SESSION 2

SORPTION AND MOBILITY (SMALL SCALE)

Chairman &   Dr R H Bromilow
Session Organiser: *IACR-Rothamsted, Harpenden, UK*

Effect of long-term sorption kinetics on leaching as calculated with the PEARL model for FOCUS scenarios

J J T I Boesten
Alterra, PO Box 47, 6700 AA Wageningen, The Netherlands
Email: boesten@alterra.wag-ur.nl

A M A van der Linden
RIVM, PO Box 1, 3720 BA Bilthoven, The Netherlands

ABSTRACT

Accurate estimation of pesticide/soil input parameters for leaching models such as PEARL is of paramount importance for meaningful use of these models in registration procedures. Adding non-equilibrium sorption into PEARL can alter the estimated transformation rate to be used as input to the model, and this effect was examined. We found that this transformation rate (as compared to the rate used when only equilibrium sorption is assumed) has to be multiplied by a correction factor whose value will often be close to 1.0 plus the quotient of the non-equilibrium Freundlich sorption coefficient divided by the equilibrium Freundlich sorption coefficient. This correction has a significant effect on calculated leaching in most cases. We recommend the re-evaluation of the available transformation rate studies whenever non-equilibrium sorption is included in leaching assessments with PEARL.

INTRODUCTION

The FOCUS groundwater scenarios have recently been developed for assessment of pesticide leaching in the EU registration process (FOCUS, 2000). These scenarios have been parameterised for four models, one of which is PEARL. Within the FOCUS scenarios, all parameters are fixed except the properties of the pesticide and its interaction with soil. Sorption parameters in PEARL have a large effect on calculated leaching, and so their estimation is of paramount importance. Sorption in PEARL is described with a two-site model: sorption at site 1 is an equilibrium process described by a Freundlich isotherm whereas sorption at site 2 is a non-equilibrium process described by pseudo first-order kinetics. The FOCUS guidance for input parameters recommends that non-equilibrium sorption should be ignored unless substance-specific data are available. Adding non-equilibrium sorption to a version of the PESTLA model that contained the same two-site sorption model as is used in PEARL considerably reduced the predicted leaching (Boesten, 1991). However, calculations with PEARL showed that adding non-equilibrium sorption had almost no effect on calculated leaching and sometimes even increased leaching (B Gottesbüren & J R van de Veen, personal communication, 2000). There is a conceptual difference in the description of the transformation rate between this PESTLA version and PEARL: in PESTLA it is assumed that the rate is proportional to the total system concentration whereas PEARL assumes that the rate is proportional to the concentration in the equilibrium domain only, thus excluding the amount sorbed at the non-equilibrium site. In this study we attempt to elucidate how this conceptual difference in the description of the transformation rate may cause the difference in calculated leaching when non-equilibrium sorption is included.

SHORT DESCRIPTION OF THE PEARL MODEL

We describe here briefly the most relevant parts of the PEARL model (Leistra *et al.*, 2001). The concentration of pesticide in the soil system, $c*$, is given by:

$$c* = \theta c + \rho X_{EQ} + \rho X_{NE} \qquad (1)$$

in which θ is volume fraction of water, ρ is dry bulk density, c is pesticide concentration in liquid phase and X_{EQ} and X_{NE} are contents of pesticide sorbed at the equilibrium and non-equilibrium site, respectively. PEARL includes also pesticide present in the gas phase but we ignore this here because it is not relevant for this study. Sorption at the equilibrium site is described by a Freundlich isotherm:

$$X_{EQ} = K_{EQ} c_R \left(\frac{c}{c_R} \right)^N \qquad (2)$$

in which K_{EQ} is the Freundlich coefficient, N is the Freundlich exponent and c_R is a reference value of c (set at 1 mg L^{-1}). Sorption at the non-equilibrium site is described with pseudo first-order kinetics:

$$\frac{\partial X_{NE}}{\partial t} = k_D \left[F K_{EQ} c_R \left(\frac{c}{c_R} \right)^N - X_{NE} \right] \qquad (3)$$

in which t is time, k_D is the desorption rate coefficient and F is the quotient of the Freundlich non-equilibrium coefficient divided by the Freundlich equilibrium coefficient.

PEARL assumes that the rate of transformation of pesticide, R_T, is proportional to the concentration in the equilibrium part of the system:

$$R_T = k_{T,EQ}(\theta c + \rho X_{EQ}) \qquad (4)$$

in which $k_{T,EQ}$ is the rate coefficient for transformation in the equilibrium part of the system. We define the half-life for transformation in the equilibrium part of the system as $H_{EQ} \equiv \ln2 / k_{T,EQ}$. Eq. 4 implies that pesticide sorbed at the non-equilibrium site is not transformed. Theoretically it would be more consistent to assume no transformation at the equilibrium site either (so only transformation in liquid phase). However, this would imply that half-lives that are usually available from pesticide registration procedures cannot be used directly as input to PEARL which is undesirable. Eq. 4 has the advantage that it is fully consistent with other models if non-equilibrium sorption is ignored. The pesticide flux in the gas phase is described by Fick's law and that in the liquid phase by a convection/dispersion equation.

EFFECT OF NON-EQUILIBRIUM SORPTION PARAMETERS ON ESTIMATED TRANSFORMATION RATES

Procedure

The normal procedure in pesticide registration is to derive half-lives from transformation rate studies in the laboratory assuming first-order kinetics. However, it is questionable whether such half-lives are accurate enough to be used as input to PEARL if sorption at non-equilibrium sites is included. This was tested as follows: (i) it was assumed that the PEARL submodel for transformation and sorption as described by Eqns 2 to 4 is valid, (ii) using this submodel (Eqns 1 to 4), the course of the remaining amount of pesticide in time was calculated with a small FORTRAN programme for hypothetical laboratory transformation studies for a range of half-lives (H_{EQ}) and sorption coefficients, (iii) this course in time was fitted to first-

order kinetics for the total remaining amount which implies that the transformation rate is assumed to be proportional to the total system concentration:

$$R_T = k_{T,SY} c * \qquad\qquad\qquad (5)$$

in which $k_{T,SY}$ is the transformation rate coefficient for the system concentration. We define the half-life for transformation of the system concentration as $H_{SY} \equiv \ln2 / k_{T,SY}$.

In the calculations, dry bulk density was 1.0 g/ml and the volume fraction of water was 0.2. The initial pesticide concentration was 1.0 mg/L (initially present in the equilibrium part of the system). The Freundlich exponent was 0.9 and pesticide was assumed not to be present in the gas phase. The Freundlich coefficient for the equilibrium site, K_{EQ}, varied from 0 to 4 L/kg (i.e ranging from 0 to about 95% sorption). The half-life H_{EQ} varied between 1 and 1000 days. The default values $F = 0.5$ and $k_D = 0.01$ d^{-1} as recommended in the PEARL manual were used (Tiktak *et al.*, 2000, p. 50). In each run, the calculation period was three times the half-life H_{EQ}. Eqns 3 and 4 were integrated using rectilinear integration with a time step of less than 2% of H_{EQ} to ensure sufficient accuracy.

The course of the amount remaining with time was characterised by 100 points in time equally spaced. These 100 points were fitted to first-order kinetics using linear regression after log-transformation which resulted in a value of H_{SY}. The results are analysed in terms of the quotient defined as $Q \equiv H_{SY} / H_{EQ}$. So the deviation of Q from unity is a measure for the differences in half-lives derived from laboratory studies via fitting to first-order kinetics and the corresponding equivalent half-lives that should be used as input for the PEARL model.

Results

Figure 1 shows that the quotient Q increases with increasing equilibrium sorption coefficient. As could be expected, Q is always 1 at zero sorption because then non-equilibrium sorption has no effect on the system. The figure shows also that Q increases when the half-life increases from 1 to about 100 days. However, when the half-life increases to higher values, Q decreases again. For a half-life of 1000 days and a sorption coefficient of about 4 L/kg, Q is about 1.5. Figure 1 shows that Q approaches 1 when the half-life approaches zero. This may be understood as follows: at very short half-lives, non-equilibrium sorption will have a negligible effect on the decline in the system for times up to three times the half-life H_{EQ} so the effect of non-equilibrium sorption is not detectable in the fitting procedure.

This explanation suggests that the fitting procedure itself has an effect on Q for short half-lives. We checked this via an alternative procedure in which the simulation period was fixed to 100 days instead of to three times the half-life H_{EQ}. This resulted indeed in a completely different relationship between Q and H_{EQ}: now Q approached infinity when H_{EQ} approached 0. This is understandable because a simulation period of 100 days for a half-life H_{EQ} of a few days implies a fast decline for about the first 10 days, followed by a slow decline of the last few percent left in the remaining 90 days. The fitting procedure for H_{SY} is then dominated by the slow decline which results in high Q values.
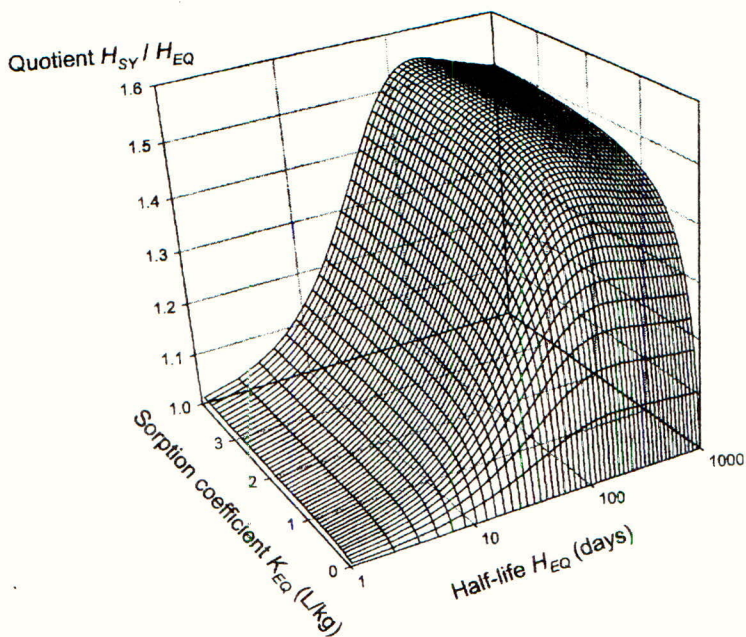
Quotient H_{SY} / H_{EQ}

Sorption coefficient K_{EQ} (L/kg)

Half-life H_{EQ} (days)

Figure 1.   The quotient Q of the half-life for transformation of the system concentration (H_{SY}) divided by the half-life for transformation of the equilibrium part of the system concentration (H_{EQ}) as a function of both the Freundlich equilibrium sorption coefficient (K_{EQ}) and the half-life H_{EQ}.

Now we attempt to analyse quantitatively the behaviour of Q at long half-lives. If the decline resulting from transformation is slow as compared to sorption kinetics, X_{NE} will approach its equilibrium value after some time and remain close to that value. In this analysis we assume that the Freundlich exponent is 1 (so linear sorption isotherm). This will be closely approximated because $N = 0.9$. It is assumed that sorption at the non-equilibrium sorption site can be approximated by assuming equilibrium. Then elimination of c from Eqn 4 using Eqn 1, leads to the following rate equation:

$$R_T = k_{T,EQ} \left[\frac{\theta + \rho \, K_{EQ}}{\theta + \rho \, (1 + F) \, K_{EQ}} \right] c* \qquad (6)$$

So these approximations imply that the transformation rate is both proportional to the equilibrium part of the system concentration and to the system concentration itself. Combination of Eqns 5 and 6 leads to the following expression for Q:

$$Q = \frac{\theta + \rho \, (1 + F) \, K_{EQ}}{\theta + \rho \, K_{EQ}} \qquad (7)$$

If sorption is high, θ can be ignored in Eqn 7 which then reduces to $Q = 1 + F$, so $Q = 1.5$ in our case. This corresponds well with the result found in Figure 1 for long half-lives and strong sorption. We checked for $H_{EQ} = 1000$ d whether Eqn 7 is also a reasonable approximation for the range of K_{EQ} from 0 to 4 and found that the value predicted by Eqn 7 differed always by

30

less than 5% from the calculated values shown in Figure 1. The approximation by Eqn 7 suggests that Q is more or less proportional to $1+F$. We checked this via calculations for $F = 4$ and found indeed a graph with a shape similar to that shown in Figure 1 but with Q approaching 5 for long half-lives and strong sorption as was expected.

SENSITIVITY OF LEACHING CALCULATED FOR FOCUS GROUNDWATER SCENARIOS: THE EFFECT OF ADDING NON-EQUILIBRIUM SORPTION

The previous analysis showed that there is interaction between the selection of the non-equilibrium sorption parameters and the selection of the half-life H_{EQ} within PEARL. We will assess the importance of this interaction via calculations for the Kremsmünster FOCUS scenario (FOCUS, 2000) using FOCUS PEARL v1.1.1. All pesticide parameters except K_{OM}, H_{EQ}, F and k_D were taken to be those for substance D as described by FOCUS (2000, p. 61). The crop was winter wheat and the pesticide was assumed to be applied to soil at a rate of 1.0 kg/ha on 1 May. Leaching was calculated as a function of K_{OM}. We compared calculations in which non-equilibrium sorption is excluded (i.e. $F = k_D = 0$) with calculations in which it is included using the default values for F and k_D recommended by Tiktak et al. (2000), so $F = 0.5$ and $k_D = 0.01$ d^{-1}. The calculations in which non-equilibrium sorption is excluded will be called "the EX calculations" and those including this sorption will be called "the IN calculations".

We consider the following case: the half-life for both EX and IN calculations was based on the same transformation rate study carried out in the laboratory with a soil having 3% organic matter and with other system properties as used for calculating Figure 1. In the normal practice of pesticide registration, four transformation rate studies would be used instead of one but we limit ourselves here to only one study for illustrative purposes. We consider two transformation rates and assume that the results of the transformation rate study can be described well with Eqn 5 using either a half-life H_{SY} of 10 or 100 days. This implies for the EX calculations that the half-life H_{EQ} was fixed at either 10 or 100 days because it is then by definition equal to the half-life H_{SY}. For the IN calculations the half-life H_{EQ} had to depend on the selected K_{OM} value to ensure consistency with the laboratory study: we calculated H_{EQ} via requiring that the selected combination of K_{EQ} and half-life H_{EQ} resulted in a half-life H_{SY} of 10 or 100 days for the transformation rate study. This was done via the same procedure as used for calculating Figure 1. This implies that the half-life H_{EQ} (used as input to PEARL) decreases with increasing K_{OM} for the IN calculations. For instance, for $H_{SY} = 10$ days, the selected half-life H_{EQ} decreased from 10 to 9.08 days if K_{OM} increased from 0 to 30 L/kg; for $H_{SY} = 100$ days, the selected half-life H_{EQ} decreased from 100 to 68 days if K_{OM} increased from 0 to 200 L/kg. The background of this is that the fraction of c^* that is present at the non-equilibrium site increases with increasing K_{OM} and that this fraction is not subject to transformation.

The predicted concentrations in leachate (Figure 2) show that the difference between IN and EX calculations increased with increasing K_{OM} as would be expected because by definition there is no difference at zero sorption. The difference between EX and IN calculations is larger at the half-life of 100 days than at the half-life of 10 days. For illustrative purposes we also made calculations in which non-equilibrium sorption was added but without correcting the half-life H_{EQ} (thus violating the requirement that the transformation rate in the laboratory study had to be described well). Figure 2 shows that then almost no difference was found between IN and EX calculations. This shows that including non-equilibrium sorption is only meaningful if the transformation rate is re-evaluated to be consistent with the results of the laboratory studies.
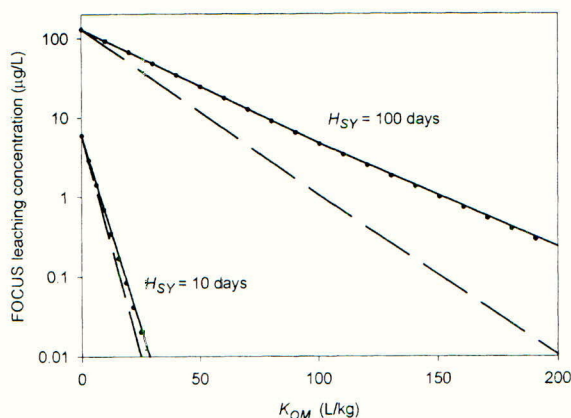
Figure 2.   The concentration of an example pesticide leaching to groundwater as a function of K_{OM} as calculated with PEARL for the Kremsmünster FOCUS scenario and winter wheat after application of 1.0 kg/ha to soil on 1 May. Solid line: equilibrium sorption only; dashed line: non-equilibrium sorption included and half-life H_{EQ} corrected based on laboratory study on transformation rate; dotted line: non-equilibrium sorption included but half-life H_{EQ} not corrected.

CONCLUSIONS AND RECOMMENDATIONS

If non-equilibrium sorption is used in a PEARL calculation, the transformation rate to be used has to be multiplied by a correction factor that ranges between 1.0 and about 1.0 plus the quotient of the non-equilibrium Freundlich sorption coefficient divided by the equilibrium Freundlich sorption coefficient. This correction leads to a substantial decrease of calculated leaching in most of the cases. We recommend the re-evaluation of the available transformation rate studies if non-equilibrium sorption is included in leaching assessments with PEARL. Given the complexity, inclusion of non-equilibrium sorption is only recommended for higher-tier evaluations.

REFERENCES

Boesten J J T I (1991) Sensitivity analysis of a mathematical model for pesticide leaching to groundwater. *Pesticide Science* **31**: 375-388.

FOCUS (2000) FOCUS groundwater scenarios in the EU review of active substances. Report of the FOCUS Groundwater Scenarios Workgroup, EC document Sanco/321/2000 rev. 2, 197 pp. Available at http://arno.ei.jrc.it/focus.

Leistra M; van der Linden A M A; Boesten J J T I; Tiktak A; Van den Berg F (2001). PEARL model for pesticide behaviour and emissions in soil-plant system; Description of the processes in FOCUS PEARL v 1.1.1. Alterra report 13, RIVM report 711401009, 117 pp. Available at www.alterra.nl/models/pearl.

Tiktak A; Van den Berg F; Boesten J J T I; Leistra M; Van der Linden A M A; Van Kraalingen D W G (2000). Manual of FOCUS PEARL version 1.1.1. RIVM report 711401008, Alterra report 28, 144 pp. Available at www.alterra.nl/models/pearl.

The measurement of time-dependent desorption and its influence on modelling movement of a pesticide metabolite through soil to groundwater

C R Leake, C M Burr, I A J Hardy, S L McMillan-Staff, G Reinken, R J Wicks
Aventis CropScience, Ongar Research Station, Ongar, Essex, CM5 0HW, UK
Email: christopher.leake@aventis.com

ABSTRACT

To explain the differences observed between modelling predictions and movement in the field of a pesticide metabolite, the influence of time on soil desorption processes was studied with eight contrasting soil types. In comparison with the standard adsorption/desorption approach, a significant increase in retention with time of the (predicted to be rather mobile) metabolite was observed. Data from four contrasting field sites showed that under European field conditions the compound remained mainly in the surface 10cm layer. Estimation of leaching using computer models has traditionally been conducted using the Freundlich adsorption K_{oc} value and the first-order-kinetics half-life as input values. When modelling potential movement to deeper soil layers, both desorption characteristics and hysteresis effects, together with their dependence with time, have an important role. In modelling the movement of this metabolite in soil, movement was over-predicted when using parameters from the non-aged samples when compared with field data. In contrast, modelling with the time-dependent desorption data, even over relatively short ageing periods of 3 days and 10 days, resulted in a significant improvement in predicted movement. To improve the model predictions of chemical movement in soil, desorption characteristics and their time dependence should be included in the model input and processing.

INTRODUCTION

In the assessment of likely leaching potential of plant protection products and their major metabolites, the accepted approach is to measure the K_{OC} in a range of soil types, normally at least four, over a range of at least five concentrations (OECD Guideline 106, 2000). Although the desorption characteristics may also be determined, it is currently not standard practice to use these data in the estimation of the movement of compounds in soil or in calculations of potential concentrations in groundwater. The phenomenon of hysteresis has been recognised for many years e.g. Bailey & White 1964; Green 1974; Calvet 1980; Koskinen 1990; Zhu & Selim 2000. More recently the effect of time on the sorption processes has also been shown to be important (Walker *et al.*, 1995; Cox & Walker 1999; Oi 1999). The FOCUS Ground-water Scenarios Working Group has identified time-dependent sorption processes as a major factor influencing the uncertainty of model predictions for those compounds that show a significant increased sorption over time (FOCUS, 2000). This investigation was conducted to determine a possible explanation for the discrepancy observed for the metabolite, between the predicted movement in soil by modelling and results from field studies.

MATERIALS AND METHODS

The adsorption of the radiolabelled metabolite was investigated in four contrasting soil types and in a sediment using four concentrations (0.04, 0.2, 1 and 5 mg L^{-1}) (Burr 1999), based on the OECD guideline 106. In preliminary studies, an adsorption equilibrium time of 48 hours and a desorption equilibrium time of 1 hour were obtained, and a soil to solution ratio of 1:3 was established. In addition to the adsorption phase, up to five desorption cycles were performed by removal of the supernatant solution and replacement with fresh 0.01M CaCl$_2$. A quantitative recovery of the radioactivity was obtained, by summation of that in the supernatant solutions, that present in the solvent extracts of the soils and that released by combustion of the remaining soil. The Freundlich adsorption constants K$_f$ and the 1/n values for each soil were calculated using the Freundlich equation taking into account the concentration of the metabolite in the residual soil water. The K$_f$ values were then expressed as K$_{OC}$ values according to the organic-carbon content of each soil.

To investigate the effect of time on the desorption process, two further experiments were conducted. In the first (McMillan-Staff 1999), the design of which was based on the OECD guideline (2000), the radiolabelled metabolite was applied to 15 g portions (dry soil equivalent) to each of four contrasting soils at four equivalent concentrations (0.04, 0.2, 1 and 5 mg L^{-1}) for each soil. The metabolite was added in this case directly to the soil so each soil sample received either 375 μg, 75 μg, 15 μg or 3 μg of the metabolite. Some soil samples then had 75 ml of 0.01M CaCl$_2$ added and were shaken at 20°C for 24 hours. This was followed by centrifugation, removal of the supernatant solution and replacement with fresh 0.01M CaCl$_2$ for a total of up to four cycles. The remaining samples were incubated at 45% of the soil moisture content at 20°C in the dark for either 3 days or 10 days. After the incubation period of either 3 days or 10 days, the samples were treated in the same manner as the time zero samples. In the second experiment to investigate the effect of time on the desorption process, a similar design was employed. Four contrasting soils were obtained from field sites in Europe. In preliminary investigations, an adsorption equilibrium time of 48 h and a desorption equilibrium time of 24 h were obtained, with a 1:3 soil to solution ratio (Burr 2000). The four concentrations were 0.04, 0.2, 1 and 5 mg L^{-1} and the samples were analysed immediately and after 3 days and 10 days ageing at 45% of maximum water holding capacity. There was identical handling of the data as in the adsorption experiment

A terrestrial field dissipation study was conducted at four sites in Europe: Bologna, Italy; Chazay, Southern France; Goch, Germany and Manningtree, UK (Wicks 1999). Plots were treated with the parent compound at a nominal rate of 1600 g a.i ha^{-1} to bare soil. Four plots at each site were sampled during the first 12 months after application with five samples per plot at 10 cm incremental depths to 30 cm and then sampling to 60 cm. Samples were composited within each plot at each depth. A limit of quantification of 0.005 mg kg^{-1} (wet weight), which was equivalent to 7.5 g ha^{-1} or about 9 g ha^{-1} on a dry weight basis, was obtained for both the parent compound and the metabolite. Soil samples were frozen, shipped and stored frozen for up to 6 months. Analysis was by Accelerated Solvent Extraction with water:acetone 20:80 followed by LC/MS/MS.

For all model calculations the simulation model PELMO (PEsticide Leaching MOdel) version 3.00 after Service Pack II (Feb 2000) was used, chosen as it is one of the recommended European registration models (Kloskowski and Nolting 1998; FOCUS 2000).

RESULTS AND DISCUSSION

The initial adsorption study with the metabolite (Burr 1999) showed that the K_{oc} value was relatively low and that the $1/n$ value was significantly below 1 (Table 1). The overall recovery of radioactivity was good, ranging from 97.8 to 99.8%.

Table 1. Organic carbon (OC), K_f, $1/n$ and K_{oc} values for the metabolite under standard adsorption conditions

Soil type (USDA)	OC (%)	K_f (L kg^{-1})	$1/n$	K_{oc} (L kg^{-1})
Silt loam	0.5	0.11	0.832	23
Sandy loam	1.2	0.43	0.867	36
Sandy clay loam (sediment)	2.3	0.64	0.957	28
Silt loam II	1.9	0.32	0.811	17
Loam	2.0	0.56	0.821	28
Overall mean values (excluding the sediment)			0.83	26

The adsorption determination for the metabolite in the four contrasting field soils confirmed the low K_{oc} value when measured by the standard OECD test (Table 2).

Table 2. Metabolite adsorption on the four field soils.

Soil type (USDA)	OC (%)	K_f (L kg^{-1})	$1/n$	K_{oc} (L kg^{-1})
Bologna (clay loam)	1.3	0.36	0.889	28
Chazay (loam)	1.5	0.38	0.895	25
Goch (silt loam)	2.5	0.88	0.858	35
Manningtree (sandy loam)	1.1	0.26	0.915	24
Overall mean values			0.89	28

This indicated that the metabolite was a potentially mobile compound under field conditions. Laboratory aerobic metabolism studies (not presented in this paper) indicated a soil half-life at 20°C in excess of 100 days. However the desorption data in the batch/equilibrium study showed significant hysteresis in all the soil types (Figure 1). Data from the field dissipation study in four contrasting soil type/climatic regions in which the precipitation plus irrigation was in excess of the historical average showed the majority of the metabolite residues remained in the surface 0-10 cm layers. During a 12-month period, no movement was detected below 20 cm at three of the sites and no movement below 30 cm at the fourth site (Table 3). These results were not consistent with the predicted movement using the standard batch/equilibrium model input parameters.
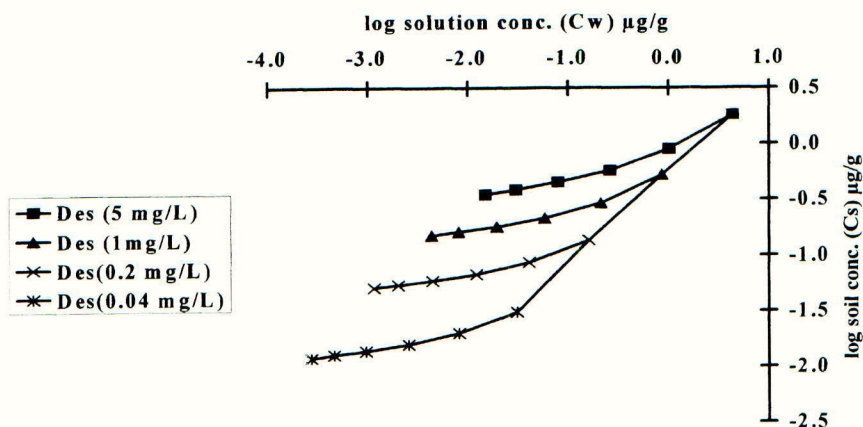
Figure 1   Desorption hysteresis as a function of treatment concentration in loam soil.

Table 3.   Distribution with depth of metabolite (concentration in g ha^{-1}) in the four field locations.

Location/ Soil	Depth (cm)	3 Day	7 Day	14 Day	1 Mon	2 Mon	4 Mon	6 Mon	9 Mon	12 Mon
Clay loam (Bologna, Italy)	0-10	<LQ	38.9	32.6	46.3	60.7	25.9	16.7	<LQ	-
	10-20	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	-
	20-30	-	-	-	<LQ	<LQ	<LQ	-	-	-
	30-60	-	-	-	-	-	-	-	-	-
Loam (Chazay, France)	0-10	34.9	47.2	98.4	40.4	53.1	<LQ	<LQ	<LQ	-
	10-20	-	<LQ	<LQ	<LQ	19.9	11.8	<LQ	<LQ	-
	20-30	-	-	<LQ	<LQ	<LQ	<LQ	<LQ	-	-
	30-60	-	-	-	-	-	-	<LQ	-	-
Silt loam (Goch, Germany)	0-10	<LQ	<LQ	34.3	68.1	71.8	55.0	28.0	20.1	18.5
	10-20	-	<LQ	<LQ	<LQ	<LQ	<LQ	12.3	11.9	<LQ
	20-30	-	-	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ	<LQ
	30-60	-	-	-	-	-	-	-	-	-
Sandy loam (Manningtree, UK)	0-10	15.7	54.0	71.7	40.8	89.1	44.5	14.3	18.5	22.4
	10-20	-	-	<LQ	<LQ	19.8	39.2	16.9	16.2	13.9
	20-30	-	-	-	<LQ	<LQ	<LQ	9.1	12.1	10.7
	30-60	-	-	-	-	-	-	<LQ	<LQ	<LQ

Mon = Month   <LQ = Less than the limit of quantification of 9 g ha^{-1} - = Not determined

The significant increase in the $K_{oc\ des1}$ value over the relatively short periods of 3 days and 10 days (Table 4) indicates the potential effect over a longer period is likely to be even greater. A linear relation can be found between the square root of the time interval for desorption ("ageing period") and the increase in the effective sorption. This linear relationship found for all eight soils is indicative of a possible diffusive-type sorption mechanism (e.g. diffusion of the metabolite into the soil or soil organic matrix).

Table 4.   Metabolite-aged desorption determinations on eight soils at three time intervals.

Soil reference (USDA)	Day 0 $K_{oc\ des1}$	Day 3 $K_{oc\ des1}$	Day 10 $K_{oc\ des1}$
Loam	18 (1)	43 (2.4)	56 (3.1)
Sand	23 (1)	70 (3.0)	105 (4.6)
Clay loam	11 (1)	34 (3.1)	57 (5.2)
Silt loam (sediment)	32 (1)	41 (1.3)	ND
Bologna (clay loam	26 (1)	43 (1.7)	61 (2.3)
Chazay (loam)	25 (1)	26 (1.0)	53 (2.1)
Goch (loam)	31 (1)	50 (1.6)	61 (2.0)
Manningtree (sandy loam)	22 (1)	52 (2.4)	62 (2.8)
Overall mean values	23.5 (1)	44.9 (1.9)	65.0 (2.8)

ND – Not determined. Figures in parentheses are ageing factors, calculated by dividing by the K_{ocdes1} at Day 0.

Modelling the movement in the soil profile was undertaken using the PELMO 3.0 model applying the actual application rates (900 g ha^{-1} every third year) and effective crop interception, (50-80% for potatoes).   In addition to the standard input values for the metabolite, the K_{OC} values were changed to reflect the aged K_{ocdes1} values. The average penetration depth after 7 months was estimated to be 14 cm using 3-day desorption data and 11 cm with 10-day desorption data (Figure 2). The inclusion of the desorption data in the model showed that the distribution with depth was more consistent with the field data where the metabolite was mainly confined to the 0-10 cm layer at all four sites, with little movement to the 10-20 cm or 20-30 cm layers. Consequently the movement of the metabolite in soil can only be accurately modelled when the time-dependent desorption is taken into account.
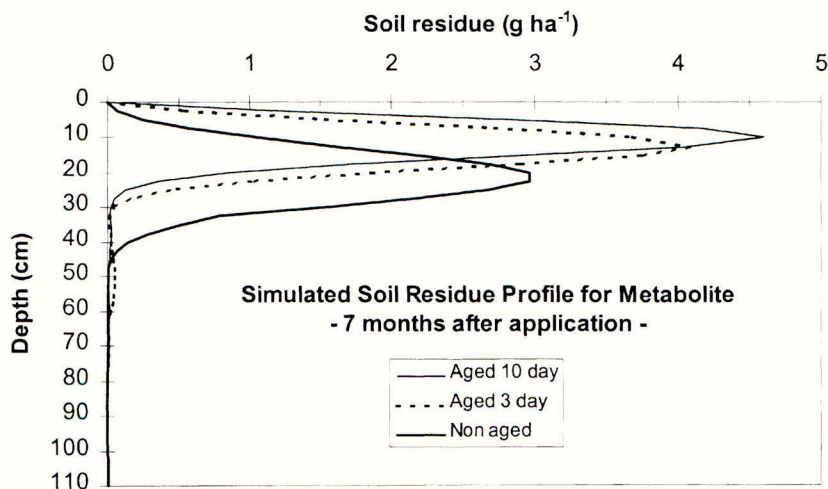

Figure 2. Example of the simulated profile for the metabolite in soil demonstrating the relative effect of ageing.

CONCLUSIONS

In modelling the movement of plant protection products and their metabolites in soil, the desorption characteristics may be of greater importance than the adsorption K_{OC}. Also, even over relatively short periods (up to 10 days), the time dependence of the desorption characteristics is important and though there is currently much less information available, it is likely that the increase will continue for longer time periods. To improve modelling predictions, both the desorption characteristics and their time dependence should be included.

REFERENCES

Bailey G W; White J L (1964). Review of adsorption and desorption of organic pesticides by soil colloids, with implications concerning pesticide bioactivity. *J. Agric. Food Chem* **12**: 324-332.

Burr C M (1999) [^{14}C]-RPA 412636: Adsorption/desorption to and from four soils and a sediment. Aventis CropScience Report 201886.

Burr C M (2000) [^{14}C]-RPA 412636: Adsorption to and aged desorption from four European soils obtained from field dissipation study sites. Aventis CropScience Report 202660.

Calvert R (1980) Adsorption-desorption phenomena In: *Interactions Between Herbicides and the Soil*.ed. R J Hance, Academic Press, London.

Cox L; Walker A (1999) Studies of time dependent sorption of linuron and isoproturon in soils. Chemophere **38**: 2707-2718.

FOCUS (2000) FOCUS groundwater scenarios in the EU plant protection product review process. Final report of the FOCUS Groundwater Scenarios Workgroup, EC Document Reference Sanco/321/2000 rev.2: 1-202.

Green R E (1974). Pesticide-clay-water interactions. In: *Pesticides in Soil and Water*. ed. W D Guenzi, pp 3-66 SSSA, Madison, WI. USA.

Kloskowski R; Nolting H-G (1998) Mitteilungen - Die Abteilung fuer Pflanzenschutz und Anwendungstechnik der Biologischen Bundesanstalt gibt bekannt: Offizialisierung von PELMO 3.00. Nachrichtenblatt des Deutschen Pflanzenschutzdienstes, Vol 50, No 10: 271.

Koskinen W C; Harper S S (1990) The retention process: Mechanisms. In: *Pesticides in the Soil Environment : Processes, Impacts and Modelling*. ed H H Cheng, pp 51-77 SSSA, Madison, WI. USA.

McMillan-Staff S L (1999) [^{14}C]-RPA 412636: Aged desorption. Aventis CropScience Report 202127.

OECD Guideline for the Testing of Chemicals- Adsorption–Desorption Using a Batch Equilibrium Method. Adopted 21st Jan 2000. OECD Paris

Oi M (1999) Time-dependent sorption of imidacloprid in two different soils. *J. Agric. Food Chem.* **47**: 327-332.

Walker A; Welch S J; Turner I J (1995) Studies of time-dependent sorption processes in soils. *Proceedings of the BCPC Symposium – Pesticide Movement to Water 1995* pp. 13-18. ed A Walker, R Allen, S W Bailey, A M Blair, C D Brown, P Gunther, C R Leake and P H Nicholls.

Wicks R J (1999) Field dissipation study in Europe. Aventis CropScience Report 202140.

Zhu H; Selim H M (2000) Hysteretic behaviour of metolachlor adsorption-desorption in soils. *Soil Science* **165**: 632-645