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Mélanie Kah, Colin D. Brown

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PhD Thesis

2007

**BEHAVIOUR OF IONISABLE
PESTICIDES IN SOILS**

Mélanie Kah

Supervisor: Professor Colin D. Brown

University of York
Environment Department

This thesis is submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy.

ABSTRACT

Ionisable pesticides can be partially ionised within the range of natural soil pH and this strongly influences their reactivity in soils. This group includes important, worldwide contaminants of groundwater and surface waters. It is essential that their specific behaviour is recognised within risk assessment procedures. Experiments were carried out with ten pesticides (six acids and four bases) and nine arable soils (range in pH, texture and organic matter content) to advance the understanding and prediction of the behaviour of ionisable pesticides in soils. The main conclusions can be summarised as follows:

- Adsorption of ionisable pesticides tends to be stronger in soils with lower pH and containing more organic carbon. A regression equation including Log D (lipophilicity corrected for pH), the soil organic carbon content and a pesticide descriptor was selected to predict the adsorption of acids. The behaviour of bases was more complex and approaches specific to each compound seem to be required.
- There were some marked differences between the soils in their ability to degrade the different ionisable pesticides. The lack of consistent behaviour renders a global approach to prediction of degradation unrealistic. Distinct types of behaviour could however be distinguished according to the main route of degradation.
- Significant correlations between sorption and degradation were only observed for three pesticides out of ten, with faster degradation in soils with stronger sorption.
- A centrifugation technique was used to measure adsorption at realistic soil moisture contents and provides a robust characterisation of the fraction of pesticide available for leaching. Time-dependent adsorption was also assessed. The increase in adsorption between one and seven days was not directly related to the level of adsorption although it was more important in soils containing more organic carbon.

Although specific interactions between pesticides and soils are still not fully understood, these results provide the basis for a more robust analysis of the behaviour of ionisable pesticides in the environment.

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AUTHOR'S DECLARATION

Chapters of the present thesis have been written as papers for international peer-reviewed journals. The current publication status of the papers is presented in Table 1-1. All these papers have been reworked, so that they are presented in a consistent style and format in this thesis. In addition, introductions and conclusions have been modified to eliminate repetition and to aid continuity. For those papers, which have been published, copyright rests with the publishers.

The papers have been written by the candidate as leading author, however it should be noted that the papers have gained in quality through suggestions, advice and editing from the co-authors. Chapters 2, 3, 4 and 7, which are published, have also benefited from the comments of the anonymous referees as part of the review process.

The work in this thesis was undertaken as a PhD student in the EcoChemistry team, first at Cranfield University in Silsoe (January 2004 – October 2004) and then at the Central Science Laboratory in York and the University of York (November 2004 – January 2007).

This work was undertaken for DEFRA-funded project PS2201, which is part of a collaboration with the BRGM (Bureau de Recherche Géologiques et Minière, Orléans, France). The final year of this collaborative project lies outside of this PhD and is: (i) integrating the results obtained in the two institutes, (ii) evaluating the impact of approaches specific to ionisable pesticides on fate models outputs and (iii) proposing guidance for a more robust risk assessment within regulatory procedures.

Chapter 1

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 pre- or early post-emergence or chemicals subject to washoff from crop surfaces. 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 in order to develop and validate computer simulation models for use as predictive tools in future environmental fate assessments.

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

Once in the soil, pesticide molecules partition between the aqueous and solid phases and this will affect many other aspects of their behaviour: sorption can be rate limiting to volatilization, bioavailability (and thus efficacy and biodegradation rate) and subsurface transport. There have been many attempts to develop either a universally applicable sorption constant, or a regression equation 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; Wauchope et al., 2002) 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.

Alongside sorption, degradation is the second important process used to predict the fate of pesticides in soils (Boesten and van der Linden, 1991). Variability in degradation rate is expected and numerous studies have provided evidence for field-to-field variation in the degradation rates of pesticides (Price et al., 2001; Walker et al., 2001; Dyson and al., 2002). Extrapolation from measurements on a set of soils to prediction for a different soil is a common problem in environmental assessment. A greater understanding of the factors that influence degradation rates is required to support this extrapolation and thus ensure the safe use of new and existing products.

The aim of this PhD is to advance the understanding and prediction of the behaviour of ionisable pesticides in soils. The main objectives of this work are:

- i) to review current knowledge regarding the behaviour of ionisable pesticides in soils,
- ii) to identify the soil and pesticides properties influencing the adsorption and degradation of ionisable pesticides in soils and investigate interactions between the two processes
- iii) to propose approaches to predict the extent of these processes when data are not available,
- iv) to study the relevance of batch experiments to determine adsorption parameters for ionisable pesticides and to investigate changes in sorption with time.

A great deal of work has been undertaken concerning the adsorption of ionisable pesticides in soils but generalised conclusions cannot be made. Several authors developed equations to predict the sorption of ionisable compounds in soils or sediments (Javfert, 1990; Lee, 1990; Fontaine et al., 1991; Shimizu et al., 1992). Unfortunately, the applicability of these models to other systems was rarely demonstrated. Approaches specific to a particular class of ionisable pesticide and/or soil type might be necessary to describe the complexity of interactions amongst ionisable molecules.

A screening approach was adopted to the work, with initial broad investigations followed up by more detailed and targeted analysis. The target was to produce a significant dataset of adsorption and degradation parameters to allow the identification of any particular behaviour linked with a pesticide or soil type and to select relevant pesticide or soil properties that could be used to predict the extent of adsorption and degradation processes. Adsorption and degradation parameters were

determined for a set of ten ionisable pesticides in nine soils. The selection of the pesticides was based on their dissociation constant, the nature of the functional group that dissociates and adsorption and degradation parameters previously reported in the literature. All the pesticides selected are currently registered and used in the EU. Nine arable soils were selected to give a gradient in pH (pH in 1M KCl from 4.4 to 8.0) and to have a range in texture (clay content from 5.6 to 41.5%) and organic carbon content (7.6-32.4 g kg⁻¹). This set of soils was designed to be representative of arable soils commonly found in the UK.

Chapters of the present thesis have been prepared as stand-alone papers for submission to international peer-reviewed journals. The status of the different papers with regard to the publication process is presented in Table 1-1.

Chapter 2 presents an extensive literature review introducing the issues concerning adsorption and the characteristics of ionisable pesticides. The mechanisms postulated for their adsorption are described. Subsequently, the review focuses on the influence of soil properties on adsorption and on potential to predict the behaviour of ionisable pesticides in soils. Finally, degradation of ionisable compounds in soil is considered, with particular emphasis on dependence of degradation on the adsorption process.

Chapter 3 reports the results of the screening experiment regarding the adsorption process. Adsorption coefficients for six acidic and four basic pesticides were measured in nine contrasting arable soils. Results were then submitted to statistical analyses against a wide range of soil and pesticide properties to identify the best

combination of properties to describe the variation in adsorption. Approaches to predict adsorption coefficients are proposed and tested on an independent dataset.

Chapter 4 reports the results of the screening experiment regarding degradation. Degradation parameters were measured for the same sets of pesticides and soils. Results were submitted to statistical analyses to (i) identify any commonalities in soil and pesticide properties influencing rate of degradation and (ii) test for any link between sorption and degradation processes.

Chapter 5 provides a short overview concerning the determination of lipophilicity corrected for pH (Log D). Chapter 3 demonstrates the importance of this parameter to predict variations in adsorption for acidic pesticides in soils. The achievement of reliable values is still a problem, especially for ionic compounds. Chapter 5 discusses the theory and options for measurement methods in order to obtain more reliable Log D values.

Chapter 6 addresses a specific issue related to adsorption mechanism that was identified in Chapter 3. Sorption isotherms were determined for two acidic herbicides, at four CaCl_2 concentrations and in three soils. Differences in the influence of ionic strength are interpreted in terms of adsorption mechanisms.

Chapter 7 presents an alternative method to the classical batch method to measure sorption of organic compounds in soils. Adsorption of six acidic pesticides in nine contrasting soils was measured using two techniques: (i) the batch method and (ii) a centrifugation method that allowed the measurement of adsorption at a realistic soil to

solution ratio. Results regarding time-dependent sorption of acidic compounds are also presented.

Chapter 8 summarizes the main conclusions and assesses the implications of the findings reported. A further analysis of the results presented in Chapter 3 supports the definition of priorities for future work.

Table 1-1 Publication status of the papers presented in the PhD thesis.

| Chapter | Authors | Title | Status | Journal |
|---------|----------------------------------|---|---------------------------|---|
| 2 | M. Kah and C.D. Brown | Adsorption of ionisable pesticides in soils | Published | Reviews of Environmental Contamination and Toxicology (2006) 188, 149-218 |
| 3 | M. Kah and C.D. Brown | Prediction of the adsorption of ionisable pesticides in soils | Published | Journal of Food and Agricultural Chemistry (2007) 55, 2312-2322 |
| 4 | M. Kah, S. Beulke and C.D. Brown | Factors influencing degradation of pesticides in soils. | Published | Journal of Food and Agricultural Chemistry (2007) 55, 4487-4492 |
| 5 | M. Kah and C.D. Brown | Log D: lipophilicity of corrected for pH | Submitted (March 2006) | Chemosphere |
| 7 | M. Kah and C.D. Brown | Changes in pesticides adsorption with time at high soil to solution ratio | Published | Chemosphere (2007) 68, 1335-1343 |

Chapter 2

ADSORPTION OF IONISABLE PESTICIDES IN SOILS

INTRODUCTION

It is estimated that ionisable compounds comprise 25% of the existing active substances currently undergoing review for re-registration 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 of pesticides 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, eight were ionisable compounds (IFEN, 2002). This pesticide category represented up to half of the pesticides detected in surface and drinking water samples in Hungary (Györfi et al., 1998). Among the nine pesticides most frequently exceeding $0.1 \mu\text{g L}^{-1}$ in surface fresh waters in the UK between 1998 and 2003, six were ionisable compounds (mecoprop, MCPA, 2,4-D, dichlorprop, simazine, and atrazine). Similarly, ionisable pesticides amounted for seven of the ten pesticides exceeding threshold concentrations in UK groundwater in 2003 (Environment Agency, monitoring data, UK, 2003). Atrazine and simazine were

amongst the three most frequently detected pesticides in ground water collected from wells of agricultural areas in USA (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 ionized within the range of normal soil pH and this strongly affects their reactivity in soils. The adsorption of neutral organic compounds in soils mainly occurs 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.

Many reviews are available on the adsorption of organic chemicals in soils (among the most recent: Calvet, 1989; Harper, 1994; Von Oepen et al., 1991; Wauchope et al., 2002). They mainly covered the behaviour of hydrophobic compounds in soils, which is now relatively well understood. Comparatively, 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/ with pesticide and soil properties. Numerous articles reported results about the 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, the review focuses on the influence of soil properties on adsorption and on 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 that often have a great importance for the sorption of ionisable pesticides (soil pH, clay and oxides contents). Finally, we briefly review degradation of ionisable compounds in soil and evidence for its dependence on the adsorption process.

BACKGROUND

Ionisation

A weakly acidic compound dissociates in water to produce protons. Thus, it exists both in 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:



Where $[\text{H}_3\text{O}^+]$, $[\text{A}^-]$ and $[\text{HA}]$ are defined as the aqueous concentration of hydronium ion (or proton), anionic species and neutral species, respectively (all in mole L^{-1}).

In addition,

$$\text{p}K_a = -\log K_a \quad \text{and} \quad \text{pH} = -\log [\text{H}_3\text{O}^+]$$

which gives

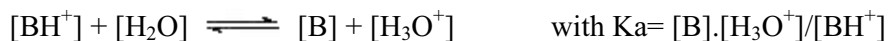
$$[\text{HA}] / [\text{A}^-] = 10^{(\text{p}K_a - \text{pH})}$$

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 (Figure 2-1).

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:



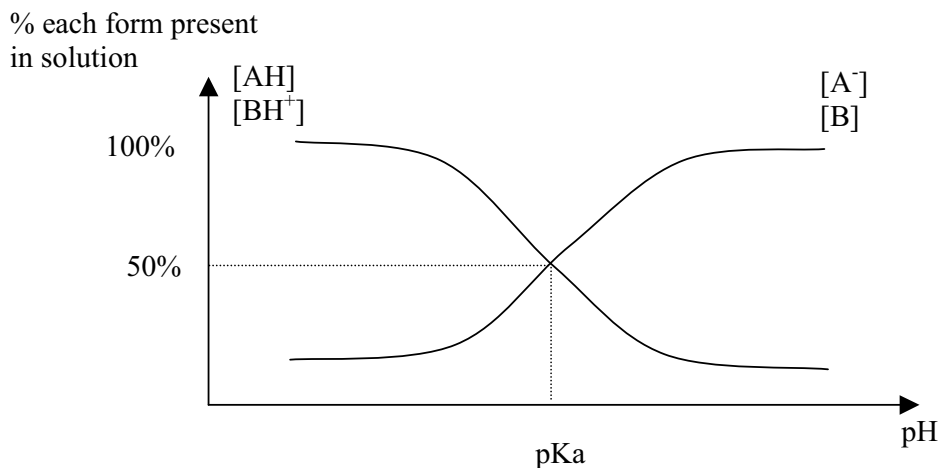
Where $[\text{OH}^-]$, $[\text{BH}^+]$ and $[\text{B}]$ are defined as the aqueous concentration of the hydroxide ions, positive and neutral species, respectively (all in mole L^{-1}). The ratio of cationic to neutral species in solution can also be calculated according to the pH of the solution. However,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



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 ($\text{p}K_a + \text{p}K_b = 14$).

Figure 2-1. Dominance of neutral or ionic form in solution according to the pH, assuming that the activity coefficient is near unity. $[\text{AH}]$ and $[\text{BH}^+]$ are the protonated forms, $[\text{A}^-]$ and $[\text{B}]$ the dissociated form, of the acidic and basic compounds respectively. With $[\text{AH}]$ the concentration of the protonated form of an acid and $\text{p}K_a$,

its dissociation constant: $[\text{A}^-] = \frac{1}{1 + 10^{\text{pH} - \text{p}K_a}}$



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 2-1 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 will be 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.

Table 2-1. Molecular structures, uses and properties for examples of ionisable pesticides (Tomlin, 1997; www.inra.fr/agritox)

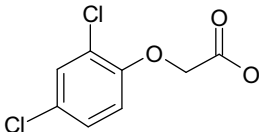
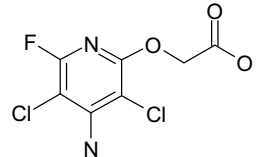
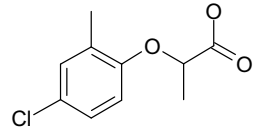
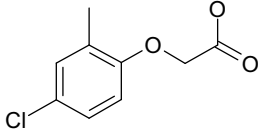
| Pesticide name [CAS RN] | Formula | Use and application rate (g ha ⁻¹) | pKa | Koc (mL g ⁻¹) | DT50 (d) | Solubility (in water, g L ⁻¹) | Log P |
|----------------------------|---|--|------|------------------------------|-------------|--|--------------------------|
| Acidic compounds | | | | | | | |
| Carboxylic acids | | | | | | | |
| 2,4-D [94-75-7] |  | Herbicide on cereals, maize, sorghum, grassland, orchards, sugar cane, rice, non crop lands (280-2300) | 2.97 | 5-212 | 5-59 | 0.6 | -1 (pH9) 2.7 (pH1) |
| fluroxypyr [69377-81-7] |  | Control of a range of broad leaved weeds in all small grain crops and pasture (200) | 2.94 | 51-81 | 5-68 | 0.091 | 156 (pH4) 0.23 (pH10) |
| mecoprop [7085-19-0] |  | Hormone type herbicide for the control of broad-leaved weeds in wheat, barley, oats, grassland and pasture (1200-1500) | 3.11 | 5- 43 | 7-13 | >250 | -0.19 |
| 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) | 3.73 | 10-157 | 7-79 | 294 | 2.7 (pH1) -1.07 (pH9) |

Table 2-1. (Continued)

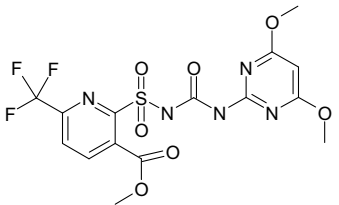
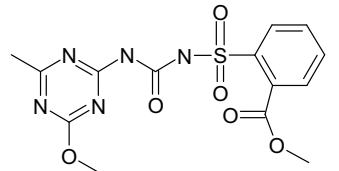
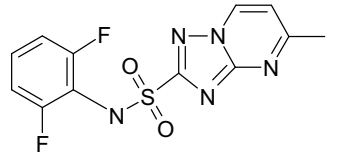
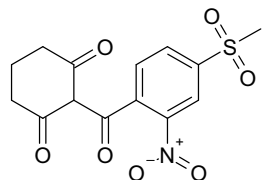
| Pesticide name [CAS RN] | Formula | Use and application rate (g ha ⁻¹) | pKa | Koc (mL g ⁻¹) | DT50 (d) | Solubility (in water, g L ⁻¹) | Log P |
|---|---|--|------|------------------------------|-------------|--|-----------------------|
| NHSO₂ acids flupysulfuron-methyl-sodium [144740-54-5] |  | Selective control of black grass and other weeds in cereals (10) | 4.94 | 15-47 | 6-26 | 0.063 (pH5) 0.600 (pH 6) | 0.06 (pH6) |
| 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) | 3.75 | 4-60 | 4-100 | 0.548 (pH7); 213 (pH9) | -1.7 (pH7) |
| flumetsulam [98967-40-9] |  | Control of broad-leaved weeds and grasses in soya beans, field peas and maize (10-20) | 4.6 | 5-182 | 30-60 | 0.049 (pH2.5) | -0.68 |
| Other acids mesotrione [104206-82-8] |  | Control of broad leaved and some grass weeds in maize (70-225) | 3.12 | 19-387 | 4-31.5 | 2.2 (pH5) 22 (pH9) | 0.9 (pH5) -1 (pH7) |

Table 2-1. (Continued)

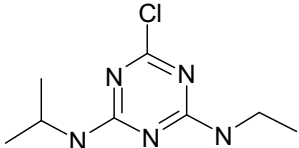
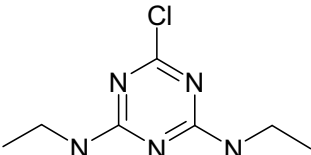
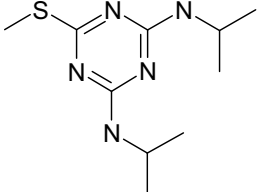
| Pesticide name [CAS RN] | Formula | Use and application rate (g ha ⁻¹) | pKa | Koc (mL g ⁻¹) | DT50 (d) | Solubility (in water, g L ⁻¹) | Log P |
|----------------------------|---|--|------|------------------------------|-------------|--|--------------------|
| Basic compounds | | | | | | | |
| Triazines | | | | | | | |
| <i>chlorotriazines</i> | | | | | | | |
| atrazine [1912-24-9] |  | Control of annual broad-leaved weeds and annual grasses in maize, sorghum, sugar cane, grassland, conifer, industrial weed control (750-1000) | 1.7 | 39-173 | 166-77 | 0.033 (pH7) | 2.5 |
| 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) | 1.62 | 103-277 | 27-102 | 0.062 (pH7) | 2.1 (unionised) |
| <i>methylthiotriazine</i> | | | | | | | |
| prometryn [7287-19-6] |  | Selective systemic herbicide on cotton, sunflowers, peanuts, potatoes, carrots peas and beans (800-2500) | 4.1 | 185-575 | 14-150 | 0.033 | 3.1 (unionised) |

Table 2-1. (Continued)

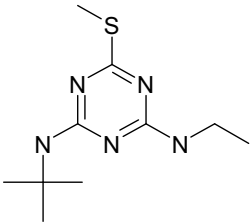
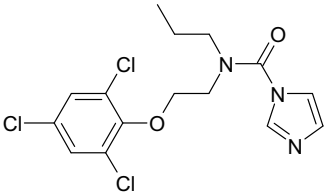
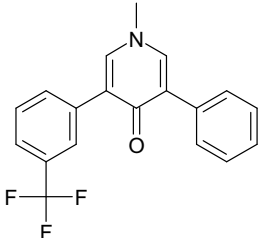
| Pesticide name [CAS RN] | Formula | Use and application rate (g ha ⁻¹) | pKa | Koc (mL g ⁻¹) | DT50 (d) | Solubility (in water, g L ⁻¹) | Log P |
|------------------------------|---|---|-----|------------------------------|-------------|--|---------------------|
| terbutryn [886-50-0] |  | Control 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) | 4.3 | 2000 | 14-50 | 0.022 | 3.65 (unionised) |
| Other basic compounds | | | | | | | |
| prochloraz [67747-09-5] |  | Protectant and eradicator fungicide effective against a wide range of diseases affecting field crops, fruit, turf and vegetables (400-600) | 3.8 | 1222-5818 | 5-37 | 0.034 | 4.12 (unionised) |
| 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) | 1.7 | 350-1100 | >343 | 0.012 (pH7) | 1.87 (pH7) |

Table 2-1. (Continued)

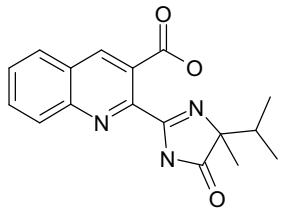
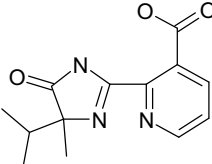
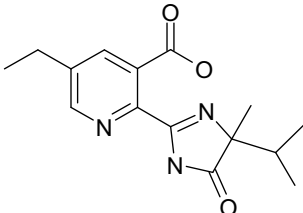
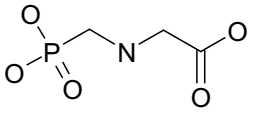
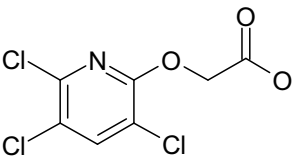
| Pesticide name [CAS RN] | Formula | Use and application rate (g ha ⁻¹) | pKa | Koc (mL g ⁻¹) | DT50 (d) | Solubility (in water, g L ⁻¹) | Log P |
|-----------------------------|---|---|------------------|------------------------------|-------------|--|--|
| Amphoteric compounds | | | | | | | |
| Imidazolinones | | | | | | | |
| imazaquin [81335-37-7] |  | Pre-planting or pre-emergence control of broad-leaved weeds in soya beans (70-140) | 3.8 | 13-40 | 60 | 0.060-0.120 | 0.34 |
| imazapyr [81334-34-1] |  | Control of annual and perennial grasses, sedges and broad-leaved weeds in non-crop areas, forestry management and plantation of rubber trees and oil palms (100-1700) | 1.9 3.6 11 | 4-170 | 30-150 | 9.74 | 0.11 |
| imazethapyr [81335-77-5] |  | Control of many major annual and perennial grass and broad-leaved weeds in soya and other leguminous crops (70-200) | 2.1 3.9 | 75-173 | 30-90 | 1.4 | 1.04 (pH 5) 1.49 (pH 7) 1.2 (pH 9) |

Table 2-1. (Continued)

| Pesticide name [CAS RN] | Formula | Use and application rate (g ha ⁻¹) | pKa | Koc (mL g ⁻¹) | DT50 (d) | Solubility (in water, g L ⁻¹) | Log P |
|--|---|---|--------------------|------------------------------|-------------|--|---|
| 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) | 2.3 5.7 10.2 | 1000-59000 | 3-174 | 11.6 | -3.2 (pH2-5) |
| 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) | 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) |

pKa: dissociation constant

Koc: distribution coefficient in soils normalised by the organic carbon content

DT50: half-life in soil, time required for 50% of the initial dose to be degraded

Log P: indicates the hydrophobicity of the compound

Measurement of soil pH

Soil pH values are usually determined in 1:5 soil:liquid suspension (in water, 0.01M CaCl₂ or 1M KCl according to ISO10390;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 NH₃ to NH₄⁺ on the surface of clay minerals (Raman and Mortland, 1969). This is due to 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. This 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 of this is that whilst 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 pKa 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 towards the formation of BH^+ and thus the amount adsorbed is greater than the amount deduced from the pKa value. This explanation was also proposed for adsorption of atrazine and simazine on clay by Celis et al. (1997a) (cf III. C. 1.).

The difference in pH between soil particles 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 still needed to better understand and determine the pH at soil interfaces.

ADSORPTION OF IONISABLE COMPOUNDS

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_d , conventionally written with a subscript d (for 'distribution'). It is 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 (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 chromatography (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 non-equilibrium conditions, whereas the batch procedure, by definition, measures quasi-equilibrium. 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 non-ionic 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 described above, and degradation also becomes a factor in reducing the accuracy of the results (Harper, 1994).

Recently, Berglöf et al. (2003) proposed the use of low-density super critical fluid extraction (0.3g 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. This could provide an easy method to predict sorption in soil at different pH levels, but still has to 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.

Factors influencing adsorption of ionisable compounds in soils

1. Soil properties

Once the organic molecule reaches the soil, its partition between the solid and liquid phase will depend to a large extent on soil properties. Non-polar 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 can additionally bind to clay and Fe/Al (hydr)oxides. These two components seem to play a significant role in certain cases. At last, unlike hydrophobic compounds, ionisable pesticides 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 D.

2. 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 complexity of the soil environment (Harper, 1994) and a variable influence of

temperature on the different binding mechanisms (Hayes, 1970). Di Vincenzo and Sparks (2001) explore the differences in the sorption mechanisms of the protonated and ionized forms of PCP (pentachlorophenol) 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 ionized 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 indicates that the effect of a colder climate on the soil formation did 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 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 and/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.

3. 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 non-polar 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.

4. Experimental factor: importance of ionic strength

Different salt solutions, including CaCl_2 or KCl , NH_4Cl , HCl , NaCl , $\text{Ca}(\text{H}_2\text{PO}_4)_2$, $\text{Na}_4\text{P}_2\text{O}_7$, 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 1M, 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 mecoprop 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), 2,4DNP, DNOC, dinoseb, 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 availability 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 (Freundlich adsorption coefficient, De Jonge and De Jonge, 1999). Lower solubility of 2,4-D in 1M NaCl compared to 0.01 and 0.1M NaCl, could explain the increasing sorption of 2,4-D on goethite with increasing ionic strength observed by Watson (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 concentrations 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 five-fold decrease in prosulfuron sorption as solution changed from 0.0015 to 1.5M 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 adsorption of ionic pesticides on calcite and alpha-alumina decreases with increasing 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 non-sorbing solution complexes, or (iii) a decrease in the activity of the charged ions caused by the increasing electrolyte concentration. The addition of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ 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 suggests that the application of large amounts of phosphorus and lime to agricultural fields could reduce pesticide sorption, and enhances pesticide concentration in solution, especially in weathered soils.

Finally, it is interesting to note that 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 0.01M caused adsorption capacity to diminish, with the greatest effect between 0 and 0.0025M. 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 0.01M CaCl_2 , but strength of sorption decreased about 5-fold when CaCl_2 increased from 0.01 to 1M, 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 0.01M CaCl_2 in standardized soil sorption experiments (OECD, 1997, Guidelines for the Testing of Chemicals, Test n°106: Adsorption-Desorption Using a Batch Equilibrium Method) will affect the sorption coefficients of ionisable pesticides. This places a constraint on the use of results from these standardized tests to predict sorption behaviour of ionisable compounds in the field.

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 (DiVincenzo and Sparks, 2001) and spectroscopic studies are often impractical due to 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 obtained are summarized in Table 2-2. 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.

Table 2-2. Experimental evidence of adsorption mechanisms.

| Pesticide | Sorbent | Adsorption mechanisms | | | | | | | Methods | Reference | |
|--------------------------------|-----------------------|-----------------------|---------------|-----------|----------------|-----------------|-----------------|-----------------|---------|---|------------------------------|
| | | hydrophobic | van der Waals | H-bonding | ionic exchange | charge transfer | ligand exchange | cation bridging | | | |
| Acidic pesticides | | | | | | | | | | | |
| mecoprop; 2,4-D; bentazone | iron oxides | | | | x | | | x | | interpretation of isotherms | Clausen and Fabricius, 2001 |
| 2,4-D | organo clays | | | x | | | | | x | FT-IR, X ray diffraction | Hermosin and Comejo, 1993 |
| acifluorfen | Cu (II) | | | | | | | x | | polarographic techniques, X-ray diffraction | Kozlowski et al., 1990 |
| fluazifop-butyl | homoionic clays | | | x | | x | | | | IR and X ray diffraction | Gessa et al., 1987 |
| fluazifop-butyl; fluazifop | smectites | | | | | x | | x | x | IR spectroscopy, X ray diffraction, TLC | Fusi et al., 1988 |
| pentachlorophenol | variable charge soils | x | | | x | | | | | interpretation of isotherms | Hyun et al., 2003 |
| azimsulfuron | iron oxides | | | | | | | x | x | IR | Pinna et al., 2004 |
| primisulfuron | oxides and soils | x | | x | x | | | | | interpretation of isotherms | Ukrainczyk et al., 1996 |
| ethamsulfuron-methyl | acidic soil | | | x | | | | | | FT-IR | Si et al., 2005 |
| Basic pesticides | | | | | | | | | | | |
| atrazine | HA | | | x | x | x | | | | FT-IR and ESR | Senesi et al., 1995 |
| atrazine | HA | | | x | | no | | | | UV-visible, FT-IR and ESR | Martin-Neto et al., 1994 |
| atrazine | HA | x | | x | | no | | | | UV-visible, FT-IR and ESR | Martin-Neto et al., 2001 |
| hydroxyatrazine | HA | x | | x | | x | | | | UV-visible, FT-IR and ESR | Martin-Neto et al., 2001 |
| atrazine | OM | | | x | | | | | | NMR spectroscopy | Welhouse and Bleam, 1993 a,b |
| Zwitterionic pesticides | | | | | | | | | | | |
| imazaquin | soils, HA | x | | x | x | no | | | x | FT-IR and ESR | Ferreira et al., 2002 |
| imazethapyr | soils, HA | | x | x | x | x | | | | FT-IR and ESR | Senesi et al., 1997 |
| glyphosate | clays and oxides | | | x | x | | | | x | IR and X ray diffraction | McConnell and Hossner, 1989 |
| glyphosate | goethite | | | | | | | x | | FT-IR | Sheals et al., 2002 |

FT-IR: Fourier transform infrared spectroscopy; ESR: electron spin resonance spectroscopy; TLC: thin layer chromatography; NMR: Nuclear magnetic resonance
no: evidence that the mechanism is not occurring

1. Hydrophobic sorption

Hydrophobic adsorption is proposed as the main mechanism for the retention of non-polar 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), pentachlorophenol (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 pKa of the herbicide. The authors demonstrated that the protonation of atrazine 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 $\text{pH} < 5$ and thus create some very hydrophobic adsorption sites at low pH.

2. 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 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 ($2-4 \text{ kJ mole}^{-1}$) comprising short-range dipolar or induced-dipolar attractions, but may be magnified by the hydrophobic effect. Since 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).

3. H-bonding

H-bonding is an intra- or inter-molecular dipole-dipole interaction that is stronger than van der Waals bonds. The energy of this binding amounts to about $2-40 \text{ KJ mole}^{-1}$. 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 $-\text{OH}$ and $-\text{NH}$. The presence of numerous oxygen and hydroxyl-containing functional groups on HS renders the formation of H-bonding highly probable for pesticides containing 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, Fourier transform infrared (FT-IR) and electron spin resonance (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, hydroxyl and carbonyl functional groups. The strong complexation 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., 1976), 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), ethametsulfuron-methyl (Si et al., 2005) and imazaquin (Ferreira et al., 2002) on soil OM.

4. Ionic exchange

Ionic exchange is a non-specific electrostatic interaction ($>20 \text{ kcal mole}^{-1}$), 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 generally either non-charged or negatively charged. Moreover, direct sorption involving the few positive charges at the edge of sheets in clays or protonated 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 non-specific ion exchange reactions (Hyun et al., 2003). Recently, Hyun and Lee (2004) demonstrated that anion exchange of prosulfuron accounted for up to 82% of overall sorption in the pH range 3 to 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 bentazon (Clausen and Fabricius, 2001) and clofenset, salicylic acid and 2,4-D (Dubus et al., 2001). However, Ukrainczyk and Ajwa (1997) 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. Since 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 $\text{pH} < \text{pK}_a$). 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 ($1.7 < \text{pK}_a < 4.3$) 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 bipyridylum 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).

5. 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 bipyridylum 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) would 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 et al., 1982). Atrazine readily converts to hydroxyatrazine, even in laboratory samples at low water contents, 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 the strength of its basic character. Fusi et al. (1988) have shown that fluzifop-butyl could apparently adsorb to Al- and Fe-

homoionic clays, by protonation of the pyridine nitrogen. 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).

6. 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 so 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 different iron oxides suggested that mecoprop adsorbs by outer and inner-sphere complexes, whereas 2,4-D and bentazon 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 azimsulfuron-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).

7. 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. As 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; Mc Donnell 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.

8. 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, 1994; 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, nine years 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 the 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 non-extractable residues. This 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 non-extractable residues may require particular attention, when assessing the behaviour and mobility of polar compounds in soil.

9. 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 2-3) 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 ligand exchange mechanism) depends on the molecular structure of the pesticide and might explain the different sorption behaviour of some compounds having similar pKa (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 like Fe and Al (hydr)oxides (Nearpass, 1976). Tropical soils and Andosols display variable charges (Fe and Al (hydr)oxides and allophanic minerals) and generally show a strong affinity for anions such as phosphate, fluoride and to a lesser degree sulphate. Competition effects are thus likely in those types of soils.

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.

Table 2-3. Potential mechanisms for the adsorption of ionisable compounds and how these are influenced by properties of the compound and the soil.

| | | | | compound | | soil | |
|------------------------------|---------------------|--|--|---|----------------------|--|--|
| | pH dependent | type | energy | positive influence | negative influence | positive influence | negative influence |
| hydrophobic partition | to a certain extent | partitioning | low | 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 |
| Van der Waals | no | short-range induced-dipolar attractions | 2-4 kJ mol ⁻¹ (Koskinen and Harper, 1990) | | | OM and clay content | |
| H bonding | to a certain extent | dipole-dipole interaction | 2-110 kJ mol ⁻¹ (Haberhauer et al., 2001; Koskinen and Harper, 1990) | non-ionic but polar molecule capable of cooperative (or multifunctional) interactions | | OM and clay content | competition with water molecules |
| anion exchange | yes | non-specific electrostatic interaction | >80 kJ mol ⁻¹ | anionic: low pKa | steric hindrance | aluminium and iron (oxi)hydroxides | OM (coating), ionic strength (competition) |
| cation exchange | yes | non-specific electrostatic interaction | >80 kJ mol ⁻¹ | cationic: high pKa | steric hindrance | high OM (functional acidity) and/or clay content | ionic strength (competition) |
| charge transfer | yes | electron donor-acceptor mechanisms (π - π reaction) | 12 KJ mol ⁻¹ (Haberhauer et al., 2001) | basicity of compound (ability to give e ⁻) or acidity (ability to accept e ⁻) | very low or high pKa | OM: capacity to give or accept electron (aromaticity) Clay: type of exchangeable cation (different acidity of water molecule surrounding) | |
| ligand exchange | yes | inner sphere complex, may be multi dentate or multinuclear | >20 kJ mol ⁻¹ | chemical structure allowing the formation of multi dentate/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) |
| water bridging | yes | outer sphere complex | 4-16 kJ mol ⁻¹ | anionic or polar functional group | | large, high valency exchangeable cations such as Fe ³⁺ , Al ³⁺ and Mg ²⁺ | |
| cation bridging | yes | inner sphere complex | 150-330 kJ mol ⁻¹ on clays 140 kJ mole ⁻¹ on OM (Haberhauer et al., 2001) | anionic or polar functional group able to displace the water surrounding the cation | | small, low valency exchangeable cations | |

Prediction of the adsorption behaviour of ionisable pesticide in soils

1. Influence of soil pH

How to obtain a range of soil pH

Soil pH has been shown to influence the sorption of many ionisable pesticides. Several strategies can be followed in order 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 prior to 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 pre-treatment histories (tillage, crop) are compared (Barriusso et al., 1992; Harper, 1988; Reddy et al., 1995; 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 can cause 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. This 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 pKa. 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 pKa of about 8 are assumed to be non-ionised, whereas uncharged and ionized forms of carboxylic groups with pKa of about 5.2 are assumed to coexist (Moreau-Kervevan and Mouvet, 1998; Stevenson, 1972).

The dissociation constant describes the sensitivity of ionisable pesticides to soil pH (Table 2-4) and four types of pH influence have been recorded (Figure 2-2). These are discussed in turn below.

Figure 2-2. Three adsorption behaviours have often been recorded for ionisable compounds as a function of soil pH (A, B, C). A pH-independent sorption can also be observed in some cases. This chart was first used by Calvet (1980b)

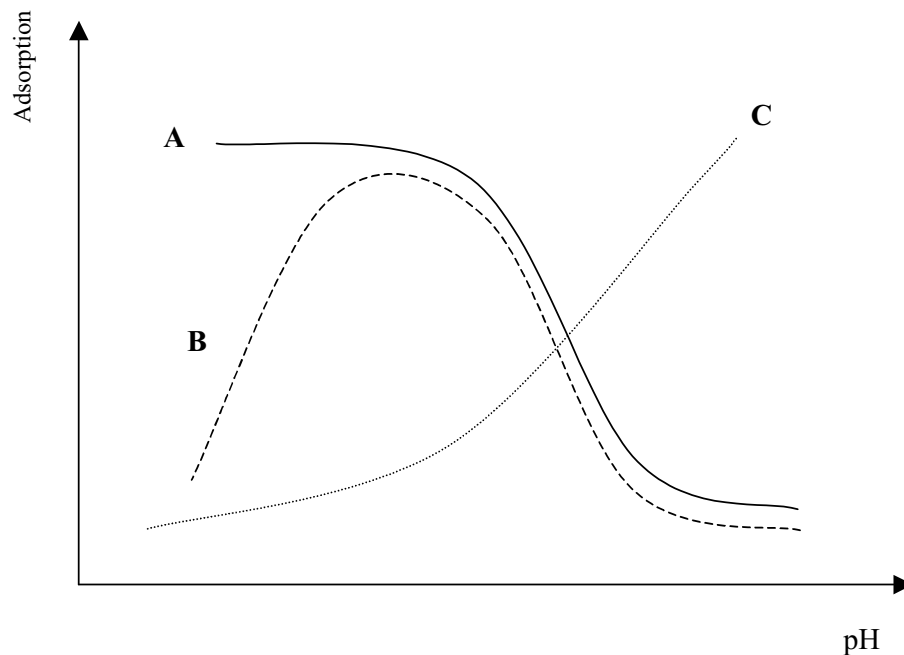


Table 2-4. Changes with pH in form, behaviour and adsorption mechanism operating for acid and basic compounds (adapted from Wauchope et al., 2002).

| pH | —————→ | | |
|-------------------------|--|--|---|
| Acidic compounds | | | |
| pKa | pKa>10 | 3<pKa<10 | pKa<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)hydroxydes, OM) cation bridging (through ligand exchange: H ₂ O-metal) | |
| Basic compounds | | | |
| pKa | pKa>10 (pKb<4) | 3<pKa<10 (4<pKb<11) | pKa<3 (pKb>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 partitionning (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.

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 pKa are generally low). Weak acids (e.g. carboxylic acids, sulfonylureas, phenols) exist predominantly in the anionic form at pH values greater than their pKa. 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 molecule 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 straight 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 present as neutral molecules under alkaline conditions and as cations at pH values below their pKa. 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 DOM at high pH levels which 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 pKa 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 positively charged (Watson et al., 1973).

A bell-shaped curve has been observed in experiments in which the pH was modified artificially for terbutryn (Barriuso 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 it 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 $\text{pH} < 8$, but remains unsaturated in alkaline solution.

Recently, 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 years. The authors explained this behaviour by two liming responses (increase of Al and Fe oxides and reduction of Olsen-P concentrations) 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 consequences 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 high to underscore any influence of pH. Finally, the difference 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.

Table 2-5. Details of experiments investigating correlation between the adsorption coefficient of ionisable pesticides and selected soil properties: OM, clay and pH

| Acidic pesticides (pKa) | Adsorbent | Native pH | pH range | Presence of correlation and r ² value ^a | | | References |
|-------------------------|----------------------------|----------------|----------|---|-----------|----------|-----------------------------|
| | | | | pH | OM | Clay | |
| <i>Carboxylic acids</i> | database | | | (-) 0.16** | (+) 0.006 | (+) 0.01 | Weber et al., 2004 |
| salicylic acid (2.8) | 10 cambisols | x ^b | 6.2-8.3 | (-) 0.76 exponential fitting (r ² =0.97) | (+)(-) | nc | Dubus et al., 2001 |
| | 8 ferralsols | x | 4.6-7.2 | bell-shaped curve | (+)(-) | nc | Dubus et al., 2001 |
| clofencet (2.83) | 10 cambisols | x | 6.2-8.3 | (-) 0.72 exponential fitting (r ² =0.98) | (+)(-) | nc | Dubus et al., 2001 |
| | 8 ferralsols | x | 4.6-7.2 | (-) | (+)(-) | nc | Dubus et al., 2001 |
| haloxifop (2.9) | 15 soils, sediments | x | 4.2-8.3 | (-) | nc | nc | Rick et al., 1987 |
| 2,4-D (2.97) | 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 | | Barriuso and Calvet, 1992 |
| | 10 soils | x | 5.3-6.1 | nc | (+) 0.96 | (+) | Bolan and Bascaran, 1996 |
| | 10 cambisols | x | 6.2-8.3 | (-) 0.18 | (+)(-) | nc | Dubus et al., 2001 |
| | 8 ferralsols | x | 4.6-7.2 | nc | (+)(-) | nc | Dubus et al., 2001 |
| | 4 soils | x | 5-6.9 | (-) 0.93 | (+) | | Johnson et al., 1995 |
| | 5 soils | x | 5.1-7.3 | regression with pH, OM, clay 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 2-5. (Continued)

| Acidic pesticides (pKa) | Adsorbent | Native pH | pH range | pH | OM | Clay | References |
|-------------------------------|---------------------|-------------------|----------|---|-------------------------------|-------------|-------------------------------|
| <i>NHSO₂ acids</i> | database | | | (-) 0.16** | (+) 0.15** | (+) 0.0025 | Weber et al., 2004 |
| <i>Sulfonylureas</i> | | | | | | | |
| 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 |
| | 6 colorado soils | x | 5.6-7.8 | exponential fitting (r ² = 0.85) (-) 0.31 | (+) 0.81* | (+) 0.82* | Vicari et al., 1996 |
| chlorsulfuron (3.6) | 1 soil | 2 w. ^d | 4.2-7.8 | (-) (*) | phytotoxicity ; (+) 0.87** | nc | Mersie et al., 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 mth. | 5.1-6.7 | (-) *** | nc | nc | Wehtje et al., 1987 |
| <i>Other NHSO₂</i> | | | | | | | |
| 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 |
| <i>Other acids</i> | | | | | | | |
| mesotrione (3.12) | 15 soils | x | 4.6-7.7 | (-) 0.66 | (+) | | Dyson et al., 2002 |

Table 2-5. (Continued)

| Basic pesticides (pKa) | Adsorbent | Native pH | pH range | pH | OM | Clay | References |
|------------------------|-------------------------|-----------|----------|---------------------------------|---------------------------------|------------------------------------|---------------------------|
| | database | | | (-) 0.18 | (+) 0.27** | (+) 0.14** | Weber et al., 2004 |
| <u>Triazines</u> | | | | | | | |
| metribuzin (0.99) | Silty clay loam profile | x | 6.5-7.2 | (-) 0.86 | (+) 0.01 | (+) 0.75 | Harper, 1988 |
| | 9 soils | x | 5.1-6.8 | (-) 0.19 | (+) 0.94** | (+) 0.45 | Peter and Weber, 1985 |
| | | | | regression with clay, pH | | | |
| 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*** | (+) | (+) | Novak et al., 1997 |
| | | | | regression with CO, pH, clay | | | |
| terbutryn (4.3) | 2 oxisols | 0 | 3.5-7 | bell shaped curve (max. at pH5) | (+) 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 |
| | | | | | | | |
| <u>Others</u> | | | | | | | |
| 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 |
| | 2 soils | 0 | 3.5-6.4 | (-) | | | Weber et al., 1986 |
| carbendazim (4.2) | 4 soils | x | 2.9-5.4 | (-) 0.35 | (+) 0.99** | (+) 0.73* | Bergl6f et al., 2002 |
| | 2 soils | 0 | 3-7 | (+) | | | Bergl6f et al., 2002 |

Table 2-5. (Continued)

| Amphoteric pesticides (pKa) | Adsorbent | Native pH | pH range | pH | OM | Clay | References |
|------------------------------|------------------|-----------|----------|--|---|------------|-----------------------|
| 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., 1989 |
| | 2 soils | 10 yr. | 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 | 3 mth. | 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 | 3 mth. | 5.1-6.7 | (-) *** | nc | nc | Wehtje et al., 1987 |
| 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., 1989 |
| Others | | | | | | | |
| glyphosate (2.6;5.6;10.6) | 2 soils | 60 yr. | 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 (r² 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 Kd measurement

^d w.,mth.,yr.: refer to the time the soil was let to equilibrate after addition of a buffer agent (in weeks, months or years respectively).

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. In order 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 2-5.

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 (pKa=2.8) and salicylic acid (pKa=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 (pKa=3) and MCPA (pKa=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 (pKa=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 (NHSO₂)

Sulfonylureas

Sorption of the weakly acidic sulfonylurea herbicides generally increases with decreasing pH as was 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 of 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 to 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 four Brazilian soils, while 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 non-linear 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 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 Koc value as a function of Koc's for the neutral and anionic form, pH and pKa. Strebe and Talbert (2001) also studied the adsorption of flumetsulam in 14 soils. Kd and Koc were correlated with OM in surface soils while Kd was correlated with extractable Fe and inversely correlated to pH in subsurface soils. The mobility of flumetsulam (TLC study) was negatively correlated with Kd values at both soil depths and with Koc in the subsurface soils. However, multiple linear regressions suggested that no soil property was an adequate predictor for mobility. For bentazon (pKa=3.3), the highest freundlich coefficient (Kf) values were in the soil with highest organic carbon content and lowest pH (Thorstensen et al., 2001).

Other acidic compounds

Mesotrione (pKa =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 from 4.6 to 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 non-ionisable 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 Kd 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 below pH=5 could be explained by its protonation (pKa=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). These 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 pKa (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 pre-treated for 15 years with ammonium sulphate or calcium nitrate to achieve different pH values (Ladlie et al. 1976 a, b) and in soils allowed to equilibrate for three months 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 (pKa = 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 which 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 range of pH 3 to 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 since 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 pH 6, whilst sorption varied only slightly above pH 6. In the above-mentioned studies on imidazolinones, soil pH was

adjusted to different levels, although soils were allowed to equilibrate in the field for at least 10 years 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 CEC (cationic exchange capacity). 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 of 4 to 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 (six with pH-dependent charges) and observed an increase in Koc with decreasing native pH (from 4.8 to 8). The Koc 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 nine 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 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), maybe due to the limited pH range. However, although 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 might be related to their mechanism of adsorption and could maybe 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 on 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 clever 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 to predict the sorptive behaviour of pesticides that dissociate to form ions. Many factors, including the dissociation constant (pKa), 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 described above, sorption of these compounds 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 pKa, 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 Koc 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 pesticide 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.

2. 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 herbicide 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 as 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 thiazafurion (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 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 the reality (Celis et al., 1999).

Soil organic matter

Many works show that adsorption of organic chemicals in soils is mainly to organic matter even though structure and properties of organic constituents are not clearly understood yet. For instance, Stephenson et al. (1990) showed that throughout a 4-month 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 (Table 2-5).

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 among others. 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., 1997a) 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 (that 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, however, 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 where 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, might also explained 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 non-ionisable 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., 2005). 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 minerals

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 been sometimes found between the clay content and the adsorption of certain ionisable pesticides, especially some sulfonylureas and basic compounds (Table 2-5). 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 . This 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 and/or 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.

Non-ionic 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; Kozłowski 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 montmorillonite. Although excluded from this review of ionisable pesticides, cationic bipyridylum 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. However, Chappell et al. (2005) concluded that atrazine could adsorb within the interlayer of smectite. Their results demonstrated that interlayer hydration status has a large influence on the affinity of smectite for atrazine and that air-drying treatments have the potential to modify the sorption affinity of smectitic soils for organic molecules such as atrazine.

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 mecoprop, 2,4-D and bentazone (Clausen and Fabricius, 2001). This sorption behaviour will probably be more common in tropical and semi-tropical 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)hydroxides.

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 negative 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 $-\text{OH}$ 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 (anionic exchange capacity) to CEC (cationic exchange capacity), 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.

3. 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 (Table 2-5). K_d values were not related to soil pH for any of the six non-ionisable 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 standardize pH, with its decrease calculated as a function of pH (ii) multiple regression equations defined for each ionisable pesticide family (Weber et al., 2004) (iii) models that take into account the influence of pH and oxides on adsorption.

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.

Alongside 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 DT50, 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 microorganisms) 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 interrelated, and may influence these processes in opposite directions, thereby exhibiting a stimulating and restricting effect on the overall degradation process. We have seen above how pH influences the adsorption of ionisable pesticides in soils. Since 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 will 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 and al., 2002), dicamba (Voos and Groffman, 1997) and flumetsulam (Lehmann et al., 1992).

Negative influence: specific case of sulfonyleureas

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 sulfonyleureas. For instance, Hultgren et al. (2002) studied prosulfuron degradation and observed that pH-dependent hydrolysis of the sulfonyleurea bridge was the primary transformation process. Significant microbial degradation occurred in only two of the ten soils. Microbial reaction tends to be faster under alkaline conditions (up to a maximum value), whereas abiotic hydrolysis of sulfonyleureas 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-times 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 relation between degradation and pH often reported for sulfonyleureas including chlorsulfuron, metsulfuron-methyl, 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 DT50 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 non-ionisable 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.

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 DT50 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, 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 relation between K_d and DT50 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 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 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).

CONCLUSION

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, 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 pesticides properties should help to better understand and predict the adsorption mechanisms that operate.

More generally, knowledge is still lacking concerning the phenomena occurring 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 influence of varying pH on the charge at the surface of soil particles also play 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 behaviours 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 truly 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. This confirms that sorption of ionisable compounds in different soils cannot be assessed simply by normalising to organic carbon content. Clay and Al, 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 assumptions necessary to take into account. 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 amongst 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.

Chapter 3

PREDICTION OF THE ADSORPTION OF IONISABLE PESTICIDES IN SOILS

INTRODUCTION

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

Several authors developed equations to predict the sorption of ionisable compounds in soils or sediments (Jafvert, 1990; Lee et al., 1990; Fontaine et al., 1991; Shimizu et al., 1997; Regitano et al., 1997). 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. Unfortunately, the applicability of these models to other systems was rarely

demonstrated. Approaches specific to a particular class of pesticide and/or soil type might be necessary to describe the complexity of interactions amongst ionisable molecules. Experiments in which the pH of a soil is adjusted artificially are useful with respect to experimental design and control, but experiments dealing with a natural pH range will give more realistic results. The two methods have generated conflicting results because the influence of some experimental factors and/or soil properties 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 truly attributable to the influence of pH.

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

MATERIALS AND METHODS

Soils

Nine arable soils were sampled from the top 20 cm in several locations in southern England, in July 2004. Soils were selected to give a gradient in pH (pH in 1M KCl from 4.4 to 8.0) and to have a range in texture (clay content from 5.6 to 41.5%) and organic carbon content (7.6-32.4 g kg⁻¹). Soils were sieved to 3 mm, air-dried and analysed by the Laboratoire d'analyses des sols (INRA Arras, France) (Table 3-1). The following properties were determined: clay (<2 µm), silt (2-50 µm) and sand (50-2000 µm) content; organic carbon and nitrogen content (ISO 10694; ISO 13878); pH in water, 0.01M CaCl₂ and 1M KCl (ISO 10390); CaCO₃ content (ISO 10693), P₂O₅ content (dyer method, NF X 31-160); cationic exchange capacity (CEC, Metson method, NF X 31-130); exchangeable Ca, Mg, K (NF X 31-108) and Mn (NF X 31-120); Si, Al, Fe content with the Tamm method (an extraction with oxalate gives the content of amorphous Si, Al and Fe, de Endredy, 1963); Al and Fe content with the Merha-Jackson method (an extraction with citrate-dithionite-bicarbonate (CDB) solubilise pedogenic oxides and hydroxides, Mehra and Jackson, 1960); total Al and Fe content (ISO 11885) and total Na content (NF X 31-108). Subsamples (triplicates of roughly 30 g) were dried overnight at 110°C to determine soil moisture content of air-dried soils.

Table 3-1. Main properties of the nine arable soils studied.

| | Soil texture | Vegetation when sampled | pH | pH | pH | CaCO ₃ | Clay | Silt | Sand | OC | C/N | Bioactivity ^c | -33 kPa water content |
|---|-----------------|-------------------------|-------|-------------------------|--------|-------------------|------|------|------|--------------------|------|--------------------------|------------------------|
| | | | water | CaCl ₂ 0.01M | KCl 1M | % | % | % | % | g kg ⁻¹ | | mg TPF kg ⁻¹ | g water/100 g dry soil |
| 1 | silty clay loam | set aside | 8.20 | 7.56 | 8.02 | 76.40 | 38.5 | 48.7 | 12.8 | 17.7 | 9.6 | 202.3 | 32.2 |
| 2 | sandy clay loam | wheat | 7.81 | 7.36 | 7.54 | 36.30 | 25.7 | 24.8 | 49.5 | 32.4 | 9.1 | 381.4 | 28.0 |
| 3 | sandy clay loam | cereals | 8.08 | 7.45 | 7.41 | 0.49 | 27.5 | 21.0 | 51.5 | 10.8 | 9.4 | 91.7 | 17.7 |
| 4 | sandy clay loam | grass/clover ley | 7.91 | 7.29 | 7.29 | 0.70 | 34.5 | 21.5 | 44.0 | 20.0 | 10.1 | 136.0 | 26.9 |
| 5 | sandy clay loam | cereals | 6.85 | 6.56 | 6.27 | 0.09 | 19.9 | 26.5 | 53.6 | 23.8 | 10.4 | 113.8 | 26.3 |
| 6 | sandy loam | maize and weeds | 7.07 | 6.61 | 6.46 | 0.21 | 5.6 | 4.6 | 89.8 | 7.65 | 12.4 | 15.2 | 9.7 |
| 7 | loam | w.wheat | 6.89 | 6.4 | 6.38 | 0.09 | 23.6 | 35.7 | 40.7 | 16.8 | 10.5 | 99.0 | 25.5 |
| 8 | clay | set aside | 5.96 | 5.39 | 4.87 | 0.09 | 41.5 | 33.0 | 25.5 | 32.3 | 11.5 | 32.1 | 35.5 |
| 9 | sandy loam | set aside | 5.28 | 4.68 | 4.40 | 0.09 | 13.5 | 20.1 | 66.4 | 15.0 | 11.4 | 52.2 | 20.1 |

| | P ₂ O ₅ | CEC | Ca exch. | Mg exch. | K exch. | Mn exch. | Si Tamm | Al Tamm | Fe Tamm | Al Mehra | Fe Mehra | Al total | Fe total | Na total |
|---|-------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| | g kg ⁻¹ | cmol ⁺ kg ⁻¹ | cmol ⁺ kg ⁻¹ | cmol ⁺ kg ⁻¹ | cmol ⁺ kg ⁻¹ | cmol ⁺ kg ⁻¹ | g 100g ⁻¹ | g 100g ⁻¹ | g 100g ⁻¹ | g 100g ⁻¹ | g 100g ⁻¹ | g 100g ⁻¹ | g 100g ⁻¹ | g 100g ⁻¹ |
| 1 | 0.043 | 6.96 | 9.0 | 0.517 | 0.385 | 3.39 | 0.019 | 0.036 | 0.058 | 0.075 | 0.55 | 1.23 | 1.07 | 0.06 |
| 2 | 0.091 | 16.60 | 41.9 | 0.613 | 0.850 | 1.79 | 0.103 | 0.217 | 0.437 | 0.326 | 2.52 | 2.89 | 3.42 | 0.22 |
| 3 | 0.683 | 12.90 | 16.0 | 3.270 | 0.479 | 0.90 | 0.172 | 0.228 | 0.376 | 0.163 | 1.72 | 4.32 | 3.26 | 0.27 |
| 4 | 0.270 | 18.10 | 31.2 | 0.924 | 0.508 | 1.47 | 0.179 | 0.266 | 0.373 | 0.288 | 2.57 | 4.79 | 3.94 | 0.30 |
| 5 | 0.243 | 11.60 | 11.4 | 1.720 | 0.276 | 1.42 | 0.102 | 0.177 | 0.378 | 0.141 | 0.64 | 3.27 | 1.55 | 0.27 |
| 6 | 0.242 | 3.41 | 4.7 | 0.187 | 0.254 | 0.90 | 0.058 | 0.153 | 0.171 | 0.159 | 0.61 | 2.20 | 0.83 | 0.09 |
| 7 | 0.225 | 10.30 | 10.5 | 0.492 | 0.594 | 2.79 | 0.028 | 0.099 | 0.288 | 0.125 | 1.33 | 4.97 | 2.59 | 0.31 |
| 8 | 0.214 | 22.30 | 16.5 | 6.120 | 0.456 | 2.68 | 0.045 | 0.166 | 0.442 | 0.150 | 0.90 | 6.25 | 3.15 | 0.35 |
| 9 | 0.264 | 6.62 | 3.0 | 0.918 | 0.393 | 4.19 | 0.036 | 0.132 | 0.268 | 0.147 | 0.61 | 4.04 | 1.36 | 0.44 |

^aOC: organic carbon content

^bC/N: ratio of carbon and nitrogen content

^cBioactivity measured on soils sampled in July 2004 after two weeks incubation. Details are provided in Chapter 4.

Table 3-2. Molecular structures, uses and properties of the pesticides (Tomlin, 1997; www.inra.fr/agritox)

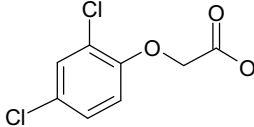
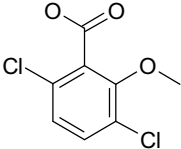
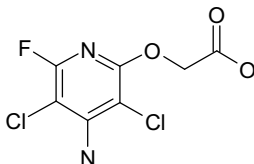
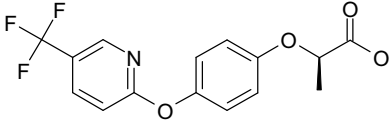
| Pesticide name [CAS RN] | Formula | Use and application rate (g ha ⁻¹) | pKa ^a | Koc ^b (mL g ⁻¹) | DT50 ^c (d) | Solubility (in water, g L ⁻¹) | Log P ^d |
|---|---|--|------------------|---|--------------------------|--|--------------------|
| Acidic compounds | | | | | | | |
| <i>Carboxylic acids</i> | | | | | | | |
| 2,4-D [94-75-7] (2,4-dichlorophenoxy)acetic acid |  | Selective systemic post-emergence control of annual and perennial broad-leaved weeds in cereals, maize, sorghum, grassland, orchards, sugar cane, rice, non crop lands (280-2300) | 2.97 | 5-212 | 5-59 | 0.6 | 2.7 |
| dicamba [1918-00-9] 3,6-dichloro-2-methoxybenzoic acid |  | Selective systemic herbicide to control annual and perennial broad-leaved weeds and brush species in cereals, maize, sorghum, sugar cane, asparagus, turf, pastures and non-crop lands (100-11200) | 1.97 | 3.5-21 | 1.4-11 | 6.5 | 2.3 |
| fluroxypyr [69377-81-7] [(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy]acetic acid |  | Post emergence herbicide to control a range of broad-leaved weeds in all small grain crops and pasture (200) | 2.94 | 51-81 | 5-68 | 0.091 | 2.2 |
| fluazifop-P [83066-88-0] (2R)-2-[4-[[5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid |  | Post-emergence control of wild oats, volunteer cereals and annual and perennial grass weeds in oilseeds rape, sugar beet, potatoes, vegetables, fruits, vines, citrus ornamentals and other broad-leaved crops (125) | 2.98 | 39-84 | 2-168 | 0.780 | 3.1 |

Table 3-2. (Continued)

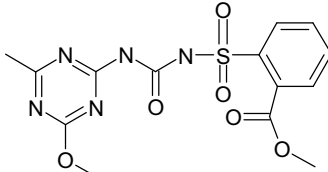
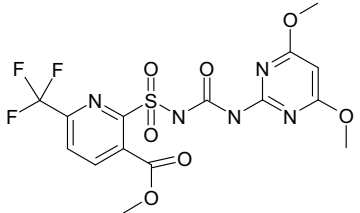
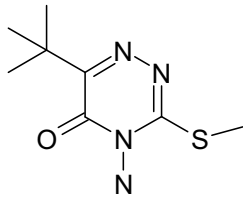
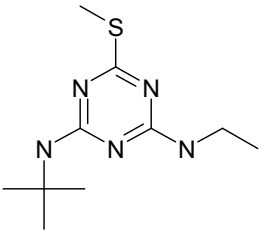
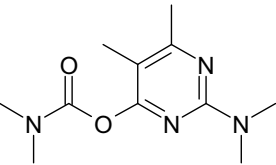
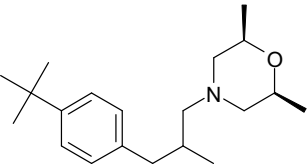
| Pesticide name [CAS RN] | Formula | Use and application rate (g ha ⁻¹) | pKa | Koc (mL g ⁻¹) | DT50 (d) | Solubility (in water, g L ⁻¹) | Log P |
|--|---|---|------|------------------------------|-------------|--|-----------------|
| <i>NHSO₂ acids (Sulfonylureas)</i> | | | | | | | |
| metsulfuron-methyl [74223-64-6] 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate |  | Selective systemic herbicide, pre- or post-emergence application to control a wide range of annual and perennial broad leaved weeds in wheat, barley, rice and oats (4-7.5) | 3.75 | 4-60 | 4-100 | 0.548 (pH7); 213 (pH9) | 1.2 |
| flupyr sulfuron-methyl [144740-54-5] methyl 2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-6-(trifluoromethyl)-3-pyridinecarboxylate monosodium salt |  | Selective, post-emergence control of black grass and other weeds in cereals (10) | 4.94 | 15-47 | 6-26 | 0.063 (pH5) 0.600 (pH 6) | 4.3 |
| Basic compounds | | | | | | | |
| <i>Triazines</i> | | | | | | | |
| metribuzin [21087-64-9] 4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one |  | Selective systemic herbicide, predominantly absorbed by roots, for pre- or post-emergence control of many grasses and broad-leaved weeds in soya beans, potatoes, sugar cane, maize and cereals (350-700) | 1 | 9-95 | 6-377 | 1.05 | 1.6 (pH 5.6) |

Table 3-2. (Continued)

| Pesticide name [CAS RN] | Formula | Use and application rate (g ha ⁻¹) | pKa | Koc (mL g ⁻¹) | DT50 (d) | Solubility (in water, g L ⁻¹) | Log P |
|--|---|--|------|------------------------------|-------------|--|---------------|
| terbutryn [886-50-0] <i>N</i> -(1,1-dimethylethyl)- <i>N'</i> -ethyl- 6-(methylthio)-1,3,5-triazine- 2,4-diamine |  | Selective herbicide, used pre-emergence in winter cereals to control blackgrass and annual meadow grass. Also used post-emergence in cereals, sugar cane and maize (1000-2000) | 4.3 | 2000 | 14-50 | 0.022 | 3.65 |
| Others | | | | | | | |
| pirimicarb [23103-98-2] 2-(dimethylamino)-5,6- dimethyl-4-pyrimidinyl dimethylcarbamate |  | Selective systemic insecticide used in cereals, fruit, ornamentals, strawberries, potatoes, sugar beet, tobacco and glasshouse crops (70-140) | 4.54 | 290 | 7-234 | 3 (pH7.4) | 1.7 |
| fenpropimorph [67564-91-4] <i>rel</i> -(2 <i>R</i> ,6 <i>S</i>)-4-[3-[4-(1,1- dimethylethyl)phenyl]-2- methylpropyl]-2,6- dimethylmorpholine |  | Systemic foliar fungicide with protective and curative action used on cereals (750) | 6.98 | 2772- 5943 | 15-127 | 0.0043 (pH7) | 4.4 (pH 9) |

^apKa: dissociation constant^bKoc: adsorption coefficient in soils normalised by the organic carbon content^cDT50: half-life in soil, time required for 50% of the initial dose to be degraded^dLog P: octanol-water partition coefficient; indicates the lipophilicity of the compound. Log P was measured for the six acids whereas data for bases are from the literature.

Pesticides and other chemicals

Ten ionisable pesticides were selected, comprising four carboxylic acids, two sulfonylureas, two triazines, one carbamate and one morpholine (Table 3-2). Pestanal analytical grade standard of 2,4-D, dicamba, fluroxypyr, metsulfuron-methyl, metribuzin, pirimicarb, fenpropimorph and terbutryn were purchased from Sigma-Aldrich (Seelze, Germany), fluazifop-P was supplied by Syngenta (Bracknell, UK) and flupyr-sulfuron-methyl was supplied by E.I. DuPont de Nemours (Wilmington, DE, USA). Fluroxypyr is applied in the field as fluroxypyr-meptyl, which is rapidly hydrolysed to the parent acid (half-life in soil-water slurries = 2-5 h at pH 6-7 and 22-24° C, Tomlin, 1997), so fluroxypyr was directly applied to the soils in this study. Similarly, the first metabolite of fluazifop-P-butyl (fluazifop-P) was used because the DT50 of the former is less than 24 h in soils (Tomlin, 1997). Based on pre-experiments (data not shown) it was assumed that no competition effects operate at low concentration. Pesticides were paired (fluroxypyr with fluazifop-P, metribuzin with pirimicarb and fenpropimorph with terbutryn) and studied together by high-pressure liquid chromatography (HPLC) and gas chromatography with mass spectrum detection (GC-MS). Details are provided in Table 3-3. Radiolabelled 2,4-D was purchased from American Radiolabelled Chemicals Inc. (St. Louis, MO, USA), dicamba from Izotop Institute of Isotopes Co., Ltd. (Budapest, Hungary) and metsulfuron-methyl and flupyr-sulfuron-methyl were supplied by E.I. DuPont de Nemours (Wilmington, DE, USA). All organic solvents were HPLC grade (Fisher Scientific, UK).

More than 700 two-dimensional properties were calculated for each pesticide using Dragon Web Version 3.0 (Talete srl, Milan, Italy). The neutral and ionic forms of ionisable compounds have different polarities. Since their ratio varies with pH, the

lipophilicity of ionisable pesticides is pH dependent. Lipophilicity profiles (Log D) represent the shift in octanol/water partition coefficient with pH as a consequence of dissociation. The decrease in Log D with pH was measured for each acid using the pH metric method (GLpKa, Sirius Analytical Instruments Ltd.; OECD, 2000). The method consists in determining the dissociation constant (pKa) by titration before and after the addition of octanol. The partitioning of the compound between water and octanol shifts the apparent pKa. The shift is then interpreted to calculate Log D at each pH.

Measurement of sorption

Sorption coefficients were determined at one concentration on nine different soils and with four replicates using a standard batch equilibrium method (OECD, 1997). Considering the application rates in the field and incorporation in the upper 2.5 cm of the soil profile, all experiments were carried out at 2 mg a.s. kg⁻¹. Sulfonylurea herbicides are applied at very low rates in the field, but were studied at a relatively high concentration (1 mg a.s. kg⁻¹) to ensure consistency with a parallel degradation study (Chapter 4). Soil suspensions in 0.01M CaCl₂ were prepared in 50 mL PTFE centrifuge tubes (Oak Ridge centrifugation tube, FEP by Nalgene Nunc International). Soil to solution ratios were chosen according to the strength of sorption reported in the literature. A ratio of 1:25 (w:w) was used for terbutryn and fenpropimorph whilst the other pesticides were studied at a ratio of 1:2 (w:w). After a pre-equilibration period of 14 h on a side-to-side shaker (300 oscillations min⁻¹), the soil suspensions were spiked with a minimal amount of pesticide solution in 0.01M CaCl₂ (0.2-0.5 mL, mixture of labelled and unlabelled when radiolabelled compounds were used) and returned to shaking until pseudo-equilibrium was reached. A 72 h equilibration period

was chosen based on a pre-experiment measuring adsorption between 12 and 120 h in soils 2 and 8 (results not shown). Samples were maintained in the dark at 4°C throughout the procedure to minimise degradation. The samples were then centrifuged at 5000 *g* for 10 min, and the supernatant analysed to measure C_e (mg L⁻¹), the concentration of pesticide remaining in solution after adsorption. Triplicates without soil were used as reference for C_i , the initial concentration (mg L⁻¹). Assuming that all pesticide removed from the solution is sorbed by the soil, the concentration of pesticide adsorbed in the solid phase C_s (mg kg⁻¹), can be calculated as:

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

where V (mL) is the volume of solution in the suspension and m_s is the mass of soil (g). The soil sorption coefficients K_d (mL g⁻¹) and K_{oc} (mL g⁻¹) were then calculated as:

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

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

For basic pesticides, a liquid-liquid extraction of the CaCl₂ supernatant was performed with ethyl acetate (ratio 1:1). After one hour shaking (200 oscillation min⁻¹), the samples were allowed to stand, and pesticide concentrations in the ethyl acetate supernatant were analysed by GC-MS.

Table 3-3. Details of analytical procedures for the ten ionisable pesticides.

| HPLC analysis (Agilent 1100 MWD multiwavelength detector) | | | | | | | | | | |
|--|-------------------------------|---|--|-----------------------|-----------------------------------|----------------------------|-------------------------|---------------------------------------|---------------------------------------|--------------|
| Pesticide | Purity (%) | HPLC Mobile phase | T (°C) | Wavelength (nm) | Flow rate (mL min ⁻¹) | Injection volume (µL) | Column | Retention time (min) | Detection limit (mg L ⁻¹) | Recovery (%) |
| fluroxypyr | 99.2 | ACN:water acidified (0.04% H ₃ PO ₄) | 30 | 200 | 1 | 20 | Agilent eclipse XDB-C8 | 2.9 | 0.02 | 90-131 |
| fluazifop-P | 90-93 | (45:55, v:v) | | | | | 4.6*150mm, 5µm | 8.8 | 0.02 | 97-112 |
| GC-MS Analysis (GC:Agilent 6890N, MS Detector: HP 5973) | | | | | | | | | | |
| Pesticide | Purity (%) | T (°C) | Helium flow rate (mL min ⁻¹) | Injection volume (µL) | column | mass to charge ratio (m/z) | Retention time (min) | Detection limit (mg L ⁻¹) | Recovery (%) | |
| metribuzin | 99.3 | | | | | 198 | 12.5 | 0.0092 | | |
| pirimicarb | 99.4 | injector:250°C | | | J&W HP5-MS, | 166 | 11.8 | 0.0036 | 71-92 | |
| fenpropimorph | 93.6 | detector:300°C | 0.7 mL min ⁻¹ | 1 | 30m*0.25mmi.d., | 128 | 13.9 | 0.0019 | | |
| terbutryn | 98.7 | | | | 0.25µm film thickness | 226 | 13.3 | 0.0053 | | |
| LSC Analysis (Liquid Scintillation Counter LS 6500, Beckman Coulter Inc., Fullerton, USA) | | | | | | | | | | |
| Samples were counted three times for five minutes and were corrected for background using blank controls. Counting efficiency and colour quenching were corrected with the external standard ratio method. | | | | | | | | | | |
| Pesticide | ¹⁴ C position | Specific activity (MBq mmol ⁻¹) | Procedure | | | | Counting efficiency (%) | Detection limit (Bq) | | |
| 2,4-D | ring- ¹⁴ C | 2960.0 | The solution to analyse was diluted in 10 mL of ecoscint A scintillation cocktail (National Diagnostics, Hessle, UK) | | | | 94-95 | 1.5 | | |
| dicamba | carboxyl- ¹⁴ C | 693.0 | | | | | | | | |
| metsulfuron-methyl | triazine-2- ¹⁴ C | 703.8 | | | | | | | | |
| flupyrsulfuron methyl | pyrimidine-2- ¹⁴ C | 739.9 | | | | | | | | |

Statistical analysis

Relationships between adsorption coefficients and soil/pesticide descriptors were investigated using two software packages. The aim was to identify the best combination of properties to describe the variation in adsorption. The three best properties to include in the regression equations were selected with (i) a forward stepwise search with Genstat (starting with no terms in the model, variables are added or dropped according to the residual mean square; Genstat for Windows, 7th edition, organisation Rothamsted Research, UK) and (ii) MobyDigs (software designed to identify an optimal regression model where a large number of potential parameters are available, using a genetic algorithm approach coupled with ordinary least squares regression; MobyDigs Version 1.0, Talete srl.; Todeschini et al., 2004). Each pesticide and soil was first considered individually. The data for the acids and bases were then integrated and the software was run again. Finally, the whole dataset was considered. The same approach was followed for the descriptors with separate analysis with soil descriptors, pesticide descriptors and finally all descriptors considered together.

RESULTS

Adsorption coefficients (Kd)

In general, sorption of the acids was weak compared to the bases, broadly following the order: dicamba < metsulfuron-methyl < fluazifop-P < metribuzin < 2,4-D < flupyr-sulfuron-methyl < fluroxypyr < terbutryn < pirimicarb < fenpropimorph (Table 3-4). The adsorption coefficient normalised to the organic carbon content of the soil (Koc) is usually much less variable than Kd for a given hydrophobic molecule (Karickhoff, 1981) and this parameter is widely used for comparing pesticide binding in soil. The normalisation of adsorption coefficients to the clay content (Kclay) has also been proposed for polar and ionic pesticides (Hermosin et al., 2000). In this study, Koc and Kclay values varied significantly between soils ($p < 0.001$). This confirms that the Koc or Kclay approaches are not suitable for ionisable compounds.

Adsorption coefficients were plotted against the pH in KCl and organic carbon content (OC) of the soils (Figure 3-1, 3-2). Those are the two soils properties expected to have the greatest influence on the fate of ionisable compounds in soils (Chapter 2).

Adsorption was generally stronger in soils with lower pH and containing more organic carbon. There were weak but significant correlations between Kd values and pH KCl ($r = -0.385$, $p < 0.001$ for the six acids; $r = -0.219$, $p < 0.01$ for the four bases) and between Kd and OC ($r = 0.513$, $p < 0.001$ for the acids; $r = 0.329$, $p < 0.001$ for the base).

Four measurements of soil pH were initially considered (i.e. pH determined in 0.01M CaCl₂, in 1M KCl, in water and in the soil suspension just before centrifugation). pH KCl provided the widest range and was the most strongly correlated with Kd. This is

probably because pH KCl is a measure of surface acidity (K^+ extracts H^+ ions present at the surface of soil particles) and provides a measure of the total potential acidity of a soil (active and exchangeable pools of acidity, Brady and Weil, 2002). This measure seems to be a better indicator for the dissociation of ionisable compounds in soil than an apparent acidity measurement (e.g. pH of a soil suspension). Therefore, only pH KCl was selected for further analysis.

Table 3-4. Adsorption coefficients (K_d , $mL\ g^{-1}$) obtained using the batch technique for six acidic and four basic pesticides in nine agricultural soils. The value between parentheses is the standard deviation for four replicates.

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

Figure 3-1. Plots of K_d (mL g^{-1}) against pH KCl (a), OC (g kg^{-1})(b) and Koc (mL g^{-1}) against soil pH KCl (c) for the six acids.

◇ 2,4-D □ dicamba ○ flupyr-sulfuron-methyl △ fluroxypyr * metsulfuron-methyl × fluazifop-P

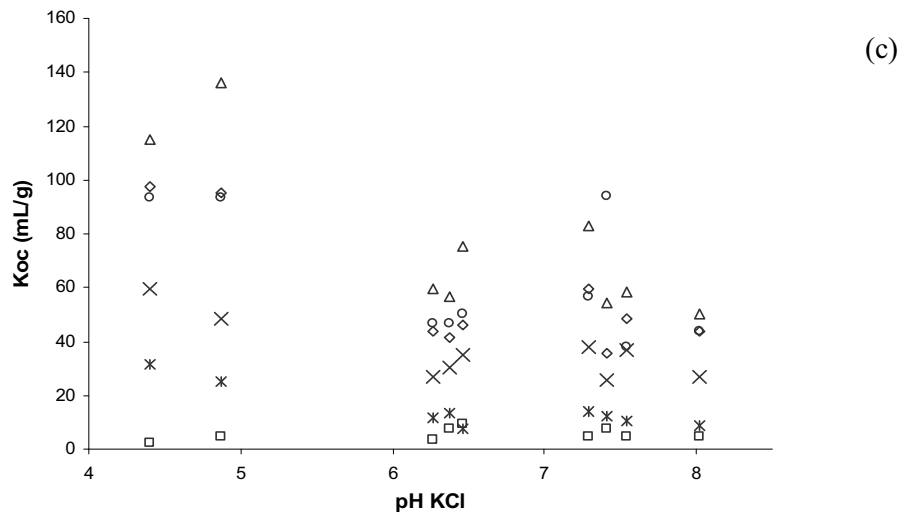
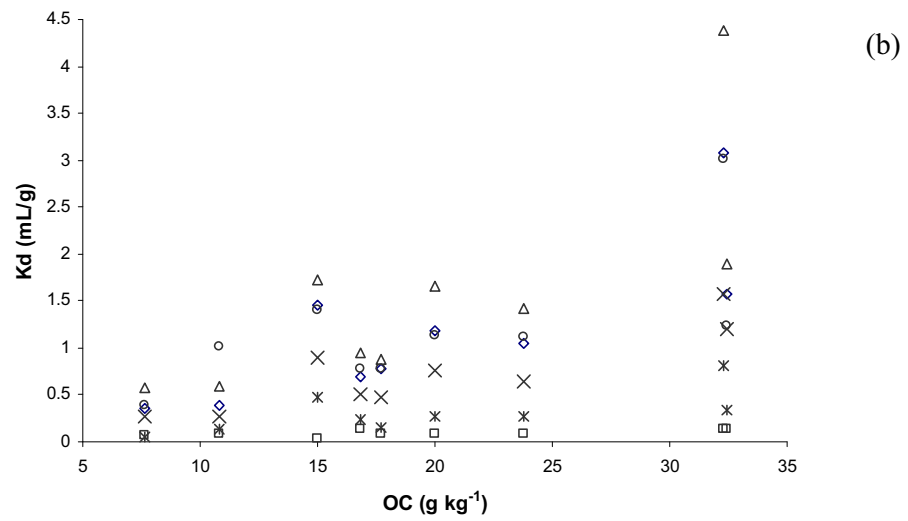
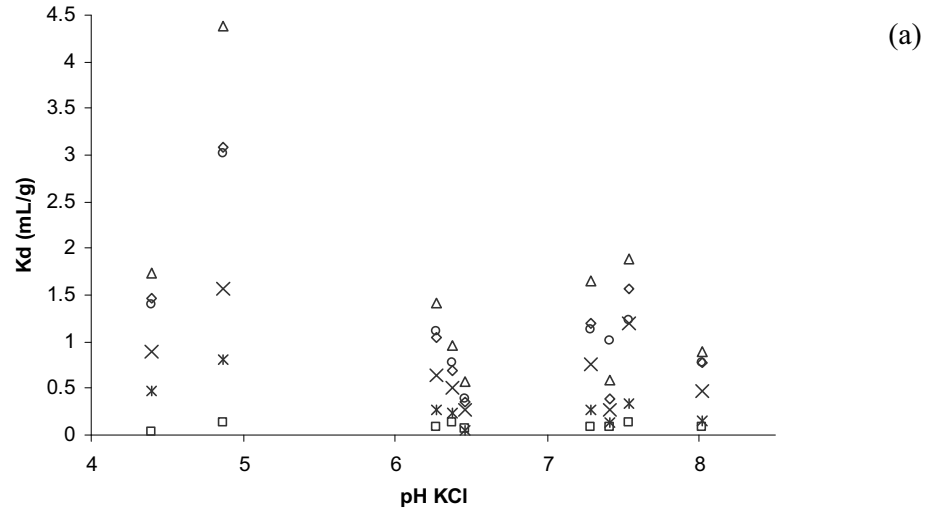
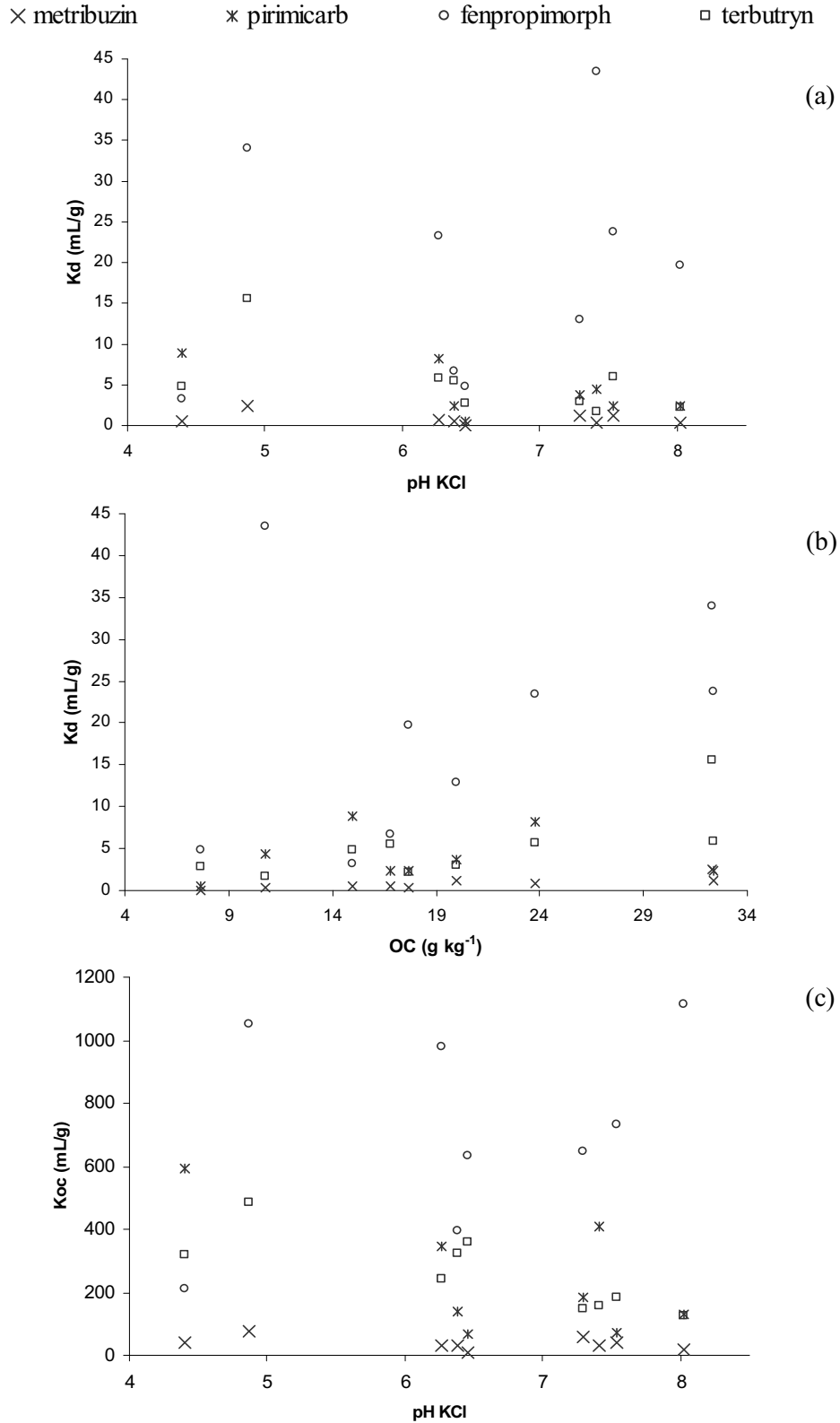


Figure 3-2. Plots of K_d (mL g^{-1}) against pH KCl (a), OC (g kg^{-1})(b) and K_{oc} (mL g^{-1}) against soil pH KCl (c) for the four basic compounds. Outlier for pirimicarb: $K_d=105$ (mL g^{-1}), $K_{oc}= 3262$ (mL g^{-1}) in soil 8 (pH = 4.87, OC=32.3) and fenpropimorph: $K_{oc}= 4026$ (mL g^{-1}) in soil 2 (pH=7.41, OC=10.8)



A negative effect of pH on the sorption of ionisable pesticides has frequently been reported and plots of K_d against pH resembling dissociation curves have been observed in experiments in which the pH of a soil was adjusted artificially (Barriuso et al., 1992; Gao et al., 1998; Mersie et al., 1985; Rocha et al., 2002). The comparison of soils representing a range of native pH is expected to provide more realistic information on the behaviour of a compound. However, variations in other soil properties, such as OC, counterbalance the effect of pH and make the interpretation of the results more difficult. Soil 8 has a large organic carbon content (Table 3-1) resulting in strong adsorption for all pesticides (Table 3-4). This explains why a peak in adsorption appears at pH 4.87 on the plot of K_d versus pH (Figure 3-1a). The plot of K_{oc} (instead of K_d) against pH eliminates a major part of the influence of organic matter and thus distinguishes the part of variation attributable to other factors such as pH.

For each acid, K_{oc} was stronger in soils with low pH (Figure 3-1c). The plots do not perfectly fit the shape of a dissociation curve, probably because the organic matter in each soil type has different characteristics and/or because adsorption depends on other soil parameters. Sorption of some acids at $pH > pK_a + 2$ is not negligible although 99% of the pesticide should be in the anionic form. This suggests that (i) some anions might adsorb even though they are generally repulsed by negatively charged soil surfaces and/or that (ii) neutral species still exist at $pH > pK_a + 2$, presumably because some surfaces or microenvironments of the soil matrix have lower pH than the bulk solution (Chapter 2). The anionic form of acidic pesticides can strongly interact with the positively charged surface of oxides. However, no influence of oxides contents (Al and Fe extracted with the Merha-Jackson method) on the adsorption of acids could be observed. This is probably because the soils studied were formed in a

temperate area where the relatively high concentration of organic compounds prevents the formation of oxides in soils.

The influence of pH and OC on the adsorption of basic compounds is less apparent than for the acids (Figure 3-2a, b). The adsorption of fenpropimorph seems independent from these two parameters and correlations between its sorption and OC or pH are not significant. Fenpropimorph has a very different molecular structure and a much higher volatility than the other basic compounds studied and this might result in a particular behaviour and/or experimental artefacts, respectively. Although no clear influence of pH on K_{oc} can be noticed for metribuzin, pirimicarb or fenpropimorph, a peak in adsorption is observed for terbutryn. This type of pH influence is sometimes observed for basic compounds and was previously reported for terbutryn in experiments in which the pH was modified artificially (Barriuso and Calvet, 1992; Barriuso et al., 1992).

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

A first analysis of the results confirmed the influence of OC and pH on the adsorption of ionisable compounds. It also suggested that other parameters are needed to predict the variability in adsorption between soils and pesticides.

Multivariate analysis

Two software packages were used to select the best combination of parameters, amongst 26 soil and 762 pesticide properties, to explain the variability in adsorption. Each pesticide and soil was considered individually before combining the data for acids, bases and for all the pesticides. Separate analyses were also undertaken with soil and pesticide descriptors and with both combined. Main results from the analysis are given in Table 3-5. Regression coefficients are generally large even when only soil properties are considered. The low level of adsorption of dicamba makes the determination of adsorption difficult and prone to error and this probably explains the low regression coefficients obtained for this compound. Results obtained with the Genstat package were generally similar to those obtained with MobyDigs (results not shown). Differences in the parameters selected and the generally lower regression coefficients obtained with the Genstat package can be attributed to the sequential nature of the stepwise approach. Indeed, the selection of new variables is conditioned on the variables already selected. The number of models examined is thus restricted compared to the genetic algorithm approach that examines all possible models.

Better predictions were generally obtained for Log K_d than for K_d probably because Log K_d gives a narrower range of values.

Different combinations of soil properties were generally selected for the different pesticides, but some trends can be identified. The lipophilicity of each compound corrected for soil pH (Log D) was selected for four of the six acids studied, one basic compound and when all acids, all bases and all pesticides were considered together. It seems therefore to be the major determinant of the variability in adsorption. Soil OC content and CEC (Cation Exchange Capacity) give a measure of the quantity of

sorption sites of each soil and one of these two properties was selected for almost all pesticides. Metsulfuron-methyl and flupyr-sulfuron-methyl are sulfonylurea herbicides. The soil parameters selected to predict their adsorption (phosphorus content, exchangeable magnesium and sodium content) differ from those for the four carboxylic acids. A link between phosphorus content (P_2O_5) and sorption of ionisable pesticide has not been reported previously and the reason why this soil property has been selected for almost all pesticides is unclear. Nevertheless, Log D appeared within the ten strongest predictors selected by the software. The content of exchangeable magnesium (Mg) was selected for the two sulfonylureas and for the basic compounds as an important parameter influencing adsorption. This is probably because sorption was particularly strong in soil 8 due to a high OC content combined with a low pH. This soil also has much more exchangeable magnesium than the other soils (6.12 compared to an average of 1.64 $cmol^+ kg^{-1}$). Exchangeable magnesium is unlikely to have a direct effect on adsorption.

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

Table 3-5. Best predictors for sorption variability (expressed as Kd and Log Kd) selected by the MobyDigs package.

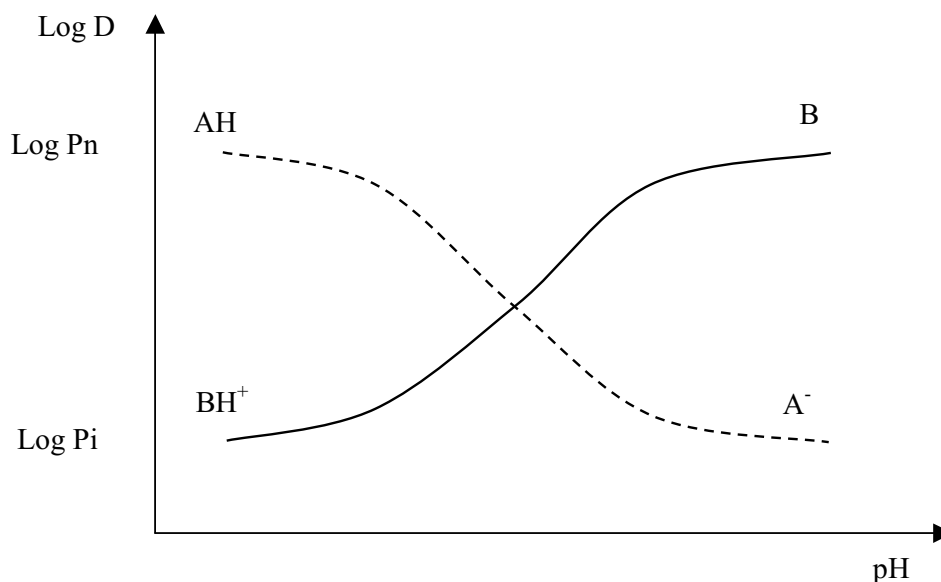
| | Soil properties selected for Kd | r ² | Soil properties selected for Log Kd | r ² |
|----------------------|--|----------------|---|----------------|
| 2,4-D | Log D, CaCO ₃ , CEC | 0.961 | P ₂ O ₅ , CEC, Al | 0.953 |
| dicamba | Log D, OC | 0.161 | CaCO ₃ , CEC, Al | 0.418 |
| fluroxypyr | Log D, CEC, K | 0.946 | pH, CEC, Al | 0.969 |
| fluazifop-P | Log D, OC, Ca | 0.952 | P ₂ O ₅ , CEC, Al | 0.957 |
| metsulfuron-methyl | P ₂ O ₅ , Mg, Na | 0.911 | sand, pH, Ca | 0.953 |
| flupyrulfuron-methyl | P ₂ O ₅ , Mg, Na | 0.961 | CaCO ₃ , CEC, K | 0.939 |
| All acids | Log D, Ca | 0.119 | Log D, OC | 0.397 |
| metribuzin | pH, CEC, K | 0.931 | clay, OC, Na | 0.922 |
| pirimicarb | C/N, P ₂ O ₅ , Mg | 0.979 | Log D, Al, Fe | 0.972 |
| fenpropimorph | pH, C/N, Mg | 0.791 | C/N, Mg, Na | 0.862 |
| terbutryn | CaCO ₃ , P ₂ O ₅ , Mg | 0.912 | OC, CaCO ₃ , Si | 0.919 |
| All bases | Mg, K | 0.303 | Log D, OC, K | 0.412 |
| All pesticides | Log D, CEC | 0.159 | Log D, OC, Al | 0.554 |
| | All properties for Kd | r ² | All properties for Log Kd | r ² |
| All acids | Log D, OC, nCs | 0.710 | Log D, OC, GATS7v | 0.906 |
| All bases | CaCO ₃ , Mg, BELp1 | 0.458 | OC, Mg, BELv3 | 0.821 |
| All pesticides | Mg, ATS1m, ATS8e | 0.360 | OC, CIC2, JGI3 | 0.838 |
| ATS1m | Broto-Moreau autocorrelation of a topological structure - lag 1 / weighted by atomic masses | | | |
| ATS8e | Broto-Moreau autocorrelation of a topological structure - lag 8 / weighted by atomic Sanderson | | | |
| BELp1 | lowest eigenvalue n. 1 of Burden matrix / weighted by atomic polarizabilities | | | |
| BELv3 | lowest eigenvalue n. 3 of Burden matrix / weighted by atomic van der Waals volumes | | | |
| CIC2 | complementary information content (neighborhood symmetry of 2-order) | | | |
| GATS7v | Geary autocorrelation - lag 7 / weighted by atomic van der Waals volumes | | | |
| JGI3 | mean topological charge index of order3 | | | |
| nCs | number of total secondary C(sp3) | | | |

Equation to predict the adsorption of acids

When all descriptors were considered together, Log D and OC were selected as the best predictors for the adsorption of acids (Table 3-5). Better predictions were obtained for Log K_d than for K_d and to be consistent with linear free energy relationships, the OC content was transformed to logarithmic values as well. Several authors previously used the partition coefficient between octanol and water to predict hydrophobic partitioning of neutral compounds (Sabljic et al., 1995; Dearden, 2004) as well as ionisable compounds such as dichlorprop (Riise and Salbu, 1992) and 2,4-D (Hyun and Lee, 2005). The neutral and ionic forms of ionisable compounds have different polarities. Since their ratio varies with pH, the lipophilicity of ionisable pesticides is pH dependent. For acids, Log D decreases with increasing pH as the proportion of anionic species increases. For bases, Log D increases with pH since the dominant form at pH > pK_a is neutral (Figure 3-3). The parameter Log D describes two sources of variability in adsorption. When Log D is selected for a single compound, it describes the shift in concentrations of the neutral and ionic forms and the difference in their strength of sorption. The correlation between K_d and Log D is thus positive for acids and negative for bases (for which the cation adsorbs more strongly than the neutral form). When several pesticides are considered together, Log D also allows ranking of pesticides according to their intrinsic tendency for hydrophobic partitioning. In this case, the relationship between K_d and Log D is always positive. Log D can thus be used to predict the adsorption of acids that mainly occurs through hydrophobic partitioning, but it is unsuitable for bases.

Figure 3-3. Variation in lipophilicity (Log D) with pH for acids (dashed line) and basic compounds (plain line). Log P_n and Log P_i are the lipophilicity of the neutral and ionic form respectively. [AH] and [BH⁺] are the protonated form, [A⁻] and [B] the dissociated form, of the acidic and basic compounds respectively.

For acids : $\text{Log D} = \text{Log} (10^{(\text{Log P}_n + 10^{(\text{Log P}_i + \text{pH} - \text{pK}_a)})} - \text{Log} (1 + 10^{(\text{pH} - \text{pK}_a)})$



Finally, two regression equations are proposed to predict the adsorption of acids in soils. When tested on our set of data, equation (1) that includes Log D and Log OC, described a large part of the variation in adsorption (Figure 3-4a). The inclusion of the pesticide parameter GATS7v (Geary autocorrelation - lag 7 / weighted by atomic van der Waals volumes) significantly improved the description (equation (2), Figure 3-4b). In combination with other pesticide descriptors, van der Waals volume has been used previously to predict the K_{oc} of 14 carbamates and 12 triazines (Reddy and Locke, 1994a, b) and to distinguish compounds that are found in groundwater from those that are not (Worrall and Thomsen, 2004). Adsorption on hydrophobic constituents of OM can be explained either in terms of solute partition between water and organic matter (solvent-motivated sorption, described by Log D) or in terms of

solute adsorption (sorbent-motivated, physical adsorption by van der Waals interactions, Chapter 2). Although it is not fully understood, the GATS7v parameter might describe the propensity of an organic compound to adsorb to OM by van der Waals interaction and thus explain the part of sorption that is not explained by Log D. The two equations were then tested on an independent dataset of adsorption coefficients comprising seven acidic pesticides (three common to both datasets: 2,4-D, metsulfuron-methyl, dicamba, and four independent phenoxy acids: MCPA, 2,4,5-T, dichlorprop, mecoprop-P) and 36 temperate soils sampled in France and the UK ($2.13 < \text{OC (g kg}^{-1}\text{)} < 47.9$ and $3.43 < \text{pH KCl} < 8.02$; Surdyk et al., 2006; Figure 3-5). Log D for MCPA, 2,4,5-T, dichlorprop and mecoprop-P were calculated based on the lipophilicity of the neutral form (K_{ow}) estimated by KowWin v.1.67 (2000) and using the equation: $\text{Log D} = \text{Log P}_n - \text{Log (1+10}^{(\text{pH-pK}_a\text{)})}$ (with Log P_n , the lipophilicity of the neutral form). Better predictions were again observed with equation (2) that includes the pesticide parameter related to van der Waals volumes (equation (1): $r^2=0.451$; equation (2): $r^2=0.721$). Although it requires further validation, this descriptor seems to be a useful indicator for the behaviour of organic compounds in soil.

Figure 3-4. Adsorption coefficients measured for the acids (Log Kd) are plotted against the values predicted with two regression equations including the lipophilicity of the compound corrected for soil pH (Log D), the soil organic carbon (Log OC) and the pesticide descriptor GATS7v (Geary autocorrelation - lag 7 / weighted by atomic van der Waals volumes). The dashed line is the 1:1 line.

◇ 2,4-D □ dicamba ○ flupyr-sulfuron-methyl △ fluroxypyr * metsulfuron-methyl × fluazifop-P

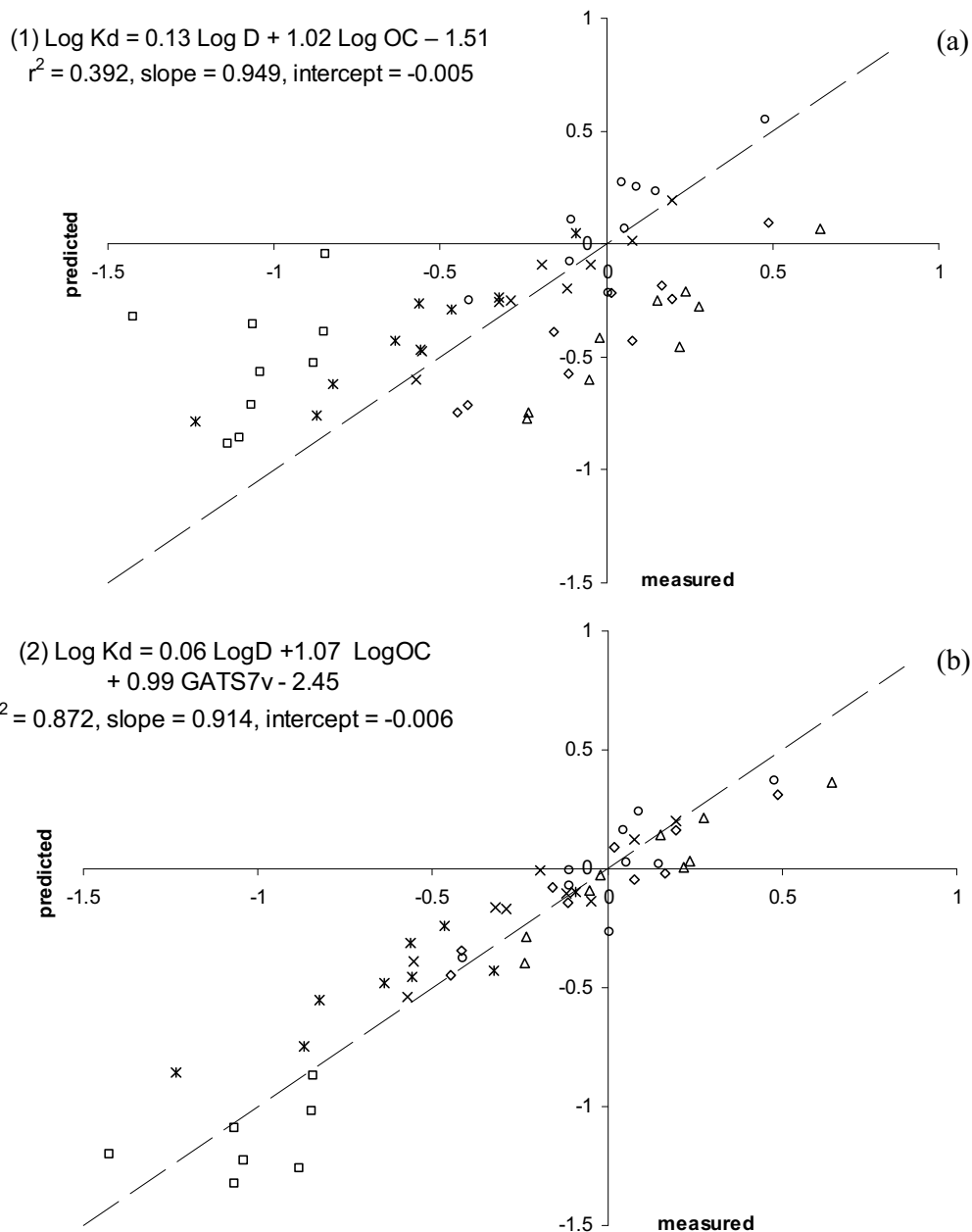
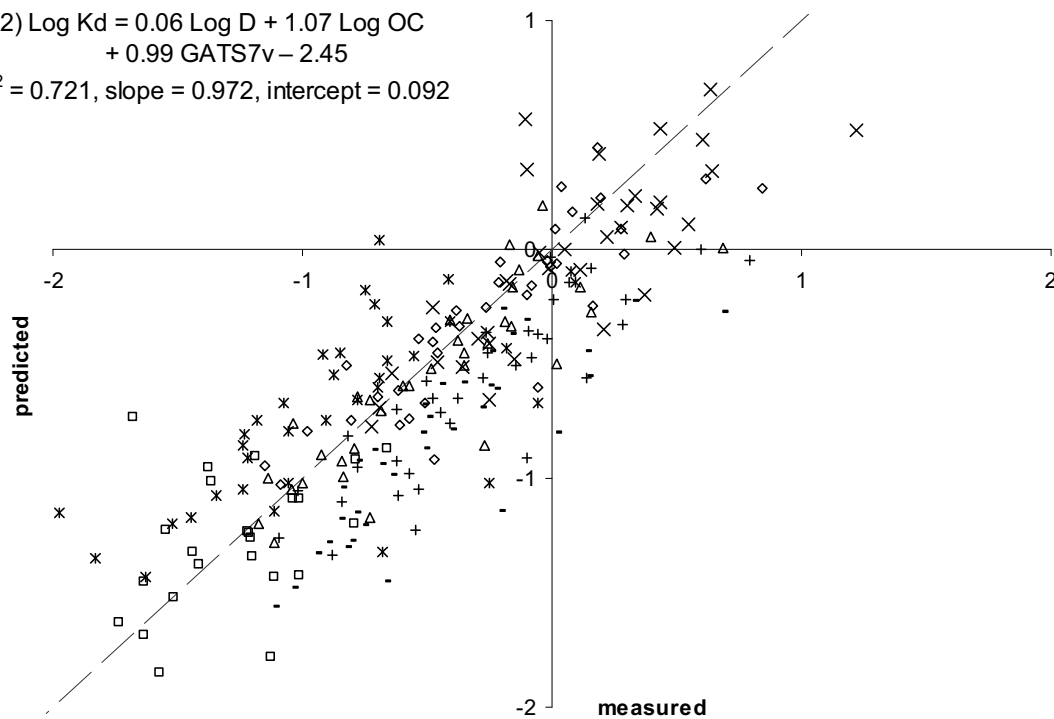


Figure 3-5. External validation of the regression equation including three parameters: lipophilicity of the compound corrected for soil pH (Log D), soil organic carbon content (Log OC) and pesticide descriptor (GATS7v). The dataset comprises adsorption coefficients (Log Kd) measured for seven acids in 36 temperate soils. The dashed line is the 1:1 line.

◇ 2,4-D □ dicamba × metsulfuron-methyl △ dichlorprop × 2,4,5 T + MCPA - mecoprop-P

$$(2) \text{ Log Kd} = 0.06 \text{ Log D} + 1.07 \text{ Log OC} + 0.99 \text{ GATS7v} - 2.45$$

$$r^2 = 0.721, \text{ slope} = 0.972, \text{ intercept} = 0.092$$



Equation to predict the adsorption of bases

When the four bases were considered together, the MobyDigs package selected the parameters OC, exchangeable magnesium and BELv3 to predict adsorption (Table 3-5, Figure 3-6). Nevertheless, as previously noted, the influence of magnesium content is probably due to the set of soils studied (very high content in soil 8) and since this property is rarely reported in the literature, its relevance is difficult to test on external datasets.

Fenpropimorph had a different behaviour relative to the other bases (no significant influence of pH or OC). When this compound was excluded from the dataset, the best properties selected for the three bases remaining were then pH, CEC and BELm8 (lowest eigenvalue n. 8 of Burden matrix/weighted by atomic masses). The equation that only included the soil properties pH and CEC gave a good match to adsorption data for terbutryn reported by Barriuso and Calvet (1992) but failed to predict sorption of metribuzin (Harper, 1988, Figure 3-7). In the latter study, clay content was the single best predictor of the adsorption of metribuzin. In contrast to results for the acids, the inclusion of the pesticide parameter (BELm8) did not improve the match to independent datasets for the bases.

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

and the balance between these processes is not fully understood (Chapter 2). Equations specific to a particular compound are thus preferred at present.

Based on numerous literature data, Weber et al. (2004) proposed regression equations to predict the adsorption of several basic compounds. The equation for metribuzin ($pK_a=0.99$) included pH, OC and clay content whereas the equation for terbutryn ($pK_a=4.3$) only included OC. No equation was proposed for fenpropimorph or pirimicarb, probably because too few data were available. When applied to our dataset, the equations proposed by Weber et al. (2004) provided a good match to data for metribuzin ($r^2=0.863$, $p<0.001$) but consistently underestimated sorption for terbutryn ($r^2=0.452$; $p=0.028$) (Figure 3-8). More experimental data are needed to achieve a greater level of accuracy and to provide equations for other basic compounds.

Figure 3-6. Prediction of the adsorption coefficient of four basic compounds using three parameters: the soil organic carbon content (g kg^{-1}), magnesium content (cmol^+ kg^{-1}) and a pesticide descriptors (BELv3). The dashed line is the 1:1 line.

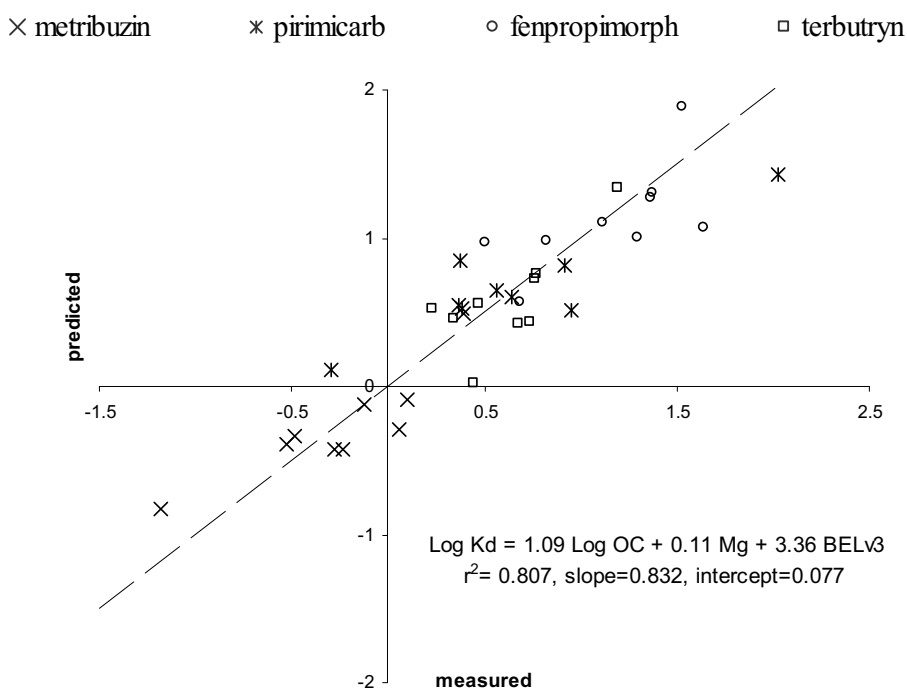


Figure 3-7. Prediction of the adsorption coefficient measured for metribuzin (Harper, 1988) and terbutryn (Barriuso and Calvet, 1992) with the regression equation including two parameters: soil pH and cation exchange capacity (CEC). The dashed line is the 1:1 line.

× metribuzin: $r^2=0.833$, slope=1.930, intercept=1.203

□ terbutryn : $r^2=0.751$, slope=1.182, intercept=0.074

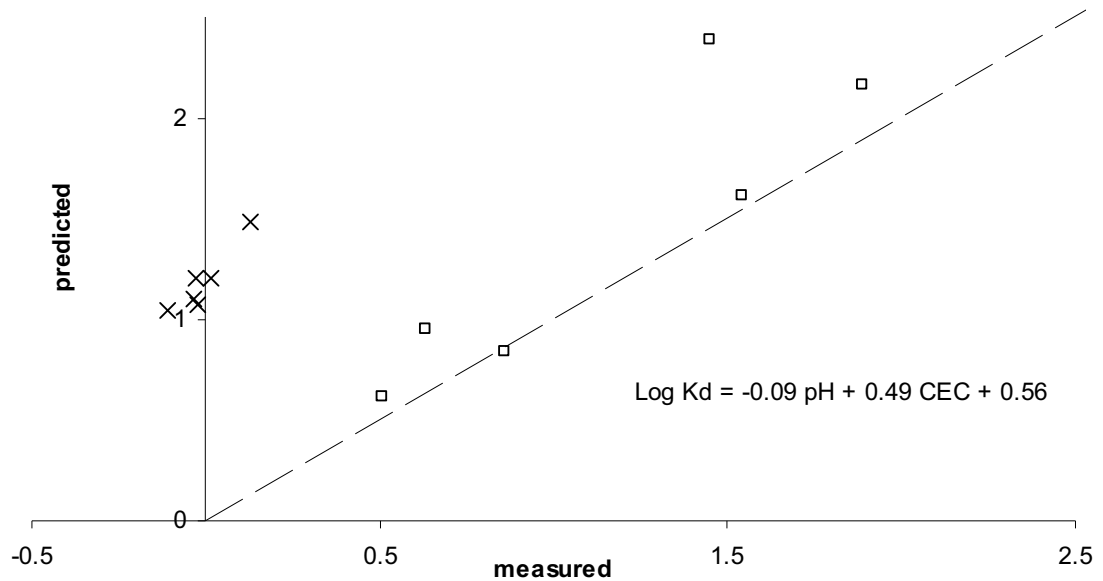
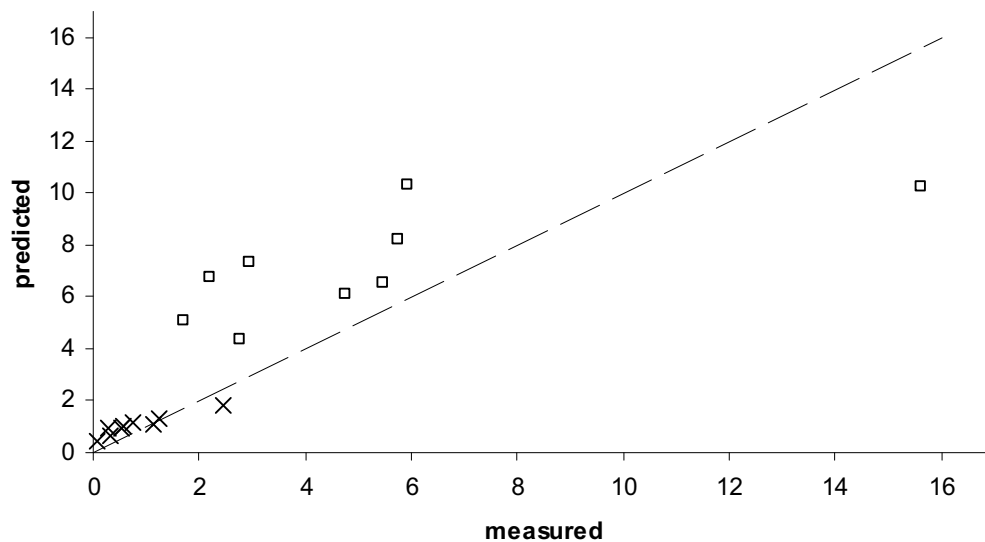


Figure 3-8. Prediction of the adsorption of two bases measured in the current study with the equations proposed by Weber et al. (2004). The dashed line is the 1:1 line.

× metribuzin : $K_d = -0.12 \text{ pH} + 0.18 \text{ OM} (\%) + 0.01 \text{ clay} (\%) + 0.9$, $r^2=0.863$, slope=0.502, intercept=0.623

□ terbutryn : $K_d = 1.39 \text{ OM} (\%) + 2.5$, $r^2=0.452$ slope=0.355, intercept=5.354



CONCLUSION

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

For the acids, the two strongest descriptors of the variability in adsorption were (i) the lipophilicity of the compound corrected for soil pH (Log D) and (ii) the soil organic carbon content (OC). A regression equation including these two parameters described a large part of the variability in sorption of the acids ($r^2=0.454$). The inclusion of a pesticide descriptor related to the van der Waals volume of the molecule (GATS7v) significantly improved the prediction ($r^2=0.721$) but requires further validation. Reliable determination of the lipophilicity of ionisable compounds is still a problem (Finizio et al., 1997) and the value used in any regression equation needs to be either measured or selected from the literature with great care.

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

Chapter 4

FACTORS INFLUENCING DEGRADATION OF PESTICIDES IN SOILS

INTRODUCTION

Alongside sorption, degradation is the second important process used to predict the fate of pesticides 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 DT50, the time required for 50% of the initial dose to disappear). Rates of degradation are influenced by physico-chemical properties of the soil (such as pH and organic carbon content), biological properties (activity and distribution of microorganisms) and environmental conditions that control soil temperature and moisture content. Both route and rate of degradation also depend on properties of the chemical. Variability in degradation rate is expected and numerous studies have provided evidence for field-to-field variation in the degradation rates of pesticides (Walker et al., 2001). Extrapolation from measurements on a set of soils to prediction for a different soil is a common problem in environmental assessment. A greater understanding of the factors that influence degradation rates is required to support this extrapolation and thus ensure the safe use of new and existing products.

For non-ionisable 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. for most sulfonylureas), pH generally has a negative influence on rates of degradation (Chapter 2).

Sorption processes may affect biodegradation mainly by modifying chemical bioavailability. A positive relationship between adsorption coefficient (K_d) and half-life has been reported for many ionisable pesticides (Chapter 2). However, several factors might counterbalance the influence of sorption on degradation and the link between sorption and degradation is not always obvious (Barriuso et al., 1997; Radosevish et al., 1996; Shaw and Burns, 1998). Conflicting results were sometimes observed for the same compounds and no general trend is apparent at present. Even a weak correlation between sorption and degradation greatly influences probabilistic analysis of leaching through soil and reduces the predicted extent of leaching (Beulke and Brown, 2006). More experiments coupling measurement of adsorption and degradation under differing conditions are required to better understand the extent and mechanisms of interactions between these processes.

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

MATERIALS AND METHODS

The soils and pesticides used in this experiment were the same as those used in Chapter 3. Detailed descriptions of the soils, the pesticides and the measurement of adsorption can be found in the Materials and Methods section of Chapter 3.

Soils

Nine arable soils were sampled from the top 20 cm in several locations in southern England in July 2004 (2,4-D and dicamba degradation study and all sorption experiments), September 2004 (degradation of fluroxypyr, fluazifop-P, metsulfuron-methyl and flupyrsulfuron-methyl) and April 2005 (degradation of the four bases). Soils properties are presented in Table 3-1. The soil water content for the incubation was determined with a pressure membrane system for samples of sieved soil loosely repacked into a ring of 1 cm height and 4 cm diameter (roughly 20 g of soil, 3 replicates). Samples were left in cells under a pressure of -33 kPa until there was no further change in weight. Moisture content was then determined by difference in weight from oven-dried samples.

Pesticides

The main properties of the six acids and four bases studied in this chapter are presented in Table 3-2. Assuming that no competition effects operate at low concentration, pesticides were paired (2,4-D with dicamba, fluroxypyr with

fluazifop-P, metsulfuron-methyl with flupyr-sulfuron-methyl, metribuzin with pirimicarb and fenpropimorph with terbutryn) and studied together. Sorption of the weakly sorbed pesticides was measured using radioisotopes as described in Chapter 3. Considering the application rates in the field and incorporation in the upper 2.5 cm of the soil profile, degradation experiments for eight of the pesticides were carried out at 2 mg a.s. kg⁻¹. Sulfonylurea herbicides are applied at very low rates in the field, but were studied at a relatively high concentration (1 mg a.s. kg⁻¹) to facilitate analysis. Two-dimensional molecular properties were calculated for each pesticide using AdmeWorks ModelBuilder Version 2.1 (Fujitsu Kyushu System Engineering Ltd.). Estimates of degradation potential were included in the list of pesticide descriptors. Six estimates of aerobic biodegradability were determined using BIOWINTM (2000) and three DT50 values from the literature were included for each pesticide (laboratory, field and typical half-life reported in the Footprint database (www.eu-footprint.org/ppdb.html)).

Incubation to measure degradation and analysis

Samples of fresh soil were pre-incubated for 8 days prior to application of pesticide (moisture content just below -33 kPa, 15°C, in the dark) to allow germination and removal of seeds and establish equilibrium of microbial metabolism following the change from sampling or storage conditions to incubation conditions. The period between sampling and the beginning of incubation never exceeded 3 months to comply with OECD guidelines (OECD, 2002).

Technical grade pesticide solution in deionised water (5 mL) was applied dropwise to the equivalent of 200 g of dry soil (3 replicates) to reach an initial concentration of 2

mg a.s. kg⁻¹ (1 mg a.s. kg⁻¹ for the two sulfonylureas). When the chemical properties did not allow dissolution in water (terbutryn and fenpropimorph), the pesticides were dissolved in acetone and 0.5 mL of pesticide solution was applied to the soil with a 0.5 mL syringe (Agilent Technology). Soil was thoroughly mixed and the moisture content was adjusted by weight to exactly -33 kPa. The soil was then transferred to a 500 mL glass flask and incubated at 15°C in the dark. During the incubation, moisture content was maintained by weight twice a week and lids were not tightly closed to avoid anaerobic conditions being created. At appropriate time intervals, samples of 20 g of soil were weighed into 125 mL amber glass jars and immediately frozen. Nine samples were taken during the incubation period. The duration of incubation was chosen according to half-lives previously reported in the literature. It ranged from 42 days (2,4-D and dicamba) up to 119 days (metsulfuron-methyl and flupyr-sulfuron-methyl).

Soil bioactivity was evaluated by measuring dehydrogenase activity after 2 and 6 weeks of incubation (triplicates, Table 3-1). This enzyme is only active in living organisms and thus is an indicator for soil microbial activity (Viswanath et al., 1977). Soil samples (5 g) were incubated at 30°C with 5 mL of colourless TTC solution (0.5% by weight, 2,3,5-triphenyl-2H-tetrazolium chloride, 98%, Avocado Research Chemicals Limited) in 0.1M tris buffer adjusted to pH 7.6 with HCl (tris(hydroxymethyl)aminomethane, general purpose grade, Merck Science). TTC is reduced by dehydrogenase enzymes to red water-insoluble TPF (triphenylformazane) and was extracted with 25 mL acetone after 24 hours of incubation. The samples were shaken for one hour (end-over-end shaker, 22 rpm) and centrifuged at 2500 g for ten minutes. The intensity of the red colour of the supernatant was measured by spectrophotometry at 485 nm (UV-160A, UV-visible recording spectrophotometer,

Shimadzu) and converted to bioactivity (mg TPF kg^{-1}) based on a set of TPF standards (1,3,5-triphenylformazane, Sigma-Aldrich Company Ltd.).

Extraction and quantification of pesticide remaining in soil was undertaken at the end of the respective incubation period. Degradation was measured through the relative decline of residues extracted with an appropriate organic solvent (soil to solution 1:2, see details in Table 4-1). After one hour of end-over-end shaking (22 rpm), the samples were allowed to stand until the soil had settled (one hour), and pesticide concentration in the clear supernatant was determined. Subsamples of supernatant containing metsulfuron-methyl and flupyr-sulfuron-methyl were concentrated two-fold by evaporation under nitrogen flow prior to analysis. Basic pesticides were extracted with acetone. Subsamples of supernatant were evaporated to dryness under nitrogen flow and redissolved in ethyl acetate. Analysis was by high-pressure liquid chromatography and gas chromatography with mass spectrum detection. Details are provided in Table 3.3 and Table 4-1. Non-extractable residues were considered to be degraded and the extraction efficiency was assumed to remain constant over the course of the experiment.

Three kinetic models were fitted to the degradation curves: a simple first-order equation, a first-order multi-compartment (Gustafson & Holden) model and first-order sequential (Hockey-Stick) model. Parameters were optimised according to recommendations by FOCUS (2006) using the least squares method with Microsoft Excel Solver. The simple first-order kinetic model always described the data adequately (and often better than the other two models). The first-order rate of degradation and the DT50 (time required for 50% of the initial dose of pesticide to be degraded) of each compound in each soil were determined with the following equations:

Table 4-1. Details of extraction and analytical procedures to study degradation of the acidic pesticides. Analysis of basic and radiolabelled compounds is described in Chapter 3 (Table 3-3).

| HPLC analysis | | | | | | | | | | | |
|-----------------------|------------|---|---|--------|-----------------|--------------------|-----------------------|--|----------------------|---------------------------------------|--------------|
| Pesticide | Purity (%) | Extraction (soil:solvent ratio: 1:2, v:v) | HPLC Mobile phase | T (°C) | Wavelength (nm) | Flow rate (mL/min) | Injection volume (µL) | Column | Retention time (min) | Detection limit (mg L ⁻¹) | Recovery (%) |
| 2,4-D | 99.6 | Methanol acidified | ACN:water acidified (0.04% H ₃ PO ₄) | 30 | 202 | 1 | 20 | Discovery® C18 4.6*150mm, 5µm | 4.7 | 0.01 | 95-106 |
| dicamba | 97.1 | (0.25% H ₃ PO ₄) | (40:60, v:v) | | | | | | 6.7 | 0.01 | 95-106 |
| fluroxypyr | 99.2 | Methanol acidified (1% H ₃ PO ₄) | ACN:water acidified (0.04% H ₃ PO ₄) | 30 | 200 | 1 | 20 | Agilent eclipse XDB-C8 4.6*150mm, 5µm | 2.9 | 0.02 | 90-131 |
| fluazifop-P | 90-93 | | (45:55, v:v) | | | | | | 8.8 | 0.02 | 97-112 |
| metsulfuron-methyl | 99.3 | ACN:Sodium acetate 0.1M | ACN:water acidified (0.25% H ₃ PO ₄) | 25 | 225 | 0.5 | 20 | Agilent eclipse XDB-C8, 4.6*150mm, 5µm | 5.9 | 0.02 | 93-106 |
| flupyrsulfuron methyl | 99.0 | pH 6.5 (75:25) | (50:50, v:v) | | | | | | 12 | 0.17 | 59-120 |

$$C_t = C_o \cdot e^{-rt} \text{ and } DT50 = \frac{\ln 2}{r}$$

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

Measurement of adsorption

Sorption coefficients (K_d , mL g^{-1}) were determined at one concentration and with four replicates using a standard batch equilibrium method (OECD, 1997) as described in Chapter 3.

Statistical analysis

The first objective was to identify the best combination of properties to describe the variation in rates of degradation. The three best properties to include in the regression equations were selected with MobyDigs Version 1.0 (Todeschini et al., 2004), a program designed to identify an optimal regression model where a large number of potential parameters are available (previously described in Chapter 3, section Statistical Analysis). Each pesticide and soil was first considered individually. The data for the acids and bases were then integrated and the software was run again. Finally, the whole dataset was considered. The same approach was followed for the descriptors with separate analysis for soil descriptors, pesticide descriptors and finally all descriptors considered together. Correlation analysis was performed using Genstat for Windows (7th edition, Rothamsted Research).

RESULTS

There was no initial lag phase on any degradation curve. A lag phase is normally attributed to adaptation of the microbial population. First-order half-lives are reported in Table 4-2. There were some marked differences between soils in their ability to degrade different pesticides. DT50 values for the acids were generally much larger in soil 6 and this was probably related to the very weak bioactivity of this soil.

Table 4-2. DT50 (days) of 10 ionisable pesticides measured in nine arable soils. The value between parentheses is the standard error associated with the estimation of DT50 with a first-order kinetic model (3 replicates).

| Soils | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-----------------------|----------------|----------------|----------------|----------------|----------------|------------------|----------------|----------------|----------------|
| 2.4-D | 2.9 (0.26) | 2.6 (0.37) | 4.7 (0.52) | 5.5 (0.38) | 3.0 (0.36) | 6.2 (0.56) | 3.7 (0.22) | 4.6 (0.12) | 4.6 (0.36) |
| dicamba | 15.1 (0.68) | 7.6 (0.42) | 24.2 (0.42) | 11.3 (0.44) | 9.1 (0.58) | 46.1 (1.16) | 9.1 (0.67) | 8.2 (0.31) | 15.0 (0.91) |
| fluroxypyr | 8.6 (0.62) | 8.6 (0.27) | 13.4 (0.36) | 9.9 (0.36) | 7.4 (0.81) | 21.3 (0.78) | 9.2 (0.42) | 9.3 (0.33) | 6.6 (0.73) |
| fluazifop-P | 6.0 (0.18) | 6.1 (0.10) | 10.3 (0.37) | 6.3 (0.14) | 11.3 (0.40) | 16.6 (0.76) | 7.0 (0.49) | 10.6 (0.80) | 13.0 (0.92) |
| metsulfuron-methyl | 54.4 (0.97) | 35.0 (1.11) | 89.4 (2.16) | 40.9 (1.22) | 37.1 (1.05) | 175.9 (22.95) | 71.8 (3.04) | 23.8 (1.30) | 35.2 (1.30) |
| flupyrsulfuron-methyl | 7.8 (0.42) | 7.9 (0.68) | 16.1 (1.09) | 10.5 (1.53) | 21.3 (0.88) | 12.2 (1.39) | 21.7 (1.40) | 7.5 (0.60) | 21.5 (5.46) |
| metribuzin | 9.3 (0.31) | 10.6 (0.60) | 23.3 (1.11) | 15.6 (0.60) | 16.6 (0.74) | 49.4 (2.15) | 15.7 (0.70) | 21.4 (1.37) | 19.5 (0.85) |
| pirimicarb | 12.5 (0.38) | 14.4 (0.61) | 57.2 (1.77) | 20.9 (0.54) | 17.1 (0.46) | 47.8 (2.05) | 7.9 (0.46) | 6.6 (0.62) | 15.4 (0.55) |
| fenpropimorph | 7.9 (0.27) | 8.3 (0.58) | 42.1 (3.81) | 14.3 (0.75) | 44.5 (4.82) | 20.6 (2.63) | 53.9 (3.34) | 30.7 (3.12) | 62 (6.33) |
| terbutryn | 8.5 (0.11) | 7.1 (0.11) | 15.1 (0.55) | 8.8 (0.29) | 12 (0.35) | 56.8 (1.37) | 16.6 (0.53) | 14.1 (0.47) | 22.3 (0.62) |

Multivariate statistical analysis

The MobyDigs package was used to select the best combination of parameters, amongst 26 soil and almost 200 pesticide properties, to explain the variability in degradation rate. Each pesticide and soil was considered individually before combining the data for acids, bases and for all the pesticides. Separate analyses were also undertaken with soil and pesticide descriptors and with both combined. When several pesticides were considered, rates of degradation were expressed as a percentage of the median. Main results from the analysis are given in Table 4-3.

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

The same procedure was applied with pesticides properties and each soil to determine whether a particular behaviour could be deduced from the characteristics of the pesticide (results partially shown in Table 4-3). The combinations of pesticide descriptors selected were different for the different soils. The descriptor ALLP was selected for all soils except soil 6 and when all pesticides were considered together. The parameter describes the topological complexity in a molecule and might be useful to rank pesticides according to their intrinsic degradability. No other pesticide descriptor was common to several soils and the large regression coefficients are probably due to the great number and variety of parameters available.

Table 4-3. Best predictors for variability in rate of degradation selected by the MobyDigs package. Rates were expressed as the percentage of the median when several compounds were considered together.

| | Soil properties | r^2 |
|------------------------|--|-------|
| 2,4-D | bioactivity, P ₂ O ₅ , Al | 0.929 |
| dicamba | pH, Log (OC), Al | 0.971 |
| fluroxypyr | Fe, K, Na | 0.768 |
| fluzifop-P | clay, Mg, K | 0.979 |
| metsulfuron-methyl | bioactivity, OC, Al | 0.926 |
| flupyr-sulfuron-methyl | CEC, Al, Na | 0.936 |
| All acids | C/N, P ₂ O ₅ , Mg | 0.098 |
| metribuzine | C/N, P ₂ O ₅ , Mn | 0.968 |
| pirimicarb | Si, Al, K | 0.945 |
| fenpropimorph | Mg, Al, K | 0.914 |
| terbutryn | Mg, K, Na | 0.985 |
| All bases | bioactivity, sand, P ₂ O ₅ | 0.463 |
| All pesticides | C/N, P ₂ O ₅ , Mg | 0.131 |
| | Pesticide properties (all soils) | r^2 |
| All acids | N3C, S0, V6P | 0.742 |
| All bases | NDB, EDMN | 0.690 |
| All pesticides | ALLP2, S6C, EDMX | 0.635 |
| | All properties (all soils) | r^2 |
| All acids | Log (OC), NATM, V6P | 0.801 |
| All bases | Log (OC), CaCO ₃ , ALLP4 | 0.496 |
| All pesticides | loam, ALLP2, EDMX | 0.670 |
| ALLP2 | ALLP 1/number of atoms in structure | |
| ALLP4 | ALLP 3/number of atoms in structure | |
| EDMN | Minimum electron density value | |
| EDMX | Maximum electron density value | |
| N3C | 3rd order molecular connectivity number | |
| NATM | Number of nonhydrogen atoms | |
| NDB | Number of double bonds | |
| S6C | 6th order cluster molecular connectivity | |
| S0 | Zero-order molecular connectivity | |
| V6P | 6th order path molecular connectivity valence | |

Calculated biodegradability (BioWin6, BioWin1) and DT50 reported in the literature (typical value, Footprint, 2006) were selected to discriminate the pesticides in only three of the nine soils (soil 5, 7 and 9 respectively). This confirms that values from the literature must be used with care since degradation rates strongly depend on both the compound and the soil type.

An equation predicting degradation of a range of compounds has not been proposed to date and is not supported by results from the current study. The failure of such a global approach (QSAR type approach) could be expected considering the complexity of interactions between different processes that influence breakdown of organic compounds in soils. The routes and rates of degradation are influenced by chemical, biological and physical properties of soils and also depend on the properties of the pesticide. Soil properties are interrelated and may influence these processes in opposite directions, thereby exhibiting a stimulating and restricting effect on the overall degradation process. The dominance of one process over another depends on the soil-pesticide combination and cannot therefore be generalised.

Correlation analysis

Correlations between rates of degradation and main soil parameters were investigated for each pesticide and are reported in Table 4-4. A positive influence of OC content on degradation rates was observed for all pesticides in this study (Table 4-4). This relationship is generally seen as the reflection of an enhanced bioactivity in soils with larger OC content (the positive correlation between OC content and bioactivity was strong but not significant for the set of soils studied here). Any inhibition of

degradation due to stronger sorption and thus reduced bioavailability in soils with large OC content was insufficient to overcome this positive correlation.

Table 4-4: Correlations coefficients between degradation rates, some soil properties and adsorption coefficients. *, ** and *** indicate a significance at $p < 0.05$, 0.01 and 0.001 levels, respectively.

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

Moreover, adsorption to humic substances could facilitate the abiotic transformation of the molecule, reinforcing the positive effect of OC on degradation rate. This effect has been previously shown for metribuzin and its metabolites (Henriksen et al., 2004), for azimsulfuron (Pinna et al, 2004) and triasulfuron (Said-Pullicino, 2004).

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

Several studies suggest that the determination of the type and activity of degrading microorganisms is necessary to describe the influence of microbial population on dissipation of pesticides (Issa and Wood, 1999; Hultgren et al., 2002). Particularly slow degradation was observed in the soil exhibiting the weakest bioactivity (soil 6) and this parameter was significantly correlated with degradation rates for six of the pesticides studied, as well as when all pesticides were considered together. Numerous methods are available to characterise the microbial activity of soils and the determination of dehydrogenase activity is one of the simplest techniques. Although it provided a good indicator for ranking the soils according to their biodegradation potential, more specific measurements would provide further information.

Many studies have demonstrated a positive influence of pH on total microbial biomass and activity (Price et al., 2001; Walker et al., 2001) and a positive correlation was observed in the present study as well ($r=0.619$). This probably explains the positive influence of pH on the degradation of fluazifop-P, metribuzin, fenpropimorph and terbutryn (Table 4-4). A similar influence of pH was previously reported for metribuzin (Ladlie et al., 1976). Conversely, pH had a significant negative influence on the degradation of metsulfuron-methyl and pirimicarb. Degradation rates for these two compounds were not correlated to soil bioactivity and this supports a dominance of abiotic hydrolysis over biodegradation. The abiotic hydrolysis of sulfonylureas is generally more favoured under acidic conditions and a negative relationship between degradation and pH was reported for chlorsulfuron, prosulfuron, primisulfuron methyl, rimsulfuron, thifensulfuron methyl and triasulfuron (Chapter 2). Flupyrsulfuron-methyl is a sulfonylurea herbicide as well. However, its hydrolysis was reported to be faster at alkaline pH (Singles et al., 1999). No significant influence

of pH on its degradation was observed in the present study and this confirms that common rules are difficult to apply, even for chemicals with similar structures.

Link between adsorption and degradation processes

There was no statistical relationship between sorption and degradation for most of the pesticides (Table 4-4, Figure 4-1). Significant correlations were only observed for dicamba, metsulfuron-methyl and pirimicarb, with faster degradation in soils with stronger sorption. As discussed above, metsulfuron-methyl and pirimicarb seem particularly sensitive to chemical hydrolysis and adsorption onto humic acids might have catalyzed their degradation.

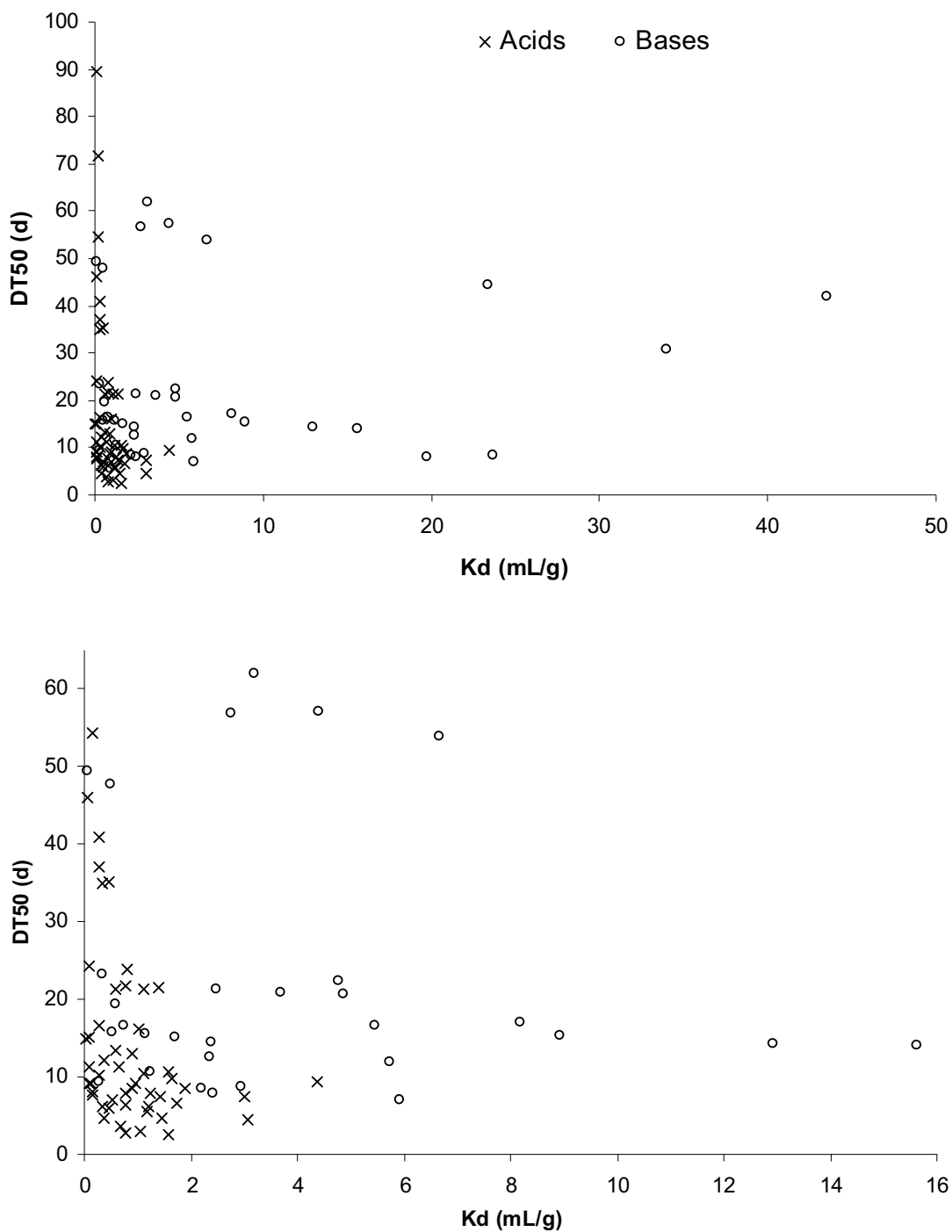
Acidic compounds are generally weakly sorbed in temperate soils and their sorption might be too weak to counterbalance the effect of OC on degradation through an increase in bioactivity. Indeed, OC content has a positive influence on both degradation and adsorption processes and this might lead to mistaken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

Although the adsorption of basic compounds was generally much stronger than that of acids, no relationship between adsorption and degradation rates could be observed except for pirimicarb. Metribuzin, fenpropimorph and terbutryn seem to be primarily degraded by microorganisms in this set of soils (strong correlation between degradation and soil bioactivity). The following possibilities need thus to be considered: (i) microorganisms are generally more abundant at, or near soil particle surfaces (Stotzky, 1986) and sorption may thus concentrate the pesticide in regions of greatest microbial activity and (ii) biodegradation might not always be restricted to

chemical in solution as suggested by Khan and Ivarson (1981), Eberbach (1998), Guo et al. (2000) and Park et al. (2001).

Beulke and Brown (2006) suggested that the effect of sorption on degradation might be dominant if soils with a wide range of OC contents are compared. For instance, a strong positive relationship between K_d and DT50 was noticed for metazachlor when studied in 10 plots within the same field ($r=0.9$, $1.5 < OC(\%) < 6.6$) while no clear relationship appeared when 18 soils were considered ($0.6 < OC(\%) < 2.4$; Allen and Walker, 1987). Significant relationships between adsorption or degradation processes and soil properties are more likely when similar types of soils are compared because the range in other influences on degradation is somewhat restricted. The set of soils considered in the present study does not represent an extreme range in OC content (0.7 to 3.4 %) but it presents large differences regarding texture and pH. These characteristics might not be favourable to emphasize a link between adsorption and degradation processes.

Figure 4-1. Plot of adsorption (K_d) and degradation (DT50) parameters for six acidic and four basic pesticides in nine agricultural soils. Outlier for metsulfuron-methyl: $K_d = 0.058$ and $DT50 = 175.9$ days in soil 6 and pirimicarb: $K_d = 105.34$, $DT50 = 6.6$ in soil 8. Lower figure shows detail from the figure above.



CONCLUSION

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

On the other hand, a correlation analysis permitted to identify distinct types of behaviour. Metsulfuron-methyl, pirimicarb (and perhaps dicamba) seemed mainly degraded by abiotic acidic hydrolysis. The degradation rates of these three pesticides were positively influenced by soil OC content and negatively influenced by soil pH. A positive relationship linked their adsorption and degradation parameters, probably as a consequence of a catalyzed hydrolysis after adsorption onto soil organic matter. In contrast, microbial degradation seemed to dominate the breakdown of 2,4-D, fluzifop-P, flupyrsulfuron-methyl, metribuzin, fenpropimorph and terbutryn. As a consequence, degradation rates of those pesticides were very sensitive to soil bioactivity level, positively influenced by soil pH and not related to adsorption. Finally, fluroxypyr had an intermediate behavior and the influence of soil properties on its degradation was unclear. The dominance of one route of degradation over another strongly depends on the characteristic of the pesticide. Pesticides with similar structures may also behave differently as shown in the current study for the two sulfonylureas.

Chapter 5

LOG D: LIPOPHILICITY CORRECTED FOR PH

INTRODUCTION

In the last 25 years, the octanol/water partition coefficient (K_{ow}) for organic compounds has been widely used in predictive environmental studies. Lipophilicity is a very important molecular descriptor that often correlates well with the bioactivity of chemicals. This parameter has been used in models to predict the distribution of organic molecules among environmental compartments (Sabljić et al., 1995), in equations for estimating bioaccumulation in animals and plants (Neely et al., 1974) or to predict the toxic effects of a substance in QSAR studies (Lin et al., 2002; Di Marzio and Saenz, 2004). Lipophilicity of organic chemicals has also been identified as an important parameter to predict adsorption in soils and sediments (Chapter 3). Literature reviews can yield K_{ow} values that differ by more than one order of magnitude for some compounds (Benfenati et al., 2003). Reliable determination of the lipophilicity of ionisable compounds is still a problem (Finizio et al., 1997) and the value used in any regression equation needs to be either measured or selected from the literature with great care.

THEORY

Ionisable compounds may be partially ionized dependent on the pH. Since the neutral and ionic species exhibit different polarities, the Kow value of ionisable pesticides is pH dependent. Numerous studies report Kow values for ionisable compounds (e.g. Benfenati et al., 2003; Donovan and Pescatore, 2002; Finizio et al., 1997; Machatha and Yalkowsky, 2005). However, most of them determined a single Kow value (also called P), reflecting the lipophilicity of the neutral species only. It is essential to determine Kow values over the full range of pH that occurs in the environment in order to get an appropriate predictor. When the Kow for the neutral (P) and ionic forms (P_i) are known, theoretical equations can be used to calculate the change in lipophilicity with pH.

There is a clear distinction between the partition coefficient P (partition of neutral species between octanol and water) and the distribution ratio D, defined for the total analytical concentration (Nowosielski and Fein, 1998):

$$P = \frac{[AH]_o}{[AH]_w} \qquad D = \frac{[AH]_o + [A^-]_o}{[AH]_w + [A^-]_w}$$

With [HA] and [A⁻], the concentrations of neutral and anionic species, the subscript o and w referring to the concentration in the octanol and aqueous phases, respectively.

In the case of non-ionisable compounds, only neutral species exist and thus P and D are identical. For ionisable compounds, D should be used instead of P in the pH range where ionic species exist.

Assuming that only the neutral species are present in the non-aqueous phase and activity corrections are neglected, D of acidic compounds can be calculated from the dissociation constant, pKa and P:

$$D = \frac{P}{1 + 10^{(pH - pKa)}} \quad (1)$$

However, in many systems, ionic species enter the non-aqueous phase and a more complex approach is required (Westall et al., 1985). For instance, measurement of Kow of 10 phenols and carboxylic acids at pH 12 indicates that both free ions and ion pairs were present in the octanol phase at significant concentrations (Jafvert et al., 1990). Introducing P_i , the octanol-water partition coefficient for ionic species:

$$P_i = \frac{[A^-]_o}{[A^-]_w} \quad D \text{ can be defined as: } D = P \cdot [AH] + P_i \cdot [A^-]$$

Since:

$$[HA] = \frac{1}{1 + 10^{(pH - pKa)}} \quad \wedge \quad [HA] + [A^-] = 1$$

$$\Rightarrow D = \frac{P}{1 + 10^{(pH - pKa)}} + P_i \cdot \left(1 - \frac{1}{1 + 10^{(pH - pKa)}}\right) \Leftrightarrow D = \frac{P + P_i \cdot 10^{(pH - pKa)}}{1 + 10^{(pH - pKa)}} \quad (2)$$

For acidic compounds, a sigmoidal decrease of Log D is obtained with pH (Figure 5-1). The curve closely resembles the speciation curves but is offset towards higher pH values. This behaviour has been observed experimentally for 23 ionisable pharmaceuticals (Log D measured at three pH values using a counter-current chromatography technique, Berthod, 1999), 2,4,6-trichlorophenol and

pentachlorophenol (Nowosielsky and Fein, 1998), and for PCP, DDA, DNOC and 2,4,5-T (Jafvert et al., 1990). Decreasing Kow value with increasing pH has also been recorded for dichlorprop (Riise and Salbu, 1992) and pentachlorophenol (Kaiser and Valdmanis, 1982).

The difference in lipophilicity between the neutral and ionic species varies with the compound and is difficult to predict. Although Nowosielski and Fein (1998) observed a similar difference between Log P and Log P_i for the two chlorophenols studied ($\Delta\text{Log Kow} = 2.9$), Riise and Salbu (1992) reported that $\Delta\text{Log Kow}$ was 2.2 for dichlorprop and the correlation between P_i and P for 10 phenols and carboxylic acids was poor in the study of Jafvert et al. (1990). This indicates that both Log P and Log P_i need to be determined for a given compound.

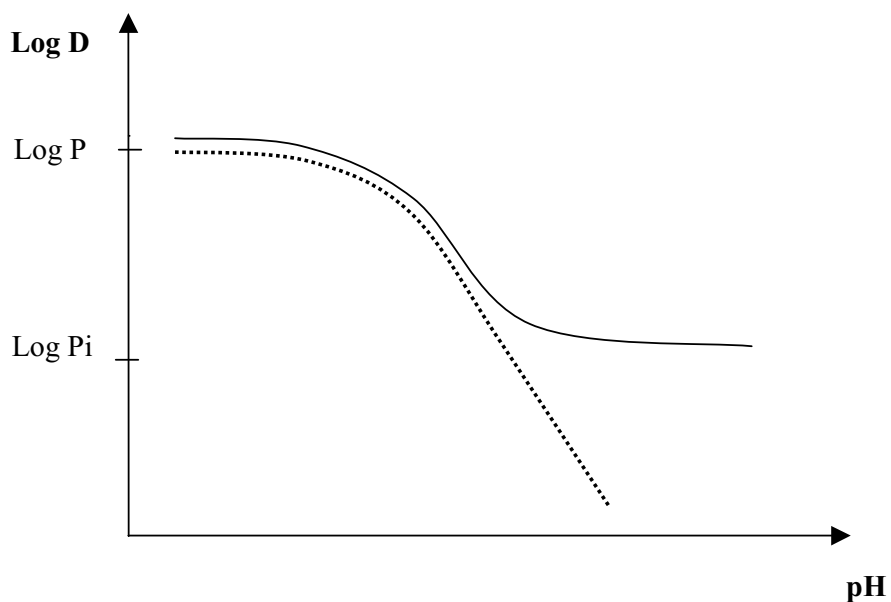
Two pH units below the pK_a of acidic compounds, Log D corresponds to Log P (Berthod, 1999). Log P_i is measured above a pH value that depends on the difference in lipophilicity of the neutral and ionic forms. Empirically, this pH is close to pK_a + Log (P/P_i) + 2. When P_i is very small and/or close to zero, the [Log(P/P_i) + 2] interval becomes large and Log D never reaches the Log P_i value. At pH values larger than pK_a, Log D seems to decrease linearly with pH according to: $\text{Log D} = \text{Log P} + \text{pK}_a - \text{pH}$ (Berthod, 1999).

For basic compounds, the change in lipophilicity with pH can be similarly studied and D calculated as:

$$D = \frac{P + P_i \cdot 10^{(\text{pK}_a - \text{pH})}}{1 + 10^{(\text{pK}_a - \text{pH})}}$$

D decreases with pH as the proportion of neutral species decreases. Similarly, if P_i is very small, D seems to decrease linearly with pH at pH values smaller than pKa according to: $\text{Log } D = \text{Log } P - \text{pKa} + \text{pH}$ (Berthod, 1999).

Figure 5-1. When the lipophilicity of the anionic form ($\text{Log } P_i$) is not taken into account, $\text{Log } D$ decreases indefinitely with increasing pH (dashed line, equation (1)). If the partitioning of the ionic form is considered, $\text{Log } D$ tends to $\text{Log } P_i$ when pH increases (solid line, equation (2)).



The determination of the partition coefficient of the neutral and ionic form requires a pH modification of the octanol-water system and this must be done very carefully. Nowosielski and Fein (1998) used the shaking flask method and noticed a significant difference between initial and equilibrium pH of the aqueous phase (up to 3 pH units), especially for pH values greater than the pKa. This pH shift could be explained by the deprotonation occurring when neutral species are transferred from or to the aqueous

phase. Since K_{ow} is a measure of the equilibrium concentration ratio, the authors advised that only the equilibrium pH should be associated with a measured K_{ow} .

One must also be careful when adjusting the pH to very high values. This requires a large concentration of base and might significantly increase the ionic strength. Charged species may complex with reagent ions and partition as ion-pairs. Ionic strength has thus an increasingly strong influence on K_{ow} as the concentration of the ionic species increases and this complicates the experimental determination. Nowosielsky and Fein (1998) observed a positive and linear relationship between the Log K_{ow} of pentachlorophenol and the Logarithm of the ionic strength of the aqueous solution. Increasing K_{ow} values with increasing ionic strength were also observed for PCP at pH > 10 (Lee et al., 1990; Westall et al., 1985), PCP, DDA and 2,4,5-T at pH 12 (Jafvert et al., 1990). Typically 0.1M of a background electrolyte is used during the measurement.

Both the ionic strength and the type of counter ion present in solution have a pronounced effect on the ion-pairing phenomenon. Log D values obtained for aqueous solutions containing $MgCl_2$ and $CaCl_2$ were greater than those containing NaCl and KCl at equal concentration (Jafvert et al., 1990) whereas the presence of Cd^{2+} reduced the K_{ow} for pentachlorophenol (Nowosielsky and Fein, 1998).

Table 5-1. Methods to determine the partition coefficient between octanol and water of the neutral form (P) and its variation with pH (D).

| Method (measurement) | Advantage | Drawback | Not applicable if | References |
|--|--|--|--|--|
| DIRECT | | | | |
| Shaking flask (P) | Most realistic method, reliable | Time, quantity of product used, formation of octanol emulsions in water | Log P > 6; the tested substance dissociates (Kow depends on concentration) | OECD, 1981 |
| Slow stirring method (P) | Avoid the formation of emulsions, reliable | Time, quantity of product used | The tested substance dissociates (Kow depends on concentration) | Brooke et al., 1986; de Bruijn et al., 1989 |
| CHROMATOGRAPHIC METHODS | | | | |
| Classical HPLC approach (P) | Rapid and cheap, does not require chemical quantification | Different retention mechanisms; poor reproducibility; pH range limited to 2-7.5 | Very low Kow values | Sicbaldi and Finizio, 1993; Finizio et al., 1997; OECD, 2004 |
| Micellar and microemulsion electrokinetic chromatography (P) | Rapid and cheap, | Requires the establishment of solvation parameter model | Ionic substance | Poole and Poole, 2003 |
| Methanol-water gradient and a short octadecyl-poly(vinyl alcohol) column (P) | Good agreement with shake-flask method | | Ionic substance | Donovan and Pescatore, 2002 |
| OTHERS | | | | |
| Filter probe method (P, D) | Rapid; well adapted to construct a Log D/pH profile | Expensive equipment required, slow to set up | Log P < 0.2; no isobestic point | Takacs-Novak, 1995; Leo, 2000 |
| pH metric method (or potentiometric method) (P, D) | Rapid | Expensive equipment required | Insoluble compound | OECD, 2000 |
| CALCULATION | | | | |
| Regressions with other properties (P, D) | Quick and cheap | Results depends on the dataset | | Xing and Glen, 2002 |
| Theoretical calculation (fragmental approach) (P, D) | Wide range of chemical; reliable for neutral compounds; only reliable method for Kow>5 | Not reliable for zwitterionic, tautomeric, charged compounds and strongly hydrogen bonding compounds | Fragment not available in the software database | Leo, 2000; Machatha and Yalkowski, 2005 |

METHODS TO MEASURE LOG D

Numerous methods are available to measure or estimate the partition coefficient of chemicals between octanol and water phases. All these methods have strengths and weaknesses and all can be unreliable for certain categories of compounds (Table 5-1).

Direct methods

Kow is traditionally measured with the shaking flask method (OECD n°107, 1981). An octanol/water mixture is spiked with the tested chemical and shaken until equilibrium is achieved. The organic and aqueous phases are then separated and the concentration of chemical in one or both phases is determined. This method presents some drawbacks concerning time, quantity of product used and lack of reliability for substances with high lipophilicity ($\text{Log Kow} > 6$) due to the formation of octanol emulsions in water (Finizio et al., 1997). Deviations also occur if the tested molecule dissociates as the partition coefficient then becomes dependent upon concentration. Thus, the method should only be applied to the non-ionised form of ionisable substances using an appropriate buffer (OECD, 1981).

The slow stirring method follows the same principle as the shaking flask method. The only difference concerns the slow stirring conditions in order to avoid the formation of emulsions (Brooke et al., 1986; de Bruijn et al., 1990). Although expensive and time consuming, both methods are relatively reliable to determine the lipophilicity of neutral compounds. They are however inappropriate for the determination of Kow of ionic species.

Estimation of Kow by indirect methods

The RP-HPLC approach (OECD n°117, 2004) is based on substance partition between a non-polar liquid organic phase and a polar aqueous phase in a column. This is the most rapid and cheap method because it does not require any chemical quantification (Finizio et al., 1997). However, as the retention mechanisms are different from those occurring in direct determination, multivariate techniques and molecular descriptors might need to be applied for chemicals differing from the reference substances (Sicbaldi and Finizio, 1993). This technique seems to be relatively ineffective for organochlorinated hydrocarbons and more generally for compounds with very low Kow values (Finizio et al., 1997). Moreover, the reproducibility is often poor and the operating pH range for silica based column material is limited (pH 2-7.5) (Poole and Poole, 2003). Micellar/microemulsion electrokinetic chromatography is an improvement of the chromatographic method that uses various surfactants above their critical micelle concentration. These systems seem suitable for the rapid determination of Log P for neutral compounds. However, the method is inaccurate for ionic compounds and requires the establishment of a solvation model. Donovan and Pescatore (2002) also described an alternative HPLC method using a methanol-water gradient and a short octadecyl-poly(vinyl alcohol) column. The results correlated well with those obtained with the traditional shake-flask method but the method is only suitable for the determination of Log P (neutral form).

Counter-current chromatography (CCC) is a liquid chromatography technique in which the stationary phase is also a liquid. Solute separation is based on partitioning between the two immiscible liquid phases (Berthod, 1999). The Log P values obtained with CCC for the neutral form of 17 beta-blockers differed significantly from

computed literature values and/or experimental values obtained via extrapolation (Carda-Broch and Berthod, 2003). In contrast, the Log P of 23 ionisable pharmaceuticals measured with CCC agreed with the literature values (Berthod, 1999).

The column generator technique consists in filling a column with glass beads covered with water-saturated octanol containing the chemical. Water is then pumped through the column and directly extracted with organic solvent or using a C18 column eluted with hexane or methanol (Woodburn et al., 1984).

The pH metric technique (OECD proposal for a new guideline n°122, 2000) consists of two linked titrations. Typically, a pre-acidified solution of a weak acid is titrated with standardised 0.5M KOH to some appropriately high pH. Octanol is then added (in relatively low and high amounts for lipophilic and hydrophilic molecules, respectively) and the dual-solvent mixture is titrated with standardised 0.5M HCl back to the starting pH (pH is measured after each addition). If the weak acid partitions in the octanol phase, the two assays show non-overlapping titration curves. The greatest divergence between the two curves occurs in the buffer region. Since the pKa is approximately equal to the pH at the mid-buffer inflection point, the two part assay yields two constants: pKa and p_oKa (the apparent constant derived from the octanol-containing segment of data). A large difference between pKa and p_oKa indicates a large value of Log P. The pH-metric procedure had been validated against the standard shake-flask method (Avdeef, 2001). It lacks the speed of HPLC methods but is well positioned to replace the shake-flask procedure as the primary validation method for ionisable molecules (the sample molecule must be ionisable and have a pKa in the measurable pH range, Avdeef, 2001).

The filter probe method is similar to the potentiometric method except that the determination is made by spectroscopy rather than by potentiometry. An aqueous solution of the sample under test is placed in a reaction vessel and circulated through a UV flow cell. The absorbance of the aqueous solution is measured before and after the addition of octanol. A solvent inlet filter prevents any octanol from passing through the detector. This method is well adapted to construct a Log D/pH profile (Leo, 2000). The method is reliable and rapid but does not apply to $\text{Log } P < 0.2$. The critical part is to determine the isobestic point of the compound in its UV spectrum (wavelength at which the absorption spectra of the two species cross each other).

Theoretical calculation

Several approaches exist for the theoretical calculation of K_{ow} . Many studies report regression equations between K_{ow} and water solubility (Finizio et al., 1997). However, the results rely on selection of the most appropriate equation and the quality of the solubility data. Shiu et al. (1990) reported solubility data ranging over one order of magnitude, especially for compounds with very low solubility values. Xing and Glen (2002) investigated a novel method to predict Log K_{ow} with an equation including three molecular properties (polarizability and partial atomic charges on nitrogen and oxygen). Calculated values were in good agreement with the training dataset comprising 592 Log P values ($r^2=0.89$).

Finally, several software packages such as ClogP (Bio-Byte, Claremont, USA.), ACD/LogD (Advanced Chemistry Development, Inc., Canada) and KowWin (component of the EPI SuiteTM package, U.S. Environmental Protection Agency, available at <http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm>) estimate the

lipophilicity of a chemical by theoretical calculation based on the additive-constitutive nature of K_{ow} . The molecular structure is divided into fragments (atoms or larger functional groups) and the values for each group are summed (sometimes with correction factors) to estimate $\text{Log } P$. This method is applicable to a wide range of chemicals (e.g. highly lipophilic classes of compounds) and can be greatly improved when experimental K_{ow} values of similar molecules are known. Although the results are in good agreement with direct measurement for neutral compounds, the method tends to be inaccurate for compounds having interacting functional groups or complex molecules with fragments that are not available in the software database (Finizio et al., 1997). The programs are designed to determine the partition coefficient of the non-ionised form of a compound. Predictions are not particularly good for $\text{Log } K_{ow}$ of zwitterionic, tautomeric and charged compounds as well as for strongly hydrogen-bonding compounds (Machatha and Yalkowski, 2005). Results may however be satisfactory for the more common acids and bases (Leo, 2000). ACD/LogP and ClogP propose program extensions to predict the $\text{Log } D$ profile for ionisable molecules. Sources of these programs can be found in van de Waterbeemd and Mannhold (1996).

Comparison of results obtained with various methods

Finizio et al. (1997) compared the K_{ow} values of 87 chemicals obtained from estimation methods (RP-HPLC, calculation and estimation from the water solubility) to experimental values (shaking flask and slow stirring methods). After a critical evaluation of all available data, the authors selected one value for each compound, preferring the method (when available) in the order: slow stirring, shaking flask, RP-HPLC or calculation. The RP-HPLC method gave good results for compounds with

Log P < 5 although it is likely to fail for compounds with very small Kow values. The Clog P method gave good results but seems only to be reliable for large Log P values (Log P > 5). The method of calculating from water solubility was generally the least precise estimation method and should be used only for preliminary screening purposes (Finizio et al., 1997). Similarly, Leo (2000) concludes that the traditional shaking-flask methods or the slow-stirring technique still provide the most reliable values. Benfenati et al. (2003) compared experimental (from four different sources) and calculated (HyperChem, KowWin, TOPKAT and Pallas) Log P values of 235 pesticides. They concluded that reliable Log P values for pesticides are still limited and experimental values show a certain degree of variability. All software programs gave both overestimates and underestimates of the experimental Log P and their performance seemed to depend on the chemical class. The authors advocated using values obtained by a single procedure to obtain consistent results.

The reliable determination of Kow is still a problem, especially for ionisable compounds. Phenomena such as ion pairing or ionic strength effects can operate and very different values are often measured by direct methods. A significant uncertainty is often associated with the values generated by software packages using additive-constitutive approaches as well. Amongst the numerous methods available, the pH metric and filter probe methods seem to be the most appropriate at present for ionisable pesticides.

Comparison of Log P values for acidic herbicides

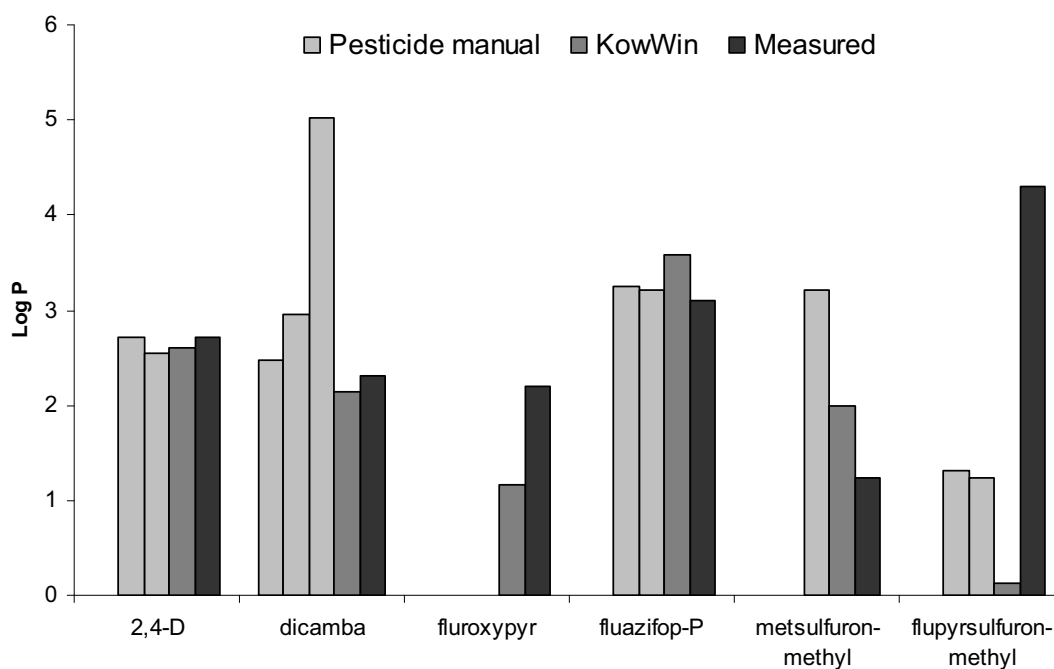
Three methods for obtaining Log P were compared for six acidic compounds. Log P were (1) calculated using values reported in the Pesticide Manual (Tomlin, 2005) with the equation: $\text{Log P} = \text{Log D} + \text{Log}(1+10^{(\text{pH}-\text{pKa})})$, (2) estimated by the software KowWin v.1.67 (2000) and (3) measured (as part of a lipophilicity profile in the pH range 2-11) using the pH metric method (OECD, 2000; GLpKa from Sirius Analytical Instrument Ltd).

Although the three methods gave relatively similar results for 2,4-D and fluazifop-P, significant differences were observed for the other compounds (Table 5-2 and Figure 5-2).

Table 5-2. Log P values obtained with three different methods for six acidic pesticides.

| | pKa | Pesticide Manual | | | KowWin | pH metric method | |
|------------------------|------|-------------------------|-------------------|----------------------|-----------------|------------------|--------------------|
| | | Log D reported | pH | Log P calculated | Log P estimated | Log P measured | Log P _i |
| 2,4-D | 2.64 | 2.71 0.19 | 1.0 5.0 | 2.71 2.55 | 2.61 | 2.72 | |
| dicamba | 1.97 | -0.55 -1.88 -1.90 | 5.0 6.8 8.9 | 2.48 2.95 5.03 | 2.14 | 2.30 | |
| fluroxypyr | 2.94 | -1.24 | unstated | ? | 1.17 | 2.20 | |
| fluazifop-P | 2.98 | 3.10 -0.80 | 2.6 7.0 | 3.25 3.22 | 3.58 | 3.10 | -0.21 |
| metsulfuron-methyl | 3.80 | 0.02 | 7.0 | 3.22 | 2.00 | 1.23 | |
| flupyr-sulfuron-methyl | 4.90 | 0.96 0.10 | 5.0 6.0 | 1.31 1.23 | 0.13 | 4.31 | -0.57 |

Figure 5-2. Differences in Log P values obtained with three different methods for six acidic pesticides.



Log P for fluroxypyr could not be calculated because no pH value was associated with the Log D value reported in the Pesticide Manual (Tomlin, 2005). On the other hand, three different Log P values could be calculated for dicamba. The Pesticide Manual and most databases do not report the method and/or the pH associated with octanol-water partition coefficients. When dealing with ionisable pesticides, these two pieces of information are essential to calculate Log P values and to allow discrimination when several values are available.

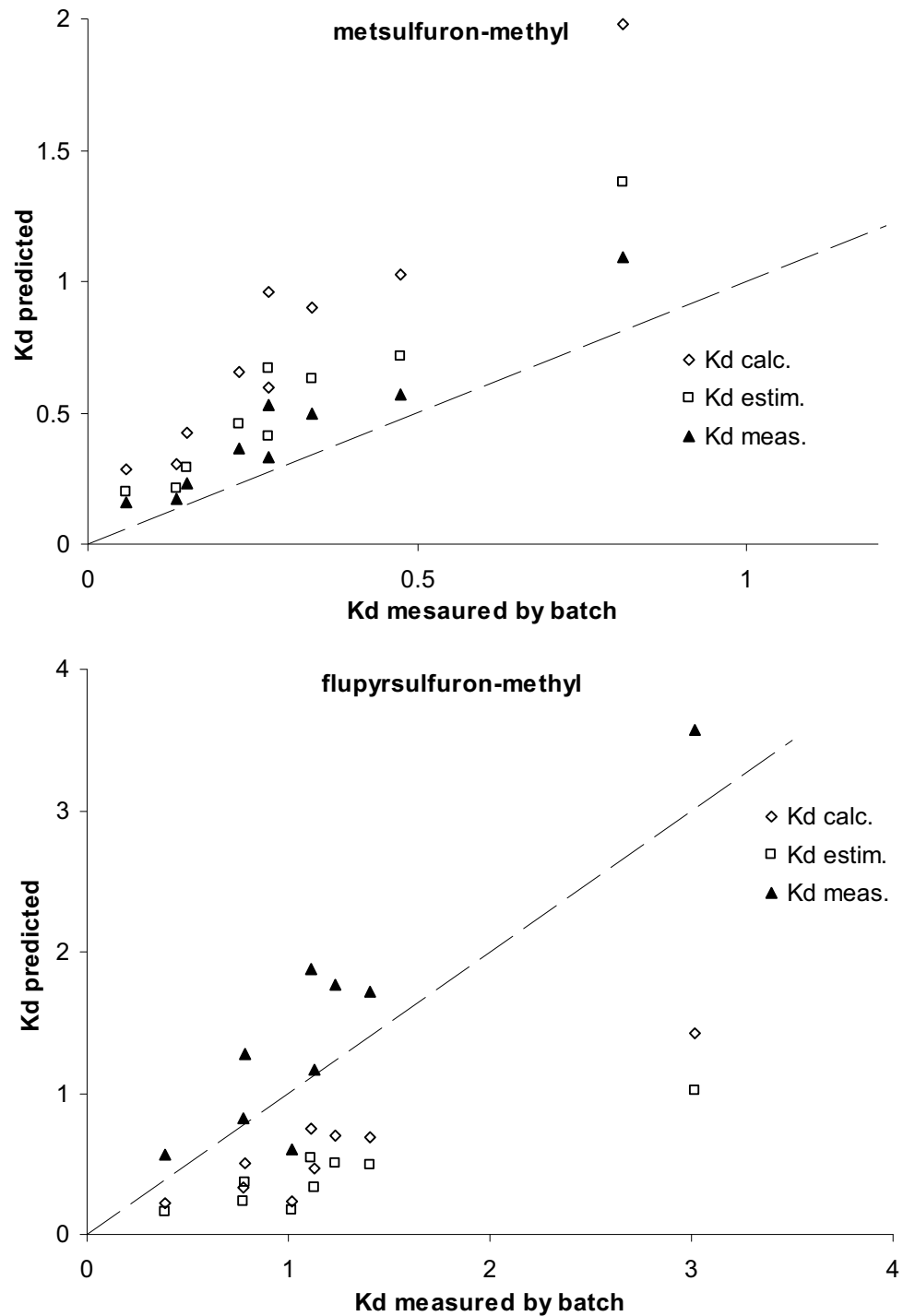
Depending on the compound, the software KowWin under or overestimated measured Log P. The software could not predict Log P for flupyrulfuron-methyl but estimations were generally quite close to the measured values for the other compounds. Another advantage of this method is that a unique value is generated.

Log P_i (K_{ow} of the anion) was only measured for fluazifop-P and flupyr-sulfuron-methyl, the two most hydrophobic compounds. The ionic form can only partition in octanol if a counter-ion is available in the solution. In the pH metric method, the counter ion could come from either the background electrolyte (water, 0.15M KCl) or the acid titrant (0.5M HCl) used in the titration. The measurement range of this assay was -1 to +5 and the lowest Log P_i value that could be successfully measured was thus -1. When no Log P_i was reported, it did not mean that the compound would not show ion-pair partitioning under any circumstances. It only means that the value for the ion-pair partitioning is outside the measurement range of the assay. This is to be expected for compounds having small neutral Log P values (< 3).

The ion-pairing process is highly dependent on the ionic strength and the type of cation present in solution. Composition of soil solution is very variable and difficult to assess. It seems thus difficult to predict the consequences of ion pairing even though it is known to occur.

A regression equation to predict the adsorption of acidic compounds in soils (K_d) was proposed in Chapter 3. The equation considers the soil organic carbon content and the lipophilicity of each compound in each soil. The selection of an appropriate Log P value to derive Log D is essential since it might lead to large differences in the prediction of adsorption as shown in Figure 5-2.

Figure 5-3. Adsorption coefficients (K_d) for two pesticides in nine soils predicted with the Log P reported in the literature ($K_{d_{calc.}}$; Tomlin, 2005), estimated by KowWin ($K_{d_{estim.}}$) and measured by the pH metric method ($K_{d_{meas.}}$) plotted against K_d measured by batch method.



CONCLUSION

As a consequence of dissociation, the lipophilicity of ionisable compounds is pH dependent. The difference in lipophilicity between the neutral and ionic species varies with the compound and the determination of both values is recommended. When the lipophilicity of each species is known, theoretical equations can be used to calculate the change in lipophilicity with pH.

Although numerous methods are available to measure the partition coefficient of chemicals between octanol and water phases, only a few are appropriate for ionisable pesticides. When working with ionisable compounds, pH must be carefully controlled and has to reach levels at which only one species exists ($pK_a \pm 2$). Both the ionic strength and the type of counter ion present in solution have a pronounced effect on the ion-pairing phenomenon. These two factors must thus be controlled carefully. Variation in these parameters probably explains why literature often yields very different lipophilicity values for ionisable compounds. At present, the pH metric and filter probe methods seem to be the most appropriate experimental settings to construct a Log D/pH profile. Their drawback is that they require expensive equipment and trained personnel.

When comparing the lipophilicity of several compounds, the use of Log P (or Log D) values obtained with a single method should be preferred. If data are gathered from the literature, they should always be associated with a measurement method and a specified pH. If unavailable, software such as KowWin can provide a good estimation of Log P in most cases. A new version of this software (vsKowWin) is available and

can improve estimation when melting point and experimental Kow values are also provided.

Chapter 6

INFLUENCE OF IONIC STRENGTH ON ADSORPTION: DIFFERENCES BETWEEN 2,4-D AND FLUPYRSULFURON-METHYL

INTRODUCTION

In Chapter 3, adsorption of six acids was measured in nine different soils. The results showed that the major part of variability in adsorption could be explained by variations in the soil organic carbon (OC) content and the hydrophobicity of each pesticide corrected for pH (Log D). These results confirm that adsorption of acidic compounds is mainly due to hydrophobic partitioning of the neutral form onto soil organic matter. In contrast to the other acids studied, fluroxypyr and 2,4-D adsorbed more than would be predicted based on soil OC content and Log D. Significant adsorption occurred in some soils having a pH > 7, where more than 99.99% of the pesticides molecules are in the anionic form. This suggests that the anionic forms of these two pesticides have the ability to adsorb through mechanisms not occurring with other acids.

Several articles reported that some acidic pesticides are likely to adsorb by cation bridging in temperate soils. Cation bridging arises from the formation of an inner-sphere complex between an exchangeable cation (at a clay or organic matter

surface) and an anionic or polar functional group on a pesticide (Chapter 2). As cations are normally surrounded by hydrating water molecules, the organic functional group must be able to displace the water to form an inner-sphere complex (Koskinen and Harper, 1990). Fluazifop, fluazifop-butyl (Fusi et al., 1988), mecoprop and 2,4-D (Clausen et al., 2001) have been shown to form direct coordination with a cation at the surface of clays (smectite, kaolinite respectively), whereas cation bridging does not seem to occur for pesticides such as bentazone (Clausen et al., 2001) and primisulfuron (Ukrainczyk et al., 1996). The latter authors concluded that the negative charge on the sulfonylurea bridge is too sterically hindered to allow inner-sphere complex formation between the surface metal and primisulfuron.

Flupyrifluron-methyl has a greater pKa and hydrophobicity than 2,4-D (Table 3-2) and this would suggest a stronger adsorption than 2,4-D in soils. However, similar adsorption coefficients were measured for these two pesticides in eight out of nine arable soils ((Figure 3-1c). In one soil only (soil 3, pH=7.41 in 1M KCl), adsorption of 2,4-D was much weaker than that of flupyrifluron-methyl. It is thus hypothesised that a specific sorption mechanism was operating for 2,4-D but not for flupyrifluron-methyl, that this mechanism was cation bridging and that cation bridging was either not operating or was much reduced in soil 3.

The aim of this experiment was to characterise the sorption mechanism operating for 2,4-D and not for flupyrifluron-methyl and to understand how it is influenced by soil properties. Three soils with similar pH were selected from the previous study. In soils 2 and 4, adsorption of 2,4-D and flupyrifluron-methyl was similar when measured in 0.01M CaCl₂ whereas adsorption of 2,4-D was much weaker than that of flupyrifluron-methyl in soil 3. Adsorption isotherms for the two acids were determined at four concentrations of CaCl₂. The objectives were (i) to investigate any

influence on adsorption mechanisms from adding CaCl_2 as an electrolyte, and (ii) to identify the soil and/or pesticide characteristics that could explain differences in behaviour.

MATERIAL AND METHODS

Soils

Properties of soils 2, 3 and 4 are presented in Table 3-1. Additionally, the clay fraction of each soil was extracted using the sedimentation method (Pansu and Gautheyrou, 2006). Clays were subsequently freeze-dried and saturated with Mg^{2+} . The oriented clay aggregates were then characterised by X-ray diffraction (Siemens Kristalloflex D-5000 diffractometer, with Ni-filtered $\text{Cu K}\alpha$ radiation; scanning speed: 1° min^{-1} ; chart speed: 1 cm min^{-1}). Diffraction patterns were produced before and after treatment with ethylene glycol at 550°C . A semi-quantitative estimate of non-iron minerals was made using the reflection powers given by Stokke and Carson (1973) (Table 6-1).

Table 6-1. Main properties and clay mineralogy of soils 2, 3 and 4.

| | pH | OC | Clay | Kaolinite | Smectite | Vermiculite | Illite | Chlorite | Quartz | Goethite |
|---|-----------|--------------------|------|------------------------------|----------|-------------|--------|----------|--------|----------|
| | 1M KCl | g kg^{-1} | % | $\text{g } 100\text{g}^{-1}$ | | | | | | |
| 2 | 7.54 | 32.4 | 25.7 | 12.9 | - | 2.6 | 7.7 | 2.6 | traces | traces |
| 3 | 7.41 | 10.8 | 27.5 | 6.9 | <1.4 | - | 16.5 | 2.8 | traces | |
| 4 | 7.29 | 20.0 | 34.5 | 24.2 | - | <1.7 | 8.6 | <1.7 | traces | traces |

Pesticides

The main properties of unlabelled and radiolabelled 2,4-D and flupyrsulfuron-methyl can be found in Chapter 3 (Table 3-2 and Table 3-3).

Measurement of adsorption

Sorption was measured for four pesticide concentrations (0.1, 0.4, 1 and 4 mg kg⁻¹) and with four background electrolytes (milliQ water, 0.01, 0.1 or 1M CaCl₂) using the batch equilibrium method described in Chapter 3 (three replicates). The Freundlich equation was fitted to the data: $C_s = K_f.C_e^{1/n}$, with C_s , the concentration adsorbed on the solid phase (mg g⁻¹) and C_e , the concentration in solution at equilibrium (mg mL⁻¹). The parameters K_f (Freundlich constant, mg mL^{-1/n}) and $1/n$ (measure of isotherm linearity, dimensionless) were optimised using the least squares method with Microsoft Excel Solver.

RESULTS

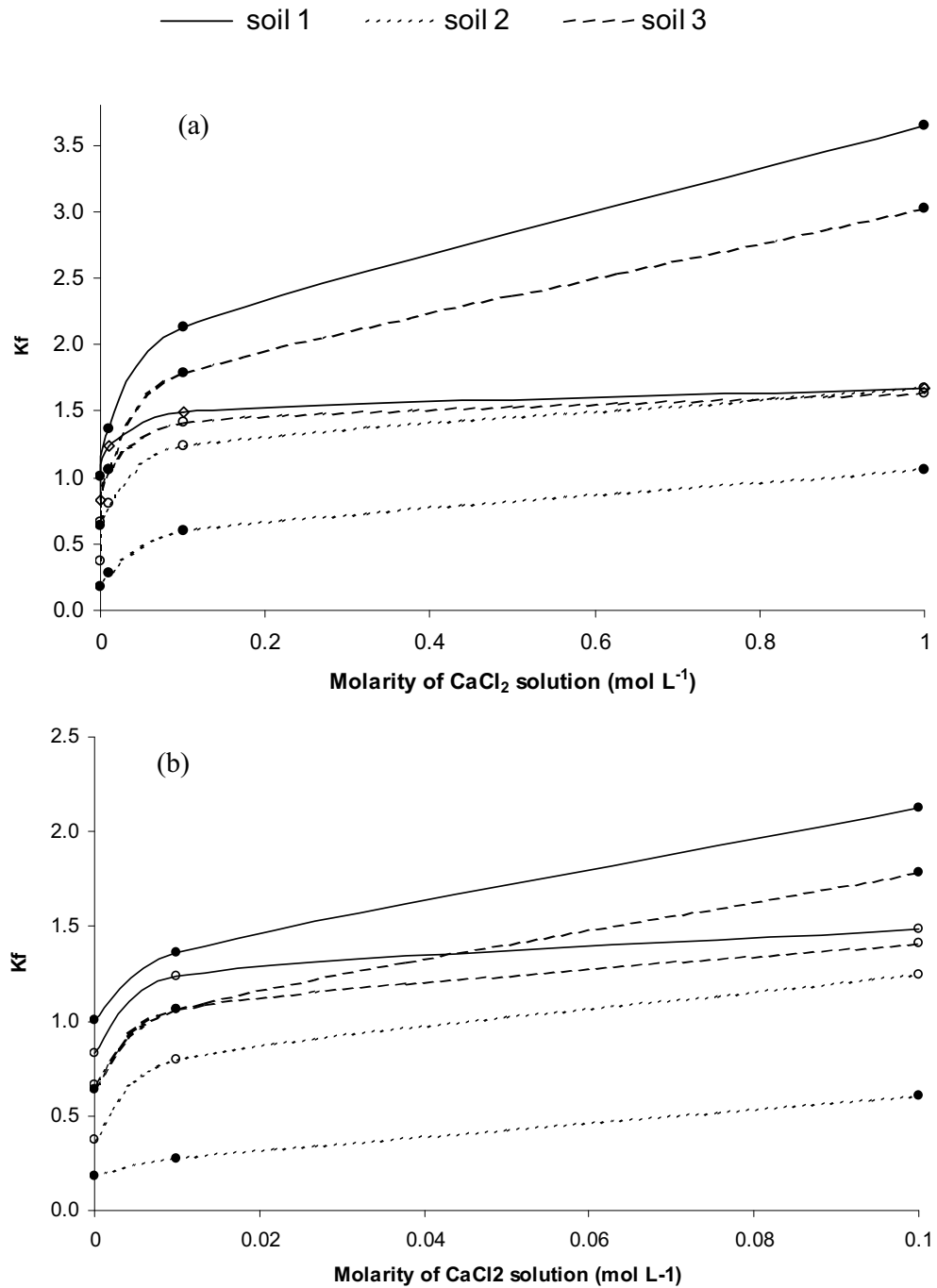
The Freundlich equation fitted the data very well ($r^2 > 0.99$). The curvature of the isotherms ($1/n$) ranged from 0.81 to 1.10 (Table 6-2) and indicated that adsorption generally decreased as concentration increased. The curvature was not consistently related to the soil type or CaCl₂ concentrations. On the other hand, a significantly greater curvature (smaller $1/n$) was observed for 2,4-D and this could indicate that more specific adsorption mechanisms are operative (Weber et al., 1993). Strength of adsorption for both pesticides generally followed the order soil 2 < soil 4 < soil 3 and this can be partly explained by differences in the soil organic matter content.

Table 6-2. Freundlich adsorption parameters (K_f and $1/n$) for 2,4-D and flupyrsulfuron-methyl in three soils ($r^2 > 0.99$) and four CaCl_2 concentrations. The value between parentheses is the standard deviation for three replicates.

| soil | suspension pH | CaCl_2 | 2,4-D | | flupyrsulfuron-methyl | |
|------|---------------|-----------------|-------------|-------------|-----------------------|-------------|
| | | | K_f | $1/n$ | K_f | $1/n$ |
| 2 | 7.67 | 0 | 1.00 (0.02) | 0.87 (0.03) | 0.83 (0.02) | 0.90 (0.02) |
| | 7.40 | 0.01M | 1.36 (0.04) | 0.89 (0.05) | 1.24 (0.03) | 0.91 (0.02) |
| | 7.03 | 0.1M | 2.13 (0.02) | 0.88 (0.03) | 1.49 (0.03) | 0.99 (0.03) |
| | 6.76 | 1M | 3.65 (0.03) | 0.85 (0.01) | 1.67 (0.05) | 0.94 (0.03) |
| 3 | 8.07 | 0 | 0.18 (0.02) | 1.10 (0.23) | 0.38 (0.03) | 0.92 (0.05) |
| | 7.59 | 0.01M | 0.28 (0.02) | 0.88 (0.11) | 0.80 (0.01) | 0.99 (0.04) |
| | 7.19 | 0.1M | 0.60 (0.00) | 0.85 (0.04) | 1.24 (0.02) | 0.96 (0.04) |
| | 7.01 | 1M | 1.06 (0.18) | 0.85 (0.02) | 1.67 (0.01) | 0.94 (0.02) |
| 4 | 7.78 | 0 | 0.64 (0.02) | 0.82 (0.13) | 0.67 (0.03) | 0.93 (0.03) |
| | 7.28 | 0.01M | 1.06 (0.01) | 0.81 (0.01) | 1.06 (0.05) | 0.91 (0.02) |
| | 6.86 | 0.1M | 1.79 (0.03) | 0.82 (0.03) | 1.41 (0.06) | 0.93 (0.02) |
| | 6.59 | 1M | 3.02 (0.03) | 0.81 (0.01) | 1.63 (0.06) | 0.92 (0.01) |

Adsorption (K_f values) increased significantly with CaCl_2 concentration for both pesticides in all soils particularly up to 0.1M CaCl_2 (Table 6-2 and Figure 6-1). A positive influence of ionic strength on the adsorption of acidic pesticides has often been observed previously (Chapter 2). It is known to result in part from a decrease in pH, caused by a replacement of protons from the soil surface as ionic strength increases (De Jonge and De Jonge, 1999, Regitano et al., 1997). The pH of the soil suspensions decreased by approximately one pH unit between soil suspensions in water and 1M CaCl_2 (Table 6-2). Decreasing pH shifts acidic compounds toward neutral forms that are more strongly adsorbed than the anionic forms and results therefore in an increase in adsorption.

Figure 6-1. Freundlich adsorption coefficients (mg mL^{-1}) for 2,4-D (\bullet) and flupyr-sulfuron-methyl (\circ) in three soils as a function of CaCl_2 concentration. Lower figure shows detail from the figure above.



Measured adsorption coefficients (K_f) were compared to coefficients predicted using the equation proposed in Chapter 3. The regression equation takes into account the shift in hydrophobicity of acidic compounds as a function of pH (Log D) and the OC content of the soil. The comparison between the observed and predicted values permits therefore to distinguish the part of variation attributable to factors other than the shift in pH (Figure 6-2).

The increase in adsorption observed for 2,4-D was much greater than what would be predicted based on the shift in pH (Figure 6-2, 6-3) and this supports the occurrence of adsorption mechanisms directly dependent on Ca^{2+} concentration. Complexation of the pesticide molecules with surface-exchanged multivalent cations (cation bridging) has probably contributed to stronger adsorption at higher ionic strengths, as proposed for glyphosate (De Jonge and De Jonge, 1999) and for mecoprop and 2,4-D on kaolinite (Clausen et al., 2001). Adsorption of flupyr-sulfuron-methyl was much less affected by the addition of CaCl_2 than 2,4-D (Figure 6-3). The formation of Ca-pesticide complexes depends on the type of anion involved in the formation (Clausen et al., 2001). The negative charge on the sulfonylurea bridge of flupyr-sulfuron-methyl might be too sterically hindered to allow inner-sphere complex formation, as suggested by Ukrainczyk et al. (1996) for primisulfuron.

Figure 6-2. Comparison of adsorption coefficients measured at different CaCl₂ concentrations (Kf linear) with Kd predicted using the equation proposed in Chapter 3, that takes into account the decrease in pH with increasing ionic strength: $\text{Log } K_d = 0.13 \text{ Log } D + 1.02 \text{ Log } OC - 1.51$

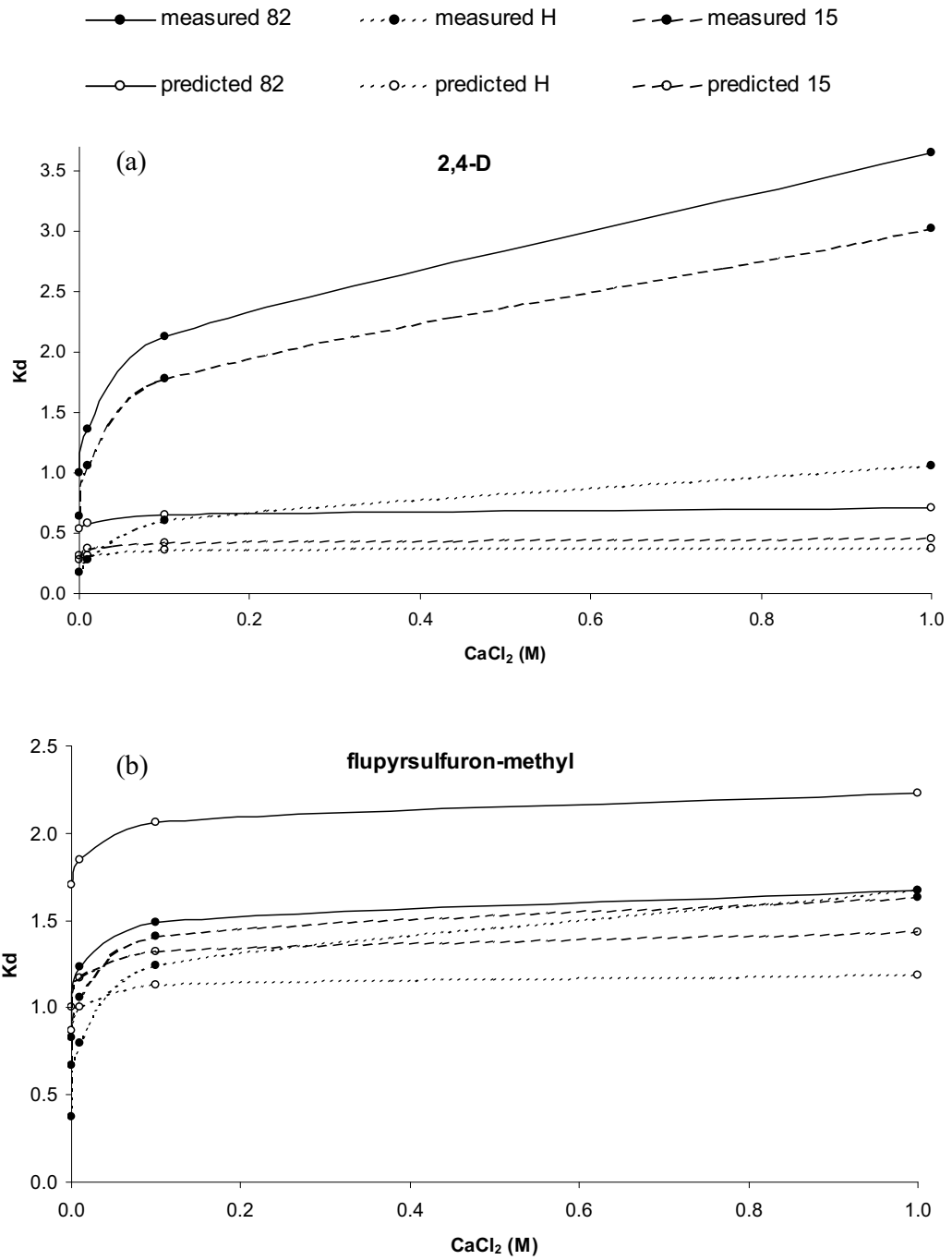
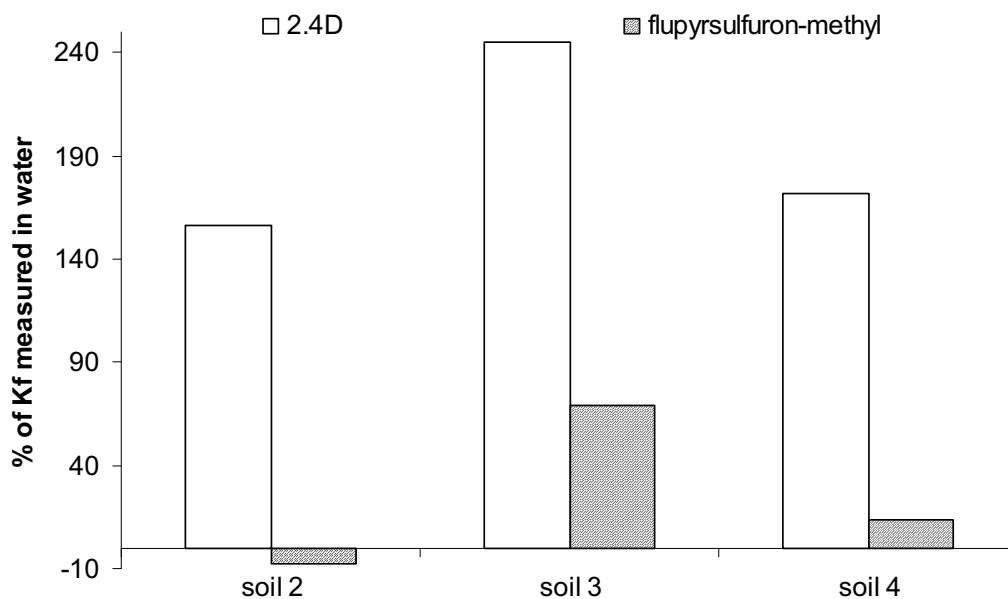


Figure 6-3. Part of the increase in adsorption, observed between 0.01M and 1M CaCl₂, attributable to other factors than the shift in pH and calculated as:

$(K_f \text{ measured} - K_d \text{ predicted})_{1M} - (K_f \text{ measured} - K_d \text{ predicted})_{0.01M}$, and expressed as a percentage of K_f measured in 0.01M CaCl₂.



Adsorption of flupyr sulfuron-methyl became similar in the three soils at the highest CaCl₂ concentration (1M, Figure 6-1). A salting-out effect could explain this behaviour. Watson (1973) and Lee et al. (1990) reported that an increase in ionic strength often provokes a drop in the solubility of pesticides. Considering the poor solubility of flupyr sulfuron-methyl (Table 3-2), precipitation might have occurred in 1M CaCl₂ solution. Calculation of adsorption coefficients was based on the concentration of pesticide remaining in solution and thus does not permit any distinction between precipitation and adsorption phenomena.

When measured in 0.01M CaCl₂, adsorption of flupyr sulfuron-methyl was much stronger than that of 2,4-D in soil 3, whereas the two pesticides have similar adsorption levels in the other soils (Table 6-2 and Figure 3-1a). Since soils 2, 3 and 4

contain relatively similar amounts of strongly charged clays (smectite, vermiculite and illite, Table 6-1), a specific interaction between flupyr-sulfuron-methyl and clays of soil 3 is rather unlikely. Reasons for a particularly strong adsorption of flupyr-sulfuron-methyl in soil 3 remain therefore unclear.

CONCLUSION

These results give evidence for differences in the mechanisms of adsorption between two acidic pesticides. The application of more advanced techniques such as nuclear magnetic resonance, electron spin resonance, or fluorescence spectroscopies would help in characterising the type of bonds formed and explain differences observed for different soil-pesticide combinations. A better characterisation of soil constituent chemistry - particularly that of humic substances- also deserves further research and would help in characterizing the adsorption potential of soils for a particular compound. On the other hand, the characteristics of OM and clays fractions are very variable between soils and generalisation will always be difficult.

This experiment confirms that ionic composition of the soil solution (or background electrolyte used in batch experiments) can have a significant impact on the adsorption of acidic pesticides. The effect depends on the ionic strength, nature of ions and on the pesticide-soil combination. The ionic strength of natural soil solution does not normally exceed 10^{-3} M, so that effects of ionic strength on adsorption can usually be neglected (Lee et al., 1990). Nevertheless, the choice to use 0.01M CaCl_2 in standardized batch experiments (OECD, 1997) will affect the adsorption coefficients of ionisable pesticides. This places a constraint on the use of results from these standardized tests to predict adsorption behaviour of ionisable compounds in the field.

Chapter 7

CHANGES IN PESTICIDE ADSORPTION WITH TIME AT HIGH SOIL TO SOLUTION RATIOS

INTRODUCTION

The batch slurry method is generally used for direct measurement of the adsorption coefficient of an organic molecule in soil (K_d). The advantages of this method are that the soil and solution can be separated effectively, a large volume of solution is obtained for analysis and the method can be easily used for routine laboratory work following OECD guideline 106 (OECD, 1997). However, some important experimental features (e.g. temperature, type of vessel, type of shaking, centrifugation speed and soil to solution ratios) have not been completely standardised. This makes the results from different studies difficult to compare.

The ratio of soil to solution has been shown to influence the final adsorption coefficient obtained, although different studies have given contrasting results. The OECD guideline (OECD, 1997) advises to conduct a screening test for choosing the best ratio to achieve between 30 and 50% adsorption. After a theoretical analysis of systematic and random errors, Boesten (1990) concluded that it is desirable to obtain more than 20% adsorption because of the analytical method and preferably >50% adsorption. Based on the analytical precision of the experimental variables, McDonald

and Evangelou (1997) demonstrated that the optimal adsorption is 55% and the optimal solid to solution ratio occurs at $1.2/K_d$ or $1.2/K_f$ for linear and Freundlich type partitioning ($0.8 < 1/n < 1$), respectively. In practice, soil:solution ratios required to reach equilibrium in batch adsorption experiment range from 1:2 to 1:100. Such ratios are atypical of field soil moisture conditions and the results may not adequately reflect adsorption processes in field-moist or unsaturated soil.

Experiments using soil columns are more analogous to field conditions, but they take a long time to perform and have other disadvantages that include non-uniform flow within the column and difficulty in distinguishing between processes (e.g. adsorption, degradation) (Celorie et al., 1989). The centrifugation method has been proposed as an alternative to determine adsorption coefficients of organic contaminants in soils (Walker and Jurado-Exposito, 1998; Walker, 2000). Adsorption can be measured at a realistic soil:solution ratio whilst avoiding the disadvantages of column experiments.

Lower adsorption coefficients determined with the centrifugation technique compared to a batch method have been reported for isoproturon, diuron and metsulfuron-methyl (Walker and Jurado-Exposito, 1998), an anthranilate (Kennedy et al., 2002) and imidacloprid and carbofuran (Yazgan et al., 2005). Shaking may be the main reason for greater adsorption observed with the batch method as soil aggregates are broken down, thus significantly increasing the surface area available to interact with pesticides molecules. However, results are not fully consistent (Walker and Jurado-Exposito, 1998) and the discrepancy between the two methods appears to depend on the soil type (Kennedy et al., 2002).

The objectives of this study were to (i) measure adsorption of six acidic pesticides in nine soils using a centrifugation technique after one and seven days contact time, (ii)

compare the results to adsorption coefficients obtained with a classical batch technique, and (iii) identify any trends in behaviour in relation to properties of pesticides and/or soils.

MATERIAL AND METHODS

Soils

The nine arable soils used in the previous chapters were also used in this study. They are described in details in Chapter 3 (see Table 3-1). Although not necessary for the centrifugation technique, we used air-dried soils sieved to 3 mm in both methods for consistency. Subsamples (triplicates of roughly 30 g) were dried overnight at 110 °C to determine the moisture content of air-dried soils. The water content for the centrifugation technique was set to -33 kPa (roughly equivalent to 40% of the maximum water holding capacity, depending on the soil type). This water content was determined by weight after triplicate, repacked samples of each soil had been left on a pressure membrane system for at least one week (as described in Chapter 4).

Pesticides and other chemicals

Six acidic pesticides comprising four carboxylic acids and two sulfonylureas were considered in this chapter. They were described in details in Chapter 3 (Table 3-2).

Measurement of adsorption using the batch equilibrium method

Adsorption coefficients were determined at one concentration and with four replicates using a standard batch equilibrium method (OECD, 1997), as described in Chapter 3. For the least strongly adsorbed molecules, a ratio >1 is advised in the guideline (OECD, 1997), but is not technically achievable within the batch method. Moreover, adapting the ratio to each pesticide-soil combination makes the comparison of results less robust. A soil to solution ratio of 1:2 (w:w) was thus applied for all pesticides.

Measurement of adsorption using centrifugation

A 130 g sample of each soil was brought to a moisture content close to -33 kPa and pre-incubated for 24 h in a 500-mL glass flask at 4°C in the dark. Pesticide in 0.01M CaCl_2 was then applied drop wise and the moisture content adjusted by weighing to exactly that at -33 kPa. Volumes of pesticide solution added ranged from 5 to 6 mL ($20\text{-}50\text{ mg L}^{-1}$) for unlabelled compounds and from 0.3 to 0.5 mL for labelled compounds ($32\text{-}91.5\text{ kBq mL}^{-1}$). After mixing with a spoon for a couple of minutes to ensure a homogeneous application, the soils were incubated at 4°C and in the dark. After 1 and 7 days incubation, the moisture content was readjusted by weighing. Soils were carefully mixed and samples were taken to calculate the adsorption coefficient. For each soil, 10 g of incubated soil (4 replicates) was weighed into the insert of a 50-mL centrifuge tube (VectaSpin 20, PVDF, Whatman International Ltd., Maidstone, UK). The original filter was removed and replaced by a glass microfibre filter (MF 300, 25 mm diameter, 75 g m^{-2} , $0.45\text{ }\mu\text{m}$ thickness, Fisher Scientific, UK) pre-wetted with $100\text{ }\mu\text{L}$ of deionised water. The tubes and contents were then centrifuged at 1500 g for 30 min to collect an aliquot of soil solution (between 0.1 and

0.5 mL depending on the soil type) that was directly analysed for pesticide concentration by HPLC or LSC. The centrifugation force applied was such that the soil was subjected to a pressure of 200 kPa:

$$w = \sqrt{\frac{2.P}{\rho(2.a.L + L^2)}}$$

where w is the rotation speed (rad s^{-1}), P is the pressure to apply (Pa), ρ the volumetric mass of the sample (kg m^{-3}), a is the distance from the rotor to the sample (m) and L is the depth of the soil sample (m). We then calculate the centrifugation force in rpm (rotation min^{-1}) as:

$$rpm = \sqrt{\frac{w}{2.\pi.60}}$$

The pressure of 200 kPa was chosen following the protocol proposed by Walker and Jurado-Exposito (1998) to extract soil solution. It corresponds to the boundary between “mobile” and “immobile” water proposed by Addiscott (1977). To determine the total concentration of pesticides present in the soil (used as C_i for the calculation of K_d), soil samples (10 g, 2 replicates per soil) were weighed into PTFE tubes after 1 and 7 d and extracted by adding an appropriate organic solvent (soil to solution ratio 1:2, Table 4-1). After shaking for one hour on an end-over-end shaker (22 rev min^{-1}), the samples were allowed to stand until the soil had settled (one hour). Pesticide concentrations in the clear supernatant were quantified directly by HPLC or LSC (Table 3-3).

Variance and correlation analyses were performed using Genstat for Windows (7th edition, Rothamsted Research).

RESULTS

Table 7-1 gives the adsorption coefficients obtained by batch (Kdb) and by centrifugation methods after one and seven days (Kdc1 and Kdc7, respectively) for each combination of soil and pesticide.

In general, pesticide adsorption was weak and increased in the same order for both techniques: dicamba < metsulfuron-methyl < fluazifop-P < 2,4-D < flupyr-sulfuron-methyl < fluroxypyr. The extent of adsorption measured using the batch technique varied greatly between pesticides and soils and ranged from 3-4% for dicamba to 29-68% for fluroxypyr. The moisture content at -33 kPa is equivalent to soil to solution ratios ranging from 3 to 10 depending on the soil type. These higher ratios yielded a satisfactory level of adsorption (from 12-32% for dicamba to 82-90% for fluroxypyr) and reduced the variability in the measurement for the less sorbed pesticides (Table 7-1).

Comparison of batch and centrifugation results

For each pesticide, the adsorption coefficients obtained after one and seven days by centrifugation were plotted against the values obtained using the batch method. The coefficients of the linear trend line fitting these plots are reported in Figure 7-1. In accordance with previous studies, adsorption coefficients obtained by centrifugation were generally smaller than those from batch experiments. Adsorption coefficients measured by centrifugation after seven days approached the values obtained in the batch studies. In the case of metsulfuron-methyl adsorption coefficients were generally larger from the centrifugation technique.

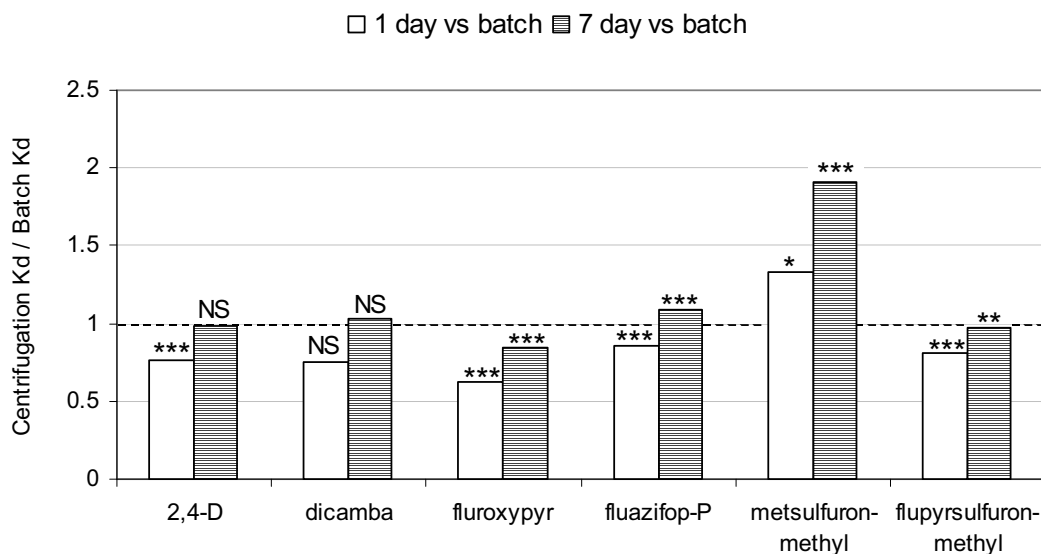
Table 7-1. Sorption coefficients (mL g^{-1}) obtained with a batch (Kdb) and centrifugation technique after one and seven days equilibrium (Kdc1 and Kdc7, respectively). Values between parentheses are the standard deviations for four replicates

| Soil | 2,4-D | | | dicamba | | | fluroxypyr | | |
|------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| | Kdb | Kdc1 | Kdc7 | Kdb | Kdc1 | Kdc7 | Kdb | Kdc1 | Kdc7 |
| 1 | 0.77 (0.03) | 0.61 (0.03) | 0.69 (0.06) | 0.09 (0.02) | 0.10 (0.03) | 0.11 (0.01) | 0.89 (0.04) | 0.58 (0.07) | 0.74 (0.04) |
| 2 | 1.57 (0.14) | 1.25 (0.05) | 1.51 (0.04) | 0.14 (0.02) | 0.04 (0.01) | 0.05 (0.01) | 1.89 (0.07) | 1.24 (0.06) | 1.52 (0.01) |
| 3 | 0.38 (0.04) | 0.59 (0.09) | 0.60 (0.06) | 0.08 (0.06) | 0.10 (0.01) | 0.14 (0.02) | 0.59 (0.02) | 0.63 (0.04) | 0.77 (0.02) |
| 4 | 1.19 (0.09) | 0.99 (0.03) | 1.25 (0.04) | 0.09 (0.04) | 0.06 (0.02) | 0.11 (0.02) | 1.66 (0.04) | 1.04 (0.05) | 1.44 (0.11) |
| 5 | 1.04 (0.09) | 0.86 (0.02) | 1.05 (0.01) | 0.09 (0.08) | 0.04 (0.01) | 0.04 (0.00) | 1.42 (0.06) | 0.86 (0.03) | 1.19 (0.02) |
| 6 | 0.36 (0.03) | 0.44 (0.02) | 0.53 (0.03) | 0.07 (0.05) | 0.06 (0.00) | 0.07 (0.00) | 0.58 (0.02) | 0.49 (0.01) | 0.66 (0.04) |
| 7 | 0.66 (0.08) | 0.67 (0.04) | 0.74 (0.05) | 0.13 (0.14) | 0.07 (0.01) | 0.11 (0.01) | 0.95 (0.05) | 0.82 (0.04) | 1.06 (0.04) |
| 8 | 3.08 (0.14) | 2.11 (0.09) | 2.88 (0.12) | 0.14 (0.04) | 0.17 (0.01) | 0.23 (0.01) | 4.39 (0.19) | 2.58 (0.06) | 3.59 (0.12) |
| 9 | 1.46 (0.06) | 1.23 (0.06) | 1.51 (0.04) | 0.04 (0.05) | 0.07 (0.00) | 0.09 (0.01) | 1.73 (0.16) | 1.16 (0.04) | 1.49 (0.01) |

| Soil | fluazifop-P | | | metsulfuron-methyl | | | flupyr-sulfuron-methyl | | |
|------|----------------|----------------|----------------|--------------------|----------------|----------------|------------------------|----------------|----------------|
| | Kdb | Kdc1 | Kdc7 | Kdb | Kdc1 | Kdc7 | Kdb | Kdc1 | Kdc7 |
| 1 | 0.48 (0.04) | 0.41 (0.06) | 0.49 (0.03) | 0.15 (0.00) | 0.25 (0.01) | 0.27 (0.03) | 0.78 (0.05) | 0.68 (0.06) | 0.77 (0.07) |
| 2 | 1.20 (0.05) | 0.86 (0.02) | 1.03 (0.01) | 0.34 (0.05) | 0.31 (0.02) | 0.42 (0.02) | 1.23 (0.11) | 0.87 (0.04) | 1.06 (0.04) |
| 3 | 0.28 (0.02) | 0.39 (0.03) | 0.48 (0.01) | 0.13 (0.01) | 0.28 (0.03) | 0.35 (0.03) | 1.02 (0.02) | 0.96 (0.02) | 1.19 (0.07) |
| 4 | 0.76 (0.07) | 0.54 (0.03) | 0.77 (0.06) | 0.28 (0.08) | 0.29 (0.03) | 0.42 (0.05) | 1.13 (0.08) | 0.89 (0.03) | 1.12 (0.09) |
| 5 | 0.64 (0.01) | 0.51 (0.01) | 0.69 (0.01) | 0.27 (0.00) | 0.25 (0.01) | 0.36 (0.01) | 1.11 (0.03) | 0.70 (0.01) | 0.86 (0.02) |
| 6 | 0.27 (0.02) | 0.26 (0.01) | 0.31 (0.02) | 0.06 (0.01) | 0.12 (0.01) | 0.15 (0.02) | 0.39 (0.02) | 0.24 (0.01) | 0.32 (0.03) |
| 7 | 0.51 (0.02) | 0.49 (0.02) | 0.60 (0.03) | 0.23 (0.02) | 0.26 (0.03) | 0.36 (0.03) | 0.78 (0.04) | 0.70 (0.05) | 0.70 (0.03) |
| 8 | 1.57 (0.04) | 1.47 (0.04) | 1.89 (0.03) | 0.81 (0.03) | 1.22 (0.08) | 1.85 (0.04) | 3.02 (0.21) | 2.53 (0.15) | 3.07 (0.15) |
| 9 | 0.89 (0.12) | 0.87 (0.03) | 1.05 (0.01) | 0.47 (0.09) | 0.58 (0.03) | 0.71 (0.02) | 1.40 (0.10) | 1.05 (0.02) | 1.16 (0.03) |

Figure 7-1. Ratio of adsorption coefficients obtained by centrifugation and batch techniques (values less than one indicate that batch results are larger).

*, **, *** indicate a significant difference between the two methods at 0.05, 0.01, 0.001 probability level respectively; NS indicates a non-significant difference.

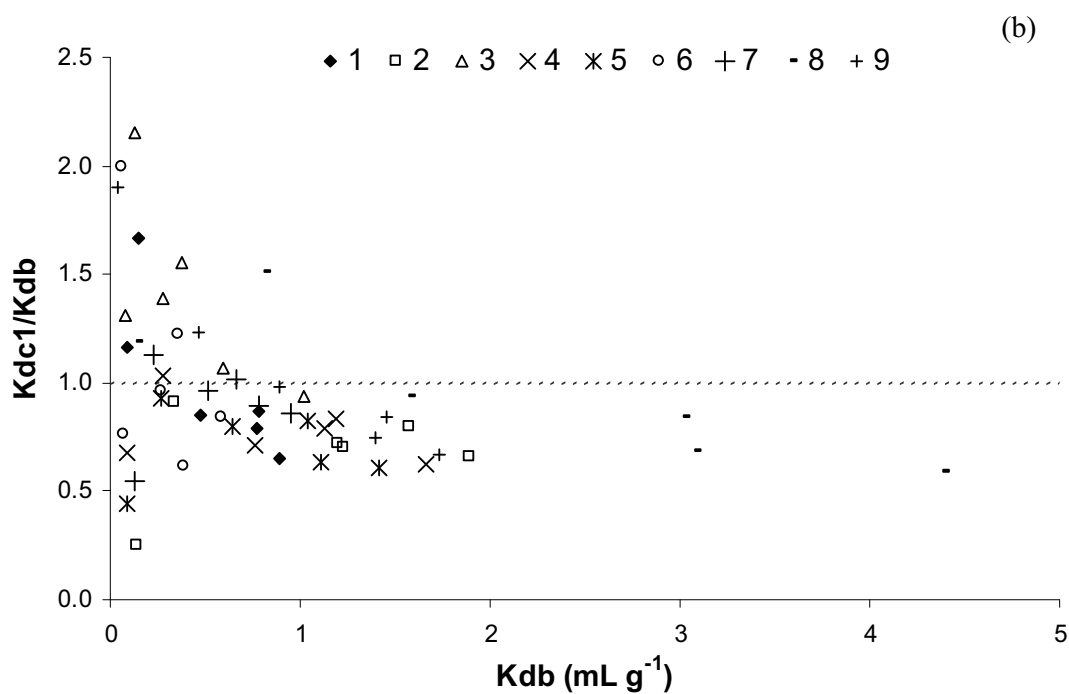
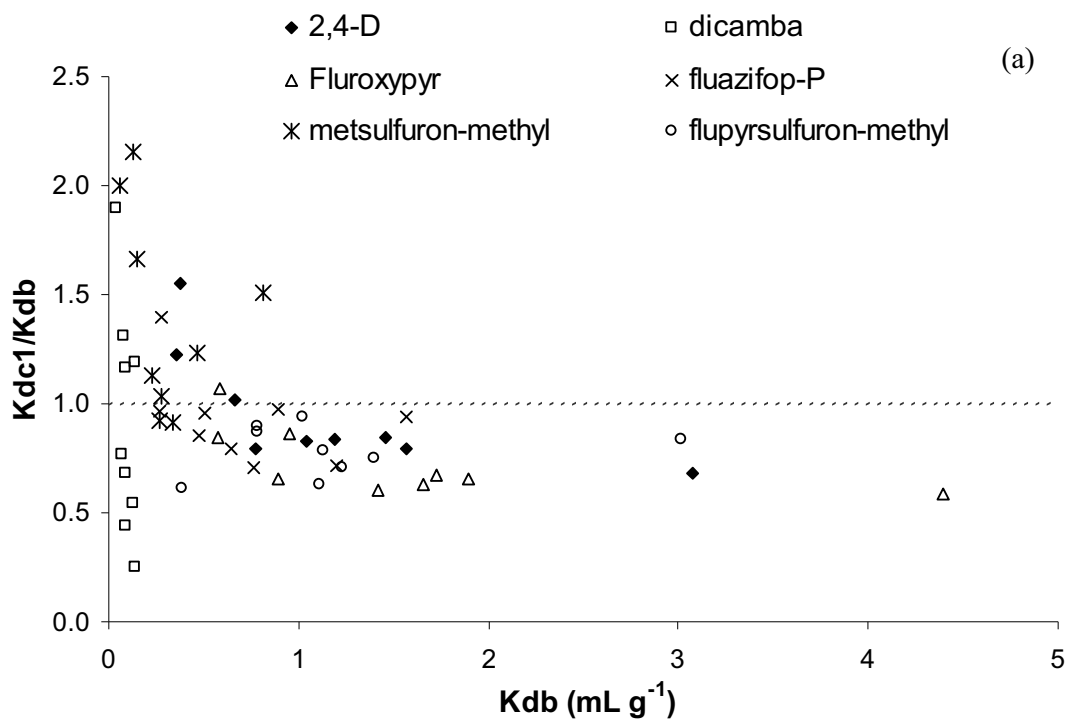


Walker and Jurado-Exposito (1998) previously measured greater adsorption of metsulfuron-methyl by batch than by centrifugation on two soils. However, K_{dc} exceeded K_{db} for incubation period greater than 15 days at 25 °C.

These conflicting results might be due to the low level of adsorption of this compound that makes the determination of adsorption by the batch method difficult and prone to error. It is probable that for the same reason, no trend could be identified for dicamba as the plot of K_{dc} versus K_{db} was not linear.

When all data are plotted together, it appears that the discrepancy between the two methods is related to the strength of adsorption (Figure 7-2).

Figure 7-2. Relative difference between sorption coefficients determined by batch (K_{db}) and centrifugation after one day (K_{dc1}) plotted against K_{db} . Data are differentiated for the different pesticides (a) and soils (b).



The batch technique only yields greater adsorption than the centrifugation technique above a certain level of adsorption. When K_{db} is very small ($K_{db} < 0.5 \text{ mL g}^{-1}$) greater adsorption is generally measured using the centrifugation technique. This might occur if rapid uptake of pesticide-rich solution into the soil aggregates resulted in a physical protection of pesticide. Alternatively, the high soil to solution ratio and small volume of soil available for adsorption in the centrifugation studies might have resulted in pesticide concentrations at the surface of aggregates that were large enough to cause some precipitation. Assuming that all the pesticide molecules were in the soil solution (very low adsorption levels) and that they dissolved in the total amount of water present in the soil, an application rate of 2 mg kg^{-1} is equivalent to a concentration of 20 mg L^{-1} in the soil solution of the driest soil. This concentration is of the same order of magnitude as some solubility data (Tomlin, 1997). All studies were undertaken at $4 \text{ }^{\circ}\text{C}$ and this would have decreased solubility and increased any potential for precipitation of pesticides at the surface of soil aggregates.

When all pesticides were considered together the ratio K_{dc1}/K_{db} was not correlated with the level of adsorption (estimated by K_{db} , $p=0.091$) or the soil organic carbon content ($p=0.212$). However, when considered individually, the relationship between the ratio K_{dc1}/K_{db} and level of adsorption was significant for four pesticides (excepting metsulfuron-methyl and flupyrsulfuron-methyl) and seven soils (excepting soil 2 and 3). Similarly, the relationship with organic carbon content was significant for 2,4-D and fluroxypyr, the two compounds that were most strongly sorbed in this study. This result is consistent with the study of Kennedy et al. (2002) that compared the adsorption of an anthranilate fungicide measured with batch and centrifugation techniques in five soils. Stronger adsorption was always obtained with the batch method and the discrepancy between the two methods was also significantly

correlated with the soil organic carbon content ($p=0.032$). The reason that soils with lower organic carbon give a better agreement between the two methods is still unclear.

Yazgan et al. (2005) also compared these two techniques to measure the adsorption of imidacloprid and carbofuran in eight different soils. The mean adsorption obtained by the batch method was 1.8 times larger than that measured by centrifugation for imidacloprid and 4.5 times larger for carbofuran. Imidacloprid and carbofuran had similar levels of adsorption (mean adsorption coefficients were 2.8 and 2.9 mL g⁻¹, respectively; Yazgan et al., 2005). No explanation for the difference in behaviour between the two compounds was proposed.

These results suggest that the discrepancy between the two methods depends on the properties of both the compound and the soil and that the difference tends to be greater when adsorption is strong. Whilst the vigorous shaking applied in the batch technique is probably the main factor leading to enhanced adsorption, further work involving more strongly sorbed pesticides and a greater variety of sorbents is necessary to determine the aspects of the methods that contribute to these differences and to better understand how they depend on soil and pesticides properties.

Time-dependent adsorption

Adsorption coefficients measured by centrifugation after seven days were significantly larger than those after one day ($p<0.001$, except for dicamba, Figure 7-3). The difference ($K_{dc7}-K_{dc1}$) was highly correlated with K_{db} . When expressed as a percentage of total adsorption, the increase in adsorption was not correlated with

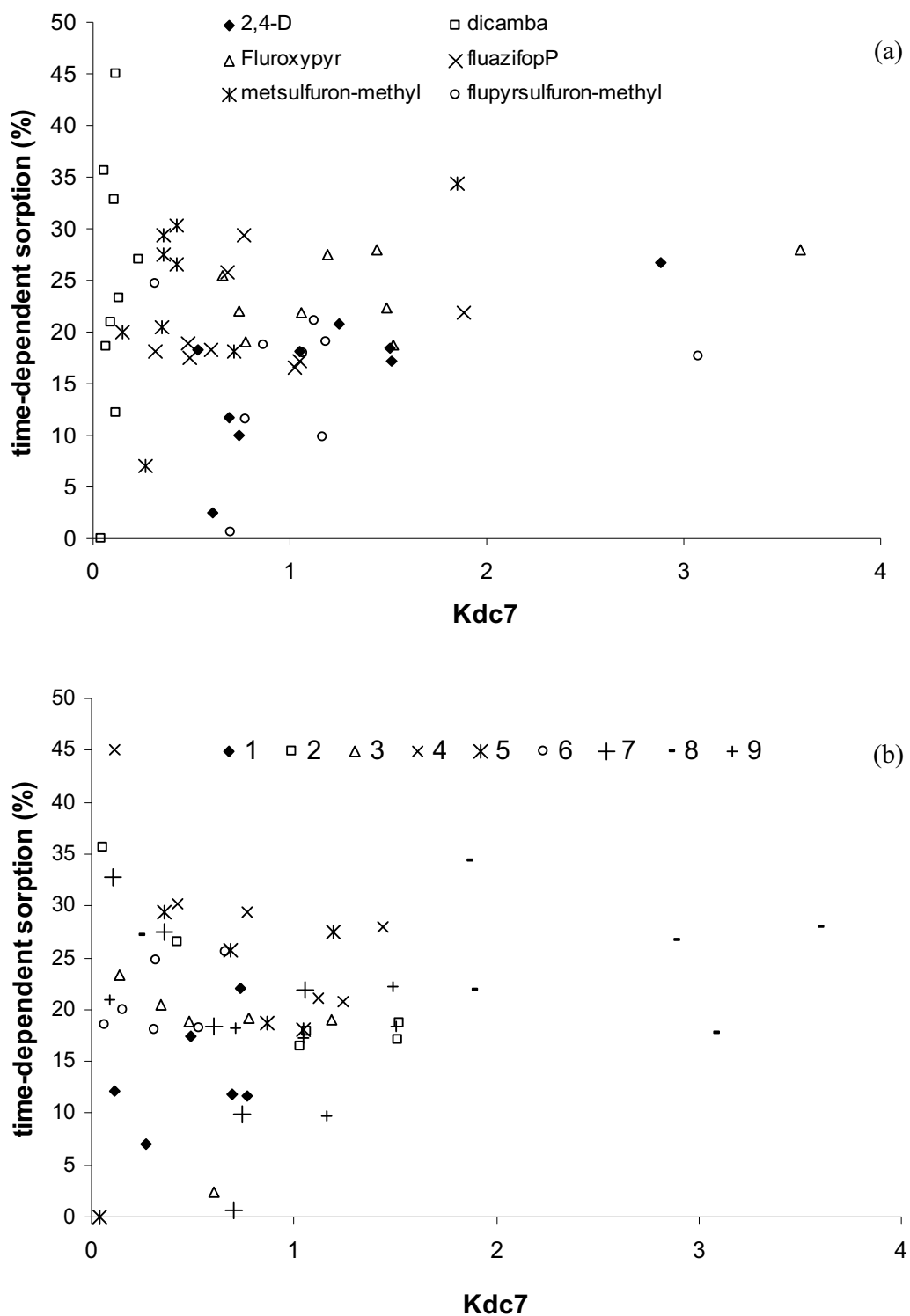
adsorption determined with the batch method ($p=0.282$), but was significantly correlated with the soil organic carbon content ($p=0.022$).

The total amount of pesticide (C_i) used to calculate K_{dc} was determined by solvent extraction after one and seven days. Adsorption coefficients determined by centrifugation are thus already corrected for possible degradation processes and even a marked curvature of the isotherm could not explain the significant increase in adsorption observed in seven days.

The increase in K_{dc} with time can thus mainly be attributed to kinetic adsorption and/or slow diffusion. By its nature, time dependent adsorption will vary with the experimental system.

The centrifugation method allows conditions that are closer to the field situation and is thus more likely to yield results of greater relevance to field soils. The relative increase in adsorption with time was greater in soils with larger organic carbon content and similar behaviour was previously observed for fluroxypyr (Lehmann et al., 1990). Nevertheless, the study of Mamy and Barriusso (2006) suggests that the increase in adsorption with time is more important for the less sorbed molecules and this was not observed in the present study. More kinetic studies, preferably with techniques representative of the field conditions, are still required to better understand how soil and pesticides properties influence the rates at which time-dependent processes occur.

Figure 7-3. Extent of time-dependent sorption (expressed as a percentage increase in sorption after seven days, Kdc7) plotted against the sorption strength. Data are differentiated for the different pesticides (a) and soils (b).



Prediction of pesticide transport through soil

Many models used to predict the behaviour of organic compounds in the environment use adsorption coefficients to estimate the transport through soil to ground and surface water. The batch technique gives an indication of maximum adsorption on disaggregated soil particles while results obtained by centrifugation are more likely to represent sorption over time in field soil. K_{db} was generally larger than K_{dc1} implying that shortly after application, more pesticide may be present in the soil solution and thus be available for degradation, plant uptake or leaching into groundwater than will be predicted from K_{db} .

It is well recognised that adsorption and desorption processes in soils are not instantaneous (Koskinen and Harper, 1990; Pignatello and Xing, 1996; Walker et al., 2005). When time dependent adsorption is measured with a batch technique, in which particles are suspended in a well-mixed aqueous solvent, phenomena occur within individual soil grains or within aggregates that are stable in water.

In the centrifugation technique, transport-related behaviour (physical nonequilibrium) may also play an important role. Physical nonequilibrium arises from slow exchange of solute between mobile and less mobile water (Pignatello and Xing, 1996). Diffusion is slow relative to that in bulk water due to the tortuosity of the paths within soil aggregates, adsorption and interferences due to pore walls and the viscosity of the water near surfaces (Pignatello, 2000). Besides, pesticide molecules might interact with new adsorption sites while diffusing into soil aggregates and become more strongly bound or entrapped within organic matrices in the soil (Koskinen and Harper, 1990). Distribution between dissolved and protected pools might require days, weeks or even months to reach equilibrium (Pignatello and Xing, 1996; Cox and Walker,

1999). In the field, events such as rainfall, degradation and uptake of pesticides deplete the readily available molecules. The direction of diffusion is then reversed and pesticide molecules are redistributed from the inner to the outer regions of soil aggregates by slow diffusion and desorption processes that become rate-limiting to pesticide availability for transport (Pignatello et al., 1993). If rainfall occurs immediately after pesticide application, the extent of time-dependent processes will be limited and a relatively high proportion of pesticide may be available to leach. As suggested by Walker et al. (2005), the timing of rainfall relative to pesticide application is one of the most important factors controlling losses via leaching.

CONCLUSION

The study of Beulke et al. (2004) showed that the concentration of three pesticides in pore water determined by the centrifugation technique declined at a similar rate to the concentration in leachate (as measured in a small soil column) and decline was faster than that could be attributed to degradation alone. The centrifugation technique may thus be an adequate technique to characterise the fraction of pesticide that is available for leaching at a given time after application. The centrifugation technique requires additional time and materials, but it provides more extensive information than the batch method. It allows measurement of adsorption at realistic soil moisture contents and characterisation of the fraction of a pesticide that is available soon after application. The importance of time-dependent retention processes can also be assessed. The technique is also advantageous for pesticides with very low adsorption coefficients since it yields satisfactory level of adsorption and significantly reduces the variability of the results.

Chapter 8

CONCLUSIONS AND PERSPECTIVES

Literature review

A great deal of work has been undertaken concerning the adsorption of ionisable pesticides in soils in the past 15 years. An extensive review of the literature introduced the main issues concerning the behaviour of ionisable pesticides in soils:

1. Many retention mechanisms in addition to hydrophobic partitioning have been postulated as contributing to the adsorption of ionisable pesticides in soils. These include ionic exchange, charge transfer, ligand exchange and cation (or water) bridging. However, relatively little experimental evidence is available.
2. 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 influence of varying pH on the charge at the surface of soil particles may also play 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 behaviours have also been reported.
3. Soil organic matter generally promotes the adsorption of ionisable pesticides in soils although a negative influence has occasionally been observed. Clay and Al, Fe

(oxi)hydroxides can also play a significant role and might have to be considered in some situations.

4. 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 select the descriptors and parameters that should be included.

5. 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 degradation mechanisms.

6. Questions remain concerning the link between the processes of adsorption and degradation.

The aim of this PhD was to advance the understanding and prediction of the behaviour of ionisable pesticides in soils. A dataset of adsorption and degradation parameters for ten ionisable pesticides and nine soils was first produced. Data were analysed by several approaches and this led onto more detailed investigations. The main conclusions of this thesis can be summarised as follows.

Adsorption of acidic pesticides

In general, adsorption of acids was weak compared to bases and followed the order: dicamba < metsulfuron-methyl < fluazifop-P < metribuzin < 2,4-D < flupyrsulfuron-methyl < fluroxypyr < terbutryn < pirimicarb < fenpropimorph. Adsorption of ionisable pesticides tends to be stronger in soils with lower pH and containing more organic carbon. Results confirmed that approaches consisting in the normalisation of

adsorption coefficients to the organic carbon (K_{oc}) or clay content (K_{clay}) are not suitable for ionisable compounds.

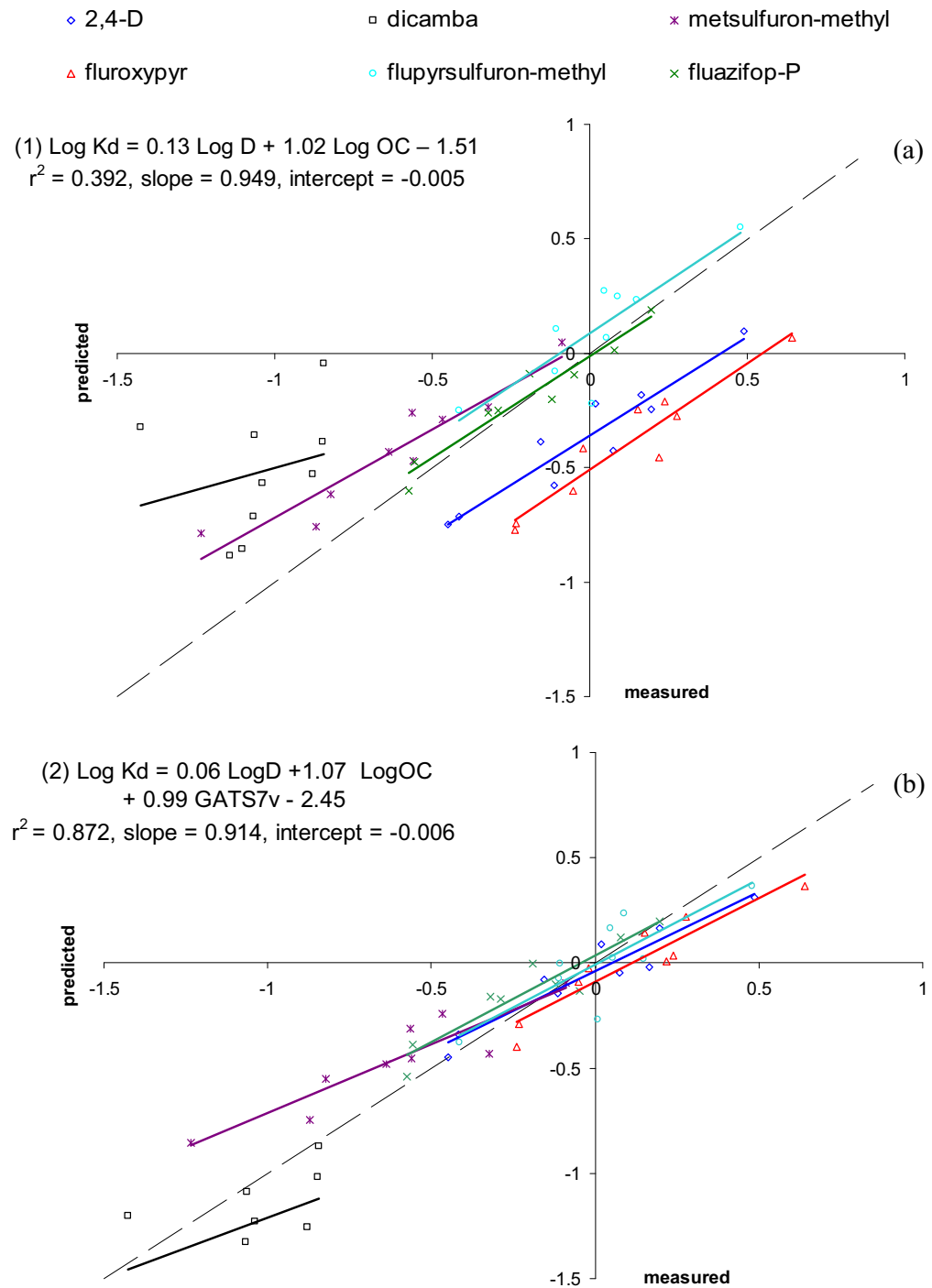
Statistical analyses against a wide range of soil and pesticide descriptors were used to identify the best combination of properties that describes the variation in adsorption. Different combinations of properties were generally selected for the different soils and pesticides but after a careful analysis of the results, some trends clearly appeared.

For the acids, the two strongest descriptors of the variability in adsorption were the lipophilicity of the compound corrected for soil pH (Log D) and the soil organic carbon content (OC). The regression equation including these two parameters (equation (1)) described a large part of the variability in adsorption.

Figure 3-4 represented adsorption coefficients measured for the acids plotted against the values predicted. The figure is reproduced here with the addition of trend lines fitting the data for each pesticide (Figure 8-1a). It clearly appears that trend lines are approximately parallel to the 1:1 line. This indicates that variations in adsorption due to differences in soil pH and OC content can be well described for different acidic pesticides in various temperate soils by a unique equation. For modelling purposes, the following assumptions can hence be reasonably made: (i) variations due to pH are a direct consequence of pesticide dissociation (variations in surface charges can be neglected in temperate soils), (ii) differences in quality of soil organic matter in the different soils can be neglected, at least for these soils from the UK, (iii) adsorption to the clay fraction can be neglected.

Equation (1) only includes Log D and the soil organic carbon content and the trend lines fitting data for 2,4-D and fluroxypyr are offset compared to the 1:1 line (Figure 8-1a). The intersection with the Y-axis needs therefore to be corrected for the pesticide considered.

Figure 8-1. Adsorption coefficients measured for the acids (Log Kd) are plotted against the values predicted with two regression equations. Trend lines for each pesticide were added to the original figure (Figure 3-4).



Two pesticide parameters are already included in equation (1) through the parameter Log D (i.e. pKa, the dissociation constant and Log P, the lipophilicity of the neutral form). Reliable pKa values can be obtained from various methods (e.g titration, spectrophotometric, conductometric methods). On the other hand, the determination of the lipophilicity of ionisable compounds is still a problem. Although numerous methods are available to measure lipophilicity, only a few are appropriate for ionisable pesticides. The offsets observed for 2,4-D and fluroxypyr could thus indicate that Log P has not been correctly evaluated for these two compounds. However, the lipophilicity of the pesticides studied was determined with a method suitable for ionisable compounds (pH-metric method) and although errors are possible, the method is expected to give consistent results for different compounds.

Another possible explanation for the offset observed for 2,4-D and fluroxypyr is that an additional characteristic of the compound is required to describe its affinity with soil organic matter. Ionisable pesticides may adsorb on soil particles through various mechanisms and experiments measuring the influence of ionic strength on adsorption confirmed differences between 2,4-D and flupyrsulfuron-methyl. In Chapter 3, the inclusion of the pesticide parameter GATS7v (Geary autocorrelation - lag 7 / weighted by atomic van der Waals volumes) was shown to significantly improve the prediction by setting the intersection of trend lines with the Y-axis to 0 on the predicted versus measured plot (equation (2), Figure 8-1b). Although this parameter was successfully tested on an independent dataset including other acidic pesticides, its applicability to other datasets needs to be further validated.

Another approach to improve prediction would consist in using the regression equation (1) (that only includes the Log D and the soil organic carbon content) and determining a correction factor that would be specific to the molecule studied using

experimental data. This solution would not require the use of software to determine the parameter $GATS7v$ and would allow correction for possible errors in the determination of Log P. In theory, the correction factor can be determined with a single adsorption measurement. Nevertheless, the use of more experimental data, obtained in contrasting soils (especially regarding pH and organic carbon content) is obviously preferable.

Adsorption of basic pesticides

The adsorption behaviour of basic pesticides is more complex than that of acids. This is probably due to the variety of mechanisms likely to retain basic compounds on soil particles. A large part of the variation in adsorption for individual compounds could be explained by variation in the soil cation exchange capacity (CEC) and pH. Nevertheless, the large differences in behaviour between bases could not be deduced from molecular properties of the compounds. Approaches specific to each basic compound are required. More experimental data are needed to achieve a greater level of accuracy and to provide equations for other basic compounds.

Centrifugation technique and time-dependent adsorption

The results discussed so far in this section were obtained with the batch-slurry method. Although this technique is the most commonly used for direct measurement of the adsorption of organic molecules in soil, the results may not adequately reflect

adsorption processes in field-moist or unsaturated soil. Results obtained by batch technique for the six acidic pesticides were compared to adsorption coefficients measured using a centrifugation technique that allows measurement at realistic soil to solution ratios. Although the batch method gave significantly higher values of K_d than the centrifugation method for the more strongly sorbed molecules in the more sorptive soils, it tended to give lower adsorption coefficients compared to the centrifugation method when adsorption was weaker. Discrepancies between the two methods were probably mainly due to the vigorous shaking applied in the batch technique that artificially enhances the availability of adsorption sites. This implies that shortly after application, more pesticide may be present in the soil solution and thus be available for degradation, plant uptake or leaching than will be predicted using an adsorption coefficient determined with the batch method.

The centrifugation method was also applied to investigate changes in adsorption with time. Adsorption of the six acidic compounds increased significantly between one and seven days and the extractability of total residues decreased with time. The increase in adsorption was not directly related to the level of adsorption although it was more important in soils containing more organic carbon. These results confirm the importance of time-dependent processes and the necessity to include them in risk assessment procedures. The centrifugation technique is a useful method to measure adsorption of pesticides at realistic soil moisture contents and seems to be an adequate technique to characterise the fraction of pesticide that is available for leaching at a given time after application.

Degradation

Results regarding degradation confirm some marked differences between soils in their ability to degrade different pesticides. Results were first submitted to the same statistical analysis as for adsorption data. The parameters selected to explain variations in rates of degradation strongly depended on the soil-pesticide combination. The lack of consistent behaviour renders a global approach to prediction of degradation unrealistic.

On the other hand, a correlation analysis permitted to identify distinct types of behaviour. Metsulfuron-methyl, pirimicarb (and perhaps dicamba) seemed mainly degraded by abiotic acidic hydrolysis. The degradation rates of these three pesticides were positively influenced by soil OC content and negatively influenced by soil pH. A positive relationship linked their adsorption and degradation parameters, probably as a consequence of a catalyzed hydrolysis after adsorption onto soil organic matter. In contrast, microbial degradation seemed to dominate the breakdown of 2,4-D, fluazifop-P, flupyrsulfuron-methyl, metribuzin, fenpropimorph and terbutryn. As a consequence, degradation rates of these pesticides were very sensitive to soil bioactivity level, positively influenced by soil pH and not related to adsorption. Fluroxypyr had an intermediate behaviour and the influence of soil properties on its degradation was unclear. The dominance of one route of degradation over another strongly depends on the characteristic of the pesticide. Pesticides with similar structures may also behave differently as shown for the two sulfonylureas.

Link between adsorption and degradation processes

Finally, there was no statistical relationship between sorption and degradation for most of the pesticides. Significant correlations were only observed for three ionisable pesticides out of ten, with faster degradation in soils with stronger sorption. Although a negative relationship between these two processes has been observed in other studies, the results cannot be generalised.

Further research

This study reports useful information about the behaviour of ionisable pesticides in soils. Adsorption of acidic pesticides was successfully predicted in a set of temperate soils using a single equation. The equation proposed provides a promising starting point to improve the risk assessment of acidic pesticides in the environment. Current assessments are normally based on three or four measurements of adsorption and the influence of pH is rarely taken into account. The equation presented would permit a more accurate assessment of adsorption, even if a wide range of soils is considered, without requiring more experimental data. The equations presented in this thesis will have to be tested on further sorption and leaching data, to see whether they are appropriate. The impact of approaches specific to ionisable pesticides on outputs from pesticide fate models will have to be evaluated and compared to approaches currently applied. Finally, it is hoped that guidance will be proposed for a more robust risk assessment of ionisable pesticides in the environment. This could take the form of advice on inputs for fate models and/or adaptation of the FOCUS scenarios applied in

the UK. The FOCUS scenarios are a set of nine standard combinations of weather, soil and cropping data which collectively represent agriculture in the EU for the purposes of a Tier 1 EU-level assessment of leaching potential (FOCUS, 2000). These scenarios could be adapted to include situations in which acidic pesticides are likely to leach (alkaline soil pH combined with low organic matter content). This will also allow for a more robust assessment of the likely impact of new molecules proposed for registration and would help to identify the sites where a particular management with respect to leaching of currently applied molecules is required.

The behaviour of basic pesticides appeared to be more complex than that of acids. More experimental data are required to establish equations specific to each basic compound to predict their adsorption in soils. The complex behaviour is probably due to the variety of mechanisms likely to retain basic compounds on soil particles. 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 nuclear magnetic resonance, electron spin resonance spectroscopy, Fourier transform infrared spectroscopy and fluorescence spectroscopies. These techniques would permit a further understanding of the behaviour of basic pesticides in soils and more generally, of organic compounds in soils.

Some aspects of the adsorption of ionisable pesticides lie outside of this thesis and would deserve further research. Complementary experiments are needed to investigate adsorption of ionisable pesticides in tropical soils. Tropical soils contain significant quantities of adsorption surfaces exhibiting variable charges according to the pH (i.e.

aluminum and iron (hydr)oxides). Additional adsorption mechanisms and a more complex influence of pH on the adsorption of ionisable pesticides have been reported in tropical soils (Chapter 2).

Experiments studying the likely competition effects between ionisable pesticides and fertilisers or between several ionisable pesticides are also required. Several recent articles reported a reduction in the adsorption of some ionisable pesticides with increasing phosphate application (Chapter 2). More experiments are needed to investigate whether significant competition phenomena might occur at realistic pesticide/fertilisers concentrations, how they depend on pesticide and soil properties and whether they should be taken into account within risk assessment procedures.

An important issue concerning the adsorption of organic compounds in soils was also raised in this thesis. The occurrence of time-dependent adsorption is still a subject of controversy. More kinetic studies, preferably with techniques representative of field conditions (such as the centrifugation technique), are still required to better understand how soil and pesticides properties influence the rates at which time-dependent processes occur.

An equation predicting degradation of a range of compounds has not been proposed to date and is not supported by results from the current study. The failure of such a global approach (QSAR type approach) could be expected considering the complexity of interactions between different processes that influence breakdown of organic compounds in soils. More detailed experiments, measuring the simultaneous decline of labelled and unlabelled compounds for instance, would permit a better distinction between processes (breakdown of parent compounds, metabolites, mineralization and

formation of bound residues). Such experiments would provide a more comprehensive image of degradation processes and permit a further understanding of the varying patterns observed for different soil-pesticide combinations.

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