_b < 4)	3 < pK_a < 10 (4 < pK_b < 11)	pK_a < 3 (pK_b > 11)
Dominant form	BH⁺ or B⁺	ratio BH⁺/B or B⁺/B(OH)	B or B(OH)
General behaviour	Extreme soil sorption and generally slow degradation	Sensitive to pH: extreme sorption of cation produces an apparent soil surface acidity effect	Like neutral compounds, except at extremely acid conditions
Adsorption mechanisms	Cation exchange (OM, clay) Charge transfert (OM)		Hydrophobic partitioning (OM, clay) van der Waals (OM, clay) H-bonding (OM, clay) Ligand exchange (OM) Charge transfer: pesticide e-donor (OM)

AH and A⁻, BH⁺ and B, are the protonated and dissociated form of weakly acidic or basic pesticides, respectively.
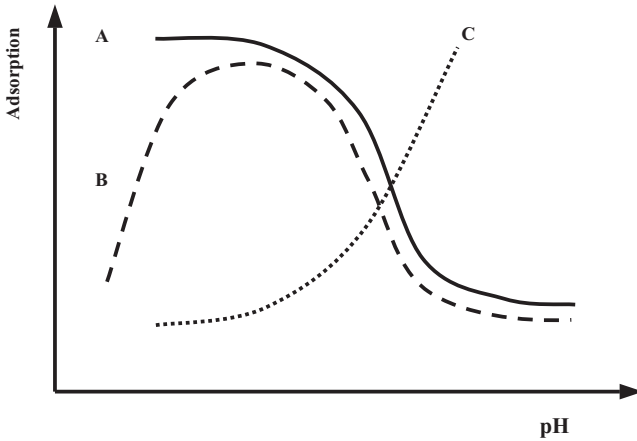Adapted from Wauchope et al. (2002).

Fig. 2. Three adsorption behaviours have often been recorded for ionisable compounds as a function of soil pH. A pH-independent sorption can also be observed in some cases. Reproduced from Calvet 1989 with permission from Environmental Health Perspectives.

present as neutral molecules under alkaline conditions and as cations at pH values below their pK_a. The cationic form is much more strongly retained than the dissociated form because of attraction by the negatively charged soils particles (cation exchange). Also, a likely solubilization of dissolved organic matter (DOM) at high pH levels that can complex with the neutral form could lead to a reduction in the measured sorption coefficient making the K_d observed at high pH lower still (Ben Hur et al. 2003; Celis et al. 1998a; de Jonge and de Jonge 1999).

Curve B. This type of curve is generally observed with weak bases. Adsorption increases with decreasing pH until a maximum is achieved and decreases thereafter. The pH corresponding to the adsorption maximum is sometimes close to the pK_a of the molecule, but it is not a general rule (Calvet et al. 1980a). The decrease in sorption at more acidic pH is generally attributed to:

Competition for anionic adsorption sites between the cationic form and other cations (H^+ and Al^{3+}) present in the solution (postulated for atrazine by Martin-Neto et al. 2001).
Increase in the cationic form that reduces the hydrophobic interaction between the pesticide and humic acid (also postulated for atrazine by Martin-Neto et al. 2001).
Ionization of acidic functional groups on OM that influences the nature of the adsorption mechanisms and could reduce the relative importance of hydrogen bonding (proposed for triazines by Moreau-Kervevan and Mouvet 1998; Wang et al. 1992).

Decrease in the concentration of anionic forms when the adsorption of an
  acidic compound is studied on some oxides where the surface is posi-
  tively charged (Watson et al. 1973).

A bell-shaped curve has been observed in experiments in which the pH was
modified artificially for terbutryn (Barrriuso and Calvet 1992; Barriuso et
al. 1992), atrazine on humic substances (Martin-Neto et al. 2001), several
dibasic carboxylic acids (Nicholls and Evans 1991a), and 2,4-D on goethite
(Watson et al. 1973). It was also observed for a weak acid (salicylic acid)
studied in soils with a range of natural pHs (Dubus et al. 2001).

Curve C. The last curve corresponds to an increase in adsorption with
increasing pH. The behaviour may occur for some weak bases that are
mainly adsorbed as neutral molecules (hydrophobic effect), and this has
been observed for simazine and atrazine on active charcoal (Yamane and
Green 1972). The behaviour can also result for molecules that are bonded by
complexation with a metallic cation as for terbutryn on Al-montmorillonite
(Calvet 1989) or carbendazim in a Vietnamese soil (Berglöf et al. 2002).
Fruhstorfer et al. (1993) also observed a higher adsorption of atrazine on
montmorillonite at pH 9.5 than at pH 4.5. The only explanation lies in the
fact that cation-exchange capacity is usually saturated by hydrogen ions in
solution at pH < 8, but remains unsaturated in alkaline solution.
    de Jonge et al. (2001) observed a significant positive correlation between
pH and adsorption of glyphosate ($p < 0.001$). The soils were from long-term
field experiments that received different additions of phosphorus and lime
over at least 60 yr. The authors explained this behaviour by two liming
responses (increase of Al and Fe oxides and reduction of Olsen-P concen-
trations) that counteract the effect of molecular charge on the strength of
sorption of glyphosate.
    It is unlikely that curve C will be observed in soils as the protonated form
of ionisable compounds always has a larger propensity for sorption than
the dissociated form.

No pH Influence.   In some cases, no influence of pH on sorption is found.
Different strategies can be applied to obtain a pH range and their conse-
quences on the other soil properties may complicate the interpretation of
the results in some cases. The pH range studied may sometimes be too
narrow or too wide to underscore any influence of pH. Finally, the differ-
ence between the pH at the surface of soil particles and in the soil solution
might also differ according to the measurement technique used and the
characteristics of the soil.

Observations.   Many articles report results concerning the influence of pH
on the adsorption of ionisable pesticides in soils. However, differences in
the experimental methods used (e.g., ionic strength, soil to solution ratio,

method to measure and modify pH, use of the formulation or technical grade) and in the range of soils considered sometimes make their interpretation and comparison difficult. Theoretical behaviour is sometimes observed, but conflicting results are also obtained. To highlight any specific behaviour that might be related to the chemical structure of the pesticide, references identifying relationships between sorption and pH are listed below, sorted by pesticide "families" (according to their ionisable functional group). The main correlations obtained between adsorption coefficients and soil properties (pH, OM, and clay contents) are summarised in Table 5.

Weak Acids: Carboxylic Acids.   The herbicide 2,4-D has often been taken as an example for the study of acidic pesticides in soils. Barriuso and Calvet (1992) studied its adsorption on 58 soils. The results of a principal-component analysis indicated a strong inverse correlation between K_d and soil pH. In the same study, the pH of three ferrasols was artificially increased and the authors observed a decrease in the K_{oc} value, confirming the importance of pH for the adsorption of 2,4-D. Similarly, the K_d value of 2,4-D decreased when the pH of some oxisols was increased from 3.5 to 7 (Barriuso et al. 1992). In this latter study, 2,4-D adsorption seemed to be dependent on pH and mineral type but independent of the OM content, whereas terbutryn adsorption was pH- and OM dependent (Barriuso et al. 1992). Johnson et al. (1995) also observed that sorption of 2,4-D was lower in slurries adjusted to pH 7 than to pH 5. In the same study, an inverse relationship between sorption and native pH of four soils was also obtained (pH between 4.2 and 5.9). However, Dubus et al. (2001) could not find any clear relationship between the adsorption of 2,4-D and the pH of 10 cambisols and eight ferralsols (pH from 4.6 to 8.3). Sorption of clofenset (pK_a = 2.8) and salicylic acid (pK_a = 2.8) (two other carboxylic acids) decreased exponentially with increasing solution pH in the 10 cambisols whereas a bell-shaped curve was obtained for the sorption of salicylic acid in the ferrasols studied (Dubus et al. 2001).

   Carrizosa et al. (2001) studied adsorption of dicamba on organoclays and found that pH had a negative effect on sorption, especially at high pesticide concentration. Greatest sorption of dichlorprop (pK_a = 3) and MCPA (pK_a = 3.7) was observed in the soil with highest organic carbon content and lowest pH (Thorstensen et al. 2001). Finally, increasing the pH (2–10) caused a fivefold decrease in the adsorption of fluroxypyr (Gao et al. 1998).

Phenols.   Hyun et al. (2003) studied adsorption of pentachlorophenol (pK_a = 4.71) in several variable-charge soils. Sorption decreased with increasing pH as the fraction of pentachlorophenolate (anionic form) increased and anion-exchange capacity decreased.

The Aminosulfonyl ($NHSO_2$): Sulfonylureas.   Sorption of the weakly acidic sulfonylurea herbicides generally increases with decreasing pH, as was

Table 5. Details of Experiments Investigating Correlation Between the Adsorption Coefficient of Ionisable Pesticides and Selected Soil Properties: OM, Clay, and pH.

Acidic pesticides (pK_a)	Adsorbent	Native pH	pH range	Presence of correlation and r^2 value[a]			References
				pH	OM	Clay	
Carboxylic acids							
Salicylic acid (2.8)	Database			(−) 0.16**	(+) 0.006	(+) 0.01	Weber et al. 2004
	10 cambisols	x[b]	6.2–8.3	(−) 0.76 / Exponential fitting ($r^2 = 0.97$)	(+)(−)	nc	Dubus et al. 2001
Clofencet (2.83)	8 ferralsols	x	4.6–7.2	Bell-shaped curve	(+)(−)	nc	Dubus et al. 2001
	10 cambisols	x	6.2–8.3	(−) 0.72 / Exponential fitting ($r^2 = 0.98$)	(+)(−)	nc	Dubus et al. 2001
Haloxifop (2.9)	8 ferralsols	x	4.6–7.2	(−)	(+)(−)	nc	Dubus et al. 2001
2,4-D (2.97)	15 soils, sediments	x	4.2–8.3	(−)	nc	nc	Rick et al. 1987
	2 oxisols	x	4.1–5.5	(−)	nc		Barriuso et al. 1992
	2 oxisols	0[c]	3.5–7	(−)	nc		Barriuso et al. 1992
	58 soils (9 soil types)	x	4.2–7.8	nc	nc		Barriuso and Calvet 1992
	10 soils	x	5.3–6.1	(−) 0.18	(+) 0.96	(+)	Bolan and Bascaran 1996
	10 cambisols	x	6.2–8.3	nc	(+)(−)	nc	Dubus et al. 2001
	8 ferralsols	x	4.6–7.2	(−) 0.93	(+)(−)	nc	Dubus et al. 2001
	4 soils	x	5–6.9	Regression with pH, OM, clay	(+)		Johnson et al. 1995
	5 soils	x	5.1–7.3	nc	(+) 0.85	nc	Picton and Farenhorst 2004
Fluazifop (3.2)	15 soils, sediments	x	4.2–8.3	(−)	nc	nc	Rick et al. 1987

Table 5. *Continued*

Acidic pesticides (pK_a)	Adsorbent	Native pH	pH range	Presence of correlation and r^2 value[a]			References
				pH	OM	Clay	
NHSO₂ acids							
Sulfonylureas							
	Database			(−) 0.16**	(+) 0.15**	(+) 0.0025	Weber et al. 2004
Metsulfuron-methyl (3.3)	24 soils	x	3.9–7.9	(−) 0.62***	(+) 0.88**	nc	Walker et al. 1989
Primisulfuron (3.47)	23 soils	x	4.6–8	(−) 0.56***	(+) 0.05	(+) 0.43***	Ukrainczyk and Ajwa 1996
				Exponential fitting ($r^2 = 0.85$)			
	6 Colorado soils	x	5.6–7.8	(−) 0.31	(+) 0.81*	(+) 0.82*	Vicari et al. 1996
Chlorsulfuron (3.6)	1 soil	2 wk.[d]	4.2–7.8	(−) (*)	Phytotoxicity; (+) 0.87**	nc	Mersie and Foy 1985
	24 soils	x	3.9–7.9	(−) 0.87***	(+) 0.74**	nc	Walker et al. 1989
Rimsulfuron (4)	6 Colorado soils	x	5.6–7.8	(−) 0.37	(+) 0.59	(+) 0.74*	Vicari et al. 1996
Nicosulfuron (4.3)	10 Iowa soils	x	6–8.2	(−) 0.12	(+) 0.75*	(+) 0.92***	Gonzalez and Ukrainczyk 1996
	4 tropical soils	x	4.6–5.2	(−) 0.88*	(+) 0.94*	(−) 0.27	Gonzalez and Ukrainczyk 1996
Sulfometuron (5.2)	5 Alabama soils	3 mon.	5.1–6.7	(−) ***	nc	nc	Wehtje et al. 1987
Other NHSO₂							
Flumetsulam (4.6)	14 surface soils	x	4.6–7.9	(−) 0.09	(+) 0.49**	(−) 0.001	Strebe and Talbert 2001
	14 subsurface soils	x	4.6–7.9	(−) 0.15	(+) 0.02	(+) 0.03	Strebe and Talbert 2001

Table 5. *Continued*

Acidic pesticides (pKₐ)	Adsorbent	Native pH	pH range	Presence of correlation and r^2 value[a]			References
				pH	OM	Clay	
Other acids							
Mesotrione (3.12)							
	15 soils	x	4.6–7.7	(−) 0.66	(+)		Dyson et al. 2002
	Database			(−) 0.18	(+) 0.27**	(+) 0.14**	Weber et al. 2004
Triazines							
Metribuzin (0.99)							
	Silty clay loam profile	x	6.5–7.2	(−) 0.86 Regression with clay, pH	(+) 0.01	(+) 0.75	Harper 1988
	9 soils	x	5.1–6.8	(−) 0.19	(+) 0.94**	(+) 0.45	Peter and Weber 1985
Atrazine (1.7)							
	58 soils (9 soil types)	x	4.2–7.8	nc	(+) 0.81		Barriuso and Calvet 1992
	241 samples (1 field)	x	5.5–7.3	(−) 0.76*** Regression with CO, pH, clay	(+)	(+)	Novak et al. 1997
Terbutryn (4.3)							
	2 oxisols	0	3.5–7	Bell-shaped curve (max. at pH 5)	(+) 0.90		Barriuso et al. 1992
	Oxisols	x	4.1–5.5	(−)	(+) 0.64		Barriuso et al. 1992
	58 soils (9 soil types)	x	4.2–7.8	(−) some correlations	(+) 0.36		Barriuso and Calvet 1992

Table 5. *Continued*

Acidic pesticides (pK_a)	Adsorbent	Native pH	pH range	Presence of correlation and r^2 value[a]			References
				pH	OM	Clay	
Others							
Fluridone (1.7)	18 soils	x	4.4–8.1	(−) 0.10	(+) 0.40** OM; (+) 0.69** OC	(+) 0.56** 0.72** with smectite	Weber et al. 1986
Carbendazim (4.2)	2 soils	0	3.5–6.4	(−)			Weber et al. 1986
	4 soils	x	2.9–5.4	(−) 0.35	(+) 0.99**	(+) 0.73*	Berglöf et al. 2002
	2 soils	0	3–7	(+)			Berglöf et al. 2002
Imidazolinones							
Imazaquin (2; 3.8)	10 soils	x	4.5–8.3	(−) <0.15	(+) 0.55 If two classes of pH 0.89 < r^2 < 0.99	(+) <0.03	Gennari et al., 1998
	22 soils	x	4.2–8.3	(−) 0.35**	(+) 0.20*	(+) 0.04	Loux et al. 1989a
	2 soils	10yr.	4.5–6.7	(−) 0.98 Quadratic relation	(−)	—	Loux and Reese 1992
	9 tropical soils	x	3.9–5.9	(−) 0.38*	(+) 0.83**	nc	Regitano et al. 2000
	3 tropical soils	3mon.	3–8	(−) 0.74**		nc	Rocha et al. 2002
Imazapyr (1.9; 3.6; 11)	10 soils	x	4.5–8.3	(−) 0.15	(+) 0.77 If two classes of pH 0.89 < r^2 < 0.99	(+) <0.03	Gennari et al. 1998
	5 Alabama soils	3mon.	5.1–6.7	(−) ***	nc	nc	Wehtje et al. 1987

Table 5. *Continued*

| Acidic pesticides (pK_a) | Adsorbent | Native pH | pH range | Presence of correlation and r^2 value[a] | | | References |
				pH	OM	Clay	
Imazethapyr (2.1; 3.9)	10 soils	x	4.5–8.3	(−) <0.15	(+) 0.61 If two classes of pH 0.89 < r^2 < 0.99	(+) <0.03	Gennari et al. 1998
	4 Minesota soils	x	4.8–7.1	nc	nc	nc	Gan et al. 1994
	22 soils	x	4.2–8.3	(−) 0.13	(+) 0.02	(+) 0.27**	Loux et al. 1989a
Others							
Glyphosate (2.6; 5.6; 10.6)	2 soils	60yr.	3.5–6.5	(+) 0.51***	nc	nc	de Jonge et al. 2001
Triclopyr (2.28; 3.35)	7 soils	x	4.4–7.7	(−) 0.37 Regression with CEC+pH ($r^2 = 0.98$)	(+) 0.87**	(+) 0.06	Pusino et al. 1994
	4 soils	x	5–6.9	(−) 0.96 Regression with pH and OM	(+)	nc	Johnson et al. 1995

[a](−) and (+) indicate a negative and positive correlation (r^2 value); *, **, and *** indicate a significance at p < 0.05, 0.01, and 0.001 levels, respectively; nc: no correlation was observed.

[b]Studies involving soils representing a range of native pH.

[c]pH was modified by adding the buffer agent into the batch soil suspension, just before K_d measurement.

[d]wk., mon., yr: the time the soil was left to equilibrate after addition of a buffer agent (in weeks, months, or years, respectively).

observed for soils with different native pH values (Gonzalez and Ukrainczyk 1996; Reddy et al. 1995; Shea 1986) and for soils adjusted to different pH levels before the sorption experiment (Mersie and Foy 1985; Shea 1986; Wehtje et al. 1987). In experiments by Walker et al. (1989), sorption of chlorsulfuron and metsulfuron-methyl was significantly negatively correlated with pH and positively correlated with the organic matter content of 23 soil samples from eight sites and three depths. Soil pH was found to be the most important variable controlling sorption. The relationship between sorption coefficients and pH was exponential; i.e., a stronger change in sorption occurred at lower pH. Ukrainczyk and Ajwa (1996) studied primisulfuron sorption on eight minerals and 23 soils and noted a great decrease of sorption with increasing pH on both adsorbents (significant negative correlation with pH with $r^2 = 0.55$). The same trend was observed for prosulfuron in 10 variable-charge soils (Hyun and Lee 2004). Vicary et al. (1996) observed maximum adsorption of rimsulfuron and primisulfuron on the soil that had the lowest pH (pH 5.6–7.8), but K_d and soil pH were not significantly correlated. Finally, Gonzalez and Ukrainczyk (1996) observed a strong negative correlation between the adsorption of nicosulfuron and the pH of 4 Brazilian soils, whereas no correlation was found for 10 Iowa soils. The explanation might lie in the lower range of pH represented by the Brazilian soils (4.6–5.2) compared to the Iowa soils (6.0–8.2).

Other Pesticides with a $NHSO_2$ Functional Group.   In 21 soils with pH ranging from 5.9 to 7.9, Fontaine et al. (1991) observed no relationship between K_d values of the weak acid flumetsulam and pH. However, a nonlinear relationship between K_{oc} and pH was obtained with a marked decrease in K_{oc} values up to pH 6–6.5 and a lesser change thereafter. This result was attributed to a strong influence of organic matter on the sorption of the neutral form of flumetsulam, which is the dominant form at low pH values. Flumetsulam sorption decreased as pH increased in four soils in which the solution pH was adjusted to 1.3–7.1. An equation was proposed to calculate the net K_{oc} value as a function of K_{oc} for the neutral and anionic form, pH, and pK_a. Strebe and Talbert (2001) also studied the adsorption of flumetsulam in 14 soils. K_d and K_{oc} were correlated with OM in surface soils while K_d was correlated with extractable Fe and inversely correlated to pH in subsurface soils. The mobility of flumetsulam (TLC study) was negatively correlated with K_d values at both soil depths and with K_{oc} in the subsurface soils. However, multiple linear regressions suggested that no soil property was an adequate predictor for mobility. For bentazone ($pK_a = 3.3$), the highest Freundlich coefficient (K_f) values were in the soil with highest organic carbon content and lowest pH (Thorstensen et al. 2001).

Other Acidic Compounds.   Mesotrione ($pK_a = 3.1$) adsorption was negatively related to pH and to a lesser extent to organic carbon content in a study carried out on 15 different soils (pH 4.6–7.7) (Dyson et al. 2002).

Overall, the results are consistent with soil pH having a major influence on the amount of mesotrione adsorbed, accounting for more than half the variation present in the data.

Weak Bases: Triazines, Triazinones.   Gao et al. (1998) studied the adsorption of seven pesticides and metabolites on sediments with different physicochemical properties, and only the nonionisable pesticide was not greatly influenced by pH. The adsorption of desethylatrazine and atrazine decreased with increasing pH (2–10), while a bell-shaped curve was obtained for terbutylazine and anilazine. The K_d of terbutryn also presented a bell-shaped curve between pH 3.5 and 7 and reached a maximum between pH 4.5 and 5.5 on oxisols with artificially stabilized pH conditions (Barriuso et al. 1992). Decrease in adsorption of terbutryn with pH < 5 could be explained by its protonation ($pK_a = 4.3$) as the soil colloids become positively charged.

Novak et al. (1997) used multiple regression analyses with data from batch experiments carried out on 241 surface soil samples from a 6.25-ha field (pH 5.5–7.3). Results revealed that atrazine sorption was positively influenced by soil organic carbon content and negatively by pH and, to a lesser extent, soil clay content. A negative influence of pH on the adsorption of simazine was also demonstrated in soils adjusted to different pH by Singh et al. (1989). Metribuzin has a very low pK_a (0.99), and pH should therefore be less important to its sorption than to the binding of other basic compounds. Nevertheless, sorption of metribuzin increased as pH decreased in soils pretreated for 15 yr with ammonium sulfate or calcium nitrate to achieve different pH values (Ladlie et al. 1976a,b) and in soils allowed to equilibrate for 3 mon after addition of HCl or NaOH (Wehtje et al. 1987).

Other Basic Compounds.   de Jonge and de Jonge (1999) observed that the pH rise (from 7.7 to 10.4) after addition of NH_4OH and NaP_2O_7 reduced the adsorption coefficient of prochloraz ($pK_a = 3.8$) by nearly 50%. As prochloraz is a neutral compound in this range of pH, the solution chemistry does not directly influence the sorption mechanism. The authors explained the observation by the solubilization of DOM at high pH levels, subsequently allowing formation complexes with prochloraz and leading to a reduction in the measured sorption coefficient. Similar behaviour has been reported for atrazine (Ben Hur et al. 2003; Celis et al. 1998a). Malik and Drennan (1990) observed that sorption of the weak base fluridone was inversely related to pH with a stronger decrease in sorption as pH increased from 2 to 5 than within the range from pH 5 to 9. Similarly, the highest Freundlich coefficient (K_f) values for propiconazole ($pK_a = 1.07$) were in the soil with highest organic carbon content and lowest pH (Thorstensen et al. 2001). The influence of pH on sorption of carbendazim ($pK_a = 4.2$) was studied on two soils that differed with respect to pH, clay, and OC. Sorption by the sandy soil (pH, 5.4; clay, 26.3%; OC, 0.3%) increased as the

pH decreased, while sorption on the second soil (pH, 2.9; clay, 49.8%; OC, 9.8%) decreased as pH decreased. One explanation may be that the solubility of carbendazim decreases with increased pH (Berglöf et al. 2002).

Zwitterionic Compounds: Imidazolinones.   Besides these results for weak acids and bases, evidence of the influence of pH on sorption exists for other ionisable compounds. The imidazolinone herbicides imazaquin, imazapyr, and imazethapyr are amphoteric compounds with acidic and basic functional groups (Stougaard et al. 1990). Their sorption was found to increase with decreasing pH in the pH range 3–8, probably due to effects on ionisation of the different ionisable functional groups (Goetz et al. 1986; Renner et al. 1988; Stougaard et al. 1990; Wehtje et al. 1987). However, in common pH ranges of agricultural soils, ionisation of the acidic groups should have a greater effect on sorption because pK_a values are very low (e.g., 1.8 for imazaquin, 1.2 for imazethapyr). For instance, Loux and Reese (1992) found a considerable decrease in imazaquin sorption when pH increased from 4.5 to below 6, while sorption varied only slightly above pH 6. In the afore mentioned studies on imidazolinones, soil pH was adjusted to different levels, although soils were allowed to equilibrate in the field for at least 10 yr in the experiments carried out by Loux and Reese (1992).

In contrast, Loux et al. (1989a) studied imazaquin and imazethapyr sorption in 22 soils and six sediment samples with a range of native pH values from 4.2 to 8.3 and a considerable variation in other soil properties. Linear regression analyses revealed a positive correlation between imazaquin sorption and organic carbon content and a negative relationship with pH. Imazethapyr sorption was positively correlated to clay content and cation-exchange capacity (CEC). In multiple regressions involving linear and quadratic terms, pH was found to be an important variable determining sorption of both compounds, but its effect on imazaquin sorption was the more significant. The authors included a quadratic term to account for the greater effect of pH in the range 4–6 as compared to that above pH 6. Imazethapyr seems to be less sensitive to soil pH than imazaquin or imazapyr. Indeed, correlation coefficients are usually very low (Gennari et al. 1998; Loux et al. 1989a), and Gan et al. (1994) could not observe any clear relationship with soil pH.

For soils relatively rich in aluminium and iron (hydr)oxides, pH-dependent charges of the adsorbents were considered to have an additional effect on imazaquin sorption (Goetz et al. 1986). Sorption of imazaquin decreased as pH values were increased from 2 to 6 for both HA and oxisol suspensions (Ferreira et al. 2002). Rocha et al. (2002) also observed a negative correlation between imazaquin sorption and artificially modified pH (from 3 to 8; $r^2 = 0.55**$) in highly weathered soils. Regitano et al. (1997) studied sorption of imazaquin on 18 soils (6 with pH-dependent charges) and observed an increase in K_{oc} with decreasing native pH (from 4.8 to 8). The K_{oc} values obtained with artificially reduced pH (to pH 3.1) show a very strong increase of adsorption at low pH level. Similarly, Regitano

et al. (2000) observed a low adsorption of imazaquin in 9 highly weathered tropical soils, with the exception being a soil with high organic carbon content and low soil-solution pH. In this article, the authors combined the results obtained in Loux et al. (1989a) and Regitano et al. (1997) and proposed a model that allowed a good prediction of imazaquin sorption in surface soils but not in subsurface samples.

Other Zwitterionic Compounds. Although Torstensson (1985) reported that sorption of glyphosate was not strongly dependent on soil pH, other studies have shown a strong dependence of sorption on pH. This effect was explained by the reduction in net charge of glyphosate as pH increases (McConnell and Hossner 1985; Nicholls and Evans 1991b) and possibly by the amount of dissolved organic matter (DOM) that went into solution at higher pH values (de Jonge and de Jonge 1999). Similarly, the relationship between triclopyr (amphoteric) sorption and the native pH of different soils was weak in the study of Pusino et al. (1994), perhaps as a result of the limited pH range. However, a combination of CEC and pH accounted for 98% of the variance in triclopyr sorption. In contrast, Johnson et al. (1995) found a strong inverse relationship between triclopyr sorption and native pH of four soils from two sites and two depths.

This listing demonstrates the great variability in the results obtained in various experiments, and highlights the difficulty in interpreting and comparing them. Although significant correlations between sorption and pH have been observed for all categories of ionisable pesticide, some sulfonylureas and imidazolinones seem to be particularly sensitive to changes in soil pH, even if they do not necessarily have higher dissociation constants. This difference might be related to their mechanism of adsorption and could be linked to some particular chemical properties of these pesticides. In some cases, pH has been shown to strongly influence sorption of a compound, while other studies cannot determine a relationship. In these cases, the influence of some experimental parameters and/or other soil properties might mask the influence of pH. The standardization of experimental settings (e.g., ionic strength, soil-to-solution ratio, method to modify pH), the inclusion of the methods used to determine soil properties, especially OM and pH, and a judicious choice of the range of soil studied would allow an easier comparison between studies and a clearer understanding of that part of variability in sorption that is attributable to variations in pH.

Attempts to Model the Influence of pH on Sorption.   Bailey et al. (1968) noted early on the difficulty in predicting the sorptive behaviour of pesticides that dissociate to form ions. Many factors, including the dissociation constant (pK_a), soil solution pH, ionic strength and ionic composition, and the type and charge of soil components may have to be considered to successfully predict sorption of ionisable compounds in soils (Koskinen and Harper 1990). Furthermore, as already described, sorption of these com-

pounds can occur through various mechanisms that depend on both the molecule and the soil properties, making any generalisation difficult.

Several authors developed equations to predict the sorption of ionisable compounds in soils or sediments (Fontaine et al. 1991; Jafvert 1990; Lee et al. 1990; Regitano et al. 1997; Shimizu et al. 1992). Different assumptions were made regarding the relationship between pH and the adsorption of the neutral and ionic forms and the pH-dependent changes to consider in the surface charges or soil components. Adsorption in the system studied could usually be predicted from the combination of two partition coefficients (one for each form coexisting in solution), with the pK_a, the soil pH, and OM content. Unfortunately, the applicability of these models to other systems in which other factors can become more important was rarely demonstrated. More recently, Spadotto and Hornsby (2003) developed a model from theoretical modelling and experimental data, initially based on the adsorption of 2,4-D in a variable-charge soil. Although the adsorption of the anion was considered to be negligible, the accessibility of OM (as a consequence of OM dissociation with increasing pH) was considered to explain the observed differences in sorption. Experimental data for sorption of 2.4-D and K_{oc} values from the literature for flumetsulam and sulfentrazone in several soils fitted the model.

Among the pesticide fate models commonly used to predict the behaviour of pesticides in the environment, only PEARL (Tiktak et al. 2000), PELMO (Jene 1998), and RZWQM (Wauchope 1992) have an option for ionisable pesticides. The parameters needed to model pH influence are generally not available and need to be determined for each soil–pesticide combination. Further experimentation should be considered to test the robustness of the equations proposed and to select the assumptions to take into account to develop a unique or specific approach if necessary, able to describe the complexity of interactions among ionisable molecules.

Influence of Soil Components.   There have been many attempts to develop a universally applicable sorption constant, or regression equations able to predict adsorption of organic contaminants in soils based on soil properties, without need for time- and cost-consuming experiments in every case. Organic carbon content has been shown to be the single most important soil property for predicting the sorption of neutral organic compounds. That is why Hamaker and Thomson (1972) proposed to refer the adsorption coefficient (K_d) to the soil organic carbon content using a normalised coefficient (K_{oc}) that appears to be much less variable for adsorption of a given hydrophobic molecule (Karickhoff 1981). It has now become a widely used parameter for comparing pesticide binding in soil. However, this approach is not suitable for ionisable compounds (Von Oepen et al. 1991) as their adsorption depends to a greater or lesser extent on soil pH and because they can interact strongly with the other soil fractions such as clay and Al, Fe (hydr)oxides.

Soil components function more as a unit than as separate entities, and the relative contributions of organic and inorganic surfaces to sorption depend on the extent to which the minerals are coated with organic substances (Stevenson 1972). The consequences of these interactions on pesticide sorption are not fully understood. Some authors have reported that the interassociation processes may block functional groups for sorption on mineral and organic surfaces (Pusino et al. 1994). This is supported by soil experiments that show that the contribution of the clay fraction to adsorption is generally much smaller than studies with the pure minerals would predict. Similarly, better fits are generally obtained with regression analysis with CEC instead of OM content because the CEC considers the sorptive capacity from both OM and clays and the likely reduction in sorption due to their interactions (Pusino et al. 1994).

Nevertheless, the different soil constituents may also complement one another, leading to enhanced sorption on the resultant aggregate. For instance, Fe coatings on montmorillonite surfaces decreased sorption of the polar uncharged herbicide thiazafluron (Celis et al. 1997b), but promoted sorption of the basic herbicides atrazine and simazine on the clay surfaces (Celis et al. 1998b). The results of Celis et al. (1999) showed how the complexity of the surface of a natural particle was far from the sum of its individual components (i.e., humic acid, clay mineral and (hydr)oxides), for the sorption fate of 2,4-D. As a consequence, the use in modelling of sorption parameters (K_{oc}, K_{ow}, $K_{mineral}$, or K_{Fe}) estimated assuming sorption on a single soil component alone may result in serious deviation from reality (Celis et al. 1999).

Soil Organic Matter.   Many studies show that adsorption of organic chemicals in soils is mainly to organic matter, even though structure and properties of organic constituents are not yet clearly understood. For instance, Stephenson et al. (1990) showed that, throughout a 4-mon experiment, 90% or more of triclopyr was recovered in the soil organic layer. Consequently, published results on pesticide adsorption frequently report some positive correlation between distribution coefficient values and soil OC content or OM content (see Table 5).

Both the type of material being decomposed and stage of decomposition are important in this process. The major HA groups include carboxylic, phenolic, hydroxyl, carbonyl, amine, amide, and aliphatic moieties. Due to this polyfunctionality, HA are one of the most powerful chelating agents among natural organic substances. The prominent role of HA, compared to other organic fractions, has been highlighted for four *s*-triazines (Stevenson 1972), imazethapyr (Senesi et al. 1997), and MCPA (Haberhauer et al. 2001).

The molecular structure of HA will also influence the adsorption of pesticide on the soil organic fraction. For instance, Gennari et al. (1998) reported that the higher the content of carboxyl groups, the higher the amount of imidazolinones adsorbed. Piccolo et al. (1992) observed a higher adsorption of atrazine on HA with higher aromaticity, polycondensation,

and molecular size. However, Piccolo et al. (1998) suggest that atrazine retention in soils might be controlled by specific molecular structure of OM rather than by its acidic functionality or aromaticity, which would indicate ionic bonding and charge transfer reaction, respectively. The aliphatic carbon content of soil OM may be a more important parameter controlling atrazine adsorption to soils because the conformational rigidity conferred to humic fractions with a large content of aromatic moieties appeared conducive only to surface adsorption and thus to easier desorption of herbicide (Piccolo et al. 1998).

Even though OM generally provides most of the adsorption sites in soils, the correlation between adsorption and OM depends more or less on the nature of both the herbicide molecule and the soil, and the positive influence of OM on the adsorption of ionisable compounds is not always obvious. For instance, Barriuso et al. (1992) did not find any relationship between the K_d value for 2,4-D and the soil OC content of two oxisols, whereas the relationship was very strong in the case of atrazine ($r^2 = 0.86$) and terbutryn ($r^2 = 0.64$). The study was carried out on two sites with plots with different crop histories, resulting in a difference in OC content, and at a pH at which the 2,4-D molecule was anionic and thus less subject to hydrophobic partitioning on the OM than the two bases. Another example was observed in three ferralsols samples, where sorption of clofenset and salicylic acid was found to increase with depth in a soil profile where organic matter decreased (Dubus et al. 2001). Enhanced sorption of weak organic acids in subsurface layers is not uncommon in soils with pH-dependent charges and has been reported in several other studies (Goetz et al. 1986; Loux et al. 1989a; Mersie and Foy 1985; Regitano et al. 2000).

In these examples, adsorption of acidic pesticides mainly involved ionic interactions with positive charges in soil, generated by iron and aluminium (hydr)oxides. The OM can adsorb some 2,4-D through weak interactions (van der Waals forces and charge transfer), but more often its overall negative charge causes charge repulsion for anionic compounds (Stevenson 1972). Coating of the mineral surfaces by soil OM might block specific sorption sites on oxide surfaces and might also explain the negative influence of OM content on adsorption observed in some cases (Dubus et al. 2001). The negative relationship between sorption and OM content observed for these profiles confirms that sorption mechanisms for ionisable compounds are different from those involved in the sorption of nonionisable compounds. However, this behaviour would never be expected for subsurface horizons of soils with permanent negative charges (temperate soils), where the higher soil-solution pH in the subsurface would enhance repulsion between anionic pesticide and the negatively charged soil sites, and where the lower OM content would provide less hydrophobic sites for sorption (Regitano et al. 2000).

Soil organic matter can also be divided into solid (SOM) and water-dissolved (DOM) fractions, both of which can associate with herbicides. The latter has been the subject of several recent studies that investigated how

organic amendments, producing soluble OM, affect pesticide adsorption. Formation of a complex between the pesticide and DOM decreases pesticide adsorption if DOM is not adsorbed to the soil, and vice versa (Barriuso et al. 1997; Ben-Hur et al. 2003; Said-Pullicino et al. 2004; Si et al. 2006). The latter case occurs where complexes adsorb in lower soil horizons that have typically a smaller OM content. In soils with large SOM contents (7% or greater), the contribution of atrazine–DOM complexes to total sorption appeared to be negligible (Ben-Hur et al. 2003; Spark and Swift 2002).

Clay.   The clay fraction of the soil is composed of both crystalline and amorphous minerals. Most of the charged and polar sorption sites are on the secondary minerals, the layer silicates. Amorphous minerals can also provide some hydrophobic sorption sites. In contrast, crystalline minerals such as quartz and feldspar typically contribute little to the sorption capacity of a soil (Harper 1994). Strong correlations have sometimes been found between the clay content and the adsorption of certain ionisable pesticides, especially some sulfonylureas and basic compounds (see Table 5). For instance, Harper (1988) studied the behaviour of metribuzin down a silty clay loam profile and observed that clay content was the single best predictor of its adsorption. Indeed, in low organic matter soils, the contribution of inorganic constituents to pesticide retention can be dominant (Barriuso et al. 1994). The results of Ben-Hur et al. (2003) indicate that clay plays a significant role in atrazine adsorption when the clay/soil organic C ratio is >30, as may occur in cultivated soils with low OM content (Barriuso et al. 1992), in deep soil horizons, and in some sediments.

It is known that *s*-triazines can be adsorbed on clay minerals as both protonated and neutral species, depending on the pH of the soil solution. The neutral form is adsorbed by relatively weak physical forces (hydrophobic partitioning, van der Waals forces, H-bonds), whereas the positively charged molecule is mostly adsorbed by cation exchange (Fruhstorfer et al. 1993). The type of surface cation seems to play a key role in the adsorption process at low pH (Herwig et al. 2001). Indeed, cations in solution may compete for negatively charged adsorption sites in cation exchange. They may also behave as adsorption sites in cation or water bridging.

Nonionic or anionic herbicides sometimes sorb to clay surfaces through the formation of a complex between the herbicide, an exchangeable cation, and the soil surface. These complexes have been found for acifluorfen, glyphosate, and some *s*-triazines (Harper 1994); they can lead to immobilization and inactivation when metal concentrations are high (Harper 1994; Kozlowski et al. 1990).

Gonzalez and Ukrainczyk (1996) observed that the sorption of nicosulfuron on Iowa soils was most correlated with clay content while in Brazilian soils it was most correlated with OC content. These differences were interpreted in terms of different clay mineralogy of Iowa (expandable 2:1 clay minerals) and Brazilian soils (kaolinite, Al and Fe oxides). Results of X-ray

diffraction analysis showed that, in some cases, sorption was not limited to the external surface of clays. Indeed, it has been demonstrated that fluazifop-butyl (Fusi et al. 1988) and fluridone (Weber et al. 1986) could enter into the interlayer space of montmorillonte. Although excluded from this review of ionisable pesticides, cationic bipyridylium herbicides (e.g., diquat and paraquat) adsorb in the internal surfaces of clays, and this process is not fully reversible (Hayes et al. 1975). Herwig et al. (2001) found atrazine adsorption to be proportional to the external surface area in Na^+ layer silicates such as kaolinite, illite, and montmorillonite, and concluded that atrazine molecules do not intercalate even in swelling Na^+ clay minerals.

Aluminium and Iron (Hydr)oxides. Positively charged oxide surfaces have been shown to play a significant role in the sorption of clofenset and salicylic acid (Dubus et al. 2001), primisulfuron (Ukrainczyk and Ajwa 1996), 2,4-D (Barriusso et al. 1992), imazaquin (Goetz et al. 1986; Regitano et al. 1997, 2000), 2,4-D and dicamba (Stolpe and Kuzila 2002), and meco-prop, 2,4-D, and bentazone (Clausen and Fabricius 2001). This sorption behaviour is probably more common in tropical and semitropical soils due to the greater prevalence of Al and Fe (hydr)oxides. In temperate areas, the relatively high concentration of organic compounds in the soil serves to complex with the Al and Fe as it is released by the weathering of soil parent material, thereby preventing the formation of their respective (oxi)hydrox-ides. Their role is particularly important when OM and clay content are low and at pH values where acidic compounds exist almost exclusively as an anion (Goetz et al. 1986). Adsorption of weak bases onto iron oxides is insignificant (Clausen and Fabricius 2001; Stolpe and Kuzila 2002).

The net charge of these surfaces varies with pH. At pH values above the point of zero charge (PZC) of the minerals, the surfaces have a net nega-tive charge. Thus, adsorption of anions is restricted due to electrostatic repulsion. At pH values lower than PZC, adsorption of anions is promoted due to electrostatic attraction to the positively charged surfaces (Dubus et al. 2001). In fact, anionic moieties can interact not only with the positive $Al(OH)^{2+}$ and $Fe(OH)^{2+}$ groups on the clay surface through electrostatic interactions (anion exchange, cation bridging), but also exchange with –OH or OH_2 and create a bridge with one or two adjacent Fe or Al atoms through a ligand-exchange mechanism (Regitano et al. 2000).

Hyun and Lee (2004) observed that the fraction of hydrophilic sorption of prosulfuron correlated well with the ratio of the AEC to CEC, whereas the correlation with only AEC led to poor fits. The authors concluded that normalizing AEC by CEC accounted for repulsion by negatively charged sites on the soil surface, which may attenuate the potential for organic anions to interact with the positively charged sites.

Conclusion. Weber et al. (2000) correlated K_d values and soil properties reported in the literature for 28 herbicides including acidic and basic

compounds. The results show that OM is the soil constituent most highly correlated with binding of most organic herbicides; clay content is correlated with retention of all cationic and many weakly basic compounds; and pH is inversely correlated with retention of many weakly acidic herbicides. A few years later, Weber et al. (2004) repeated the procedure for an assortment of 57 pesticides. K_d values for all pesticides were correlated with the OM content and a combination of OM and clay contents, but correlation coefficients were very small, and soil properties were often correlated with one another. However, after separating pesticides into chemical classes, some trends could be discerned (see Table 5). K_d values were not related to soil pH for any of the 6 nonionisable pesticide families, whereas sorption of weakly acidic pesticides in soils was most strongly related to OM content and/or inversely related to pH. Soil pH was inversely correlated with K_d for carboxylic acids, and inclusion of OM or clay content did not improve the relationship. Sorption of weakly basic pesticides was most strongly related to soil OM and clay contents and inversely related to pH. OM and clay were correlated, but pH was not related to either parameter confirming the importance of pH for the binding of ionisable pesticides.

These results, in association with the numerous studies showing a significant influence of pH on K_d or K_{oc}, confirm that the use of a unique K_{oc} is not suitable to predict the behaviour of ionisable pesticides in soils (Wauchope et al. 2002). However, it seems difficult to define a modelling approach applicable to all ionisable pesticides in all situations. The standardization of experimental settings, the inclusion of the methods used to determine soil properties, especially OM and pH, and progress in the determination of the pH at the surface of soil particles should help in comparing results of different studies and support identification of the parameters that should or should not be taken into account for a specific type of soil or compound. Better results might also be achieved by considering different categories of clay and OM rather than their total content in soil. Some fractions can adsorb ionisable pesticides very efficiently (e.g., montmorillonite clays for bases, iron and aluminium oxides for acids) while others might be essentially inert.

Until we have a better understanding and prediction of the phenomenon specific to ionisable compounds, it is advised to base assessment of the fate of ionisable pesticides on, instead of a unique K_{oc}: (i) a K_d (or K_{oc}) determined at a standardized pH, with its decrease calculated as a function of pH; (ii) multiple regression equations defined for each ionisable pesticide family (Weber et al. 2004); or (iii) models that take into account the influence of pH and oxides on adsorption.

IV. Degradation of Ionisable Compounds and Soil pH

After partitioning between the liquid and solid phases, molecules present in soil solution and molecules adsorbed on soil particles often have different potential to undergo additional processes such as volatilization, leaching,

chemical hydrolysis, or biodegradation. As a consequence, adsorption is often shown to influence the rate at which pesticides degrade in soil.

Along with sorption, degradation is the second important process used to predict the fate of organic compounds in soils (Boesten and van der Linden 1991). Standard laboratory and field dissipation studies are performed to assess the rate of degradation, often expressed as a first-order half-life or DT_{50}, the time required for 50% of the initial dose to be degraded. A greater understanding of the factors that influence biodegradation rate is required to allow prediction for soils where experimental data are not available. The rate of degradation is influenced by chemical properties of the soil (such as pH and OM content), biological properties (activity and distribution of micro-organisms), and environmental conditions that control soil temperature and moisture content. Both route and rate of degradation also depend on properties of the chemical. Degradation of pesticides in soils usually involves the activities of soil microorganisms, although abiotic transformations can become dominant in some cases. In addition, soil properties are often inter-related and may influence these processes in opposite directions, thereby exhibiting a stimulating and restricting effect on the overall degradation process. We have seen how pH influences the adsorption of ionisable pesticides in soils. Because adsorption is often important for controlling the rate of degradation, an additional pH effect on the degradation rate of ionisable pesticides might be expected. Consequently, we only focus here on the influence of soil pH on degradation rates.

Influence of Soil pH on Degradation.   A relationship between soil pH and rate of degradation has been demonstrated for many ionisable pesticides, although there are exceptions. No influence of pH on degradation was found for atrazine (Hance 1979), 2,4-D (Picton and Farenhorst 2004), and rimsulfuron (Vicari et al. 1996). Soil pH may influence the degradation of a pesticide directly if its stability is pH dependent (chemical hydrolysis) or indirectly via changes in soil microbial biomass/activity, or pesticide sorption. If degradation is influenced indirectly by pH, it tends to proceed faster at high pH.

Positive Influence: Indirect Effects via Changes to Microbial Activity and Sorption.   Soil pH significantly influences the structure of the microbial community. Many studies have demonstrated a positive influence of pH on total microbial biomass and activity (Price et al. 2001; Walker et al. 2001), although microbial degradation seems to be restricted when pH becomes greater than 8–8.5 (Awasthi et al. 2000; Fredrickson and Shea 1986; Thirunarayanan et al. 1985; Walker et al. 1989). Consequently, degradation of many neutral compounds has been shown to be faster at high pH. Moreover, we have seen that adsorption of ionisable pesticides generally decreases as pH increases. Therefore, molecules are generally more available for biodegradation under alkaline conditions, and the positive influence of pH on degradation rate is, consequently, more obvious for ionisable

compounds. A positive influence of pH on degradation has been shown for imazaquin (Loux and Reese 1992), metribuzin (Ladlie et al. 1976b), dichlorprop (Hance 1979), prochloraz (Höllrigl-Rosta et al. 1999), mesotrione (Dyson et al. 2002), dicamba (Voos and Groffman 1997), and flumetsulam (Lehmann et al. 1992).

Negative Influence: Specific Case of Sulfonylureas. Transformation of organic compounds in soils occurs through both microbial breakdown and chemical degradation. Abiotic degradation can be the dominant reaction in soils for many sulfonylureas. For instance, Hultgren et al. (2002) studied prosulfuron degradation and observed that pH-dependent hydrolysis of the sulfonylurea bridge was the primary transformation process. Significant microbial degradation occurred in only 2 of the 10 soils. Microbial reaction tends to be faster under alkaline conditions (up to a maximum value), whereas abiotic hydrolysis of sulfonylureas is generally more favoured under acidic conditions (Sabadie 1990; Said-Pullicino et al. 2004; Sarmah and Sabadie 2002; Sarmah et al. 2000; Vicari et al. 1996). For instance, Sarmah et al. (2000) observed that the hydrolysis of triasulfuron, metsulfuron-methyl, and chlorsulfuron involving attack by neutral water was at least 100 fold faster when the molecule was undissociated (acidic conditions) than when present as the anion at near-neutral pH. Chlorimuron hydrolysis also increased by 150 fold as the pH decreased from 7 to 4 in buffered aqueous solution (Brown 1990). The dominance of acidic hydrolysis explains the negative relationship between degradation and pH often reported for sulfonylureas including chlorsulfuron, metsulfuronmethyl, prosulfuron, primisulfuron methyl, rimsulfuron, and thifensulfuron methyl (Sarmah and Sabadie 2002), chlorsulfuron (Fredrickson and Shea 1986; Thirunarayanan et al. 1985; Walker et al. 1989), prosulfuron (positive correlation between DT_{50} and soil pH: $r^2 = 0.86$) (Hultgren et al. 2002), metsulfuron-methyl (Pons and Barriuso 1998; Walker et al. 1989), and chlorsulfuron and triasulfuron (Sarmah et al. 1999). Similar results have been obtained for the weak bases atrazine and simazine (Walker and Blacklow 1994; Walker and Thompson 1977).

Conclusion. Considering the complexity of interactions between the different processes, it seems to be more difficult to prove a link between degradation and pH than to demonstrate the influence of pH on sorption. However, the influence of pH on degradation seems to be more apparent for ionisable compounds. For nonionisable compounds, pH primarily controls the microbial activity of the soil, leading to a positive influence of pH on degradation rates. In the case of ionisable compounds, strength of sorption decreases and availability for degradation generally increases with increasing pH. There are thus both biological and physical processes underpinning an increase in rate of degradation with pH for ionisable compounds subject to microbial degradation. However, when abiotic degradation is dominant (e.g., sulfonylureas), pH generally has a negative influence on

degradation rates. In this case, the increase in bioactivity at high pH is less significant than the decrease in rate of chemical hydrolysis.

V. Link Between Sorption and Degradation Processes

It is quite well recognised that sorption processes may affect biodegradation mainly by modifying chemical bioavailability. Evidence that degradation can be restricted to the soil solution and that sorbed molecules may be protected from microbial attack has been provided by several studies (Ogram et al. 1985; Radosevish et al. 1996; Smith et al. 1992). The protection of a sorbed compound may arise from (i) the reduction of soil solution concentrations to levels below that necessary for microbial utilization, (ii) surface stabilisation against desorption of the compound (formation of bound residues), and (iii) inaccessibility of the micropores to microbes (Ainsworth et al. 1993).

A positive relationship between adsorption coefficient (K_d) and half-life has been reported for diallate (Anderson 1981), simazine (Walker and Blacklow 1994), 2,4-D (Bolan and Baskaran 1996), flumetsulam ($r^2 = 0.85$; Lehmann et al. 1992), several imidazolinones (Basham et al. 1987; Cantwell et al. 1989; Loux et al. 1989b; Loux and Reese 1992, 1993); metribuzin (Ladlie et al. 1976b); 2,4-D and trichlopyr (Johnson et al. 1995), mesotrione ($r^2 = 0.45$; Dyson et al. 2002), and 2,4-D (empirical power equation, $r^2 = 0.99$) (Guo et al. 2000).

Factors other than sorption also influence degradation rates, and the link between sorption and degradation is not always obvious (Barriuso et al. 1997; Radosevish et al. 1996; Shaw and Burns 1998a). A negative relationship between K_d and DT_{50} can even be observed in some cases (Walker and Thomson 1977). Several factors might counterbalance the influence of sorption on degradation:

i. Biodegradation might not always be restricted to chemical in solution (Eberbach 1998; Guo et al. 2000; Khan and Ivarson 1981; Park et al. 2001).
ii. Microorganisms are generally more abundant at or near soil particle surfaces (Stotzky 1986). Sorption may thus concentrate the pesticide in regions of greatest microbial activity, thereby facilitating degradation.
iii. Adsorption to OM can facilitate the abiotic transformation of the molecule as shown for metribuzin and its metabolites using infrared spectroscopy (Henriksen et al. 2004), for azimsulfuron (Pinna et al. 2004), and for triasulfuron (Said-Pullicino et al. 2004). This process seems to operate especially at low pH and to be related to the mechanisms of sorption.
iv. OM content can have opposing effects on degradation, either via an increase in sorption or via an increase in microbial activity.

The positive or negative correlation between OM and degradation should indicate the strength and sign of the correlation between sorption

and degradation. Bolan and Bascaran (1996) observed a bell-shaped relationship between K_d and DT_{50} of 2,4-D measured in 10 soils. The increase of degradation rate for the highest K_d values was explained by (i) the tendency of these soils to have a higher microbial activity and (ii) an inhibitory effect of 2,4-D on activity that decreased with an increase in OM content. The decrease of pesticide concentration in solution with an increasing K_d was thus compensated by an increased microbial activity, thereby increasing the rate of degradation.

More experiments coupling measurement of adsorption and degradation under differing conditions would help us to better understand the extent and mechanisms of interactions between the various processes. Nevertheless, we have seen that pH generally decreases sorption of ionisable pesticides and that pH can also influence their degradation to a great extent via changes in microbiological activity and sorption. If a negative influence of sorption on degradation can be demonstrated, it should be stronger in the case of ionisable compounds, especially for basic compounds that often show a high adsorption potential. This effect has implications, for example, in risk assessment where associating the lowest K_d with the highest DT_{50} may constitute an unrealistic and thus overly protective assumption (Dyson et al. 2002).

VI. Conclusions

Ionisable pesticides comprise a significant proportion of the existing and new active substances currently undergoing review for registration by the European Union (EU 2002). This group of pesticides includes chemicals that are frequently found in groundwater and surface waters worldwide. It is thus essential to understand their fate in the environment, and the specifics of their behaviour need to be recognised within risk assessment procedures. A great deal of work has been undertaken concerning the adsorption of ionisable pesticides in soils, but generalised conclusions cannot be made, and significant open questions remain.

Many retention mechanisms in addition to hydrophobic partitioning have been postulated to be responsible for the adsorption of ionisable pesticides in soils (e.g., ionic exchange, charge transfer, ligand exchange, and cation or water bridging). However, relatively little experimental evidence is available, and we are still unable to determine the quantitative contribution of each sorption mechanism in a particular situation. Further research using techniques such as nuclear magnetic resonance, electron spin resonance, Fourier transform infrared, and fluorescence spectroscopies, and including measurement of soil and pesticide properties, should help to better understand and predict the adsorption mechanisms that operate.

More generally, knowledge is still lacking concerning the phenomena occuring at the surface of soil particles. It is difficult to assess likely competition effects with the other ions present in soil solution, and consequently the complex effect of ionic strength, or moisture content effects, on the

adsorption of ionisable compounds. Measurements of pH do not allow the determination of the operative pH at the surface of soil particles or in microenvironments, although this is often assumed to be one to four units lower than the pH measured in the bulk solution.

The adsorption of ionisable compounds in soils is strongly influenced by pH, and this effect depends on soil composition and the characteristics of the compound. 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 varying pH on the charge at the surface of soil particles also plays a role in some cases. A decrease in adsorption with increasing pH is often observed. However, bell-shaped curves, increases in adsorption, and pH-independent behaviour have also been reported. 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 or soils equilibrated for a long period will give more realistic results. The two methods have generated conflicting results because the influence of some experimental factors and/or soil properties have superposed and often masked the influence of pH. The standardisation of experimental settings (e.g., ionic strength, soil-to-solution ratio, method to modify pH) would allow an easier determination of that part of the variance trully attributable to the influence of pH. Soil OM generally promotes the adsorption of ionisable pesticides in soils, although its negative influence has sometimes been observed as well, which confirms that sorption of ionisable compounds in different soils cannot be assessed simply by normalising to organic carbon content. Clay and Al or Fe (oxi)hydroxides can also play a significant role and might have to be considered in some situations.

So far, no modelling approach has been applied successfully to a range of ionisable pesticides to predict their adsorption in soils. Further experimental data are required to test the robustness of equations proposed and to select the necessary assumptions. Approaches specific to a particular class of pesticide, with the inclusion of QSAR for instance, and/or soil type might be necessary to describe the complexity of interactions among ionisable molecules.

Degradation of ionisable pesticides is influenced by soil pH in a particular way that relates to changes in sorption, changes in composition and activity of the microbial community, and to shifts in the balance between different degradative mechanisms. Degradation tends to proceed faster at high pH for compounds mainly degraded by microorganisms while degradation of sulfonylureas, particularly sensitive to chemical hydrolysis, is generally faster under acidic conditions.

Questions remain concerning the link between the processes of adsorption and degradation. Experiments measuring these two parameters under standardized conditions could help to better understand their relationship and their dependence regarding soil and chemical properties and could

support the choice of more realistic input parameters in risk assessment procedures.

Summary

Understanding the fate of a pesticide in soil is fundamental to the accurate assessment of its environmental behaviour and vital in ensuring the safe use of new and existing products. Ionisable pesticides comprise a significant proportion of both existing and new active substances registered for use in agriculture worldwide. This group of pesticides includes chemicals that are frequently found in groundwater and surface waters in many different countries. Despite this, approaches to predict the influence of soil properties on the behaviour of ionisable pesticides in soils are poorly developed. Current regulatory assessments frequently default to methods developed for nonionic chemicals, although it is evident that ionisable compounds do not often react like neutral molecules.

This review presents the state of knowledge on the adsorption of ionisable pesticides in soils. It first introduces the issues concerning adsorption and the characteristics of this particular kind of chemical. The mechanisms postulated for the adsorption of ionisable pesticides are then described: these are hydrophobic partitioning, ionic exchange, charge transfer, ligand exchange, cation or water bridging, and the formation of bound residues. Relatively little experimental evidence is available, and we are still unable to determine the quantitative contribution of each process in a particular situation. Knowledge is still lacking concerning phenomena occurring at the surfaces of soil particles. Measurements do not allow determination of the operative pH at the surface of soil particles or in microenvironments, and the influence of ionic strength or competition effects is difficult to assess.

Subsequently, the review focuses on the influence of soil properties on adsorption and on potential to predict the behaviour of ionisable pesticides in soils. Unlike hydrophobic compounds, adsorption of ionisable pesticides is highly sensitive to variation in pH. This relationship mainly derives from the different proportion of ionic and neutral forms of the pesticide present at each pH level but also from the presence of surfaces with pH-dependent charges in soils. Soil organic matter generally promotes adsorption, although a negative influence has sometimes been reported. Clay and oxides can also play a significant role in some cases. So far, no modelling approach has been applied successfully to a range of ionisable pesticides to predict their adsorption in soils. The standardization of experimental settings and the application of approaches specific to a particular class of pesticide or different type of soil might be necessary to describe the complexity of interactions among ionisable molecules. Degradation of ionisable pesticides is influenced by soil pH in a particular way that relates to changes in sorption, changes in composition and activity of the microbial community, and to shifts in the balance between different degradative mechanisms.

Appendix. CAS numbers and chemical names of pesticides reported.

Compound	CAS	Chemical name
Acifluorfen	50594-66-6	5-[2-Chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid
Ametryne	834-12-8	N-Ethyl-N?-(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine
Anilazine	101-05-3	4,6-Dichloro-N-(2-chlorophenyl)-1,3,5-triazin-2-amine
Atrazine	1912-24-9	6-Chloro-N-ethyl-N?-(1-methylethyl)-1,3,5-triazine-2,4-diamine
Azimsulfuron	120162-55-2	N-[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-1-methyl-4-(2-methyl-2H-tetrazol-5-yl)-1H-pyrazole-5-sulfonamid
Bentazon	25057-89-0	3-(1-Methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide
Carbendazim	10605-21-7	methyl 1H-benzimidazol-2-ylcarbamate
Chlorimuron	99283-00-8	2-[[[[(4-Chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoic acid
Chlorsulfuron	64902-72-3	2-Chloro-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide
Clofencet	129025-54-3	2-(4-Chlorophenyl)-3-ethyl-2,5-dihydro-5-oxo-4-pyridazinecarboxylic acid
Desethylatrazine	6190-65-4	2-Chloro-4-amino-6-isopropylamino-1,3,5-triazine
Diallate	2303-16-4	S-(2,3-Dichloro-2-propenyl) bis(1-methylethyl)carbamothioate
Dicamba	1918-00-9	3,6-Dichloro-2-methoxybenzoic acid
Dichlorprop	120-36-5	2-(2,4-Dichlorophenoxy)propanoic acid
Dinoseb	88-85-7	2-(1-Methylpropyl)-4,6-dinitrophenol
Dinoterb	1420-07-1	2-(1,1-Dimethylethyl)-4,6-dinitrophenol
Diquat	2764-72-9	6,7-Dihydrodipyrido[1,2-a:2?,1?-c]pyrazinediium
Diuron	330-54-1	N?-(3,4-Dichlorophenyl)-N,N-dimethylurea
DNOC	534-52-1	2-Methyl-4,6-dinitrophenol
Ethametsulfuron	111353-84-5	2-[[[[[4-Ethoxy-6-(methylamino)-1,3,5-triazin-2-yl]amino]carbonyl]amino]sulfonyl]benzoic acid
Ethametsulfuron-methyl	97780-06-8	Methyl-2-[[[[[4-ethoxy-6-(methylamino)-1,3,5-triazin-2-yl]amino]carbonyl]amino]sulfonyl]benzoic acid
Fenpropimorph	67564-91-4	rel-(2R,6S)-4-[3-[4-(1,1-Dimethylethyl)phenyl]-2-methylpropyl]-2,6-dimethylmorpholine

Appendix. *Continued*

Compound	CAS	Chemical name
Flumetsulam	98967-40-9	N-(2,6-Difluorophenyl)-5-methyl[1,2,4]triazolo[1,5-a]pyrimidine-2-sulfonamide
Fluazifop	69335-91-7	2-[4-[[5-(Trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid
Fluazifop-P	83066-88-0	(2R)-2-[4-[[5-(Trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid
Fluazifop butyl	69806-50-4	Butyl-2-[4-[[5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid
Fluridone	59756-60-4	1-Methyl-3-phenyl-5-[3-(trifluoromethyl)phenyl]-4(1H)-pyridinone
Fluroxypyr	69377-81-7	[(4-Amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy]acetic acid
Glyphosate	1071-83-6	N-(Phosphonomethyl)glycine
Haloxyfop	69806-34-4	2-[4-[[3-Chloro-5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid
Hydroxyatrazine	2163-68-0	2-Hydroxy-4-(ethylamino)-6-(isopropylamino)-s-triazine
Imazapyr	81334-34-1	2-[4,5-Dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-pyridinecarboxylic acid
Imazaquin	81335-37-7	2-[4,5-Dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinolinecarboxylic acid
Imazethapyr	81335-77-5	2-[4,5-Dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-ethyl-3-pyridinecarboxylic acid
Isoproturon	34123-59-6	N,N-Dimethyl-N'-[4-(1-methylethyl)phenyl]urea
Mesotrione	104206-82-8	2-[4-(Methylsulfonyl)-2-nitrobenzoyl]-1,3-cyclohexanedione
Metsulfuron	79510-48-8	2-[[[[(4-Methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoic acid
Metsulfuron-methyl	74223-64-6	Methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoic acid
MCPA	94-74-6	(4-Chloro-2-methylphenoxy)acetic acid
Mecoprop	7085-19-0	2-(4-Chloro-2-methylphenoxy)propanoic acid
Metribuzin	21087-64-9	4-Amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one
Nicosulfuron	111991-09-4	2-[[[[(4,6-Dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-N,N-dimethyl-3-pyridinecarboxamide
Paraquat	4685-14-7	1,1′-Dimethyl-4,4′-bipyridinium

Appendix. *Continued*

Compound	CAS	Chemical name
Pentachlorophenol (PCP)	87-86-5	Pentachlorophenol
Primisulfuron	113036-87-6	2-[[[[(4,6-bis(Difluoromethoxy)-2-pyrimidinyl]amino]carbonyl]amino]sulfonyl]benzoic acid
Primisulfuron-methyl	86209-51-0	2-[[[[(4,6-bis(Difluoromethoxy)-2-pyrimidinyl]amino]carbonyl]amino]sulfonyl]benzoic acid
Prochloraz	67747-09-5	N-Propyl-N-[2-(2,4,6-trichlorophenoxy)ethyl]-1H-imidazole-1-carboxamide
Prometon	1610-18-0	6-Methoxy-N,N'-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine
Prometryn	7287-19-6	N,N'-bis(1-Methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine
Propiconazole	60207-90-1	1-[[2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole
Prosulfuron	94125-34-5	N-[[(4-Methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]-2-(3,3,3-trifluoropropyl)benzenesulfonamide
Rimsulfuron	122931-48-0	N-[[(4,6-Dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide
Salicylic acid	69-72-7	2-Hydroxybenzoic acid
Silvex	93-72-1	2-(2,4,5-Trichlorophenoxy)propanoic acid
Simazine	122-34-9	6-Chloro-N,N²-diethyl-1,3,5-triazine-2,4-diamine
Sulfentrazone	122836-35-5	N-[2,4-Dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl]methanesulfonamide
Sulfometuron	74223-56-6	2-[[[[(4,6-Dimethyl-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoic acid
Terbutryn	886-50-0	N-(1,1-Dimethylethyl)-N²-ethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine
Terbutylazine	5915-41-3	6-Chloro-N-(1,1-dimethylethyl)-N'-ethyl-1,3,5-triazine-2,4-diamine
Thiazafluron	25366-23-8	N,N'-Dimethyl-N-[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yl]urea
Thifensulfuron-methyl	79277-27-3	Methyl-3-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylic acid
Triasulfuron	82097-50-5	2-(2-Chloroethoxy)-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide
Triclopyr	55335-06-3	[(3,5,6-Trichloro-2-pyridinyl)oxy]acetic acid
2,4-D	94-75-7	(2,4-Dichlorophenoxy)acetic acid
2,4-DNP	51-28-5	2,4-Dinitrophenol
2,4,5-T	93-76-5	(2,4,5-Trichlorophenoxy)acetic acid

Acknowledgment

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