

## **PESTICIDE VOLATILISATION FROM PLANTS: IMPROVEMENT OF THE PEARL, PELMO, AND MACRO MODELS**

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### **ABSTRACT**

Simulation of volatilisation from plants is an important part in pesticide fate models, especially for the models used to predict the concentrations of pesticides in the environment in the registration procedures. Recent efforts to harmonise registration procedures for pesticides in the European Union necessitated the development and implementation of suitable volatilisation modules within the framework of the EC project APECOP (Effective Approaches for Assessing the Predicted Environmental Concentration of Pesticides). An empirical description to estimate the cumulative volatilisation of pesticides during seven days after application to crops was included in MACRO. A mechanistic approach using a laminar air-boundary layer concept for the consideration of volatilisation from plant surfaces was developed and calibrated on the basis of a series of wind-tunnel studies performed under well-defined conditions. This description was implemented in PELMO (Pesticide Leaching Model). When key parameters had been calibrated (thickness of the air-boundary layer, phototransformation and penetration into the leaves), the approach was able to simultaneously estimate volatilisation of pesticides from plants and soil. For a more appropriate reflection of field conditions, the advanced volatilisation module to be included in PEARL (Pesticide Emission Assessment at Regional and Local Scales) could replace the concept of the laminar boundary layer with the improved description of aerodynamic and boundary-layer resistances in air.

**KEY WORDS:** MACRO, PEARL, PELMO, pesticide, volatilisation, wind tunnel

### **INTRODUCTION**

Volatilisation from plant surfaces is one of the main pathways of pesticide emission to the environment and may lead to contamination by long-range transport and deposition at locations remote from their application (Eisenreich et al., 1981; Van den Berg et al., 1999). The main factors affecting volatilisation of pesticides from crops are their physicochemical properties, their persistence on the plant surface and the environmental conditions. The persistence on the leaf surface depends on various dissipation processes, such as photodegradation, wash-off from the leaves by rainfall or irrigation, and penetration into the plant leaves (Bedos et al., 2002). As a screening-level approach for estimating the initial volatilisation rate after plant application, a correlation between physicochemical pesticide properties and measured volatilisation fluxes was used (Woodrow & Seiber, 1997). For the prediction of cumulative losses from plant surfaces, a

similar estimation method was developed by Smit et al. (1998). Despite intense research in recent years, including the development of numerous laboratory and field methods to measure volatilisation rates (Taylor & Spencer, 1990; Stork et al., 1994; Wolters et al., 2003A), knowledge of rate-determining processes is currently not sufficient for developing a reliable, physically-based model approach to predict fluxes of pesticide volatilisation from plant surfaces. The simulation of volatilisation from crops as an integral component of a complete pesticide transport model is of utmost importance, especially as a module for integration into existing models that predict environmental concentrations of pesticides (PEC models). For improving the effectiveness of risk assessment, modelling tools and methods need to be updated and evaluated continuously. In the current version of the PEARL model, which is used to evaluate the leaching of pesticides to groundwater in support of pesticide registration procedures (Tiktak et al., 2000; Leistra et al., 2001), the pesticide processes in the plant canopy are described in a simplified way. Volatilisation is described as a first-order process, for which a rate coefficient may be introduced. Recent versions of the PELMO and MACRO models have not included plant volatilisation modules yet.

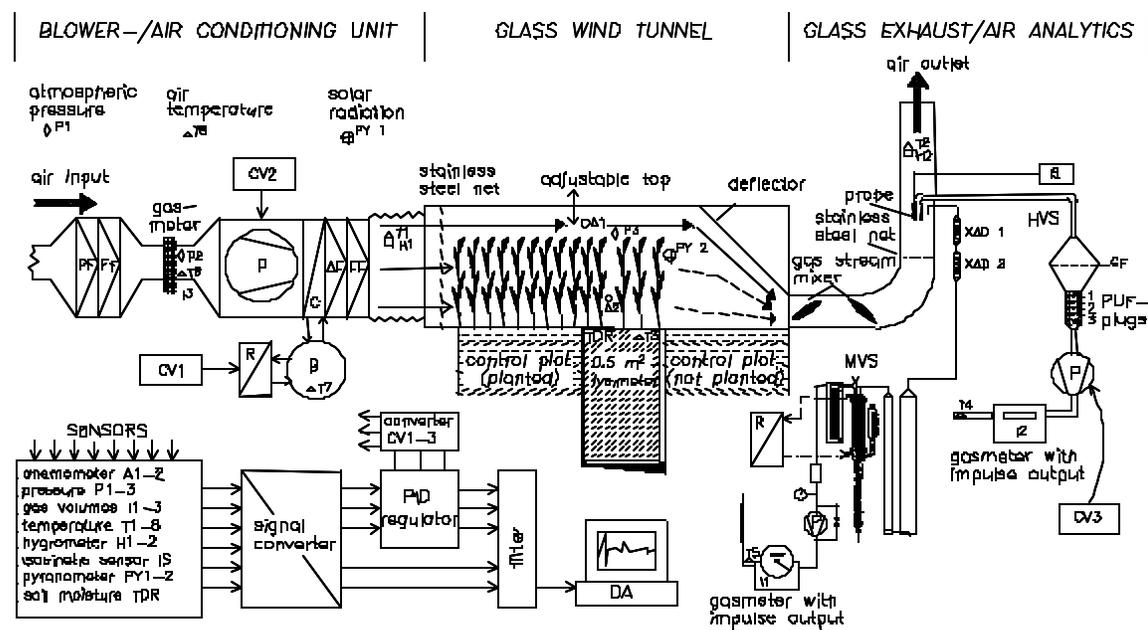
The main objective of the work within the framework of the EC project APECOP (Vanclooster et al., 2003) summarised in this paper was to develop process descriptions for pesticide volatilisation from plants and to include them in the current PEC models PEARL, PELMO, and MACRO.

## EXPERIMENTS

As an extension of the lysimeter concept (Führ et al., 1998), a glass wind tunnel was set up above a lysimeter with a soil surface area of  $0.5\text{ m}^2$  to measure the gaseous emissions of the applied pesticide (**Figure 1**). In accordance with good agricultural practice, realistic application conditions, including application rate, volume of water, and droplet spectrum of the spray emulsion were obtained by using a semiautomatic sprayer. The lysimeter can be used with two lower boundary conditions (zero moisture pressure or a defined groundwater level). A detailed description of the system was given by Stork (1995) and Linnemann (2002). The glass wind tunnel is 1.1 m high, 0.7 m wide and 2.7 m long. Its design ensures that the glass structure can withstand weather influences (wind pressure, temperature changes, rain etc.). A single blower presses air into the wind tunnel (max.  $1500\text{ m}^3\text{ h}^{-1}$ ) after intensive cleaning in various filter stages. Air filters and subsequent sieves guarantee a laminar air stream through the glass tunnel. The top of the wind tunnel can be adjusted in height and thus be adapted to the level of growing plants. In this way, constant wind velocities from  $0.3$  to  $3.5\text{ m s}^{-1}$  can be achieved with a minimum air volume. Realistic conditions are simulated inside this wind tunnel by a continuous, automatic adjustment of the air temperature to the outdoor situation. Due to the glass design, sufficient light intensity is ensured, so that experiments after application on plant surfaces can also be performed. The use of UV-transparent glass (side walls) and UV-transparent acrylic glass (lid) as construction materials guarantees sufficient irradiation and light quality. During the experiments, essential climatic parameters were monitored using various sensors, including the determination of volumetric water content in the soil by TDR measurement at various depths. Precipitation events can be simulated by irrigation nozzles in the lid of the wind tunnel.

$^{14}\text{C}$ -labelled fenpropimorph in the exhaust air was sampled with a High Volume Sampler (HVS) equipped with an adhesive-free glass fibre filter to trap particulate matter followed by three polyurethane foam plugs. Air samples were taken isokinetically based on industrial guidelines for the sampling of stack air. The maximum sampling rate was  $50\text{ m}^3\text{ h}^{-1}$ , corresponding to 3-10% of the total airflow through the wind tunnel. The sampling period of the HVS ranged between 1 h and 24 h.  $^{14}\text{C}$ -labelled carbon dioxide, formed from the mineralisation of  $^{14}\text{C}$ -

labelled fenpropimorph, was collected with a Medium Volume Sampler (MVS) at a sampling rate of 1.0 to 3.5 L min<sup>-1</sup> over a maximum sampling interval of 48 h, corresponding to a sampling rate of 10 m<sup>3</sup> in 48 h. In order to ensure sampling of <sup>14</sup>CO<sub>2</sub> only, volatile organic compounds were trapped with two cartridges filled with XAD-4 resin. Then the air sample was dried intensively by silica gel and phosphorus pentoxide. <sup>14</sup>CO<sub>2</sub> was subsequently absorbed by 2-methoxy-propylamine (Carbosorb E<sup>+</sup>, Canberra Packard, Frankfurt, Germany) using a cooled intensive-wash bottle. Losses of highly volatile 2-methoxy-propylamine were minimised by intensive cooling at a reflux temperature of -40 °C.



**Figure 1** Schematic of the wind tunnel for measuring volatilisation of pesticides from plant surfaces under field-like conditions. AF = active charcoal filter, B = brine tank, C = cooler, CV = converter, DA = data acquisition, FF = fine filter, GF = glass fibre filter, HVS = high volume sampler (<sup>14</sup>C-labelled organics), MVS = medium volume sampler (<sup>14</sup>C-labelled carbon dioxide), P = pump/blower, PF = prefilter, PUF = polyurethane foam, R = refrigeration, TDR = time domain reflectometry, XAD = adsorbent resins (Amberlite XAD-4).

Foam plugs were extracted separately with methanol using a special squeezing apparatus (Niehaus et al., 1990). Soil and plant samples, glass fibre filters, and XAD cartridges were extracted with methanol in a Soxhlet apparatus for 16 h. Radioactivity of extracts was determined by LSC (liquid scintillation counting, TRI-CARB 2500, Canberra Packard). Non-extractable radioactivity in soil and plant material was measured by combustion (TRI-CARB Sample Oxidizer 306, Canberra Packard). The active ingredients of the samples were characterised by radio-HPLC (high performance liquid chromatography) and radio-TLC (thin layer chromatography) in combination with a Bio-Imaging Analyser (Fujix BAS 100, Fuji, Tokyo, Japan).

## MODEL APPROACHES

**Empirical relationship:** The following empirical relationship was derived by Smit et al. (1998) from literature data to describe the cumulative volatilisation of pesticides during the first seven days after application to plants (fully covering the soil) in the field and in climate chambers:

$$\log(CV) = 1.528 + 0.466 \log(VP) \quad \text{for } VP \leq 10.3 \text{ mPa} \quad [1]$$

where  $CV$  = cumulative volatilisation during seven days after application [% of dosage], and  $VP$  = vapour pressure [mPa].

**Boundary-layer model:** The model simulates the environmental fate of pesticides on an hourly basis, including volatilisation from leaves, penetration into leaves, wash-off by rainfall and phototransformation. Well-known processes, e.g. pesticide transport by vapour diffusion through the laminar air-boundary layer, are described in a mechanistic way. Other processes, e.g. photochemical transformation and penetration into the plants, have not yet been quantitatively described, so a simplified description was used. In this early stage of model development, the thickness of the air-boundary layer and the rate coefficients for penetration, phototransformation and wash-off have to be calibrated on the basis of measurements. The model has the option to distinguish between two deposit classes: a well-exposed and a poorly-exposed class. The deposit in the latter class may be enclosed by plant parts (e.g. in leaf axils), it may be located on the lee side of the air flow, or it may be located deeper in the canopy. To trace the effect of assuming two deposit classes on the course of volatilisation, the portion of poorly-exposed deposit was set at 20% of the dose. In addition, the rates of the decrease processes for the poorly-exposed deposit were set at 20% of the rates of the corresponding processes for the well-exposed deposit. The definition of two deposit classes calls for the use of two mass conservation equations, one for the well-exposed and one for the poorly-exposed deposit, both of the following form:

$$\frac{dA_p}{dt} = -J_{vol,act} - R_{pen} - R_w - R_{ph} \quad [2]$$

where  $A_p$  = areic mass of pesticide on plants [ $\text{kg m}^{-2}$ ],  $t$  = time [d],  $J_{vol,act}$  = actual rate of pesticide volatilisation [ $\text{kg m}^{-2} \text{d}^{-1}$ ],  $R_{pen}$  = rate of penetration into the leaves [ $\text{kg m}^{-2} \text{d}^{-1}$ ],  $R_w$  = rate of pesticide wash-off from the leaves [ $\text{kg m}^{-2} \text{d}^{-1}$ ], and  $R_{ph}$  = rate of phototransformation on the leaves [ $\text{kg m}^{-2} \text{d}^{-1}$ ].

**Atmospheric transport resistances:** The flux density of volatilisation from plant surfaces ( $J_{v,a}$ ) is described as follows:

$$J_{v,a} = -\frac{c_{g,sur} - c_{air}}{r_a + r_b} \quad [3]$$

where  $c_{g,sur}$  = concentration of vapour in the air at the plant surface [ $\text{kg m}^{-3}$ ],  $c_{air}$  = concentration in the air outside the resistance layers [ $\text{kg m}^{-3}$ ],  $r_a$  = aerodynamic resistance [ $\text{s m}^{-1}$ ], and  $r_b$  = boundary layer resistance [ $\text{s m}^{-1}$ ].

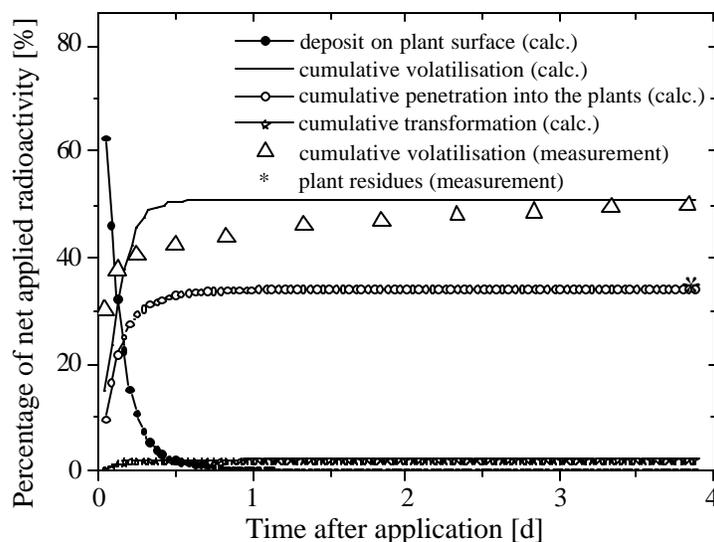
The aerodynamic resistance ( $r_a$ ) is defined as the resistance to transport between the roughness length for momentum and the height of the internal boundary layer above the field. The boundary layer resistance ( $r_b$ ) applies to the range above source height up to the roughness length for momentum. For the description of the transport resistances within and above a plant canopy, the displacement height has to be taken into account. Details on the approach based on micro-meteorological theories can be taken from Van den Berg et al. (2003).

## RESULTS AND DISCUSSION

In this publication, the comparison between experiment and model prediction is illustrated by volatilisation rates of  $^{14}\text{C}$ -fenpropimorph after application to radish plants (**Figure 2**). Detailed descriptions of the wind-tunnel studies and the underlying experimental data used for the evaluation of the model approach were given by Stork et al. (1998) and Ophoff et al. (1999).

The implementation of the empirical approach by Smit et al. (1998) in MACRO allows for an estimation of plant volatilisation on the basis of the vapour pressure of the applied pesticide. Differences in environmental conditions were not taken into consideration in this approach. Assuming an average air temperature of  $22.5^\circ\text{C}$ , cumulative volatilisation of 58% of the applied dose of fenpropimorph was predicted during seven days after application. Pesticide leaching was not considered within the computations. Although this prediction was in reasonable agreement with the measured cumulative volatilisation of approx. 50% during 4 days (**Figure 2**), the empirical relationship used for the prediction has a number of limitations. No investigations were made on the influence of weather conditions on the volatilisation from plants. Furthermore, the various transformation and penetration processes occurring on the plant leaf, having a substantial influence on the volatilisation rate, were not taken into account. Due to the lack of a sufficient number of comparative studies, a translation to field conditions is not possible (Smit et al., 1998).

A comparable estimation method (Smit et al., 1997) was already included in MACRO to calculate volatilisation from soil (Van den Berg et al., 2003). This enables MACRO users to account for the reduction in soil load due to volatilisation from plants and soil, when making calculations on pesticide movement in soil.



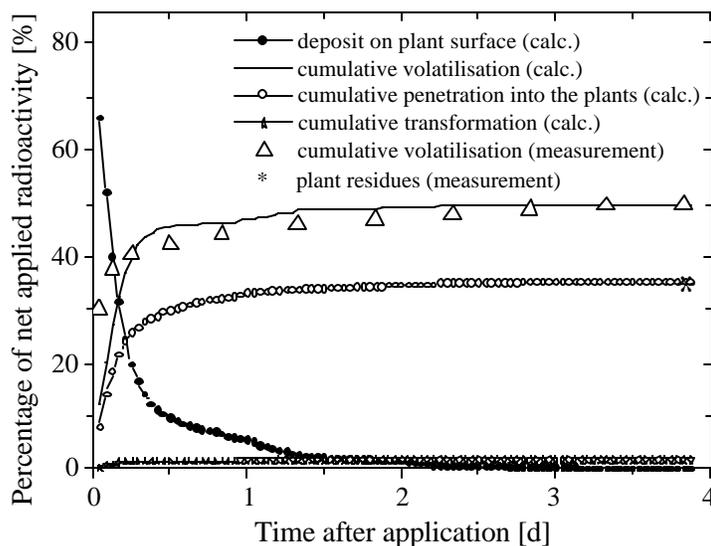
**Figure 2** Measured (wind-tunnel study) and computed (boundary-layer model) cumulative volatilisation after application of  $^{14}\text{C}$ -fenpropimorph to radish plants. Plant deposit was assumed to be well-exposed.  $k_{\text{pen}} = 3.10 \text{ d}^{-1}$ ;  $d_{\text{lam}} = 1.0 \text{ mm}$ ;  $k_{\text{ph,ref}} = 0.18 \text{ d}^{-1}$ . For the calculations, a diffusion coefficient in air of  $0.36 \text{ m}^2 \text{ d}^{-1}$  and a vapour pressure of  $3.50 \text{ mPa}$  at  $20^\circ\text{C}$  were used.

In order to calibrate the boundary-layer model for describing volatilisation from plants, the pesticide emissions determined in a series of wind-tunnel studies performed under well-defined environmental conditions were used. Most of the wind-tunnel experiments after application of  $^{14}\text{C}$ -labelled fenpropimorph (as emulsifiable concentrate) to dwarf beans and radish plants revealed volatilisation to occur as a two-stage process. Immediately after application high

volatilisation rates were measured (for about 6 to 24 hours), while during the following days volatilisation rates decreased, reaching a minimum at the end of the experiments. This volatilisation behaviour was simulated with values for the equivalent thickness of the air boundary layer in the range of 0.7 to 2.0 mm. As an example, the computed volatilisation of fenpropimorph from radish plants is compared with the measured volatilisation of fenpropimorph plus organic volatiles (**Figure 2**).

Distinction of the compounds in the volatilised fraction will require further studies. On the basis of this experiment, the rate coefficients for penetration and phototransformation were estimated to be  $3.10 \text{ d}^{-1}$  and  $0.18 \text{ d}^{-1}$ , respectively. Comparing wind-tunnel studies after application to various plants, the rate coefficients for phototransformation of fenpropimorph were estimated to be about  $0.05 \text{ d}^{-1}$  when the inlet air was filtered by activated charcoal, but were estimated to be substantially higher when the air was not filtered. These findings illustrate that enhanced amounts of OH radicals formed from ozone in non-filtered inlet air contribute to an increase of indirect photodegradation.

On the basis of the systemic activity of fenpropimorph, a fast penetration into the plant leaves was assumed. Indeed, cumulative penetration was measured to be about 34% of the dose at the end of the study (**Figure 2**). The high extent of penetration led to a decrease in deposit remaining on the plant surface, which resulted in decreasing volatilisation rates. However, the computed disappearance of detectable residues on the leaves within the first day and the subsequent disrupting of volatilisation did not correspond to the experimental findings, which revealed slight volatilisation to continue after the first day until the end of the study.



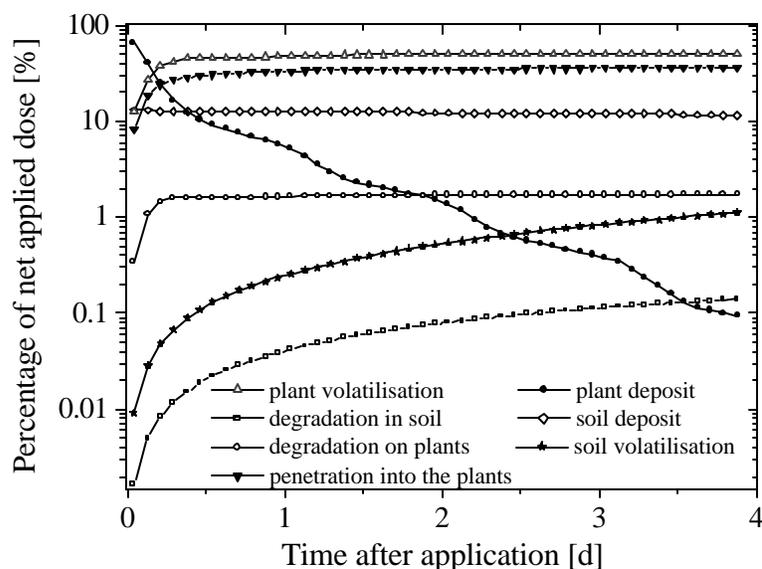
**Figure 3** Measured (wind-tunnel study) and computed (boundary-layer model) cumulative volatilisation after application of  $^{14}\text{C}$ -fenpropimorph to radish plants. Rate coefficients for the poorly-exposed deposit were set at 20% of the coefficients for the corresponding processes of the well-exposed deposit.  $k_{\text{pen}} = 3.10 \text{ d}^{-1}$ ;  $d_{\text{lam}} = 1.0 \text{ mm}$ ;  $k_{\text{ph.ref}} = 0.18 \text{ d}^{-1}$ . For the calculations, a diffusion coefficient in air of  $0.36 \text{ m}^2 \text{ d}^{-1}$  and a vapour pressure of 3.50 mPa at  $20 \text{ }^\circ\text{C}$  were used.

By replacing the assumption of all deposit on the leaves being well-exposed by a poorly-exposed scenario, a more realistic description of the course of volatilisation at the later stages of the study was obtained (**Figure 3**). Rate coefficients for the poorly-exposed deposit were set at 20% of the corresponding values for the well-exposed deposit, leading to a slower decrease of the plant deposit, accompanied by continued volatilisation until the end of the simulated period. Even though this modification generally improved the correspondence between observed and

simulated time course of fenpropimorph volatilisation by the end of the study, the underestimation during the first hours increased. Thus, reducing the deposit being available for volatilisation by introducing a poorly-exposed fraction causes a decrease of the volatilisation rates at the beginning. The lower initial volatilisation is compensated by higher rates at the end, finally leading to similar cumulative volatilisation under well-exposed and poorly-exposed conditions over the experimental period.

The measurement of pesticide residues at the end of the study enabled the calibration of the final penetration computed for  $^{14}\text{C}$ -labelled fenpropimorph. However, due to the lack of measurements on the time course of penetration, the course of the curve is uncertain. Generally, the problem of uncertainty also refers to the course of phototransformation. Thus, as part of the advanced calibration of the model approach a detailed experimental program is required to determine the kinetics of penetration and phototransformation. In addition, further testing of the model should include comparison with experimental scenarios in which combinations of pesticides are applied simultaneously to a crop, enabling the evaluation of the model's ability to reflect the behaviour of different pesticides under identical environmental conditions. Application of the model to field situations requires independent estimates for the processes missed by using non-labelled compounds.

Reliable prediction of the processes affecting the environmental fate of pesticides under field conditions is important, especially with regard to the implementation of the boundary-layer concept in PELMO, enabling an estimation of the volatilisation of pesticides from plant and soil surfaces. Application of the improved PELMO version to an environmental scenario of the wind-tunnel study after application of fenpropimorph to radish plants allows for estimation of the relevant plant and soil processes, as summarised in **Figure 4**.



**Figure 4** PELMO calculation for application of  $^{14}\text{C}$ -labelled fenpropimorph to radish plants (semi-logarithmic plot). The poorly-exposed scenario as given in Figure 3 was used for the plant processes. For the computation of the soil processes, a soil layer thickness of 1 cm was assumed. The fraction of the applied dose intercepted by the crop was estimated to be 87.1%.

Plant processes, including volatilisation from the crop, penetration into the leaves and photodegradation, were computed by PELMO assuming a poorly-exposed scenario using the boundary layer thickness and the rate coefficients summarised in **Figure 3**. For the calculation of the soil processes, including volatilisation, degradation and root-uptake, an advanced

volatilisation module developed within the framework of the APECOP project was applied to the soil deposit (Van den Berg et al., 2003). Within the calculations, PELMO was not used for the prediction of pesticide leaching. The scenario for the PELMO simulation included a default value for soil layer thickness of 1 cm and the fraction of the applied dose intercepted by the crop was taken to be 87.1%.

Computations on the plant processes in PELMO were in agreement with the predictions given in **Figure 3**, illustrated by a cumulative volatilisation from the plants of approximately 50% of the net applied dose. The predicted cumulative volatilisation from the soil was about 1.1% of the net applied dose, corresponding to 8.6% of the estimated soil deposit. Calculations indicated that degradation in soil (~0.1%) and root-uptake (<0.1%) were negligible over the time course of the study. The experimental set-up used in the wind-tunnel study did not allow distinction between volatilisation arising from soil and plant deposits. A comparison with previous studies after soil surface application revealed computed volatilisation of fenpropimorph from soil to be in the range of experimental findings. A cumulative volatilisation of 6.4% of the applied radioactivity was measured during a wind-tunnel study of 13 days after application of <sup>14</sup>C-fenpropimorph on gleyic cambisol (Wolters et al., 2003B).

At this early stage of model development, both the soil volatilisation module and the boundary-layer concept for computation of plant volatilisation implemented in PELMO need further testing (Van den Berg et al., 2003). The comparatively low extent of volatilisation from soil cannot be distinguished from the uncertainty in the computed volatilisation from plants. Further research should reveal the contribution of volatilisation from soil after application to the soil-crop system, especially under field conditions providing a soil coverage >80%. For a final evaluation of the relevance of soil volatilisation after pesticide application to plants, calibration of the PELMO computations under field conditions including various plants and soil types is required.

A volatilisation approach based on atmospheric transport resistances is currently under construction. For field conditions, the concept of a single air-boundary layer will be replaced by the description of aerodynamic resistances and boundary layer resistances (Van den Berg et al., 2003). This approach should describe the effects of soil surface conditions, nature of the vegetation and meteorological conditions on volatilisation in a more mechanistic way. The transport resistance approach is expected to be applied in a future version of the PEARL model, thus enabling a better reflection of field conditions.

## CONCLUSIONS

For the prediction of volatilisation from plants, approaches with varying degrees of accuracy were implemented in the PEC models. The different PEC models have opted for different approaches to synchronise the complexity of the plant volatilisation description with the already implemented soil volatilisation modules (Van den Berg et al., 2003).

The empirical approach for the estimation of pesticide volatilisation from plants, based on the approach by Smit et al. (1998), enables the MACRO user to include volatile losses in the determination of actual deposits available for soil processes. Taking into account the reduction of soil load due to volatilisation, an improvement of the MACRO calculations on pesticide movement in soil will be obtained.

The development of an approach based on the boundary-layer concept allows for the simulation of the environmental fate of pesticides after application to plant surfaces, including volatilisation from the leaves, penetration, wash-off and phototransformation. As the predictive use of the model is influenced by the reliability of the values for boundary layer thickness and rate

coefficients, future improvements of this approach will require a deeper understanding of the underlying processes, e.g. phototransformation and penetration.

On the basis of the experimental results obtained in wind-tunnel studies after application of radio-labelled pesticides, the boundary-layer volatilisation module was calibrated and included in PELMO, enabling the simultaneous calculation of soil and plant volatilisation. Application of PELMO to the wind-tunnel scenario was the first comprehensive PEC model calculation to imply all relevant processes affecting the post-application fate of pesticides. First calculations indicate the amount of volatilisation from soil to be comparatively small after application to soil-plant systems, but an experimental programme including various plants and soil types is required for a final evaluation of the contribution of soil volatilisation.

An advanced model based on dynamic description of atmospheric transport resistances will be developed for the improvement of the volatilisation module to be included in PEARL. In a next version of PEARL there will be two options available to describe the volatilisation processes, including both the concept based on the laminar air-boundary layer and the concept based on transport resistances. The latter approach is expected to reflect field conditions in the most appropriate way, thus its application and validation will become a main topic for future studies.

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