

IMPROVEMENT OF CONCEPTS FOR PESTICIDE VOLATILISATION FROM BARE SOIL IN PEARL, PELMO, AND MACRO MODELS

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ABSTRACT

Volatilisation is an important process to be considered when predicting the fate of a pesticide after its application to soil. At present, this emission pathway has not been described adequately in pesticide fate models used to calculate environmental concentrations as needed in the current EU risk assessment procedure under Council Directive 91/414. Moreover, little attention has been given to the concentration of pesticides in air. To remedy this, a project was started to include or improve the description of the volatilisation process in the PEARL, PELMO and MACRO models. Datasets for volatilisation under field conditions were collected and described and process studies were done in the laboratory to assess the effects of soil moisture and other environmental factors on volatilisation. Concepts to describe the volatilisation from soil surfaces were developed or improved and implemented in the models. First tests were done using measured volatilisation rates in the field to check whether the improved models could predict volatilisation better than the reference models. The inclusion of a description for the increase in the sorption coefficient at low soil water contents resulted in a better description of the volatilisation under dry soil surface conditions. Hourly input is needed to describe adequately the volatilisation process, particularly during the first day after application.

KEYWORDS: air boundary layer, emission, field conditions, laboratory conditions, model development, soil moisture, transport resistance

INTRODUCTION

In the current EU risk assessment according to Council Directive 91/414, environmental concentrations are evaluated before active substances of plant protection products can be registered. Procedures have been developed to calculate the environmental concentrations in groundwater, surface water and soil (FOCUS, 2000; FOCUS 2001). However, there is still uncertainty about the validation status of the models used to calculate the PECs. Moreover, so far, little attention has been given to the concentration of pesticides in air. To remedy the uncertainty in predicting environmental concentrations, studies were done on volatilisation of pesticides from soil and plant surfaces within the R&D project entitled 'Effective approaches for predicting environmental concentrations of pesticides' (APECOP, VanClooster et al., 2003). This project was carried out within the framework of the EU-FP5-Quality of Life Programme.

Experiments on the volatilisation of pesticides from soil were carried out in the laboratory as well as in the field. The laboratory studies were set up to gain insight in the processes affecting volatilisation of pesticide after spraying on the soil surface. A volatilisation chamber was developed to study the volatilisation from soil under constant environmental conditions, e.g. air temperature and wind speed. To approximate field conditions more closely, an experimental system was developed that consists of a wind tunnel placed above a lysimeter (See e.g. Stork et al., 1998; Wolters et al., 2003c). Datasets on volatilisation of pesticides from soil under field conditions were collected and two of these datasets were made available for use to test the validation status of current and improved model concepts for volatilisation.

For the description of the volatilisation process, literature reviews (e.g. Van den Berg et al., 1999) and recent publications on volatilisation were collected to look for concepts presented so far and possibly implemented in pesticide fate models. In the APECOP project attention was focused on the models PEARL, PELMO and MACRO. In MACRO volatilisation was not considered so far, so a simple method was selected to describe the volatilisation process.

In this paper, only the experimental studies on volatilisation from soil that have been carried out in Jülich are described briefly. The current model concept for the volatilisation process in PEARL is described as well as the concepts for volatilisation used to improve the PEARL, MACRO and PELMO models. Some results are presented to show the performance of the improved models. The experiments and model improvements for volatilisation from plants are presented by Wolters et al. (2003b).

EXPERIMENTAL

A volatilisation chamber was developed for the study of the effect of soil temperature and soil moisture on volatilisation. A small container (18 cm by 5.6 cm) filled with soil is placed under a glass dome. The humidity and temperature of the air passing through the glass dome can be adjusted to the required conditions. The design of the chamber is shown in Figure 1; more details are given by Wolters et al. (2003a).

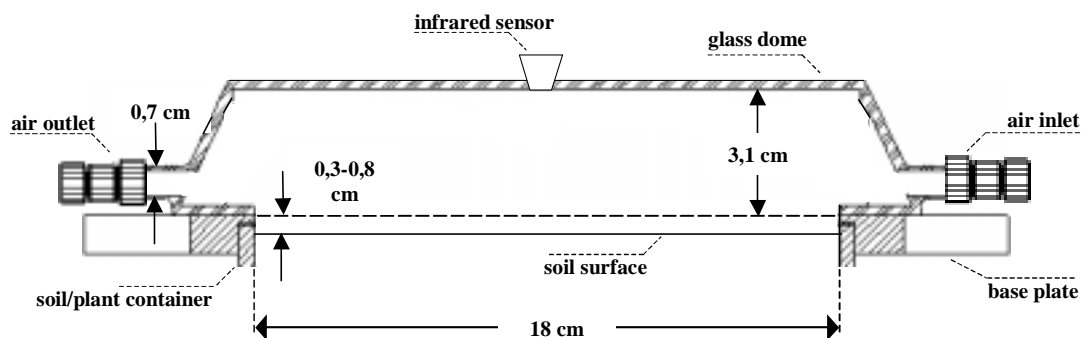


Figure 1: Design of the volatilisation chamber

Three experiments were done to study volatilisation under different soil moisture conditions. After filling the container with dry soil from a gleyic cambisol, it was placed under the glass dome and connected with a water-replenishing system under different water tensions. Air temperature was maintained at 19 °C in all experiments, while the average humidity of the air passing through the chamber at a rate of about 10 L min⁻¹ was maintained at 43, 92 and 90% for

the first, second and third experiment, respectively. The moisture content at 2.5 cm depth was monitored and between 4 to 7 days the absolute difference in the 24-h average moisture content at this depth was less than 0.1%. At the end of this equilibrium period, the moisture contents at 2.5 cm were 15.7, 14.1 and 20.3%, and in the top 7 mm they were 1.2, 3.4 and 8.7%, for the first, second and third experiment, respectively. Next ^{14}C -parathion-methyl was sprayed on the soil surface at a rate between 73 and 86 $\mu\text{g m}^{-2}$. For the subsequent 3 to 6 days, the conditions were kept constant. At intervals of up to 24 h, air samples were taken with polyurethane foam as adsorbent and they were analysed by measuring the radio-activity.

The pesticides fenpropimorph (1.4 kg ha^{-1} ; as Corbel, an emulsifiable concentrate), parathion-methyl (0.6 kg ha^{-1} , as ME605, a wettable powder) and terbuthylazine (1.18 kg ha^{-1} , an experimental formulation of Ciba Geigy) were applied in one spray mixture (202 L ha^{-1}) to a dry bare soil on a 1 ha field (80 by 125 m) near Merzenhausen (Germany) on 11 May 1995 at about 14.30 h. The soil was an Orthic luvisol (pH-KCl 7.2.; 6.4 % sand; 78.2 % silt; 14.4 % clay; 1.1% organic carbon). Dosages were about double the manufacturers recommended dosage. The aerodynamic method and the Bowen-ratio method were used to determine the pesticide volatilisation rates (Majewski et al., 1990). Data on wind speed, water vapour pressure, air temperature, radiation, soil heat flux and soil surface temperature were recorded in the field with a data logger. At 13 times during 19 days after application, concentrations of the pesticides in air were measured for calculation of the flux densities with the two methods. During 1 to 2 hours air was sampled at 0.2, 0.5 and 0.8 m above the soil surface by leading air flows of 3 $\text{m}^3 \text{h}^{-1}$ over XAD-4 cartridges (10 g) in glass tubes. Soil was sampled on 4 occasions after application. Due to dry conditions at the soil surface, volatilisation decreased drastically immediately after spraying and remained very low until rainfall events re-moistened the soil surface. Four hours after application, only the measured mass of terbuthylazine in soil (103 % of dosage) matched well with the applied mass. The masses of fenpropimorph (73%) and methyl parathion (50%) were considerably lower than that applied, probably mainly due to transformation, e.g. photodegradation under sunny and dry weather conditions. Losses by volatilisation were less than a few % of the dosage in the 4 h period between application and soil sampling.

DESCRIPTION OF MODEL IMPROVEMENTS

The description of the volatilisation process in FOCUS-PEARL version 1.1.1 (Tiktak et al., 2000; Leistra et al., 2001) is based on the assumption that a laminar boundary air layer exists through which the pesticide has to diffuse before it escapes into the atmosphere. The transport resistance of this air layer can be described as:

$$r_{bl} = \frac{d}{D_a(T)} \quad [1]$$

with:

r_{bl} = resistance for transport through boundary air layer (s m^{-1})
 d = thickness of boundary air layer (m)
 $D_a(T)$ = coefficient for diffusion in air ($\text{m}^2 \text{s}^{-1}$) at temperature T

The volatilisation flux density depends on the concentration gradient of the pesticide across the boundary air layer and this flux density is described as:

$$J_{v,a} = - \frac{(c_{g,0} - c_{air})}{r_{b1}} \quad [2]$$

with:

$$\begin{aligned} J_{v,a} &= \text{volatilisation flux density through the boundary air layer (kg m}^{-2} \text{ s}^{-1}\text{)} \\ c_{g,0} &= \text{concentration in the gas phase at the soil surface (kg m}^{-3}\text{)} \\ c_{air} &= \text{concentration in the turbulent air (kg m}^{-3}\text{)} \end{aligned}$$

It is assumed that the concentration of the pesticide in the turbulent air is negligible compared to the vapour concentration at the soil surface.

The effect of the environmental factors can be taken into account with the concept of the resistances to transport of substance from the surface to the atmosphere (Wang et al., 1997; Asman, 1998). The flux density of volatilisation is then given by:

$$J_{v,a} = - \frac{(c_{g,0} - c_{air})}{r_a + r_{b2}} \quad [3]$$

in which:

$$\begin{aligned} r_a &= \text{aerodynamic resistance (s m}^{-1}\text{)} \\ r_{b2} &= \text{boundary layer resistance (s m}^{-1}\text{)} \end{aligned}$$

The aerodynamic resistance is the resistance to transport between the roughness length for momentum z_{0h} and the height of the internal boundary layer, z_{bl} , into which the pesticide has mixed. This height depends on the length of the sprayed field, the roughness length for the experimental site and the stability conditions of the atmosphere (see Van der Molen et al., 1990). For the improvement of the concept for volatilisation in PEARL neutral atmospheric conditions are assumed, so the aerodynamic resistance can be described by:

$$r_a = \frac{\ln\left(\frac{z_{bl}}{z_0}\right)}{\kappa u_*} \quad [4]$$

in which:

$$\begin{aligned} z_{bl} &= \text{height of internal boundary layer (m)} \\ z_0 &= \text{roughness length for momentum (m)} \\ \kappa &= \text{Karman constant (dimensionless)} \\ u_* &= \text{friction velocity (m s}^{-1}\text{)} \end{aligned}$$

The roughness length for momentum can be estimated from the normalised standard deviation of the wind speed (σ_u/u) or using the Davenport classification scheme (Wieringa and Rijkoort, 1983). The height of the internal boundary layer z_{bl} can be calculated iteratively using the equation given by Van der Molen et al. (1990).

The resistance to the transport between the source height (i.e. the soil surface) and $z = z_{0m}$ can be described with the boundary resistance r_{b2} by (Hicks et al., 1987):

$$r_{b2} = \frac{2}{\kappa u_*} \left(\frac{Sc}{Pr} \right)^{2/3} \quad [5]$$

in which:

Sc = Schmidt number (-)

Pr = Prandtl number (-)

The Prandtl number can be set at 0.72, whereas the Schmidt number depends on the diffusion coefficient of pesticide in air.

The concept as described by Equations [3]-[5] was implemented in FOCUS-PEARL 1.1.1 as an option for the user to select. If this option is selected, then z_0 has to be specified.

The description of the volatilisation process in FOCUS-PELMO (FOCUS, 2000) is also based on the assumption of the existence of a laminar boundary air layer (Equations [1]-[2]). FOCUS-PELMO was improved by the inclusion of the temperature dependency of the Henry's law constant and the coefficient for diffusion in air. Further improvement was made to process hourly data. Finally, a thin surface layer of 1 mm was added on top of the soil profile into which the pesticide is mixed after spraying of the soil surface. The coefficient for diffusion through the gas phase in this layer is taken to be 0.1 times the diffusion coefficient in air. Note that all soil numerical compartments below this layer have a thickness of 5 cm.

For the inclusion of volatilisation in MACRO, a simple estimation of the volatilisation loss, as a percentage of the applied dose, was adopted based on the empirical method described by Smit et al. (1997). The cumulative volatilisation in 21 days following application, CV , is related to the fraction of the compound calculated to be present in the gas phase of the soil system, F_g :

$$CV = 71.9 + 11.6 \log(100 F_g) \quad ; \quad F_g > 6.33 \cdot 10^{-9} \quad [6a]$$

$$CV = 0.0 \quad ; \quad F_g \leq 6.33 \cdot 10^{-9} \quad [6b]$$

The fraction of the substance in the gas phase of the soil system is calculated from the partitioning of the substance between the soil phases. The fraction depends on the prevailing temperature and this temperature is set equal to the air temperature at the time of application. The air temperature is approximated from a sinusoidal variation of air temperature at the soil surface, and is calculated from the known Julian date of application, the annual average temperature and the amplitude in the annual temperature wave. A simple procedure was adopted to obtain the water content for which F_g has to be calculated. For summer applications, defined as the period from mid-June (i.e. Julian day 165) to the end of August, a water content equivalent to the wilting point (i.e. a tension of 15000 cm) is assumed, while for all other application days, a water content at a tension of 300 cm is assumed.

The concentration of the pesticide in the gas phase at the soil surface depends on the amount in the soil system and the partitioning of pesticide between the soil phases. The sorption coefficient is mostly assumed to be constant for all water contents in the soil. At low moisture contents, however, the coefficient for sorption to soil increases and this results in lower concentrations of the pesticide in the gas phase of the soil system. Thus, volatilisation of pesticides from the soil surface decreases strongly when the soil surface dries out. A simple approach to take this effect into account is to specify a maximum sorption coefficient for air-dry soil and a moisture content

below which the sorption coefficient increases. Assuming an exponential relationship the effect of the moisture content on the sorption coefficient can be described as follows:

$$K_{d,eff} = K_{d,max} \cdot e^{-\alpha \cdot w} \quad \text{for } w < w_{low} \quad [7a]$$

$$K_{d,eff} = K_d \quad \text{for } w \geq w_{low} \quad [7b]$$

in which:

$K_{d,eff}$ = effective sorption coefficient (L kg⁻¹)

$K_{d,max}$ = maximum sorption coefficient (L kg⁻¹)

K_d = sorption coefficient under moist soil conditions (L kg⁻¹)

α = coefficient (-)

w = moisture content (kg kg⁻¹)

w_{low} = moisture content below which sorption coefficient increases (kg kg⁻¹)

The coefficient α can be calculated by substituting w_{low} for w and K_d for $K_{d,eff}$ in Eq 7a. The moisture content below which the sorption coefficient increases is set equal to the moisture content at wilting point. Below wilting point, air humidity in the soil pores is no longer saturated. This concept was implemented in FOCUS-PEARL 1.1.1. The effect of increased sorption at low water contents has been implemented in FOCUS-PELMO in a somewhat different manner. A factor has to be specified to calculate the sorption coefficient for air dry soil from the standard sorption coefficient. The sorption coefficient at moisture contents between air dry and that corresponding to wilting point is obtained by interpolation using a power function.

$$K_{d,eff} = K_d \cdot F_{ss} \quad \text{for } \Theta < \Theta_{ad} \quad [8a]$$

$$K_{d,eff} = K_d \cdot 10^m \quad \text{for } \Theta_{ad} < \Theta < \Theta_{wp} \quad [8b]$$

in which:

F_{ss} = increase of soil sorption when soil is air dry (comp. to ref. conditions)

Θ = volume fraction liquid phase (m³ m⁻³)

Θ_{wp} = volume fraction liquid phase at wilting point (m³ m⁻³)

Θ_{ad} = volume fraction liquid phase when soil is air dry (m³ m⁻³)

The exponent m is given by:

$$m = \left[{}^{10}\log F_{ss} \frac{({}^{10}\log \Theta - {}^{10}\log \Theta_{wp})}{({}^{10}\log \Theta_{ad} - {}^{10}\log \Theta_{wp})} \right] \quad [8c]$$

In MACRO the increase of the sorption coefficient at low moisture contents is not considered.

COLLECTION OF INPUT PARAMETERS

The modified PELMO and MACRO models were tested with data obtained during the Jülich-1 field experiment. In the MACRO parameterisation, values taken for the vapour pressure, the water solubility and the Koc were those presented in Table 1. The soil water contents at 15000 and 300 cm water tension were 9.8 and 26.8%, respectively. The annual mean air temperature was taken to be 11 °C, and the annual amplitude was set at 7 °C. In the PELMO

parameterisation, the Henry's law coefficients of fenpropimorph at 15 and 25 °C were set at 0.087 and 0.17. The thickness of the laminar boundary air layer as well as the coefficient F_{ss} for the increase of sorption were obtained via calibration. The values for these parameters were 10 mm and 100 (-), respectively. In the PEARL parameterisation, input data for fenpropimorph were taken from Table 1. A boundary air layer was assumed and the thickness of this layer was set at 1 mm. This thickness is about the same as the value for the roughness length during daytime as calculated from wind speed data and assuming neutral atmospheric conditions. The amount of fenpropimorph applied was assigned to the top 1 mm of the soil profile. The Van Genuchten parameters for each soil layer were obtained using the Staring Reeks shell and database. The input data on the clay and organic matter contents were taken from the measurements on the composition of the layers in the Jülich soil.

Table 1: Some physico-chemical properties (at 20 ° C) of the pesticides studied in the Jülich-1 field experiment.

Property	Fenpropimorph	Terbutylazine	Parathion-methyl
Vapour pressure (mPa)	2.3	0.15 [¶]	2.0
Solubility (mg L ⁻¹)	4.3	8.5	55
Koc (L kg ⁻¹)	3569	310	243

[¶] At 25 ° C

RESULTS AND DISCUSSION

The results of the experiments on the volatilisation of parathion-methyl from soil at different moisture contents in the top 7 mm of the soil are presented in Figure 1. For all three experiments, the volatilisation decreased strongly during the first 24 h. Thereafter, the decrease became more gradual. The volatilisation rates were highest for the soil with the highest moisture content. Decreasing the soil moisture content resulted in a decrease of the volatilisation rate. A decrease in the soil moisture content from 3.4 to 1.2% resulted in a decrease of the volatilisation rate by about an order of magnitude. This strong decrease in volatilisation could be explained by a stronger sorption of pesticide to the soil particles. Under dry and sunny conditions in the field, the soil surface layer dries out, so a strong decrease in volatilisation flux can be expected. After re-wetting the topsoil, the volatilisation flux densities is expected to increase again.

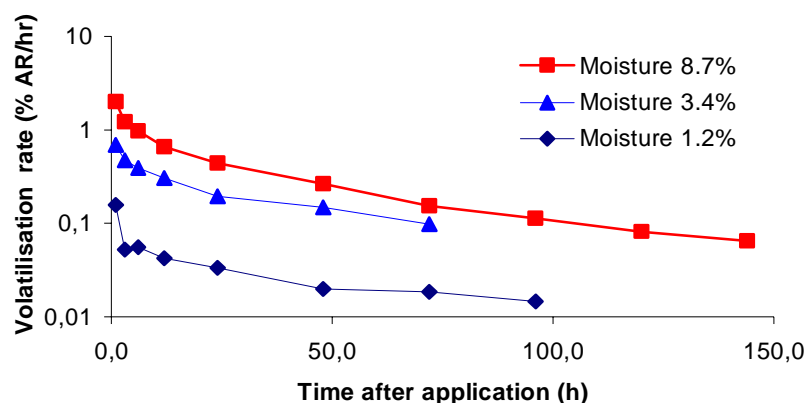


Figure 1: Volatilisation rates of ¹⁴C-parathion-methyl from soil measured in the volatilisation chamber. AR= Applied radio-activity. Moisture content measured gravimetrically in top 7 mm of soil.

The results of the comparison between the volatilisation rates calculated with FOCUS-PELMO, the new PELMO and the rates measured in the field are shown in Figure 2. The decrease in the volatilisation rate of fenpropimorph during the first hours after application, as measured in the field, could not be simulated by the new PELMO model. At later days, the calculated rates corresponded reasonably well with those measured. For those days, the rates calculated with FOCUS-PELMO substantially underestimated the volatilisation.

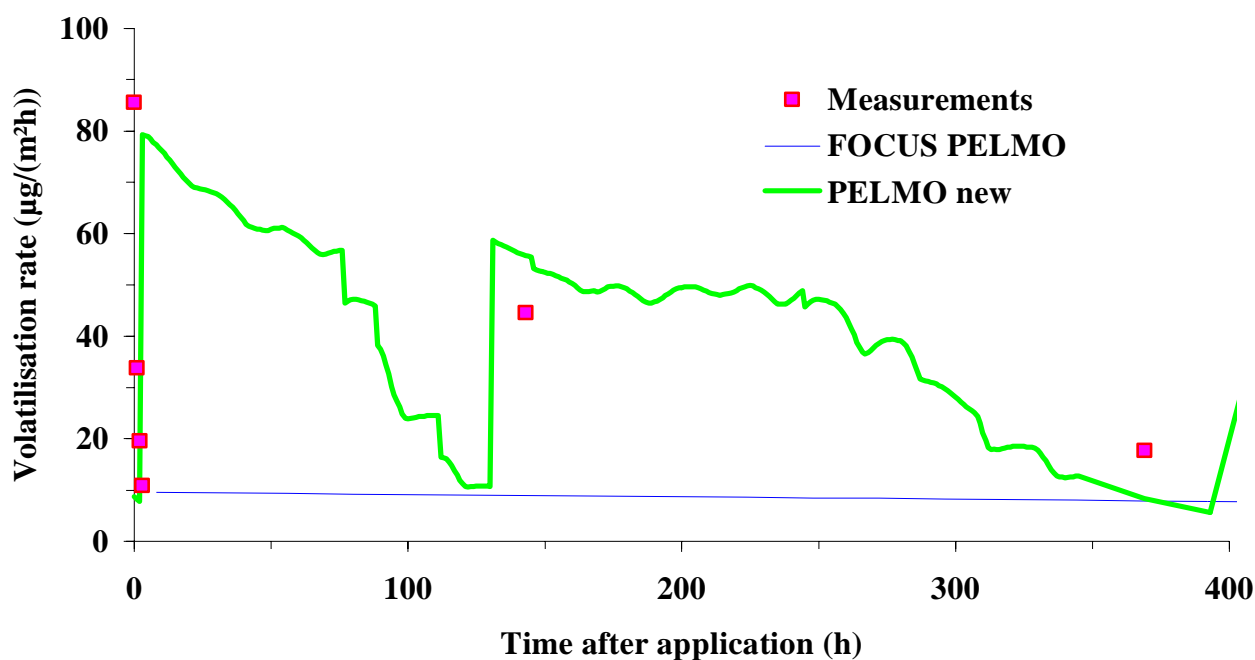


Figure 2: Comparison of the volatilisation rates of fenpropimorph from soil calculated with FOCUS-PELMO and the modified PELMO, with those measured during the field experiment at Jülich in May 1995.

The preliminary results of the comparison between the rates of volatilisation of fenpropimorph calculated with FOCUS-PEARL and the new PEARL model, and the rates measured in the field are shown in Figure 3. During the day of application, the volatilisation rate computed with FOCUS-PEARL was up to a factor 4 higher than most of the rates measured. Using the new PEARL model, the volatilisation rate computed was not much different from that measured. This improvement is due to the inclusion of the effect of an increased sorption coefficient at low soil water contents in the new PEARL. Both FOCUS-PEARL and the new PEARL model underestimated the volatilisation rate on the 6th day after the day of application. As the hydrological model only produces output on a daily basis, the wetting and drying out of the soil surface during the day cannot be taken into account. On this day 10 mm of rain fell and in the simulation this was distributed equally over 24 h. Modification of the hydrological model to handle input and output on a hourly basis can be expected to give a more accurate description of the soil moisture condition at the surface.

When increasing the thickness of the boundary air layer, the volatilisation flux as calculated with Equations [1]-[2] decreases. Because it is assumed that there is no sink of substance at the soil surface, the concentration of the substance at the soil surface depends on the resistance to transport in the top soil compartment and on that to transport through the boundary air layer.

Thus, the net effect of an increase in the boundary air layer thickness on the volatilisation flux can be substantially smaller than that expected from the difference in this thickness alone.

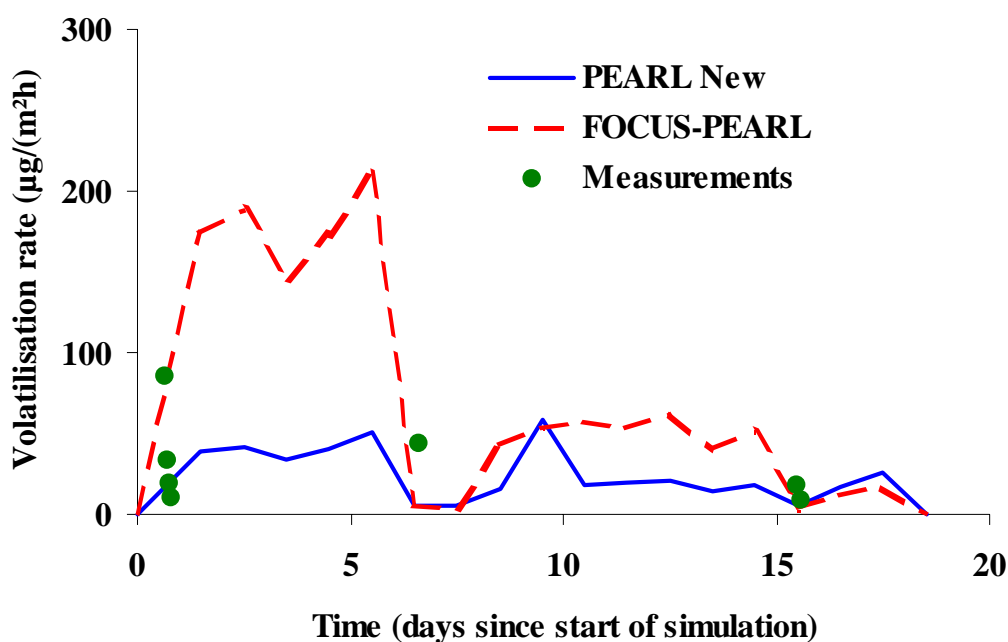


Figure 3: Comparison of the volatilisation rate of fenpropimorph calculated with FOCUS PEARL and the modified PEARL model, with those measured during the field experiment at Jülich in May 1995. Start of simulation, 11 May 0.00

The volatilisation losses during the first 21 d after application as calculated in MACRO using the method developed by Smit et al. (1997) were 15.7, 9.4 and 14.9% of the dosage for fenpropimorph, terbuthylazine and parathion-methyl, respectively. The cumulative volatilisation losses as estimated from the measured volatilisation rates were 6, 9 and 25%, respectively. The estimated loss of terbuthylazine corresponded very well with that measured, but the estimated loss of fenpropimorph was higher than that measured. It should be noted that, if different values are reported for e.g. the vapour pressure, then an estimated volatilisation loss can be obtained with the method of Smit et al. (1997) for each vapour pressure. If there is uncertainty in more input parameters, then the overall effect of these uncertainties on the volatilisation loss needs to be evaluated.

CONCLUSION

The simple empirical method as developed by Smit et al. (1997) seems to be appropriate to estimate the volatilisation loss of a pesticide in a leaching model. This total volatilisation loss is then subtracted from the applied dosage to obtain the actual load of the soil with the pesticide. It should be noted that the half-life of the pesticide is not taken into account explicitly in this method, so the volatilisation loss can be overestimated for substances with a comparatively short half-life.

Because the method described by Smit et al. (1997) only gives the total volatilisation loss over 21 days, it cannot be used to describe the short-term fate of the pesticide in the topsoil on a hourly or daily basis.

The stronger sorption of pesticide at low soil water contents can be described with a simple exponential function that gives the relation between sorption coefficient and water content. The water content below which the sorption coefficient increases can be taken to be the moisture content of the soil layer at wilting point.

At present, daily meteorological data are used to calculate the transport resistances, so the diurnal pattern of volatilisation cannot be described. This limitation can be remedied by a further model improvement to process hourly meteorological data.

The introduction of the aerodynamic transport resistance for neutral atmospheric conditions in the concept to describe volatilisation is a first step to improve the description of this process in pesticide fate models. Further improvements are needed to take atmospheric stability into account.

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