

## Modeling Pesticide Leaching and Dissipation in a Mediterranean Littoral Greenhouse

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The one-dimensional chromatographic flow model PEARL was used to simulate the movement of the insecticide imidacloprid and the fungicide procymidone through a greenhouse soil. The model was parametrized using measured and literature values of soil hydrological parameters. Soil water movement and soil temperature were reasonably well described by the model. The ability of PEARL to simulate the fate of imidacloprid and procymidone following four applications of each compound was evaluated against greenhouse data. Simulated imidacloprid residues in the 0–10 cm layer were in good agreement with measured data. Below 10 cm, the model overestimated imidacloprid remaining following the spray applications, whereas simulated residues following the chemigation applications were in reasonable agreement with measured data. Simulated residues of procymidone in the 0–10 cm layer were in general agreement with measured values. In the 10–20 cm layer, peaks in simulated concentrations occurred later than observed in the greenhouse. Predictions of procymidone residues below 20 cm were poor and underestimated compared to the measured data. For both pesticides, discrepancies between modeled and measured data in the 10–20 cm layer were attributed to the drip irrigation method used in the greenhouse. The model was unable to satisfactorily predict pesticide movement from the soil surface by irrigation water unless the scenario was modified to reflect the localized pattern of water application. Scenario analysis indicated that air boundary layer thickness is a key parameter for readily volatilized pesticides such as procymidone. This is of particular relevance to the greenhouse environment, where the boundary layer thickness may be greater than that in outdoor conditions.

**KEYWORDS:** PEARL; pesticide leaching model; leaching; imidacloprid; procymidone; drip irrigation

### INTRODUCTION

Intensive greenhouse horticulture is practiced in many regions of southern Europe, including areas of Spain, Italy, and Greece. The climate of these regions, intensive cultivation, and semiopen greenhouse structures provide conditions conducive to pest problems (1), and high levels of pesticide use are common. Although integrated crop management strategies are under development, they are not yet as economically viable as chemical control measures (1, 2).

The greenhouse environment differs from that of the field in several ways. Enclosure protects crops from the wind and, as a result, the layer of still air above the soil surface may be greater than that found in the field. This influences the potential for losses of pesticides through volatilization. Wavelengths involved in photodegradation may be filtered by greenhouse materials, and transformation by this process may be reduced compared to that in the field; air flow is reduced, and there is a tendency toward increased temperatures and humidity (3). Plants may be grown in artificial substrates rather than natural soil, and water inputs to the system may be limited to irrigation rather than natural rainfall, both of which influence the hydrology of

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the growing medium and the potential for leaching of pesticides to drainage and groundwater. Pesticides have been detected in groundwater in areas of greenhouse horticulture, and the minimization of any further contamination is a priority. The protection of groundwater resources from pesticide contamination requires the careful management of pesticide use and an understanding of pesticide dissipation, particularly leaching, under greenhouse conditions.

To date, a limited number of studies have examined the fate of pesticides in greenhouses. Many of these have focused on pesticide concentrations in the air following application (4–6). Among those studies considering other environmental compartments, Hatzilazarou et al. (7) examined the dissipation of several pesticides used in the cultivation of *Gerbera* in open and closed hydroponic systems. Concentrations in the air following application and concentrations of pesticides in liquid waste discharged from the greenhouse were assessed. González-Pradas et al. (8) performed studies to investigate the leaching of the insecticide imidacloprid [1-(6-chloro-3-pyridinyl)methyl-*N*-nitro-2-imidazolidinimine] and the fungicide procymidone [N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide] in a greenhouse in Almería (Spain). Four separate applications of each pesticide were made. Soil tension, water content, and temperature were measured throughout the experiment. Imidacloprid and procymidone were transported through the upper 40 cm of the soil profile within 2 years of their first application. Leaching was attributed to preferential flow pathways or interactions between the pesticides and the soluble organic carbon fraction. On the basis of their greenhouse experiments, González-Pradas et al. (8) noted that imidacloprid and procymidone could potentially contaminate groundwater when used in greenhouses and that the application of modeling would be useful to more fully understand pesticide fate under such conditions.

Mathematical models can be used to investigate pesticide leaching under various conditions. Although models are important tools for the evaluation of pesticide fate, they are not universally valid. Some argue that a model can never be said to be truly valid and should be evaluated only in relative terms (9). The evaluation of models is an iterative process, starting with the selection of input parameter values, followed by validation of the model against an experimental data set. Model predictions of the physical characteristics of the environment (such as soil water content, water tension, and temperature) must be evaluated and simulated pesticide behavior compared to observations (10). In the evaluation of pesticide leaching models, a stepwise approach should be adopted. The ability of the model to simulate the hydrology of the environment should first be assessed, followed by an evaluation of the simulation of pesticide fate.

Several models have been developed for the prediction of pesticide fate in the environment. Many studies have been performed to evaluate the ability of models to describe soil hydrology and pesticide dissipation in lysimeters and under field conditions (see, e.g., refs 11–17). The findings of these studies are variable. In some cases, models could not adequately describe field data, mechanistic models were not found to more accurately predict pesticide fate than empirical models, and predictions of the vertical distribution of pesticides through the soil profile were generally in better agreement with measured data than were predictions of leaching concentrations.

The objectives of the present work are (i) to evaluate the ability of a one-dimensional pesticide leaching model (PEARL) to describe the behavior of imidacloprid and procymidone in a

greenhouse environment, as reported in ref 8; (ii) to identify the key processes determining the fate of imidacloprid and procymidone under greenhouse conditions; and (iii) to determine sensitive model parameters for the prediction of imidacloprid and procymidone concentrations in the soil profile.

## MATERIALS AND METHODS

**Greenhouse Experiment.** Details of the greenhouse experiment upon which the present modeling study is based were reported by González-Pradas et al. (8). The experiment was performed over two years (September 1997–June 1999), incorporating four crops of green beans (*Phaseolus vulgaris*) and four applications each of imidacloprid and procymidone. Plants were grown in a layered substrate overlying the native soil. The artificial layers comprised a clay-rich layer (8–10 cm depth) to improve water retention, overlain by a layer of sand (10 cm depth) to provide a good rooting environment for the crop. The artificial layers overlaid a calcareous native soil with two distinct horizons. All applications of procymidone were made by spraying. The spray was directed at the soil surface, thus reducing interception by the crop canopy. Imidacloprid was applied by spraying (during the first and second cropping periods) and in irrigation water (during the third and fourth cropping periods). Procymidone and imidacloprid were both applied on October 30, 1997, January 15, 1998, October 13, 1998, and February 8, 1999. The application rates of procymidone were 6.75, 2.26, 6.15, and 8.53 kg ha<sup>-1</sup>, respectively. The application rates of imidacloprid were 1.74, 0.58, 1.48, and 1.44 kg ha<sup>-1</sup>. These application rates are substantially greater than recommended for applications to crops in Spain (1 and 0.14 kg ha<sup>-1</sup> for procymidone and imidacloprid, respectively) and were selected to facilitate the analysis of pesticide residues. Drip irrigation was used in the greenhouse. Following a large irrigation event presowing, irrigation was applied three to four times per week for a period of 30–45 min, at a rate of 0.057 L min<sup>-1</sup>. For each of the four cropping periods, the equivalent depths of water provided, including the large presowing irrigation, were 228, 379, 237, and 429 mm. The irrigation system comprised a main pipe with lateral pipes spaced at 1 m intervals, along which were located irrigation drippers at 0.5 m intervals. The lateral pipes were positioned to each side of the plant rows, in such a way that the drippers were 23–35 cm from the plant. Two plots within the greenhouse were used during the study, one for the first and third cropping periods and the other for the second and fourth cropping periods.

During the experiment the following data were collected: concentrations of imidacloprid and procymidone in 10 cm soil layers to a depth of 40 cm at 32 time points; soil moisture content (measured in the same samples as the pesticide residues); soil tension at three depths (20, 40, and 70 cm) measured between 9 a.m. and 10 a.m. on 54 days (most measurements were made in the period between November 1997 and May 1998); and daily soil temperature at three depths (20, 40, and 70 cm) during two periods (January–March 1998 and October 1998–June 1999).

Pesticide residue data were obtained from triplicate soil samples collected using an Ackermann soil core sampler. Soil cores were removed midway between two plants, at randomly selected locations around the greenhouse. The resulting holes were back-filled with fresh soil to avoid preferential flow pathways for the movement of pesticide and water. The depth of sampling was usually 40 cm, although in some cases the ground was too hard to be sampled below 30 cm.

**Modeling Studies.** Due to the high evaporative demand of the greenhouse environment, capillary rise was anticipated to be an important process. It was therefore considered to be necessary to use a model with a Darcy-based, rather than a capacity-based, description of water movement, in order to allow a mechanistic description of upward movement. The chromatographic flow model PEARL (18, 19) is a one-dimensional, multilayer model used in the assessment of leaching in pesticide registration procedures (20). PEARL (version 3.3.3) was selected for the simulation of imidacloprid and procymidone fate in the greenhouse. Soil water flow and temperature in PEARL are described using the model SWAP (21). PEARL simulates pesticide transport in water and as vapor. The processes considered by the model include losses through leaching and volatilization, pesticide degradation

**Table 1.** Properties of the Soil Layers of the Almería Greenhouse Soil

horizon name	depth (cm)	texture class	% H <sub>2</sub> O <sup>a,b</sup> (w/w)	pH <sup>a</sup>	OM <sup>a</sup> (%)	$\theta_s^c$ (cm <sup>3</sup> cm <sup>-3</sup> )	$\theta_r^c$ (cm <sup>3</sup> cm <sup>-3</sup> )	$\alpha^c$ (cm <sup>-1</sup> )	$n^d$	$K_s^d$ (m day <sup>-1</sup> )	$\lambda^{d,e}$
sand	0–10	sand	3.86	8.7	0.3	0.3275	0.0275	0.0383	2.68	7.128	1.68
clay	10–20	sandy clay loam	15.4	8.8	0.4	0.4756	0.1000	0.0792	1.48	0.3144	0.48
native 1	20–60	sandy loam	11.1	8.6	1.1	0.3442	0.0846	0.0978	1.89	1.061	0.89
native 2	>60	loamy sand	7.82	8.9	0.4	0.2128	0.0315	0.0828	2.28	3.502	1.28

<sup>a</sup> Measured values. <sup>b</sup> Gravimetric water content at 40% moisture-holding capacity. <sup>c</sup> Fitted to measured values. <sup>d</sup> Literature values. <sup>e</sup>  $\lambda = n - 1$ .

(according to first-order kinetics and adjusted to account for the effects of soil moisture, temperature, and depth), and plant uptake.

It is important when an attempt is made to simulate pesticide fate that soil water and temperature dynamics are well described. To evaluate this, model predictions of soil water content, water tension, and soil temperature were compared to measured greenhouse data prior to the simulation of pesticide behavior. On the basis of the pesticide simulations, several hypotheses were formulated and tested using further simulations. PEARL was not calibrated: all inputs came either from measured data or from appropriate literature sources.

**Input Parameter Values. Boundary Conditions.** The simulated soil profile consisted of 1 m of soil containing a variable amount of plant roots. The upper boundary condition was controlled by irrigation, soil evaporation, and crop transpiration from four crops of green beans over the two-year simulation period. The lower boundary condition was assumed to be free-draining as the groundwater table was over 100 m below the surface. A total of 58 numerical soil layers were considered in simulations.

**Soil Parameters.** The texture class and organic matter of the soils as reported in ref 8 are shown in **Table 1**. In PEARL, soil hydraulic properties are simulated using the retentivity–conductivity relationships by van Genuchten (22) and Mualem (23). Values for the parameters  $\alpha$ ,  $n$ ,  $\theta_s$ , and  $\theta_r$  were obtained from water outflow experiments (**Table 1**). The water contents of sieved and repacked soil cores were determined using tension tables (0–10 kPa) and pressure plates (10–1500 kPa). Sieved soil was used in place of undisturbed soil due to difficulties in extracting intact soil cores. Soil water content was measured in repacked soils (from which the stones had been removed). To account for the fact that stones are not involved in the water retention process, the volume of stones removed from the soil was determined, and the measured water content was adjusted accordingly. The corrected data were fitted to the van Genuchten (22) equation using the curve-fitting software RETC (24) to obtain values of  $\alpha$ ,  $\theta_s$ , and  $\theta_r$ . Determination coefficients ( $r^2$ ) were  $>0.98$  for each layer. Values of  $K_s$ ,  $n$ , and  $\lambda$  corresponding to sand, sandy clay loam, sandy loam, and loamy sand soils were taken from ref 25 to represent the sand, clay, and native layers of the profile, respectively.

**Climatic Parameters.** Potential evapotranspiration (ET<sub>0</sub>, mm day<sup>-1</sup>) was entered directly into PEARL. Daily measures of pan evaporation ( $E_{\text{pan}}$ , mm day<sup>-1</sup>) under standard conditions (grass sward) inside a similar greenhouse were available from a nearby meteorological station (Estación experimental “Las Palmerillas”, Caja Rural de Almería). ET<sub>0</sub> was estimated from  $E_{\text{pan}}$  by multiplying by a pan coefficient,  $K_p$  (26). The value of  $K_p$  was estimated as 0.85 [relating to a light wind speed ( $<2$  m/s), 1000 m windward side distance of a green crop and medium humidity (40–70%)].

The only inputs of water into the soil were from drip irrigation. Detailed records of irrigation timings were kept during the study. The drippers were calibrated to allow conversion of irrigation into equivalent rainfall depths, which were entered directly into the model.

The air temperature was recorded inside the greenhouse at times when a crop was present. During the noncropped periods, data from the meteorological station “Las Palmerillas” were used. The maximum and minimum daily temperatures measured in the greenhouse were used for the temperature inputs in PEARL.

**Cropping Parameters.** Four cropping periods were included in the simulations: September 21–December 30, 1997; January 27–June 17, 1998; October 2, 1998–January 12, 1999; and January 15–May 26, 1999. The crop type was field beans. The crop development routine in PEARL is based on the development stage, a linear scale from 0

(emergence) to 1 (harvest). Three crop stages (0, 0.5, and 1) were considered. The leaf area index was 0 m<sup>2</sup> m<sup>-2</sup> at stage 0 and 4 m<sup>2</sup> m<sup>-2</sup> at stages 0.5 and 1. This is the default FOCUS value for field beans (20). The maximum rooting depths were 0.1, 0.3, and 0.4 m at stages 0, 0.5, and 1, respectively.

**Pesticide Parameters.** Pesticide parameters used in simulations are presented in **Table 2**. Values of water solubility and vapor pressure were taken from literature sources (27, 28). The half-lives of imidacloprid (measured in soil at 70% of moisture-holding capacity and 20 °C) were 177.7, 247.5, 165.0, and 173.3 days in the sand, clay, native 1, and native 2 layers, respectively (29). Half-lives were corrected to the equivalent values at field capacity using the FOCUS method (20). Corrected half-lives were 80.3, 192.5, 112.9, and 115.3 days for the sand, clay, native 1, and native 2 layers, respectively. Degradation studies with procymidone performed in soil at 70% moisture-holding capacity and 20 °C (30) found that a residue of procymidone remained in the soil following an initial period of declining soil concentration. In reporting the aforementioned degradation study, the authors calculated a rate of loss of procymidone using pseudo-first-order kinetics, including a term for the residue of procymidone in the soil. To derive a half-life value suitable for use in PEARL, the rate constants and residue values reported in ref 30 were reanalyzed, and the time for a 50% decline in concentration was used as a surrogate for a first-order half-life as required by PEARL. Recalculated half-lives for procymidone were 48.1, 12.3, 16.2, and 10.0 days for the sand, clay, native 1, and native 2 soil layers, respectively. These then corrected to field capacity, giving half-lives of 21.5, 9.54, 11.1, and 6.64 days.

A factor was included in simulations to represent changes in imidacloprid and procymidone half-lives with soil depth. This factor was calculated by dividing the half-life in the clay and native soil layers by the half-life in the sand layer. The correction factors for half-life in the 10–20, 20–60, and 60–100 cm soil layers were 1.39, 0.93, and 0.93, respectively, for imidacloprid and 0.26, 0.34, and 0.34 for procymidone.

Activation energies for degradation were taken from laboratory studies (29, 30), and the Walker constant for the effect of moisture on degradation was taken from FOCUS guidance (31).

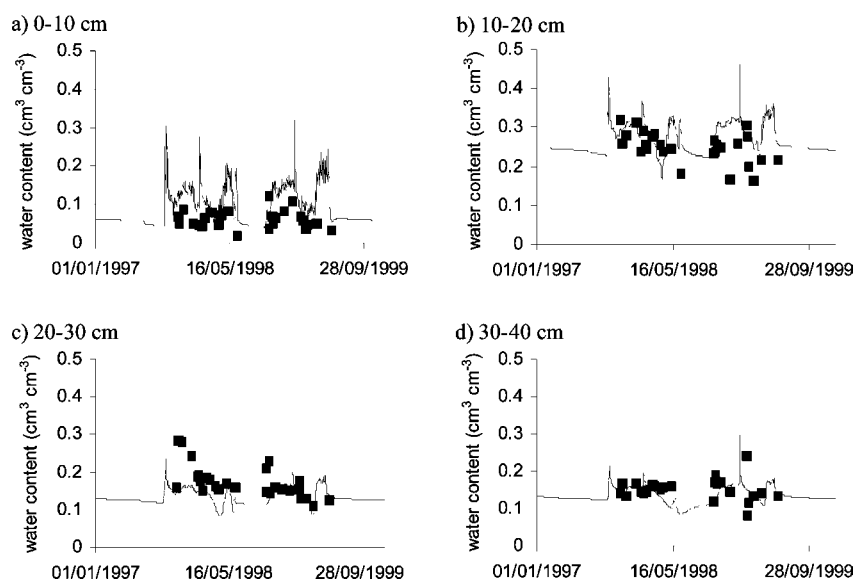
Values of the linear sorption coefficient, determined for the sand, clay, and native soil layers, reported in ref 8 were used in simulations. To take into account changes in sorption with depth, the sorption coefficient for the 0–10 cm layer was entered into the model. Correction factors were calculated by dividing the sorption coefficients for subsequent soil layers by that derived in the 0–10 cm layer. The correction factors applied to sorption in the 10–20, 20–60, and 60–100 cm soil layers were 1.26, 2.26, and 2.26, respectively, for imidacloprid and 1.61, 2.76, and 2.26 for procymidone. Due to the layered nature of the greenhouse soil, sorption was greater in the deeper soil layers than in the sandy surface layer. The Freundlich exponent,  $1/n$ , was set to 1 in order to represent linearity of sorption. To calculate volatilization of pesticides, the thickness of the boundary layer of still air above the soil surface must be estimated. The value used in simulations (0.01 m) is the same as used in FOCUS scenarios for groundwater (20) and among the largest mentioned by Jury (32), who reported a range of 0.0013–0.013 m. Crop uptake factors were taken from ref 27.

**Scenario Analysis.** Two scenario analyses were performed. The first was designed to better represent the localized application of water during drip irrigation. The second investigated the loss of procymidone through volatilization using alternate boundary layer thicknesses of 0.001 and 0.1 m.

**Table 2.** Properties of Imidacloprid and Procymidone Used in Simulations with PEARL

	imidacloprid	ref	procymidone	ref
water solubility	510 mg L <sup>-1</sup> <sup>a</sup>	26	4.5 mg L <sup>-1</sup> <sup>b</sup>	27
vapor pressure	$2 \times 10^{-7}$ Pa <sup>a</sup>	26	$1.8 \times 10^{-2}$ Pa <sup>b</sup>	27
$K_d^c$	0–10 cm = 0.19 L kg <sup>-1</sup> 10–20 cm = 0.24 L kg <sup>-1</sup> 20–60 cm = 0.43 L kg <sup>-1</sup> 60–100 cm = 0.43 L kg <sup>-1</sup>	7	0–10 cm = 0.62 L kg <sup>-1</sup> 10–20 cm = 1.01 L kg <sup>-1</sup> 20–60 cm = 1.71 L kg <sup>-1</sup> 60–100 cm = 1.38 L kg <sup>-1</sup>	7
1/n	1 <sup>d</sup>		1 <sup>d</sup>	
soil DT <sub>50</sub>	0–10 cm = 80.3 days <sup>e</sup> 10–20 cm = 192.5 days 20–60 cm = 112.9 days 60–100 cm = 115.3 days	28	0–10 cm = 21.5 days <sup>f</sup> 10–20 cm = 9.54 days 20–60 cm = 11.1 days 60–100 cm = 6.64 days	29
activation energy for degradation	38400 J mol <sup>-1</sup>	28	27800 J mol <sup>-1</sup>	29
Walker constant for degradation	0.7	30	0.7	30
TSCF <sup>g</sup>	0.331	26	0.371	26
incorporation depth	cropping periods 1 and 2, 0 cm <sup>h</sup> cropping periods 3 and 4, 10 cm <sup>i</sup>		0 cm <sup>h</sup>	
application rate	1.74, 0.58, 1.48, 1.44 kg ha <sup>-1</sup> <sup>j</sup>	7	6.75, 2.26, 6.15, 8.53 kg ha <sup>-1</sup> <sup>j</sup>	7

<sup>a</sup> Measured at 20 °C. <sup>b</sup> Measured at 25 °C. <sup>c</sup> Linear sorption coefficients measured in four soil layers. <sup>d</sup> Default selected to represent linearity of sorption. <sup>e</sup> DT<sub>50</sub> values reported in ref 28 corrected to field capacity. <sup>f</sup> DT<sub>50</sub> values reported in ref 29 corrected to field capacity. <sup>g</sup> Transpiration stream concentration factor. <sup>h</sup> Spray applications. <sup>i</sup> Estimated distribution depth following application in irrigation. <sup>j</sup> Applications made in four subsequent cropping periods.

**Figure 1.** Measured (■) and simulated (solid line) water contents simulated using SWAP for the (a) 0–10 cm, (b) 10–20 cm, (c) 20–30 cm, and (d) 30–40 cm soil layers.

## RESULTS AND DISCUSSION

**Water Flow and Soil Temperature.** Simulated soil water contents were close to the measured data (Figure 1). For the 0–10 cm layer, water content was overestimated and more variable compared to measured values. For the 10–20 cm layer, water content was accurately simulated during the first and second cropping periods, but overestimated at later times. The reverse was the case for the 20–30 cm soil layer; water content was accurately simulated during the third and fourth cropping periods but underestimated earlier in the experiment. Water content in the 30–40 cm layer was accurately simulated throughout the experiment.

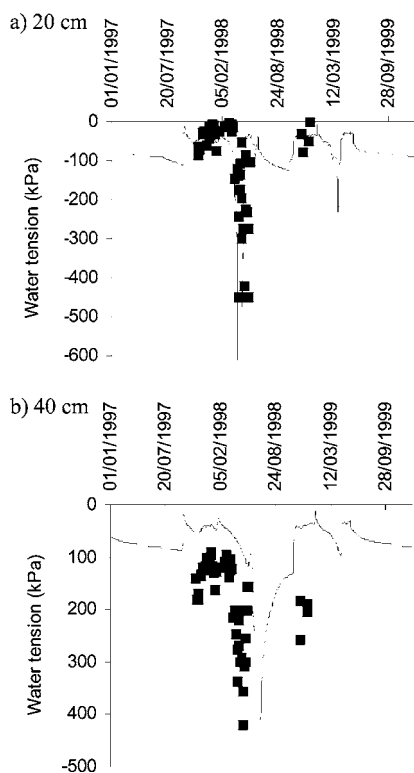
At 20 cm depth, the measured data indicate that the soil was near saturation for much of the cropping period, and there is a clear increase in tension with depth (Figure 2). In contrast, SWAP simulated fairly similar tensions at 20 and 40 cm depths. This suggests that downward water flow might have been greater

in the greenhouse than was simulated by SWAP. Measured soil water tension increased between April and June 1998. The model simulated an increase for both depths, but the increase was rather extreme (and beyond the measuring capability of the tensiometers used).

Explanations for the discrepancies between simulated and measured data can be grouped into inadequacies in measurements and inadequacies in model predictions. Due to the stoniness of the soil, insertion of the tensiometers was difficult. The structure of the soil near the tensiometers may have been altered in the insertion process, and this may have had an influence on the results obtained.

Parametrization may have been inadequate because repacked cores were used for the determination of the water retention curves. Undisturbed samples could not be removed due to the stoniness of the soil. Sieved soil was used for the measurements, and the results were corrected on the basis of the volume of





**Figure 2.** Measured (■) and simulated (solid line) soil water tension simulated using SWAP at depths of (a) 20 cm and (b) 40 cm.

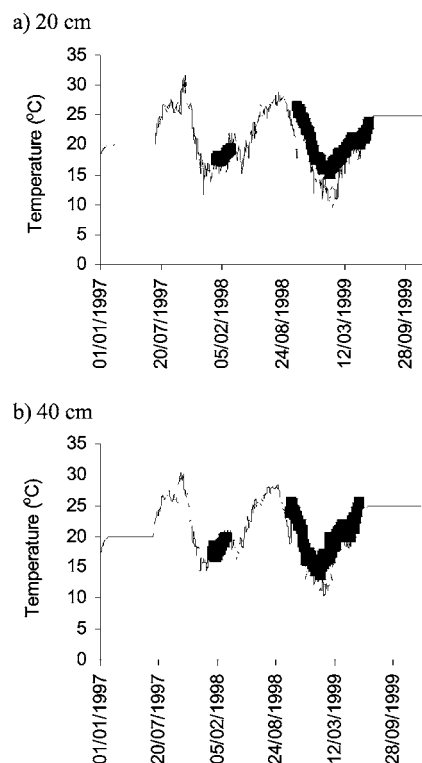
stones removed. However, this method would not include the structural influence that the stones had on the water retention curves or other structural features of the soil.

Hysteresis in the soil water retention curve was assumed to be negligible and was ignored in the parametrization of the model. Hysteresis implies that, at a given water content, soil water may have a range of potentials, depending on whether the soil is wetting or drying. Differences between the simulated and measured water retention curves may be partially explained by hysteresis in water retention in the greenhouse soil.

Fluctuations in soil temperature were well predicted by SWAP (**Figure 3**). Simulated temperatures were approximately 2–3 °C lower than the measured temperatures.

The simulated water balance (daily irrigation, water flux below 20 and 40 cm in the soil, and evapotranspiration) (**Table 3** and **Figure 4**) indicates that fluxes of water below 40 cm depth are related to the large volumes of irrigation applied before each sowing date. During the growing period, when irrigation is applied to meet crop development needs, there is very little water flux below 40 cm. Over the entire growing season, 18.5–49.6% of applied irrigation is transported through the soil to below 40 cm depth. The data presented in **Figure 4** suggest that, should pesticide leaching occur, it is most likely to be intermittent, occurring at times when the ground is prepared for the next crop. The pesticide residues in the soil from the previous crop may therefore be more important in terms of pesticide leaching than pesticide applied to a growing crop.

**Pesticide Fate.** The total amount of pesticide recovered from the soil is shown in **Figure 5**. For imidacloprid (**Figure 5a**), peak concentrations measured in the first and second cropping periods (with spray application) are accurately simulated by the model, although the decline was faster in the greenhouse soil than in the simulations. During the third and fourth cropping periods (with chemigation), peak concentrations are slightly underpredicted by the model, and the decline in residues is



**Figure 3.** Measured (■) and simulated (solid line) soil temperature simulated using SWAP at depths of (a) 20 cm and (b) 40 cm.

slower in the greenhouse soil than in the simulations. For procymidone (**Figure 5b**), the simulated peaks and declines agree reasonably well with the measured values (bearing in mind the scatter of the measured data).

The results from **Figure 5** have been split into individual soil layers in **Figures 6** and **7**. Simulated residues of imidacloprid in the 0–10 cm layer are close to measured residues over the whole experimental period (**Figure 6**). Residues of imidacloprid in the 10–20, 20–30, and 30–40 cm layers during the first and second cropping periods (spray application) are overestimated by the model, whereas those measured during the third and fourth cropping periods (chemigation) are reasonably well simulated.

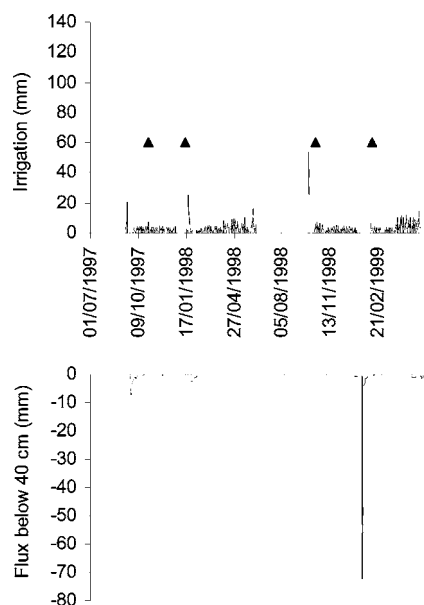
Simulated residues of procymidone in the 0–10 cm layer agree with measured residues (**Figure 7**). Peaks in simulated residues in the 10–20 cm layer occur marginally later than peaks in measured concentrations, and actual concentrations are generally overpredicted. Although procymidone concentrations measured in soil samples from the 20–30 and 30–40 cm layers were below the limit of detection in many samples, particularly in the first half of the experiment, quantifiable concentrations were detected at the later stages of the study. The model underestimated residues of procymidone measured in the 20–30 and 30–40 cm soil layers.

For comparison of measured residues at different soil depths, there are occasions when the residues measured in lower soil layers are higher than might be expected given the residues measured in the upper soil layers at the same time point. The maximum measured concentrations of procymidone in the 20–30 and 30–40 cm soil layers are 2.0 and 1.8 kg ha<sup>-1</sup>, compared to maximum simulated concentrations of 0.138 and 0.03 kg ha<sup>-1</sup>. The peak measured concentrations of procymidone in the 20–30 and 30–40 cm layers, recorded on February 10, 1999, and October 15, 1998, are approximately 4 and 10 times higher, respectively, than procymidone measured in the 10–20 cm layer at the same time point. As procymidone is moderately sorbed

**Table 3.** Water Balance for Each Cropping Period Simulated by SWAP

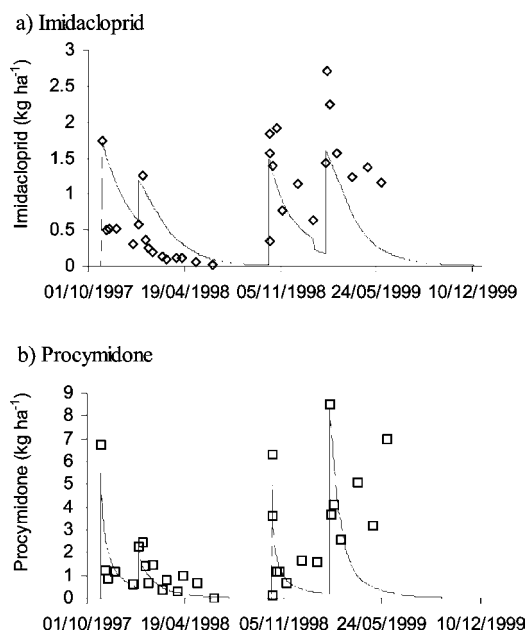
crop	date <sup>a</sup>	irrigation (mm)	evapotranspiration <sup>b</sup> (mm)	flux below 20 cm (mm)	flux below 40 cm (mm)	irrigation flux below 40 cm (%)
1	July 1–Dec 30, 1997	228.4	135.1	−101.9	−82.9	36.3
2	Dec 31, 1997–June 17, 1998	378.9	350.8	−131.9	−70.1	18.5
3	Jun 18, 1998–Jan 12, 1999	236.8	108.2	−70.9	−47.8	49.6
4	Jan 13–May 26, 1999	431.2	264.1	−247.4	−188.8	45.1

<sup>a</sup> Dates refer to the entire cropping period. For crops 2–4 this includes the period between removal of the previous crop and sowing. <sup>b</sup> Evapotranspiration is the sum of evaporation from the soil surface and root transpiration.

**Figure 4.** Actual daily irrigation and simulated flux below 40 cm. Solid triangles indicate application dates.

in the 0–10 and 10–20 cm soil layers ( $K_d = 0.62$  and  $1.01 \text{ L kg}^{-1}$ , respectively), the occurrence of concentrations in the lower soil layers comparable to those in the 10–20 cm layer suggests contamination. This may be the result of problems with the collection of soil samples. The soil was very hard when the samples were collected, and samples from the lower soil layers may have been contaminated with material containing higher concentrations of procymidone from the upper layers. However, the general agreement of simulated and measured residues suggests that incidents of contamination were infrequent.

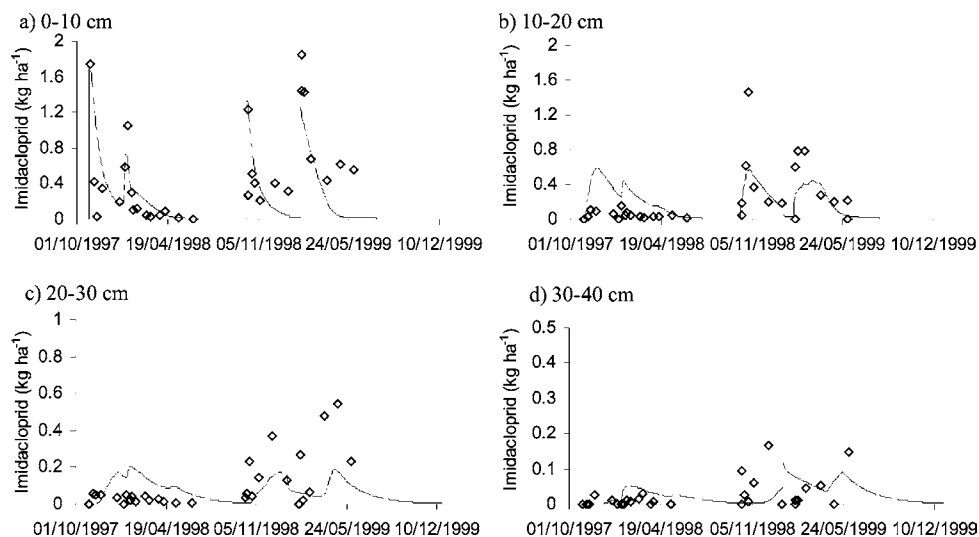
The general trend for comparison of measured and simulated residues of imidacloprid and procymidone in the soil is (i) an overprediction of imidacloprid residues at depths of  $>10$  cm during the first and second cropping periods (i.e., after spray application) and (ii) a delay in simulated procymidone residues at depths  $>10$  cm. These discrepancies may be due to the irrigation technique used in the greenhouse. One-dimensional models such as PEARL simulate a vertical movement of water through the soil profile. Water is assumed to be evenly distributed over the soil surface and to move downward from the surface, transporting pesticide into the profile. Drip irrigation is the only water input to the greenhouse, and irrigation data were used as a surrogate for rainfall in PEARL. Whereas the model assumed an even distribution of water over the soil surface and vertical movement of water and pesticide into the soil, the actual situation in the greenhouse was localized water and pesticide inputs to the soil profile, subject to both vertical

**Figure 5.** Total measured ( $\diamond$ ) and simulated (solid line) residues of (a) imidacloprid and (b) procymidone in the soil profile.

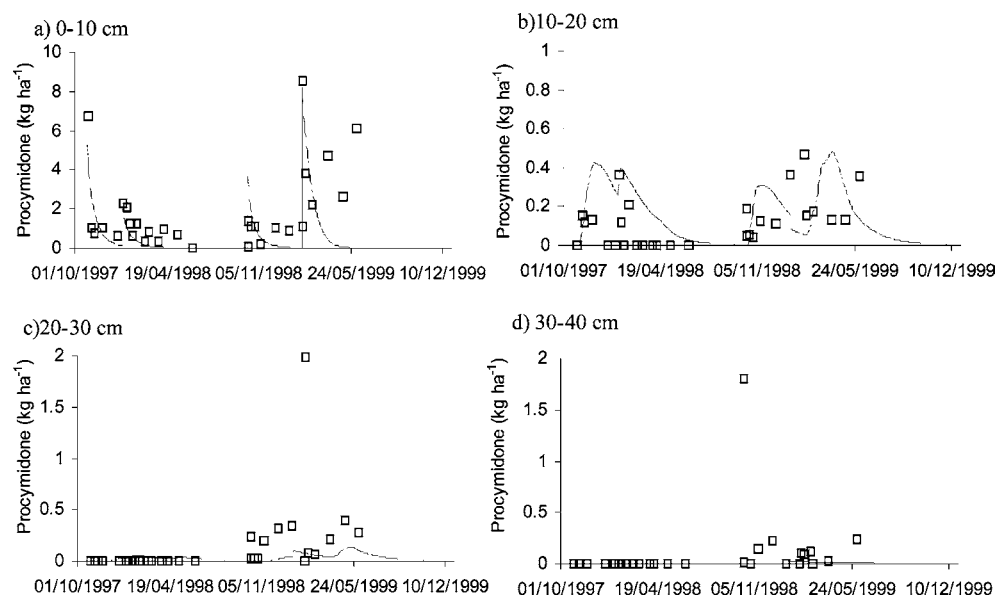
and lateral movements (33). Only the portion of pesticide applied in the vicinity of the irrigation dripper will be transported into the soil.

On the basis of its low  $K_d$  ( $0.19 \text{ L kg}^{-1}$ ), imidacloprid is not retained by the 0–10 cm layer. Coupled with the assumption of a uniform rather than localized movement of water, PEARL predicts that much of the imidacloprid is transported to the 10–20 cm soil layer within a few weeks. The low concentrations of imidacloprid measured in this layer in the greenhouse study may be the result of localized movement of small amounts of imidacloprid directly below the irrigation drippers. Whereas application to the first and second crops was by spraying to the soil surface, imidacloprid was applied to the third and fourth crops by chemigation. Using this method, imidacloprid enters the soil with irrigation water, rather than by being washed into the soil following spraying. This results in a higher concentration of imidacloprid in the 10–20 cm layer. Actual measured concentrations in the 10–20 cm are higher for the third and fourth applications, presumably because the entire applied dose has been transported through the sand. Therefore, simulated and measured values appear to have better agreement than for the first and second applications.

Peak residues of procymidone in the 10–20 cm layer were simulated to occur later than measured maximum residues. PEARL assumes some retention of procymidone by the 0–10 cm layer ( $K_d = 0.62 \text{ L kg}^{-1}$ ) and thus slower movement than for imidacloprid. However, the drip irrigation system may have



**Figure 6.** Measured ( $\diamond$ ) and simulated (solid line) residues of imidacloprid in the (a) 0–10 cm, (b) 10–20 cm, (c) 20–30 cm, and (d) 30–40 cm soil layers.



**Figure 7.** Measured ( $\square$ ) and simulated (solid line) residues of procymidone in the (a) 0–10 cm, (b) 10–20 cm, (c) 20–30 cm, and (d) 30–40 cm soil layers.

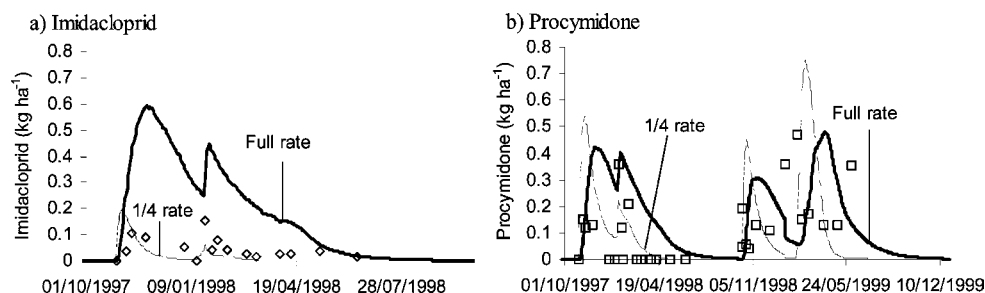
caused dissolution and transport of a portion of the applied procymidone, without time for equilibrium sorption to be reached.

To test this hypothesis, additional simulations were performed in which the application rates of imidacloprid and procymidone were 25% of those reported in **Table 2**, and the irrigation volumes (used to represent rainfall in the climate data file) were multiplied by 4. This approach was used to represent the portion of applied pesticide present in the vicinity of the irrigation drippers potentially available for transport by irrigation water and the localized inputs of water to the soil system from the irrigation system. Simulations were concerned only with spray applications of the pesticides and so were performed for the first and second applications of imidacloprid and all applications of procymidone. Simulated residues in the 10–20 cm layer are compared to measured values and the results of the initial simulations in **Figure 8**. For both compounds, the simulated concentrations agree more closely with the measured data, and for procymidone the timing of peak concentrations is improved. These results support the hypothesis that the inability of PEARL to accurately predict water and pesticide movement from drip

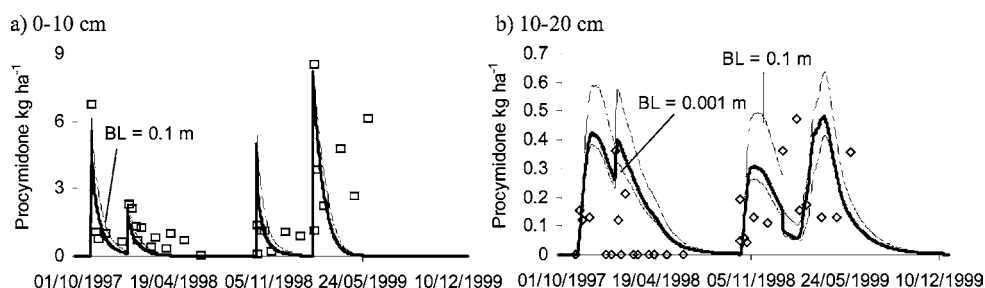
irrigation limits the usefulness of the model in predicting imidacloprid and procymidone movement.

**Important Processes for Fate of Imidacloprid and Procymidone in Greenhouse Soils.** For imidacloprid, the key process influencing fate was transformation; a maximum of 89% of the imidacloprid applied over the course of the experiment was degraded. For procymidone, the key process was volatilization; a maximum of 66% of the procymidone applied over the course of the experiment was volatilized.

Procymidone is known to be vulnerable to volatilization: Garratt and Wilkins (34) performed model simulations that predicted 83% of applied procymidone to be lost in airflow from a greenhouse over a 58 h period. In field studies in Italy (35), 15.9% of applied procymidone was lost by volatilization 6 days after an application in December, and 41.5% was lost 16 days after an application in September. The simulations reported thus far assumed a boundary layer thickness of 0.01 m, as did those reported in ref 34. In the context of PEARL, the boundary layer thickness refers to the laminar air boundary layer, the distance over which pesticide vapor moves via diffusion prior to turbulent mixing with the overlying atmospheric layer. To assess the



**Figure 8.** Measured residues of (a) imidacloprid ( $\diamond$ ) and (b) procymidone ( $\square$ ) in the 10–20 cm layer and simulated concentrations calculated with the standard application rate and irrigation (bold solid line) and with 25% application rate and  $\times 4$  irrigation (solid line).



**Figure 9.** Simulated concentrations of procymidone in the (a) 0–10 cm and (b) 10–20 cm layer calculated using PEARL with a boundary layer thicknesses (BL) of 0.001, 0.01 (bold solid line), and 0.1 m.

influence of the boundary layer on procymidone fate, residues of procymidone in the 0–10 and 10–20 cm layers were simulated using boundary layer thicknesses of 0.001, 0.01, and 0.1 m (Figure 9). Increasing the boundary layer thickness did not have a large effect on simulated procymidone residues in the 0–10 cm layer: the results of simulations with boundary layer thicknesses of 0.001 and 0.01 m are indistinguishable in Figure 9a. However, increasing the boundary layer thickness from 0.001 to 0.1 m increased procymidone concentrations in the 10–20 cm layer, on average, by a factor of 1.5.

This result is of particular interest for procymidone fate in the greenhouse environment, where the layer of still air above the soil surface is anticipated to be greater than that under outdoor conditions. Under such conditions, pesticides prone to volatilization (such as procymidone) may be more persistent in the soil. This could then have implications for movement to deeper soil layers and potentially to groundwater.

**Conclusions.** The model PEARL was evaluated in terms of its ability to predict soil hydrology and concentrations of imidacloprid and procymidone in a layered greenhouse soil. When parametrized using measured values of hydrological characteristics, the simulated water content of the 0–10 and 10–20 cm layers was in reasonable agreement with measured values. Agreement between measured and simulated values was poorer for the deeper soil layers, and the model had a tendency to underestimate soil water content, particularly in the 20–30 cm layer. Soil water tension was generally overpredicted by the model at low pressures at 20 and 40 cm depths. However, the model simulated extreme fluctuations in soil water tension between low and high pressures, which were not supported by the measured data. On the basis of these comparisons, the modeled soil hydrology was generally drier (in particular the lower soil layers) and more variable than actual greenhouse conditions. This suggests that downward water flow may have been greater in the greenhouse than was simulated by the model. Simulated soil temperature agreed well with measured data.

Residues of imidacloprid and procymidone throughout the soil profile were, on the whole, reasonably simulated by PEARL. However, comparisons between the modeled and measured data

suggest areas where the model cannot predict concentrations well. This appears to be linked to the irrigation method used in the greenhouse. In the simulations, irrigation data were used as a surrogate for rainfall. PEARL assumes a uniform distribution of rainfall over the soil surface, rather than a localized influx of water, as is the case for drip irrigation. This resulted in a general overprediction of spray-applied imidacloprid concentrations and a delayed breakthrough of procymidone concentrations. Simulated concentrations of both pesticides were in closer agreement with measured data when simulations were set up to approximate conditions under drip irrigation.

One of the key drivers for research of this type is to help provide a standardized and reliable framework for regulators and the crop protection industry, to assess the safety of pesticides. Obviously we have not yet arrived at this point. The main reason is the difficulty in simulating a multidimensional system with a one-dimensional model. Other issues that have yet to be addressed include the presence of pesticide residues prior to treatment and the relocation of irrigation drippers between cropping periods.

There are a number of avenues that could be explored to get closer to the goal. The first point is that a survey of the hydrological characteristics of greenhouse soils in Almería would be useful to more fully calibrate and evaluate mathematical modeling of the greenhouse environment. The second point is that simulations using a two-dimensional flow model would be useful, preferably supported by appropriate greenhouse experiments. These should include an improved sampling strategy to avoid contamination between samples collected from different depths, improved soil moisture and soil water tension measurements, and the direct measurement of soil hydraulic properties to permit full calibration of the model.

The third point is to perform additional simulations to check whether one-dimensional models can, in fact, be used to approximate the conditions of drip irrigation and spray application of pesticides. We propose this may be possible by splitting each pesticide application into two: the first on the actual day of application, and the second at a later time, just before the drip pipes are moved. The thickness of the simulated sand layer



could be reduced to ensure that transport of the pesticide to the clay layer below was not retarded.

The results of this study indicate that one-dimensional models cannot yet be recommended for the simulation of pesticide leaching in greenhouses under drip irrigation. However, this may be possible in the future given enough experimental information to develop a reliably calibrated scenario.

## ABBREVIATIONS USED

PEARL, pesticide emission assessment at regional and local scales (model name); SWAP, soil water atmosphere plant (model name); FOCUS, forum for the co-ordination of pesticide fate models and their use.

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