Dynamic plant uptake model applied for drip irrigation of an insecticide to pepper fruit plants

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Abstract

BACKGROUND: Drip application of insecticides is an effective way to deliver the chemical to the plant that avoids off-site movement via spray drift and minimizes applicator exposure. The aim of this paper is to present a cascade model for the uptake of pesticide into plants following drip irrigation, its application for a soil-applied insecticide and a sensitivity analysis of the model parameters.

RESULTS: The model predicted the measured increase and decline of residues following two soil applications of an insecticide to peppers, with an absolute error between model and measurement ranging from 0.002 to 0.034 mg kg \( \text{fw}^{-1} \). Maximum measured concentrations in pepper fruit were approximately 0.22 mg kg \( \text{fw}^{-1} \). Temperature was the most sensitive component for predicting the peak and final concentration in pepper fruit, through its influence on soil and plant degradation rates.

CONCLUSION: Repeated simulations of pulse inputs with the cascade model adequately describe soil pesticide applications to an actual cropped system and reasonably mimic it. The model has the potential to be used for the optimization of practical features, such as application rates and waiting times between applications and before harvest, through the integrated accounting of soil, plant and environmental influences.

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Keywords: pesticide; matrix; crops; residues; plant protection; insecticide

1 INTRODUCTION

Dynamic mathematical models that predict uptake of pesticides by roots and translocation to leaves and fruit were developed earlier. These models consider the physiological processes of plants (water transport, gas exchange, adsorption and reaction) and treat the main plant organs, i.e. roots, stem, leaves and fruit, as compartments. The resulting ordinary differential equation systems have been solved either for the steady state or by numerical methods. Steady-state solutions are simple and can also be implemented easily in spreadsheets. However, only constant scenarios can be considered, such as soil pollution with persistent compounds or regional air-borne pollution. Numerical solutions can principally handle any type of input, i.e. pulse input, constant input or irregular input, but the stepwise integration of differential equations is not well suited for implementation into spreadsheets, which are common tools applied for modelling.

Analytical solutions of differential equation systems do not have these disadvantages, but they are only known for some types of input, and mostly for linear systems. Here, a five-compartment plant uptake model is presented that considers concentrations in soil, roots, stem, leaves and fruit. The matrix is solved analytically for pulse input. Using the superposition principle, an unlimited number of periods can be considered, with each period having its own set of input and plant parameters. This allows all types of input and the simulation of real scenarios to be approached practically, but avoids the disadvantages of numerical integration methods.

Use of crop protection products such as insecticides is part of standard agronomic practice to ensure the health and yield of crops. Drip application of insecticides is an effective way to deliver protection for the plant that avoids off-site movement via spray drift and minimizes applicator exposure. Empirical methods are often used to determine the optimum amount of the crop protection product to apply in order to provide the required protection of the plant while minimizing the crop protection residues in the produce. However, empirical models such as regressions are limited in their predictive power to the range of input, and do not provide a mechanistic interpretation of the processes and results. Availability of a physiologically based model...
such as described in this paper has the potential to provide a more variable and accurate predictive tool to estimate the chemical product concentration in growing plants and final produce, or even to determine whether the product has the potential to provide plant protection via soil application.

Such a model would provide a predictive tool for the agronomist that looks for a soil-applied solution, as is currently enjoyed by those that protect the plant through foliar application. The model thus developed for uptake from soil was evaluated against information derived from drip application of a representative systemic insecticide. The example used here is methomyl applied to peppers. The product use scenario represented in this paper (drip irrigation in peppers) is not relevant to any registered use of methomyl by DuPont at the time of publication. Therefore, the measured concentrations are relevant for model validation purposes only. Methomyl, a member of the carbamate class of insecticides, was introduced in 1968 by DuPont. It is a fast-acting foliar-applied insecticide, has a broad spectrum of insecticidal activity and exhibits short residual activity.

The primary objective of this paper is to present the model as it can be used to represent a drip irrigation application. In addition, a sensitivity analysis will be conducted to evaluate the importance of the parameters for the model predictions.

2 DYNAMIC PLANT UPTAKE MODEL

2.1 Model overview

The model has five compartments, namely soil, roots, stem, leaf and fruit. Soil, roots, stem and leaf or fruit are considered as a cascade (i.e. the flow is from roots to stem and to leaves and fruit). Leaf and fruit are parallel (Fig. 1). The following processes are considered in the model:

- pulse input to soil or any plant compartment;
- loss from soil and all plant compartments to air;
- uptake into roots with the transpiration water;
- translocation from roots to stem and from stem to leaves and fruit with the transpiration stream;
- transport to fruit with phloem;
- transport to leaves and fruit with attached soil;
- growth dilution and metabolism in all plant compartments;
- leaching from soil;
- degradation of chemical in soil;
- calculation of transpiration and growth rates from plant mass at various time points;
- temperature dependency of rates.

Loss and transfer rates are first order. All inputs and rates may vary from period to period. Twenty-four periods were considered in the present simulation. Principally, deposition from air can be considered, but in the present scenario it was neglected, assuming negligible background concentration of methomyl in air.

2.2 Differential equations

The model is based on earlier approaches, where details of the processes are described. Here, only the differential equations for the concentration in each compartment are given.

The differential equation for concentration in soil is

$$\frac{dC_S}{dt} = - \left( \frac{Q_{inf}K_{WS}}{M_S} + \frac{Q_{i}K_{WS}}{M_S} + \frac{A_S P_{S} P_{S, wet} 1000 L m^{-3}}{M_S} \right) + k_{deg} \times C_S \quad (1)$$

where $C_S$ (mg kg $ww^{-1}$) is the concentration in soil, $M_S$ (kg $ww$) is the mass of soil available for plant uptake, $P_S$ (m $day^{-1}$) is the permeability of the soil, i.e. the transfer velocity of the chemical from soil to air, $Q_{inf}$ (L $day^{-1}$) is the leaching of water, $Q_i$ (L $day^{-1}$) is the water taken up by roots, $P_{S, wet}$ (kg $ww$ L$^{-1}$) is the soil wet density, $A_S$ (1 m$^2$) is the surface area of soil, $k_{deg}$ (day$^{-1}$) is the degradation rate in soil and $K_{WS}$ (kg $ww$ L$^{-1}$) is the water to bulk soil partition coefficient.

Drip irrigation is modelled as a pulse input. The mass of methomyl in the irrigation water is added to the (calculated) mass of methomyl in soil at the end of the preceding period. The resulting concentration in soil serves as the starting concentration for the following period.

The differential equation for concentration in roots is

$$\frac{dC_R}{dt} = + \frac{Q_i K_{WS}}{M_R} C_S - \left( \frac{Q_R}{M_R K_{rw}} + k_G + k_m \right) \times C_R \quad (2)$$

where $C_R$ (mg kg $fw^{-1}$) is the concentration in roots, $M_R$ (kg $fw$) is the root mass [equation (13)], $k_G$ (day$^{-1}$) is the growth rate of roots [equation (14)] and $k_m$ (day$^{-1}$) is the metabolism rate of roots.

The partition coefficients between plant tissue (roots, stem, leaves or fruit) and water, $K_{pw}$ (L $kg$ $fw^{-1}$), are all calculated from the octanol-water partition coefficient, $K_{ow}$ (L $L^{-1}$), the lipid content $L$ (kg kg $fw^{-1}$) and the water content $W$ (L kg $fw^{-1}$) of the respective tissue:

$$K_{pw} = W + L \times 1.22 \times K_{ow}^b \quad (3)$$

The exponent $b$ considers differences between plant lipids and octanol and is 0.77 for roots and 0.95 for stem, leaves and fruit.

The differential equation for the concentration in stem is

$$\frac{dC_{St}}{dt} = + \frac{Q_R}{K_{rw} M_{St}} C_R - \left( \frac{Q_R}{M_{St} K_{sw}} + \frac{A_S g_{r/St} K_{sw} 1000 L m^{-3}}{K_{sw} M_{St}} \right) + k_G \times C_{St} \quad (4)$$

where the subscript ‘St’ denotes stem. The conductance of roots and stem, $g_{r/St}$ (m $day^{-1}$), is the transfer velocity via the cuticle pathway, including the additional resistance of a gaseous and an
The differential equation for the concentration in leaves is

$$\frac{dC_l}{dt} = + \frac{Q_L}{K_{SW} M_L} C_{St} - \left( \frac{A_L g_{l,t} K_{AW} 1000 L m^{-3}}{K_{SW} M_L} + k_G + k_m \right) \times C_L$$

where the subscript 'L' denotes leaf, and Q_L is the net flux of xylem to leaves and phloem from leaves [equation (15b)]. The conductance of leaf and fruit, g_{l,t} (m day^{-1}), is composed of the parallel resistances of the stomatal and cuticular pathways. The resistance of the stomata is calculated for each period from transpiration, temperature, relative humidity and surface area of the plant.\textsuperscript{13}

The differential equation for the concentration in fruit is

$$\frac{dC_f}{dt} = + \frac{Q_F}{K_{SW} M_F} C_{St} - \left( \frac{A_F g_{f,t} K_{AW} 1000 L m^{-3}}{K_{SW} M_F} + k_G + k_m \right) \times C_F$$

where the subscript 'F' denotes fruit, and Q_F (L day^{-1}) is the sum of xylem and phloem flux to fruit [equation (15c)].

### 2.3 Solution of the differential equation system

With compartment 1 equal to soil, compartment 2 equal to roots, compartment 3 equal to stem and compartment 4 equal either to fruit or leaves (fruit and leaves are parallel), the differential equations can be rewritten as a matrix:

$$\frac{d\mathbf{C}}{dt} = \begin{pmatrix} -k_1 & 0 & 0 & 0 \\ k_{12} & -k_2 & 0 & 0 \\ 0 & k_{23} & -k_3 & 0 \\ 0 & 0 & k_{34} & -k_4 \end{pmatrix} \mathbf{C}$$

where the symbols k_1, \ldots, k_4 denote the first-order loss rates (unit day^{-1}) from the compartments, and rates k_{12}, k_{23} and k_{34} are the transfer rates from compartment 1 to 2, compartment 2 to 3 and compartment 3 to 4 respectively (unit day^{-1}). This is a linear diagonal matrix for which solutions exist.

#### 2.3.1 Pulse input

A pulse input leads to an initial concentration (at t = 0) in one or more compartments:

$$C(0) = \frac{I}{M}$$

where I is the pulse input (mg) and M is the mass of the compartment (kg). Thus, the analytical solution for a pulse input is the same as for initial concentrations unequal to zero, C(0) \neq 0:

$$C_1(t) = C_1(0) \times e^{-k_1 t}$$

$$C_2(t) = k_{12} C_1(0) \times \left( \frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2} \right) + C_2(0) \times e^{-k_2 t}$$

$$C_3(t) = k_{12} k_{23} C_1(0) \times \left( \frac{e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)(k_3 - k_2)} + \frac{e^{-k_3 t}}{(k_1 - k_3)(k_2 - k_3)} \right)$$

$$+ k_{23} C_2(0) \times \left( \frac{e^{-k_2 t}}{k_3 - k_2} + \frac{e^{-k_3 t}}{k_2 - k_3} \right)$$

$$C_4(t) = k_{13} k_{24} C_1(0) \times \left( \frac{e^{-k_1 t}}{(k_4 - k_1)(k_3 - k_1)} + \frac{e^{-k_2 t}}{(k_4 - k_2)(k_3 - k_2)} + \frac{e^{-k_3 t}}{(k_4 - k_3)(k_2 - k_3)} \right)$$

$$+ \frac{k_{23} k_{34} C_2(0) \times \left( e^{-k_2 t} \right)}{(k_4 - k_2)(k_3 - k_2) + (k_3 - k_4)(k_2 - k_4)}$$

$$+ \frac{k_{34} C_3(0) \times \left( e^{-k_3 t} \right)}{k_4 - k_3 + k_3 - k_4}$$

$$+ C_4(0) \times e^{-k_4 t}$$

### 2.3.2 Superposition

The simulation is divided into n periods during which the conditions are constant. Each period is further subdivided into 30 time intervals for output only. The above analytical solution is applied for each period, and the result from one period is entered as the initial value for the following period. This makes it possible to vary all rates and constants for each period, and thus also to approach a non-linear input (such as logistic growth of plants, or changing weather conditions). The analytical solution extended with an inhomogeneous term for constant input was tested elsewhere against a numerical solution. Even though the scenario was non-linear (logistic growth), practically no difference was seen for the two solution methods if the chosen periods were sufficiently short (1–5 days).\textsuperscript{16}

### 2.4 Parameterization

Model input parameters are based on the experimental settings described below and are presented in Table 1. No other input of methomyl than by drip irrigation was considered.

The simulation was over 35 days, which corresponds to the time period from the date of the first insecticide application to the date of last sampling, and was divided into 24 periods, each with a length of 1.5 days. During this simulation period, the pepper fruit plants were continuously ripening and harvested. To account for harvesting, the mass, transpiration and growth rates of the different plant parts were kept constant for all 24 time periods (each with a length of 1.5 days) of the model. Also, growth rates (and so growth dilution) were derived for each plant part.

The planting density was 2 plants m^{-2}. The yield per plant was estimated to be 14 fruits. The average weight of the sampled pepper fruit was 50 g fresh weight (fw). Altogether, fruit mass at harvest was 1.40 kg fresh weight (fw). Mass, growth and transpiration rates were calculated assuming logistic growth of the plant.
Table 1. Model parameters (unless otherwise noted, values were taken from the experiment)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry density</td>
<td>$\rho_{\text{dry}}$</td>
<td>1.58</td>
<td>kg dw L$^{-1}$</td>
</tr>
<tr>
<td>Infiltration flux$^a$</td>
<td>$Q_{\text{in}}$</td>
<td>0.27</td>
<td>L m$^{-2}$ day$^{-1}$</td>
</tr>
<tr>
<td>Organic carbon content</td>
<td>$f_{\text{OC}}$</td>
<td>1.16</td>
<td>g kg dw$^{-1}$</td>
</tr>
<tr>
<td>Water content</td>
<td>$W_0$</td>
<td>0.45</td>
<td>L $^{-1}$</td>
</tr>
<tr>
<td>Soil depth (rooting depth)</td>
<td>$z_s$</td>
<td>0.6</td>
<td>m</td>
</tr>
<tr>
<td>Roots</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water content$^b$</td>
<td>$W_R$</td>
<td>0.89</td>
<td>L kg fw$^{-1}$</td>
</tr>
<tr>
<td>Lipid content$^b$</td>
<td>$L_R$</td>
<td>0.025</td>
<td>kg kg fw$^{-1}$</td>
</tr>
<tr>
<td>Stem</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water content$^a$</td>
<td>$W_{S1}$</td>
<td>0.5</td>
<td>L kg fw$^{-1}$</td>
</tr>
<tr>
<td>Lipid content$^b$</td>
<td>$L_{S1}$</td>
<td>0.02</td>
<td>kg kg fw$^{-1}$</td>
</tr>
<tr>
<td>Stem specific surface area$^a$</td>
<td>$A_{S1}$</td>
<td>2</td>
<td>m$^2$ kg fw$^{-1}$</td>
</tr>
<tr>
<td>Leaf</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water content$^c$</td>
<td>$W_L$</td>
<td>0.8</td>
<td>L kg fw$^{-1}$</td>
</tr>
<tr>
<td>Lipid content$^c$</td>
<td>$L_L$</td>
<td>0.02</td>
<td>kg kg fw$^{-1}$</td>
</tr>
<tr>
<td>Leaf specific surface area$^c$</td>
<td>$A_L$</td>
<td>0.0063</td>
<td>m$^2$ kg fw$^{-1}$</td>
</tr>
<tr>
<td>Soil attachment$^d$</td>
<td>$T_S$</td>
<td>0.01</td>
<td>g ww g fw$^{-1}$</td>
</tr>
<tr>
<td>Fruit</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water content$^d$</td>
<td>$W_F$</td>
<td>0.938</td>
<td>L kg fw$^{-1}$</td>
</tr>
<tr>
<td>Lipid content$^d$</td>
<td>$L_F$</td>
<td>0.003</td>
<td>kg kg fw$^{-1}$</td>
</tr>
<tr>
<td>Fruit specific surface area$^d$</td>
<td>$A_F$</td>
<td>0.32</td>
<td>m$^2$ kg$^{-1}$</td>
</tr>
<tr>
<td>Soil attachment$^d$</td>
<td>$T_S$</td>
<td>0.001</td>
<td>g ww g fw$^{-1}$</td>
</tr>
</tbody>
</table>

$^a$ Generic values. 
$^b$ Trapp. 
$^c$ Trapp and Matthies. 
$^d$ Only at harvest, Legind and Trapp. 
$^e$ DTU Food.

...rapid equilibration of concentrations in phloem and xylem, this approach is valid. Neutral compounds equilibrate, unless they are very polar.

The temperature dependence of soil degradation and plant metabolism rates was accounted for by using the following expression:

$$k_{\text{deg/m}} = k_{\text{deg/m}}(20 \degree C)k_{\text{Arr}}(T - 20 \degree C)$$

where $k_{\text{Arr}}$ (1.099) is the Arrhenius constant for temperature correction, calculated from the temperature coefficient $Q_10$ (2.58). This value was derived for pesticide degradation in soil and is here also applied for plant metabolism owing to the present lack of better knowledge.

2.5 Sensitivity analysis

The sensitivity of the model was tested by Monte Carlo analysis by 5000 trials for each run using the Crystal Ball software. The sensitivity of input parameters was investigated separately for chemical parameters, plant parameters and environmental parameters. The forecast parameter was the maximum concentration in fruit (over the whole period) and the final concentration in fruit (at $t = 35$ days). All parameters were varied with a standard deviation of 0.1 times the default and using a normal distribution. The sensitivity was expressed by the correlation between input and output parameters.

3 EXPERIMENTAL METHODS

3.1 Physicochemical properties of methomyl

Methomyl is a water-soluble, non-volatile and xylem-mobile chemical (Table 3).
3.2 Experimental settings

Sweet pepper plants (*Capsicum frutescens* L. cv. *Italico*) were planted in six rows of 53 plants each, three control and three treatment rows, on 6 June 2005 in a sandy soil in a plastic house at the Chipiona Platform, Spain. There were two treatments with methomyl, the first on 1 August, which was the start of the experiment (day 0), and the second on 15 August (day 14). The insecticide was applied by drip irrigation using carbon-dioxide-pressurized equipment applying 3019 L solution ha$^{-1}$, resulting in an input of 100 mg m$^{-2}$ of methomyl to the soil per application. The insecticide was applied in a narrow band of 7.62 cm around the roots. For the simulation, the input per m$^{2}$ was averaged, assuming that the plants, which had grown up, drew water from the entire area.

The average temperature in the plastic house was 30 °C, and the relative humidity was 49%. Plants were watered using drip irrigation over the period from 1 August 1 to 5 September 2005. Water irrigation was conducted as appropriate to meet crop needs and environmental conditions. That is, adequate soil moisture was maintained so that water levels allowed crop growth without water stress. The chemical was injected during the middle third of the irrigation cycle for optimum placement of the chemical in the root zone.

The treated plants were sampled 9 times (2 h after the first treatment (day 0.08), day 3, day 7, day 14, 2 h after the second treatment (day 14.08), day 17, day 21, day 28 and day 35). The control plants were sampled once (day 21). Each sample consisted of 24 fruits (weight 1.1–1.4 kg fw) that were put in sample bags and frozen at −22 to −28 °C.

3.3 Analysis of pepper fruit residues

Determinations of methomyl were carried out by extraction from pepper fruit homogenate by shaking with a mixture of organic solvents (acetone + dichloromethane + petroleum ether), followed by sample clean-up by solid-phase extractions using an aminopropyl cartridge. Additional detail is available in the Netherlands multiresidue method for N-methylcarbamate pesticides. A single analysis of each unique pepper fruit sample was performed.

Chromatographic separation of the extract was performed using a C18 column (Agilent Hypersil ODS, 3 μm particle size, length 100 × 2.1 mm inner diameter). The injection volume was 30 μL, the flow rate was 0.3 mL min$^{-1}$, the autosampler temperature was 4 °C and the column temperature was 30 °C. Residues were detected and quantified by high-performance liquid chromatography with tandem mass spectrometry detection methodology (LC-MS/MS, turbo ion spray, positive). Quantification was based on the gas-phase dissociation reaction of protonated methomyl, (M + H)$^{+}$ at m/z 163.1, to the most abundant fragment ion at m/z 106.1. The confirmatory ion transition monitored was m/z 163.1 to m/z 88.1. The analyte identity was also confirmed by comparison of the retention time obtained from an analytical standard to that of peaks observed in field samples.

Method behavior was monitored during the analysis of treated pepper fruits by fortification of control pepper fruit samples with known amounts of methomyl. Recoveries of methomyl from fortified samples were monitored as a quality check of the ability of the method adequately to quantify the level of methomyl in the pepper fruit. Recoveries ranged from 85 to 93% (n = 5). Separately, the stability of methomyl under frozen storage conditions and the robustness of the extraction technique to remove incurred residues of methomyl were determined. The level of quantification of this method for methomyl was 0.010 mg kg fw$^{-1}$ pepper fruit tissue.

4 RESULTS

Methomyl is approved for use as a crop protection chemical in various countries. However, the product use scenario represented in this paper is not relevant to evaluation of any registered use for the product. It is useful, however, for the purposes of validation of this model.

No methomyl could be detected in the control pepper fruit. Figure 2 shows the calculated model results compared with the measured concentration of methomyl in pepper fruit. The concentration in fruit reaches a maximum 3 days after application and then declines until the second application appears. At the end of the simulation (t = 35 days), measured concentrations were below the detection limit (0.005 mg kg fw$^{-1}$), and simulated concentrations were below 0.01 mg kg fw$^{-1}$. The figure shows the model result before calibration. This demonstrates that the overall model structure (i.e. the compartments and fluxes) describe the system adequately.

Figure 3 shows the calculated concentrations in all compartments. The concentrations in roots and stem follow closely the concentration in soil, indicating rapid uptake and translocation. Concentration in roots is higher than in stem owing to a calculated transpiration stream concentration factor (TSCF) of 0.57 (unitless ratio). The TSCF is defined as the concentration of pesticide in xylem sap divided by the concentration in soil solution. Translocation into leaves and fruit occurs some days later, because the acropetal transport through stem takes time. However, at the end of the period, residues in leaves and fruit are also higher than in

![Figure 2](image-url) Concentration in pepper fruit versus time (days); model results compared with measurements (values below the detection limit shown as half the detection limit (0.0025 mg kg fw$^{-1}$)).

![Figure 3](image-url) Calculated concentrations in soil (CS), roots (CR), stem (CSt), leaves (CL) and fruit (CF) (mg kg fw$^{-1}$) versus time (days); y-axis in log scale.
soil, roots or stem. The highest concentrations are calculated for leaves. Maximum concentrations are at 4.5 mg kg⁻¹ because methomyl is xylem mobile and non-volatile, and leaves transpire most of the water.

5 DISCUSSION

5.1 Sensitivity analysis

Of the chemical parameters (K₆W, K₉W, M, degradation rate k₈deg, metabolism rate k₈m, pulse input I and Arrhenius temperature correction constant k₈Arr), the temperature correction constant k₈Arr had by far the highest sensitivity [correlation S = −0.99 to both C₉fruit (max) and C₉fruit (end)]. The next sensitive parameters were input I at t = 0 days and t = 14 days, with S = 0.05 and 0.06. The degradation rate in soil and the metabolism rate in fruit also had some (low) sensitivity (S = −0.02 to −0.05). All other model input parameters had less than 2% (0.02) sensitivity. An explanation is that k₈Arr has an exponential impact and acts on all degradation and metabolism rates simultaneously. If the analysis was repeated without considering k₈Arr, the degradation rate in soil (S = −0.84) and the metabolism rate in fruit (S = −0.46) had the highest impact on final concentration in fruit, followed by the second input (S = +0.23). For the maximum concentration in fruit, the second input showed the largest correlation (S = +0.60), followed by metabolism rate in fruit (−0.54), degradation rate in soil (−0.43) and the first input to soil (+0.22).

Among the environmental and plant parameters, temperature is the most significant (S = −0.88). As a result of the Arrhenius temperature correction of rates, increasing temperature leads to increasing degradation and metabolism rate constants in all compartments, and therefore decreasing maximum and final concentration in fruit. Besides, fruit mass (S = −0.25), water flux to fruit (S = 0.24) and soil mass (S = −0.23) are relevant for the maximum concentration in fruit. For the final concentration in fruit, again temperature is most significant (S = −0.99), followed by mass of soil (S = −0.09) and fruit (S = −0.07), water flux to fruit (S = +0.07) and growth rate of fruit (S = −0.04). All other environmental parameters have S ≤ 0.02.

In reality, temperature also has a (positive and exponential) effect on transpiration. This effect was not seen here because transpiration was calculated from plant mass and not calculated from temperature and humidity. The effect of temperature on the rate of cyanide metabolism of two woody plants gave Arrhenius constants between 1.063 and 1.076. Values of the Arrhenius rate constant for metabolism in plants range from 1.01 to 1.11. The constant used here (1.099) lies in this range, but close to the higher end. The problem is that the Arrhenius constant depends on enzyme reaction and on plant species, and a generally valid value does not exist. Furthermore, the increase in metabolism rates with temperature does not continue infinitely. Yu et al. have shown that, above 30 °C, the metabolism rate does not further increase, while uptake does. Additionally, the situation is complicated by the high diurnal variation in leaf and fruit temperature.

5.2 Model calibration and fit of parameters

The model can be calibrated by changing one or more of the sensitive parameters. An increase in concentration is achieved by increasing input or water flux to fruit, or by decreasing soil mass (rooting depth), fruit mass, temperature, metabolism or degradation rates. Many combinations of parameters can yield a closer result to the measured values. Figure 4 shows such a fit, which was achieved by setting the rooting depth (depth of soil) to 0.3 m and the temperature to 35 °C (the same effect can be achieved by changing other parameters such as, for example, the metabolism rates in plants). Given the many input parameters, and their variation in space and time (which is rarely known in detail), it can be expected that the concentrations measured in the harvested fruit also show considerable variations. Subsequently, mathematical modeling should probably not mainly target to meet a single measured value, but rather to rebuild the most important (and thus sensitive) processes and to indicate the key parameters.

5.3 Limitations and advantages of the new model approach

The presented model approach is limited to neutral organic compounds. Uptake can be from soil or air, and pulse emissions in/on soil, roots, stem, leaves or fruit may also occur. Principally, n separate periods can be simulated (the whole model is implemented as one spreadsheet line), with variable input for each period. Nonetheless, all results are calculated using analytical solutions of the underlying equations. This makes this new approach a flexible, stable and exact tool for many practical purposes. In another version of the multicascade approach, constant input to soil and all plant compartments, in addition to pulse input and background concentrations, can be considered. Many input parameters are needed for the simulation. Even though most of these parameters have almost no or a very small impact on the calculated result in the present scenario, the uncertainty of the predicted concentrations may be rather high. For example, if chemical and environmental input parameters are varied at the same time, and all by only 10% of the mean value, the calculated maximum concentration in fruit ranges from 0.05 mg kg⁻¹ (10th percentile) to 1.13 mg kg⁻¹ (90th percentile), which is a variation by a factor of 22.6 or 2260%. In experiments, too, large variations between measured concentrations in plants could be found. McKone and Maddalena list BCF values for the explosive RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine). RDX is a polar and non-volatile compound (in this respect similar to methomyl). Experimentally determined BCF values for fruit range from 0.07 to 5.50 kg L⁻¹ or kg kg⁻¹, i.e. the maximum BCF is 79-fold larger than the minimum BCF. This shows that uptake of chemicals into plants generally depends on many parameters and conditions, and is accompanied with large variations and uncertainty.

5.4 Comparison with earlier approaches

In the processes considered and in the underlying differential equations, the new cascade model resembles the early PlantX
model\textsuperscript{1} and the recent fruit tree model,\textsuperscript{13} but differs in that it is parameterized for crops grown annually and outdoors. Unlike the analytical cascade model presented here, the differential equations in the PlantX model are solved numerically and the model is programmed in Fortran. The fruit tree model is a steady-state solution that allows only constant input and parameters, and therefore could be implemented in a spreadsheet. The major difference to these precursors is thus not the description of processes, but the input, the solution method and the implementation.

6 CONCLUSION
Repeated simulations of pulse inputs with the cascade model adequately describe soil pesticide applications to an actual cropped system and reasonably mimic it. The model has the potential to be used for the optimization of practical features, such as application rates and waiting times between applications and before harvest, through the integrated accounting for soil, plant, and environmental influences. The large number of influences brought together is subject to large variations with accompanying uncertainties. As such, additional work is needed to adapt the model to other crops, as well as to other environmental scenarios of economic importance, such as application of manure and sewage sludge and irrigation with polluted surface water.

The model presented and other plant models, with manuals, are freely available online (http://homepage.env.dtu.dk/stt/).

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REFERENCES
9 Kennedy CM, McEuen SF and Anderson JJ, Use of crop protection product global regulatory magnitude and decline of residue data on produce for residue prediction purposes. \textit{American Chemical Society, 234th National Meeting, Boston, MA} (2007).
23 Scientific Opinion of the Panel on Plant Protection Products and their Residues on a request from EFSA related to the default Q10 value used to describe the temperature effect on transformation rates of pesticides in soil. \textit{The EFSA Journal} \textbf{62}:1–32 (2007).