Sorption kinetics of clomazone and pendimethalin in Tasmanian soils – problems for the licit opium poppy industry?

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ABSTRACT

Clomazone and pendimethalin sorption kinetics were examined on the separated fractions of four Tasmanian soils. In all soils the Kd of clomazone and pendimethalin sorption increased in the order; sand<silt<clay<particulate organic matter. The kinetics of sorption increased in the order of slowest to fastest; clay<silt<sand<particulate organic matter. The degree of sorption of both herbicides increased with increasing humification of organic matter associated with soil fractions. Pendimethalin exhibited greater sorption and faster kinetics on all soil fractions compared with clomazone, which may explain accumulation of pendimethalin soil residues.

INTRODUCTION

The Tasmanian cropping industry, and in particular the licit morphine poppy industry, relies upon the use of residual herbicides for seasonal weed control. Clomazone and pendimethalin are two such products gaining wide use, but with this has come carry-over problems. Clomazone (2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone) applied post-emergence to opium poppies (*Papaver somniferum*) has caused damage in a subsequent crop of malting barley (*Hordeum vulgare*). Pendimethalin (*N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine) provides residual weed control in pyrethrum daisies (*Tanacetum cinerariaefolium*) but with potential for subsequent carry-over effects upon opium poppy crops. As a result, accurate herbicide application is required to avoid carry-over effects and maintain crop-rotation choice in the Tasmanian production system. Initial soil sorption measurements indicated that herbicide persistence was linked to adsorption to soil colloids. Furthermore, this initial study indicated that the varied nature of individual soil constituents may have a large bearing upon sorption. The objective of this research was to evaluate the kinetics and degree of sorption to various soil fractions in four important agricultural soils in Tasmania.

METHODS AND MATERIALS

Soils

The kinetics of clomazone and pendimethalin sorption were studied in soil fractions of four soils; clay loam ferrosol with > 5% free iron oxides (ferrosol), acidic silty loam

(sodosol), smectitic black cracking clay (vertosol), and a hydrophobic loamy sand with large amounts of particulate organic matter (kurosol). All soils were classified according to the Australian soil classification system (Isbell 1996).

Soils were fractionated into sand (>20µm), silt (2-20µm) and clay (2µm) by sedimentation according to the method of Kunze and Dixon (1986). No chemical agents were used, disruption of aggregates being achieved by mechanical agitation and sonification. Particulate organic matter (POM) was separated using an aqueous solution of sodium polytungstate ($Na_6(H_2W_{12}O_{40}).H_2O$) of density 1.6 Mg m^{-3} (Golchin et al., 1994). Clay-fraction separation of whole clay (<2 µm) and fine clay (<0.02 µm) fractions was achieved by sedimentation and centrifugation (Laird et al., 1991. A sample of the clay fractions extracted from the ferrosol and vertosol was also treated with 30% H_2O_2 for removal of organic matter (Kunze and Dixon 1986). This oxidised ferrosol sample was also treated with sodium dithionite and sodium citrate in a system buffered with sodium bicarbonate (DCB treatment) for removal of free Fe compounds (Kunze and Dixon 1986).

The chemistry of the clay fractions was investigated by X-ray diffraction (XRD), selected fractions also being examined by scanning electron microscopy (SEM). Total carbon was determined by dry combustion in a LECO furnace, and total N by Kjeldahl digestion.

Sorption kinetics of herbicides onto the soils

The kinetics of clomazone and pendimethalin adsorption by the soil fractions were determined using the batch equilibration method. Each soil fraction (1.0 g or 0.5 g for POM, in triplicate) was equilibrated with 0.01M $CaCl_2$ (5 ml) containing clomazone (1 mg L^{-1}) or pendimethalin (0.4 mg L^{-1}). Incubation times were 0.5, 1, 2, 4, 8 and 24 hours, after which samples were centrifuged for 5 min at 10,000 rpm, filtered to 0.45 µm and extracted with dichloromethane.

Chemicals and analysis

Analytical grade (99.1%) clomazone and pendimethalin were obtained from the Australian Standards Laboratory. All quantification was performed using a Varian Saturn GC-MS/MS operated at 28°C. Samples (2 µL) were injected into the column at 40°C using a carrier gas of helium at a flow rate of 2 ml min^{-1}. This column temperature was maintained for 1 minute, increased to 190°C at 30°C min^{-1}, and finally increased at 10°C min^{-1} to 280°C and held there for 6 minutes.

RESULTS

The key chemical components of each soil fraction are presented in Table 1. The organic matter associated with each soil fraction was qualitatively assessed according to palynological classification (Tyson 1995) to determine the most dominant type of organic matter present.

Table 1.   Characteristics of soil fractions and organic matter

Soil fraction	Mass (%)[a]	Total carbon (%)	C:N ratio	Organic matter type[b]	Clay matrix[c]
Kurosol	100	2.1	21	PH/AOM/CH	SM/IL
POM	1.2	27	29	PH/CH	-
Sand	90	1.35	22	AOMc	-
Silt & clay	9	9.29	13	CM	
Sand-OM	-	-	-	-	-
Sodosol	100	2.4	19	AOM/PH/CM	Kaolin
POM	1	28	25	PH	-
Sand	85		23	AOM	-
Silt & clay	12		15	CM/AOM	Kaolin
Silt & clay-OM[d]	-	-	-	-	
Ferrosol	100	5.3	12	CM/PH/OAM	Kaolin
POM	2.1	25	24	PH	-
Sand & silt	12	6.28	21	OAM	-
Clay	82	5.22	10	CM	Kaolin
Clay–OM&Fe[e]	-	-	-	-	-
Vertosol	100	3.4	14	CM/OAM/PH	Smectite
POM	0.8	26	29	PH/CH	-
Sand & silt	46	1.72	34	OAM	-
Clay	33	4.33	10	CM	Smectite
Fine clay	18	1.84	7	CM	SM/IL
Fine clay -OM	-	-	-	-	SM/IL

[a] Percentage of the total soil mass.

[b] Dominant organic matter present in order of content in each fraction; PH- phytoclast material, AOM- amorphic organic matter, CH– charcoal, CM- clay/humic association.

[c] Clay mineralogy as determined by XRD; a single entry represents greater than 90% of a dominant mineral present, SM/IL indicates mixed smectite/illmenite.

[d] Treated with H_2O_2 to remove organic matter.

[e] Treated with H_2O_2 to remove organic matter and DCB to remove free iron compounds.

The POM fractions in all soils contained large amounts of relatively undegraded plant debris or phytoclast (PH) material. In addition, the POM fraction of the vertosol, and to a lesser extent of the kurosol, contained appreciable amounts of charcoal. As has been reported previously (Karapanagioti *et al.*, 2000) the presence of charcoal may explain the comparatively high Kd value (Table 2) and slow sorption kinetics (Figure 1) for clomazone on the vertosol POM fraction. In contrast, the presence of amorphic organic coatings (AOM) in the sand fraction of the kurosol provided an important sorptive site for rapid uptake of clomazone (Figure 1). The silt/clay fraction of the sodosol shown in Figure 1 exhibited an intermediate reaction rate for the uptake of clomazone, which is indicative of a clay/humic association (CM).

Clomazone sorption kinetics increased in the order of slowest to fastest; clay < sand < POM. The relative contribution of each soil fraction to the sorption of clomazone by the whole soil was affected by the type and distribution of organic matter. Soil clay fractions with a lower C:N ratio (Table 1), and hence more humified organic matter, exhibited a greater affinity for clomazone (Table 2). The readily accessible POM, which constituted less than 2% of soil mass in all soils, contributed over 5% to clomazone sorption by each soil (Table 2). Clomazone also exhibited an apparent affinity for pure clay fractions, in particular the smectite clay fraction of the vertosol (Table 2).

Table 2.   Sorption of clomazone and pendimethalin by the soil fractions.

Soil fraction	% soil mass[a]	Clomazone Kd (ml g^{-1})	% contribution to soil Kd[b]	Pendimethalin Kd (ml g^{-1})	% contribution to soil Kd[c]
Kurosol	100	1.8	-	157	-
POM	1.2	7.6	5	1806	14
Sand	90	1.5	85	111	79
Silt & clay	9	3.5	10	202	8
Sand-OM	-	0.1	-	26	-
Sodosol	100	1.7	-	170	-
POM	1	6.6	5	1962	13
Sand	85	1.2	68	115	63
Silt & clay	12	2.7	27	247	24
Silt & clay-OM[d]	-	0.8	-	88	-
Ferrosol	100	3.6	-	194	-
POM	2.1	7.2	5	1693	19
Sand & silt	12	3.7	55	108	28
Clay	82	2.5	46	176	53
Clay–OM&Fe[e]	-	1.2	-	112	-
Vertosol	100	2.4	-	191	-
POM	0.8	13	6	1994	11
Sand & silt	46	1.1	21	80	17
Clay	33	2.6	51	218	48
Fine clay	18	2.1	22	203	24
Fine clay-OM	-	1.8	-	164	-

[a] Percentage of the total soil mass.
[b] Percentage contribution of soil fraction to whole-soil clomazone sorption.
[c] Percentage contribution of soil fraction to whole-soil pendimethalin sorption.
[d] Treated with H_2O_2 to remove organic matter.
[e] Treated with H_2O_2 to remove organic matter and DCB to remove free iron compounds.

The hydrophobic pendimethalin molecule had a very strong affinity for organic surfaces, with very rapid sorption kinetics in each soil fraction (Figure 2), and in particular POM. In all soil fractions, pendimethalin sorption reached equilibrium before 4 hours, if not 2

hours. In addition, POM fractions exhibited large Kd values for pendimethalin, and contributed significantly to whole soil sorption (Table 2). Pendimethalin also showed greater adsorption to clay than sand fractions, which is most likely linked to the degree of humification of OM in the clay fractions. Importantly, clay fractions treated to remove organic matter also exhibited a strong affinity for pendimethalin, with relatively slow sorption kinetics (Table 2 and Figure 2).
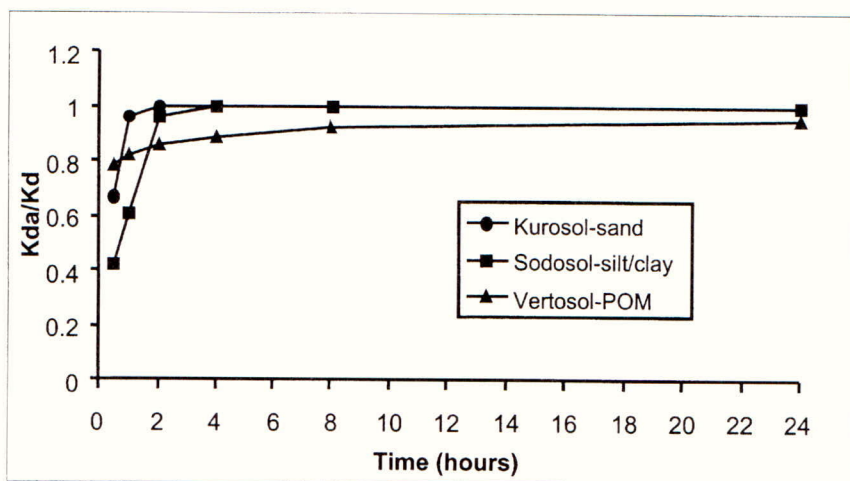

Figure 1.   The apparent sorption coefficient of clomazone normalized by equilibrium sorption coefficient (Kda/Kd) versus time.
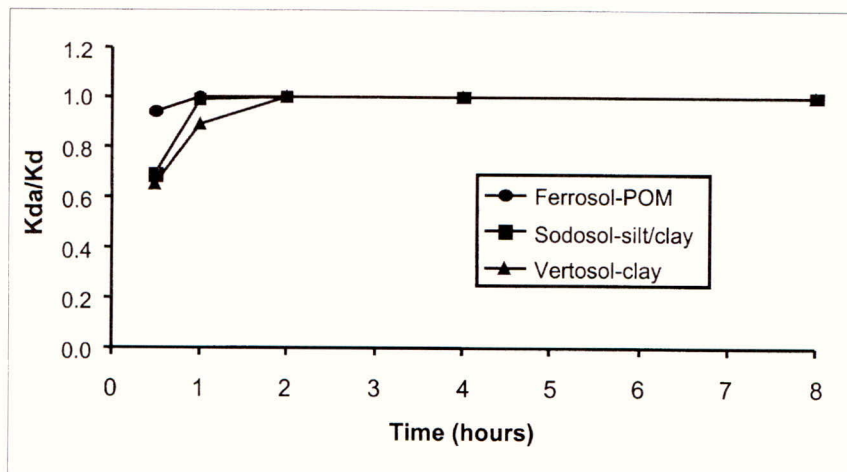

Figure 2.   The apparent sorption coefficient of pendimethalin normalized by equilibrium sorption coefficient (Kda/Kd) versus time.

CONCLUSION

Clomazone and pendimethalin exhibited a strong affinity for clay/humic associations (CM) which may result in accumulation of residues in the clay-rich ferrosol and vertosol. In addition, exposed organic surfaces such as POM provide a site for rapid strong binding of herbicide. It is likely that exposed POM surfaces and AOM coatings in sand fractions represent a labile pool of bound herbicide in each soil. Such of a pool of herbicide would be readily subject to desorption given mechanical disruption and/or increased soil moisture.

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Incorporation of soil-pH dependent behaviour in pesticide leaching assessment

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ABSTRACT

Until now, pH effects have been assessed in a simplified way in the evaluation of the leaching potential of pesticides in the Netherlands. If a substance shows pH-dependent sorption, a conservative approach is followed in which the sorption constant under worst-case conditions is taken for the assessment. In general this means that a relatively low value for the sorption coefficient is used in the calculations.

Some models used in the evaluation for pesticide registration have built-in routines that describe pH-dependent sorption, so this aspect can be taken explicitly into account. For instance, the PEARL model uses a routine that calculates the overall sorption coefficient from the sorption coefficients of the low-pH and high-pH species, as determined by the pK_a of the pesticide and the pH of the soil.

The rate of pesticide transformation in soil may also be pH-dependent, in which case the selection of the transformation rate coefficient (or half-life) differs from normal selection procedures. As none of the commonly available models has options for taking pH-dependent transformation into account, the leaching potential must be assessed by analysing the full range of possible soil-pH values.

As an example, calculating the leaching of a herbicide for the range of soil-pH values normally encountered in arable fields shows that the selection of the right parameters is very important. Surprisingly, the highest leaching of this substance appeared to be in the middle of the pH range. Certainly, such sensitivity analysis allows optimisation of the further testing of other substances, if needed.

INTRODUCTION

Reference scenarios for the assessment of the leaching potential of plant protection products have recently been developed (FOCUS, 2000), to be used in first-tier assessments. Pesticide sorption and transformation parameters and these scenarios can be used as input to appropriate leaching models and the leaching potential can be calculated. The results of the calculations are then used in the registration evaluation at the EU level. This procedure can probably be applied to approximately 80% of the substances registered in the Netherlands. The pH of the soil was not a selection criterion in the search for representative profiles, so the general procedure cannot be used for substances liable to charge transitions at typical soil pH

values; for example substances having a pK_a value (for acid dissociation) in the range 3 to 8. For such substances, a more refined approach, involving expert judgement, is recommended. In the Netherlands to date, generally a conservative approach has been followed, taking into consideration worst-case conditions with respect to leaching including the sorption constants having to be determined in soils with pH between 7 and 8.

For many substances, not only plant protection products, a relatively high correlation has been found between the sorption coefficient and the pH of the soil or sediment (for example, Moreale and van Bladel (1980), Schellenberg *et al.*, (1984), Fontaine *et al.*, (1991)). Schellenberg *et al.*, (1984) found that for chlorophenols the sorption is related to the proportion of the neutral species, although deviations were found for the highly substituted congeners. The deviations were attributed to sorption of phenolate ions in soils of higher pH. Nicholls and Evans (1991) elaborated on the theory and suggested the use of a sorption coefficient derived from both neutral and ionised species, together with the pK_a of the substance and the soil pH.

Information in *The Pesticide Manual* (Tomlin 1997) revealed that pH-dependent sorption behaviour might be relevant for approximately 20% of the pesticides registered in the Netherlands. Furthermore, such behaviour might also be relevant for metabolites of other substances. It was therefore decided to include pH-dependent sorption behaviour as an option in the PEARL model (Leistra *et al.*, 2001; Tiktak *et al.*, 2000). The use of this option in PEARL and the effect of taking pH-dependent sorption into account in the evaluation procedure and on a national scale is demonstrated below.

RELEVANT CONCEPTS IN PEARL

PEARL uses a concept of equilibrium sorption according to the Freundlich equation, with non-equilibrium sorption being optional (Leistra *et al.*, 2001; Tiktak *et al.*, 2001). A second option, pH-dependent sorption, is relevant for this study and is described below in more detail. The combination of non-equilibrium sorption and pH-dependent sorption is possible in the PEARL model, but not used in this study.

The dissociation of monovalent weak acids is described by:

$$HA \Leftrightarrow H^+ + A^-$$ (Eq. 1)

in which HA is the neutral molecule, H^+ is the hydrogen ion and A^- is the anion. The degree of dissociation of the weak acid is described by:

$$pH = pK_a + \log \frac{(A^-)}{(HA)}$$ (Eq. 2)

with the brackets indicating the activity of the species and pK_a defined as $pK_a = -\log_{10}(K_a)$ and K_a the acid dissociation constant. In the remainder of the text activities are set equal to molarities.

For each of the substances a sorption coefficient may be defined:

$$K_{om,HA} = \frac{X_{om,HA}}{c_{HA}}, \qquad K_{om,A^-} = \frac{X_{om,A^-}}{c_{A^-}}$$ (Eq. 3a, b)

with for each species, HA and A⁻:

X_{om} = content sorbed to organic matter (kg/kg)

c = concentration in solution (kg/m³)

K_{om} = sorption coefficient on basis of soil organic matter (m³/kg)

The combined coefficient $K_{om,com}$ for sorption as a function of pK_a and pH can be expressed as:

$$K_{om,com} = \frac{K_{om,HA} + K_{om,A^-} M_{rel} 10^{pH-pK_a-\Delta pH}}{1 + M_{rel} 10^{pH-pK_a-\Delta pH}}$$ (Eq. 4)

with:

Kom,com = coefficient for the sorption of the combination of HA and A⁻ on soil organic matter (m³/kg)

M_{rel} = relative molar mass of A⁻ as compared to HA

ΔpH = pH-shift, pH-units (see below)

At low pH-values, mainly HA is present and the sorption is dominated by sorption of the neutral molecule; the exponent in Eq. 4 becomes negative, almost eliminating the second term at the right-hand side while the denominator approaches 1. In contrast, at high pH the denominator becomes large, therewith eliminating the contribution of the neutral molecule. The anions are repelled by the negative charge of the surfaces of organic matter and clay minerals, so sorption is often low. However, the anions may show some residual sorption due to hydrophobic interactions between a more hydrophobic part of the molecule and organic matter. Equation 4 can also be used for weak bases, where the protonated species is more strongly sorbed than the neutral molecule. In Eq. 4 an additional term ΔpH or pH-shift is included to account for discrepancies between experimental conditions in sorption tests and the conditions for which one wants to calculate the leaching of a substance. The pH of the soil is dependent on the way it is measured. Several methods exist, of which the most obvious differences between the methods are the composition and the concentration of the solution used to prepare the slurry, usually H_2O, KCl or $CaCl_2$. It is likely that the concentration of exchangeable cations and the way in which the pH is measured affect the pH-value obtained.

RESULTS

Dinoseb, a herbicide that is no longer on the market (Tomlin, 1997), has a pK_a of 4.62 and therefore is expected to show pH-dependent sorption behaviour. Indeed, re-evaluation of sorption data in the (old) registration dossier revealed a relationship with pH. As different methods were used for measuring the pH of the soil, all pH values were converted to $pH(CaCl_2)$. Values of $pH(H_2O)$ were lowered by 0.6, whereas $pH(KCl)$ values were raised by 0.1. The fitting to the PEARL formula, using the PRISM2 package (Graphpad Software, Inc.), led to K_{om} sorption coefficients of 500 L/kg for the neutral molecule and 23 L/kg for the anion. The average half-life for dinoseb was 50.2 days. Using these sorption and transformation data in the standard Dutch evaluation procedure (net application rate 1 kg/ha), the predicted leaching of dinoseb below 1 m depth is 2.8% (maximum average concentration in the groundwater between 1 and 2 m depth is 5.7 μg/L). This would lead to a negative decision in the registration procedure. Using GeoPEARL (PEARL in combination with a GIS) (Tiktak *et al.*, 2001), we investigated whether this relatively high leaching would be predicted to occur in extensive areas of the Netherlands. The potential leaching of the substance was calculated for over 6000 different input combinations, derived from the soil map and climatic conditions as

registered by the 15 main weather stations in the Netherlands. These calculations show that in large areas of the Netherlands leaching above the 0.1 µg/L would indeed be expected (Figure 1, the 300 mg/ha leaching level roughly corresponds with this registration threshold). There are also large areas where leaching would be expected to be low. The main reason for the limited leaching is the lower pH, with corresponding higher sorption coefficient. Application of dinoseb took place to a large part in the vulnerable areas i.e. areas with soil pH around 7, so the denial of the registration seems justified.
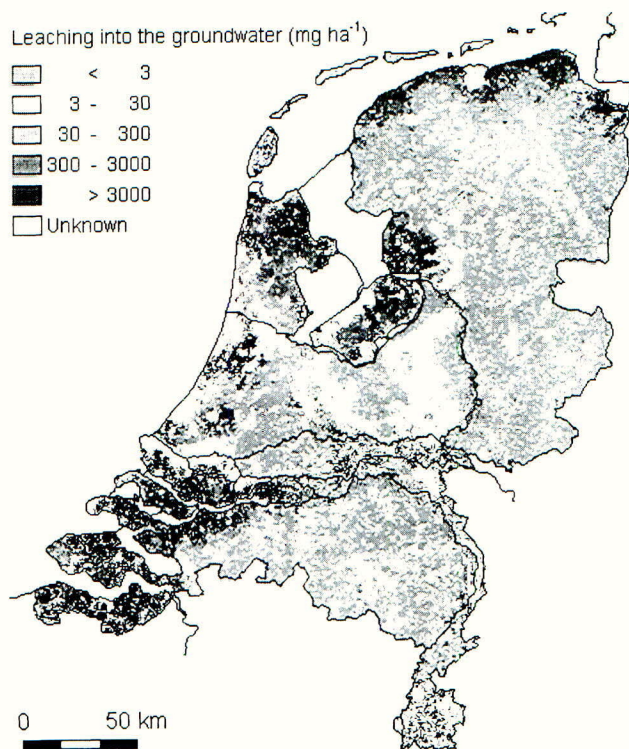

Figure 1. Potential leaching of dinoseb as calculated with GeoPEARL.

Not only sorption might be pH-dependent but transformation also. This was recently shown for a newly developed herbicide, submitted for registration in the Netherlands (name and properties are not given here because of confidentiality), which has two principal metabolites. As for other weak acids, the sorption coefficients declined with increasing pH and the sorption data could be fitted well to the PEARL formula, using the default value of zero for the pH-shift. The transformation rate of this herbicide is also correlated with the pH; the transformation rate increased with pH. As the correlation with pH for the metabolites was rather poor, constant rates were assumed. With both sorption and transformation dependent on the pH, the definition of any potentially vulnerable situations is not obvious. Using corresponding values as input into the PEARL model (while keeping all other input constant), one might cross one or more contour lines in leaching diagrams (Boesten and van der Linden 1991); indicating one or more orders of magnitude difference in leaching. The leaching of this new herbicide and its metabolites was calculated for five scenarios, differing only in pH (Table 1). The pH was assumed to be constant over the whole soil profile. The leaching is indicated as

fraction of the leaching in the scenario with pH 6. It turned out that the calculated leaching for the parent was greatest at pH 6 while for the second metabolite the leaching was greatest at pH 5.5. The calculated leaching for the first metabolite showed a slightly increasing trend towards pH5. The differences are probably due to different relationships of sorption with pH.

Table 1. Leaching of a herbicide and its two principal metabolites showing both pH-dependent sorption and pH-dependent transformation as function of the soil pH.

Substance	Relative leaching (pH 6 = 1) at pH(CaCl$_2$)				
	5	5.5	6	6.5	7
Parent	0.07	0.97	1.00	0.11	0.00
Metabolite 1	2.59	2.50	1.00	0.55	0.36
Metabolite 2	1.00	1.80	1.00	0.60	0.50

DISCUSSION

The pH(CaCl$_2$), with the CaCl$_2$ concentration at 0.005 moles per litre, is usually thought to reflect best the pH of the soil solution under normal field soil conditions. Sorption experiments almost always are performed using such a solution. In transformation experiments, the water content is intended to reflect field conditions, so there also the pH(CaCl$_2$) will best describe the incubation conditions. If other pH measurements are available, it seems best to correct to the pH(CaCl$_2$) value. The correction can be done in the PEARL model by introducing the appropriate pH-shift value. It is however recommended to correct outside PEARL if data from different methods are available.

The surface of soil minerals and soil particulate organic matter is usually charged. The pH value at the surface is up to 2 pH-units lower than the pH of the soil solution. Some authors, e.g. Nicholls and Evans (1984), developed formulae to account for this difference in pH. By means of the pH-shift parameter in the PEARL model, it is also possible to correct for this surface acidity. In the examples shown, but also in other cases, it was not necessary to correct for this effect and the default value of zero led to reasonably good fits. When the pH-shift parameter was fitted, it was not possible to obtain a value between 0 and 2 in any of the cases. The lack of sorption data below the pK$_a$ of the substances made it impossible to draw conclusions on the necessity of the pH-shift parameter.

Often the relation between the sorption coefficient and the pH is described as a log-linear sorption relation (for example, Schellenberg et al., 1984). Such a relation may describe the measured coefficients reasonably well if the pH of the soils is within a few pH units of the pK$_a$ value of the substances. To determine which approach more accurately represents the sorption changes with pH means using sorption data for pH ranges beyond those normally found in agricultural soils, particularly for pH values below the pK$_a$ of the substance. At higher pH, anions may contribute to the sorption and then the overall sorption is underestimated when using a log-linear approach. It will depend on the transformation rate whether in such cases the leaching is also underestimated.

CONCLUSIONS AND RECOMMENDATIONS

The PEARL model has an option to account for pH-dependent sorption. This option is very useful in simulating the leaching behaviour of substances having a pK$_a$ value in the range 3 to

8. With this option, the evaluation of leaching for these substances can be refined and tailor-made decisions can be taken. The theoretical basis of this option has a potential advantage over an approach using empirical log-linear relationships, which are generally used. To determine whether this approach more accurately represents sorption changes with pH further investigations, especially with data from sorption experiments performed at pH values below the pK_a of the substance, are necessary.

The transformation of substances can also be dependent on the soil pH value. PEARL has no option to account for this and therefore a scenario analysis, in which the pH of the soil changes over the relevant range, is recommended to evaluate the leaching in such cases. At the moment it is unclear whether the effect of the pH on the transformation is attributable to the availability of the substance or whether other processes are involved.

The use of information in soil maps and climatic databases is very useful to get insight in the variability of the leaching of substances. This improved knowledge might be used in the registration evaluation process. If transformation is pH-dependent, such evaluations have to be performed for several relevant scenarios.

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Characterisation of sorption for the modelling of pesticide fate

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ABSTRACT

This paper discusses the implications of simplifying assumptions concerning sorption on which the modelling of pesticide fate is traditionally based. Sorption is often measured by intense shaking of soil with large volumes of water. Evidence indicates that the values obtained are not fully applicable to field conditions. The assumption of a characteristic, instantaneous sorption equilibrium is also not valid. This is partly due to the slow diffusion of pesticides into soil aggregates. An inverse relationship is found between the rate of equilibration and aggregate size. The calculation of sorption parameters from Koc values and soil organic carbon content is of sufficient accuracy in many cases, but predictions for soils with low organic carbon contents, including many subsoils, are subject to considerable error. Sorption coefficients and Freundlich exponents from different experiments are often averaged and used as input data for modelling. This approach is not mathematically valid and can introduce bias into environmental risk assessments.

INTRODUCTION

Mathematical simulation models are important tools for assessing the risk that pesticides may pose to the environment. Their capacity to provide a realistic assessment depends to a large extent on a correct description of pesticide sorption. Sorption controls the availablity of a pesticide in the soil solution and hence its potential for transport to water resources. Models have been shown to be very sensitive to sorption parameters, particularly the Freundlich exponent (Dubus *et al.*, 2000). Nonetheless, simplistic assumptions are often made in the characterisation of sorption which necessarily introduce uncertainty into the assessment.

SORPTION EXPERIMENTS AND MODEL PARAMETERISATION

Influence of soil:solution ratio

It is generally assumed that sorption in undisturbed soils in the field can be characterised by the results from batch studies which allow intense contact between the pesticide and soil particles and are carried out at a low soil:water ratio. In the field, soil moisture rarely exceeds field capacity which raises the question of the extent to which measurements in soil slurries give an accurate estimate of sorption in natural soils at realistic moisture contents.

Soil:solution ratio has been shown to influence the sorption coefficients obtained although different studies have given contrasting results. Greater dispersion of soil aggregates during

shaking of the soil-water suspension may expose additional sorption sites and may result in increasing sorption coefficients with increasing soil:solution ratio (Grover and Hance 1970). Conversely, a decrease in sorption coefficients with increasing soil:solution ratios was found by Celorie *et al.*, (1989). Pesticide molecules can be sorbed to suspended solids or dissolved organic matter (Chiou *et al.*, 1986), whereby the apparent concentration in the liquid phase is increased and the sorption coefficient decreased. This effect is more pronounced at larger water contents because the concentration of suspended particles is greater under these conditions. Boesten (1990) concluded from a literature review and a statistical analysis that sorption coefficients are independent of water contents, but sorption experiments should be conducted at water contents as close as possible to field conditions to increase accuracy.

Several methods to determine sorption coefficients under more realistic moisture conditions are available (e.g. Celorie *et al.*, 1989). Walker and Jurado-Exposito (1998) compared sorption determined by standard methodology with that derived from a centrifugation technique which used small volumes of water relative to the mass of soil. Sorption of the herbicides isoproturon, diuron and metsulfuron-methyl was initially smaller using the centrifugation technique than the standard method. This was probably due to the ready availability of sorption sites in the shaken systems. Thus more pesticide may be available for leaching to depth shortly after application than will be predicted from equilibrium sorption coefficients measured in shaken laboratory systems at high water contents.

Sorption non-equilibrium

In standard laboratory experiments, air-dried and sieved soil (2 mm) is shaken with an aqueous pesticide solution. It is assumed that a characteristic distribution of the pesticide between the solid phase of the soil and the solution is established within two to four hours. In longer-term experiments, however, an initial decrease in solution concentration is often followed by a slow further decrease and sorption equilibrium is not reached until several hours or days have passed (Ma and Selim 1994). Natural soils in the field do not comprise uniform 2-mm sieved particles, but are made up of variable-sized aggregates which, during significant leaching events, will be at moisture contents close to field capacity. Recent data have shown that slow equilibration becomes more pronounced as the aggregate size increases, indicating that diffusion to the internal matrix can be a rate-limiting step (Walker *et al.*, 1999; Figure 1).
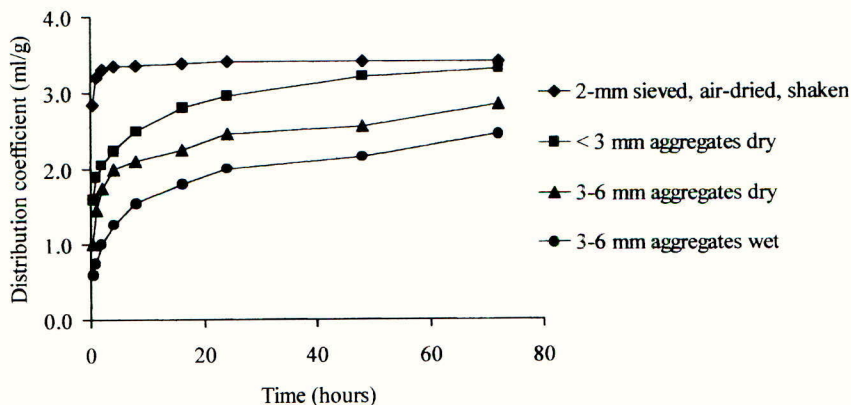

Figure 1. Kinetics of isoproturon sorption by different aggregate classes from a heavy clay soil

Under intense rainfall conditions that promote leaching events, the time for interaction between the pesticide and a soil aggregate is short and equilibrium between sorbed and solution phases will only rarely be achieved. The mechanisms of sorption in flowing systems have not been extensively studied and the true applicability of parameters derived in static systems in the laboratory to flowing systems in the field has not been established.

Influence of soil properties

Sorption is often assumed to be mainly associated with soil organic matter and sorption coefficients are expressed per unit of organic carbon content of the soil (Koc value). The data package for pesticide registration requires estimates of Koc from laboratory studies with a number of soils. Sorption of the pesticide in an untested soil can then be estimated from a knowledge of its organic carbon content and the Koc value. Although this approach can give a good approximation to the average situation, Koc values can vary considerably amongst soils. Koc values for ethofumesate determined in sandy loam soils with organic carbon contents of 1.3 to 7.1% ranged from 203 to 307 ml/g with a coefficient of variation of 14% (Beulke 1998). For metazachlor they varied from 75 to 136 ml/g with a CV of 21% (Figure 2).
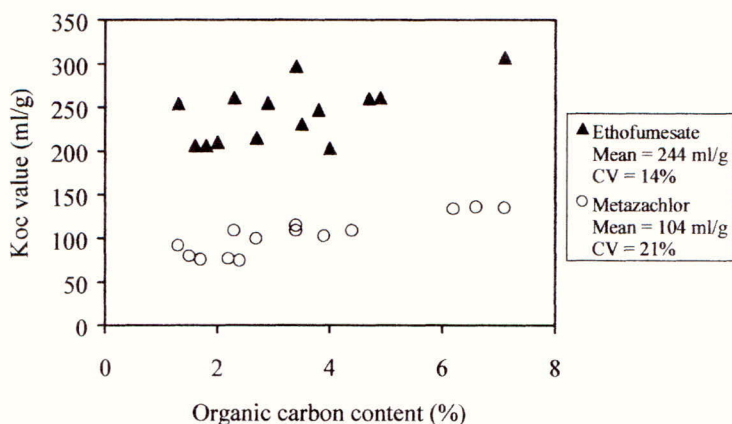

Figure 2. Koc values for ethofumesate and metazachlor in ten soils

The Koc concept assumes that sorption of pesticides to mineral soil constituents can be neglected and that the sorption capacity of organic matter is similar in all soils. These assumptions seem to be valid for hydrophobic, non-polar compounds (Businelli 1993) although Chiou (1989) pointed out that the dominant role of organic matter is restricted to saturated systems. The importance of mineral soil components increases under unsaturated conditions. For polar substances, a strong relationship between sorption and organic matter often cannot be found unless soil organic carbon content varies over a wide range (Calvet 1993).

A further illustration of the limitations in use of the Koc to predict sorption (Figure 3) has been derived from data of Walker and Crawford (1968). There was a highly significant linear correlation between atrazine sorption and soil organic carbon content ($R^2 = 0.97$) with an average Koc of 105 ml/g. However, the data show that use of the Koc concept to predict sorption in soils with low soil organic carbon will be subject to considerable error. Five of the soils used by Walker and Crawford were subsoils, and these had the five lowest organic carbon contents in the dataset shown in Figure 3. Clearly, this raises serious questions over

the confidence with which the Koc approach can be used to derive sorption parameters in deeper soil layers. In this example, however, the selection of the average Koc of 105 ml/g would result in an over-estimation of pesticide leaching and thus be a conservative assessment.
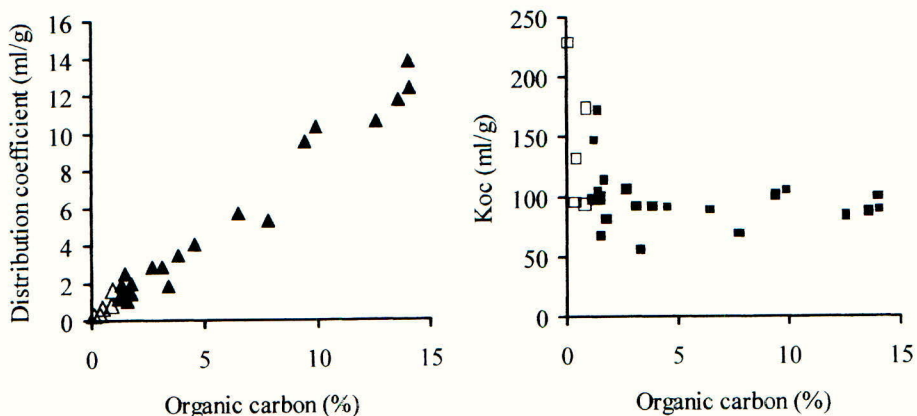

Figure 3. Distribution coefficients and Koc values for atrazine plotted against organic carbon content for five subsoils (Δ, □) and 22 topsoils (σ, v)

The variability in Koc values of a pesticide can be incorporated into assessments of pesticide leaching by probabilistic modelling. This involves sampling a large number of Koc values from statistical distributions and running a simulation model with each of the sampled values. The likelihood of exceeding a threshold concentration in leachate can be quantified on the basis of the resulting distribution of model output. A log-normal distribution is often appropriate to characterise the variability in Koc values (e.g. Novak *et al.* 1997). Data compiled by Gottesbüren (1991) indicate that the distribution of Koc values may follow variable patterns, although the size of the dataset was limited (Figure 4). Further work is needed to evaluate whether Koc values do follow typical statistical distributions and how many measurements are required for their characterisation.
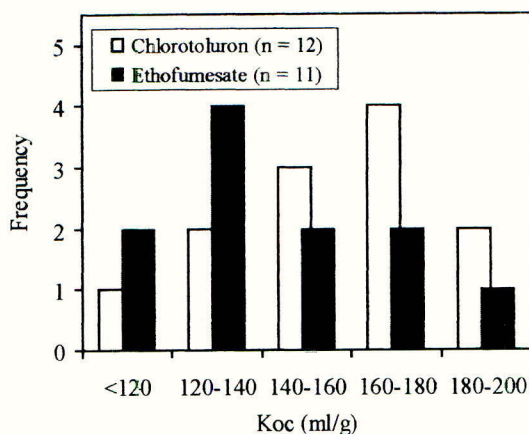

Figure 4. Frequency distributions of Koc values for chlorotoluron and ethofumesate

Averaging non-linear sorption coefficients

The Freundlich isotherm is often used to characterise sorption and another source of error in modelling pesticide fate is associated with the parameterisation of this particular relationship. The Freundlich isotherm has the generalised form:

$$S = K_f \, C^{\frac{1}{n}}$$

with S = sorbed amount (mg/kg), K_f = sorption coefficient (ml/g), C = concentration in solution (mg/l), 1/n = Freundlich exponent. This relationship has two parameters, Kf and 1/n, which must be considered as paired values. For pesticide registration purposes, sorption is determined in experiments with a number of soils. Kf or Koc values from these experiments are averaged and used to predict concentrations of the pesticide in surface water or groundwater. The same procedure is usually followed for the Freundlich exponent. This approach is not valid in a mathematical sense The predicted concentration resulting from the mean sorption coefficient and 1/n value differs from the average of simulations carried out separately for each of the four combinations. This is due to non-linearity in the Freundlich isotherm and in the relationship between sorption and pesticide leaching.

Concentrations in leachate of two hypothetical pesticides were calculated using the FOCUS groundwater scenario for Hamburg (FOCUS 2000) to demonstrate the effect of averaging sorption parameters. It was assumed that sorption was measured in four soils (Table 1). Application was made once a year at 1 kg/ha to winter cereals one day before crop emergence. Simulations were carried for 26 years using the model PELMO FOCUS 1.1.1. Concentrations for the years 6-26 were used for evaluation (FOCUS 2000). Data simulated for these 20 years and each of the four pairs of Koc and 1/n values (80 concentrations) were combined, sorted in ascending order and the overall 80th percentile concentration was derived. This was compared with the 80th percentile concentration for average Koc and 1/n values (Table 1).

Table 1. 80th percentile concentrations in leachate at 1-m depth simulated with PELMO for 4 pairs of Koc and 1/n values and for average parameters (degradation half-life = 30 d)

Pesticide 1			Pesticide 2		
Koc	1/n	80th percentile concentration	Koc	1/n	80th percentile concentration
(ml/g)		(μg/l)	(ml/g)		(μg/l)
50	0.87	6.68	100	0.87	0.117
59	0.70	0.001	118	0.70	<0.001
45	0.95	15.3	90	0.95	1.97
70	0.90	2.69	140	0.90	0.020
Overall		**8.35**	Overall		**0.55**
56 (mean)	0.86 (mean)	**4.05**	112 (mean)	0.86 (mean)	**0.019**

Large differences were found between the overall 80th percentile concentration derived from individual runs with paired Koc and 1/n values and the concentration simulated on the basis of average parameters (Table 1). Discrepancies were larger for the more strongly sorbed pesticide 2 (factor 28) than for pesticide 1 (factor 2.1). Results for the two hypothetical pesticides and the single soil scenario used in this study cannot be generalised and the effect is likely to be smaller when 1/n is closer to 1. However, simulated pesticide leaching is often very sensitive to Koc and 1/n and averaged parameters should be used with care.

CONCLUSIONS

The modelling of pesticide sorption is based on simple concepts which were developed several decades ago. Some simplifications may be insignificant at the macroscopic scale, but others restrict our ability to accurately assess the transport of pesticides to water resources. The implications of the strong variability and uncertainty in sorption parameters are just beginning to be considered. A refinement of sorption concepts and further work on innovative experimental and modelling techniques are needed to address these issues.

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