

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

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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:

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

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:

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

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:

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

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:

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

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 $H_{EQ} \equiv \ln 2 / k_{T,EQ}$. 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:

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

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 $H_{SY} \equiv \ln 2 / k_{T,SY}$.

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 $k_D = 0.01 \text{ d}^{-1}$ 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.

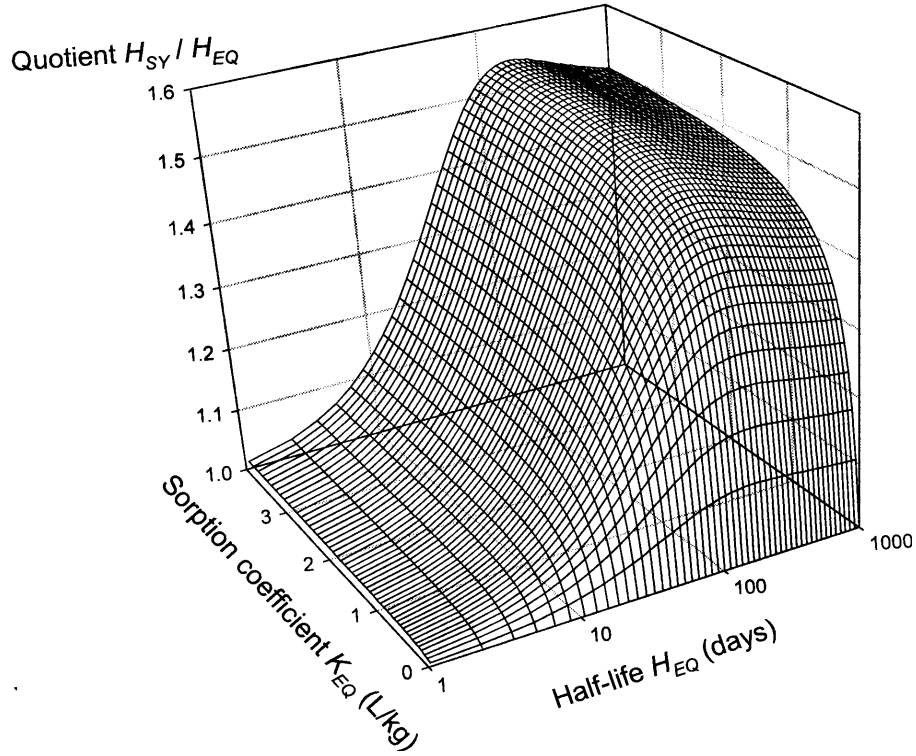


Figure 1. The quotient Q of the half-life for transformation of the system concentration (H_{SY}) divided by the half-life for transformation of the equilibrium part of the system concentration (H_{EQ}) as a function of both the Freundlich equilibrium sorption coefficient (K_{EQ}) and the half-life H_{EQ}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

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:

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

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 :

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

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

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 $k_D = 0.01 \text{ d}^{-1}$. 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.

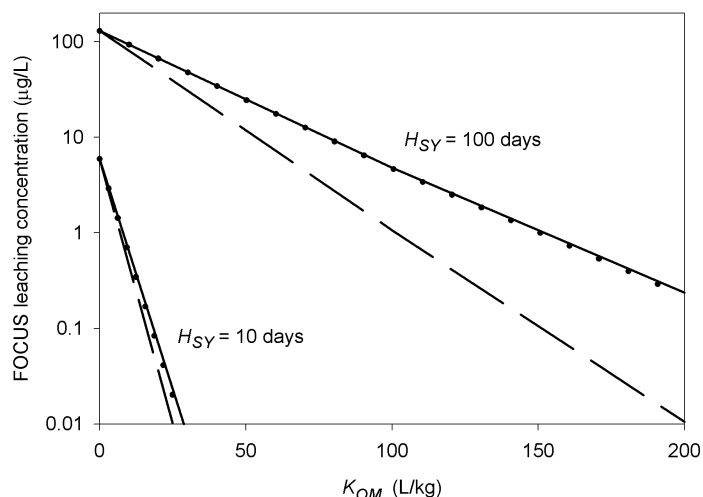


Figure 2. The concentration of an example pesticide leaching to groundwater as a function of K_{OM} as calculated with PEARL for the Kremsmünster FOCUS scenario and winter wheat after application of 1.0 kg/ha to soil on 1 May. Solid line: equilibrium sorption only; dashed line: non-equilibrium sorption 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.

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