Downloaded from orbit.dtu.dk on: May 10, 2024

DTU Library

Considering degradation kinetics of pesticides in plant uptake models

proof of concept for potato

Li, Zijian; Fantke, Peter

Published in:
Pest Management Science

Link to article, DOI:
10.1002/ps.7288

Publication date:
2023

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Li, Z., & Fantke, P. (2023). Considering degradation kinetics of pesticides in plant uptake models: proof of concept for potato. *Pest Management Science*, *79*(3), 1154-1163. https://doi.org/10.1002/ps.7288

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Research Article

Received: 31 July 2022 Revised: 7 November 2022 Accepted article published: 13 November 2022 Published online in Wiley Online Library: 24 November 2022

(wileyonlinelibrary.com) DOI 10.1002/ps.7288

Considering degradation kinetics of pesticides in plant uptake models: proof of concept for potato

Zijian Li[a*] and Peter Fantke[b]

Abstract

BACKGROUND: Degradation kinetics of pesticides in plants are crucial for modeling mechanism-based pesticide residual concentrations. However, due to complex open-field conditions that involve multiple pesticide plant uptake and elimination processes, it is difficult to directly measure degradation kinetics of pesticides in plants. To address this limitation, we proposed a modeling approach for estimating degradation rate constants of pesticides in plants, using potato as a model crop. An operational tool was developed to backward-estimate degradation rate constants, and three pesticides were selected to perform example simulations.

RESULTS: The simulation results of thiamethoxam indicated that the growth dynamics of the potato had a significant impact on the degradation kinetic estimates when the pesticide was applied during the early growth stage, as the size of the potato determined the uptake and elimination kinetics via diffusion. Using mepiquat, we demonstrated that geographical variations in weather conditions and soil properties led to significant differences in the dissipation kinetics in both potato plants and soil, which propagated the variability of the degradation rate constant. Simulation results of chlorpyrifos differed between two reported field studies, which is due to the effect of the vertical distribution of the residue concentration in the soil, which is not considered in the majority of recent studies.

CONCLUSIONS: Our proposed approach is adaptable to plant growth dynamics, preharvest intervals, and multiple pesticide application events. In future research, it is expected that the proposed method will enable region-specific inputs to improve the estimation of the degradation kinetics of pesticides in plants.
© 2022 The Authors. *Pest Management Science* published by John Wiley & Sons Ltd on behalf of Society of Chemical Industry.
Supporting information may be found in the online version of this article.

Keywords: dissipation; degradation rate constant; plant protection product; pesticide residues

1 INTRODUCTION

The protection of plants from pests, insects, pathogens, diseases, and weeds by pesticides supports the safety and quality of food.[1] Pesticides are designed to affect target living organisms, but also may harm human health.[2–7] As pesticides are predominantly used in agriculture, the consumption of residue-contaminated plants (crops) can contribute significantly to the overall exposure of humans and livestock to pesticides.[8–12] This has caused increased interest in studying the fate of pesticide residues in plants in support of improving health risk and impact assessments. The fate of pesticide residues in plant tissues is highly dependent on chemical species, plant varieties, pesticide application patterns, environmental conditions, and postharvest processing.[13,14] Measuring residue concentrations for numerous active ingredients and plant species is, however, cumbersome. Instead, modeling approaches are a promising alternative for evaluating the fate of pesticide residues and predicting residue levels in plants in an efficient manner, and can be evaluated against field measurements.[15–21]

Pesticide uptake models have been studied extensively, ranging from one-compartment foliar to multi-compartment dynamic models.[8,22–27] These mechanic models evaluate the plant uptake of pesticides via absorption, transpiration, diffusion, surface deposition, metabolism, and advection processes, performing simulations to predict residual concentrations in various crops and their components. Among these processes, the metabolism of pesticide residues in plants is not fully understood,[28,29] mainly due to a lack of data for estimating the degradation kinetics (e.g. rate constants). Since most environmental assessment tools for pesticides require such information, this is an important knowledge gap, despite initial studies evaluating degradation pathways, modes of action, and pesticide metabolites in plant

* Correspondence to: Z Li, School of Public Health (Shenzhen), Sun Yat-sen University, Shenzhen, Guangdong, 518107, China, E-mail: lizijian3@mail.sysu.edu.cn

a School of Public Health (Shenzhen), Sun Yat-sen University, Shenzhen, China

b Quantitative Sustainability Assessment, Department of Environmental and Resource Engineering, Technical University of Denmark, Kongens Lyngby, Denmark

© 2022 The Authors. *Pest Management Science* published by John Wiley & Sons Ltd on behalf of Society of Chemical Industry.
This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

15264998, 2023, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/ps.7288 by Danish Technical Knowledge, Wiley Online Library on [16/02/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

tissues.[30] Due to the lack of degradation rates of pesticides in plant tissues, some plant uptake models do not include the metabolism route,[25,27,31] while other models approximate degradation kinetics using bulk dissipation data to simulate residue concentrations in plants.[8,24,32–34] Both introduce assumptions regarding metabolism of pesticides in plants, which may hamper a proper comparison of pesticide residues in different assessment contexts.

Jacobsen *et al.*[28] evaluated in an illustrative case study the contributions of individual elimination routes to the dissipation of pesticide residues in plants in order to derive degradation rates. Their model simulated the dissipation kinetics of pesticides in wheat and tomato by breaking the dissipation process down into bulk degradation, growth dilution, and volatilization as frequently reported main elimination processes. The method employed by Jacobsen *et al.*[28] shed first light on the evaluation of the degradation kinetics of pesticides in plant tissues, which can be further improved for the following reasons. First, the fruits of wheat and tomato plants grow above ground, reflecting a more dynamic environment (i.e. sunlight, wind, precipitation, etc.) than for belowground crops, resulting in a relatively high degree of variability in the estimated within-plant degradation kinetics. Second, the fate of pesticides in the fruits of wheat and tomato plants includes not only metabolism, photolysis, volatilization, and dilution, but also inter-tissue transport that is influenced by transport and elimination mechanisms across all plant parts (such as the root, stem, and leaf).[23] Consequently, the estimation of degradation kinetics must take into account the fate, transport, and distribution of pesticides in the entire plant as well as the surrounding environmental compartments (soil and air), which can complicate simulation and propagate uncertainty. In addition, plant growth dynamics can significantly affect the uptake and elimination of pesticides in plants, especially during the early growth stage.[33] Incorporating growth dynamics into the plant uptake model can therefore more accurately reflect real-world conditions.

The main goal of our study was to advance the initial modeling approach used by Jacobsen *et al.*[28] to evaluate the degradation kinetics of pesticides in plant tissues. Potatoes were selected as the model crop, with main emphasis on degradation in harvested potato tubers. The specific objectives of this study are (i) to use a potato uptake model to investigate the degradation kinetics of pesticides, (ii) to propose a curve-fitting approach to derive degradation rate constants using the dissipation kinetics of pesticides (experimental curves), and (iii) to develop an operational tool to estimate degradation rate constants of pesticides in potatoes.

2 MATERIALS AND METHODS

2.1 General framework

In this study, first-order kinetic rate constants were used to describe the uptake and elimination processes of pesticides in potatoes, as the mass gain or loss of pesticides is assumed proportional to residual concentrations.[8,35] Figure 1(A) depicts the modeling approach for estimating the degradation rate constants of pesticide residues in potatoes by fitting a curve to the measured dissipation kinetics. Pesticide residues in potatoes are determined through considering growth dilution (elimination), diffusion (uptake and elimination), degradation (elimination), and active transport (phloem flux).[25] Specifically for organic compounds, the active transport of pesticide residues into potato tubers via phloem transport is negligible,[35] indicating that the majority of pesticide residues are likely

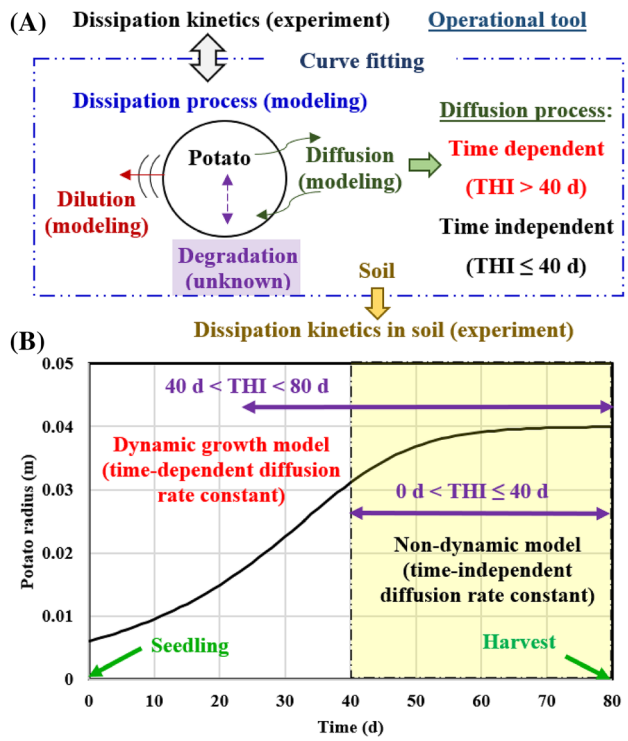

Figure 1. (A) Conceptual diagram of the modeling approach for estimating degradation rate constants of pesticides in plant tissues using potatoes as a model plant. (B) Potato radius (m) plotted against time (day) using a logistic growth function (calculation inputs are provided in Supporting Information, Table S1). THI: time-to-harvest interval. Half of the potato growth period is selected as the modeling illustration (i.e. 40 days).

taken up by potatoes through the soil compartment.[25] Simulating the rate constants of dilution and diffusion is possible using mechanistic process descriptions. In contrast, the degradation rate constant cannot be modeled directly (demonstrated in Methods S1 of the Supporting Information) and will be determined by fitting the simulated and measured curves of pesticide dissipation kinetics in potatoes.

Due to potato growth following a logistic function, the dilution rate constant (due to tissue and cell growth) can be kept constant throughout the potato's growth stages.[33] In contrast, the diffusion rate constants for both uptake (from soil to potato) and elimination (from potato to soil) depend on the radius of the potato, which can significantly affect the dissipation kinetics of pesticide residues in potatoes (Fig. 2).[33] Therefore, diffusion rate constants are dependent on time and are correlated with the dynamics of potato growth. When the potato reaches maturity [assumed to be half of the potato growth period (i.e. 40 days) after planting the seedling] (Fig. 1(B)), the radius is approximately 80% of its maximum value at harvest. Thus, when pesticide application occurs less than 40 days prior to harvest [i.e. the time-to-harvest interval (THI) ≤ 40 days], the radius and diffusion rate constants can be approximated as time-independent values to facilitate simulation of the dissipation kinetics. In contrast, when THI > 40 days, the diffusion rate constants change rapidly due to the rapid growth of the potato, which is considered to simulate the time-dependent rate constants of the diffusion processes. An operational tool (Microsoft Excel) was developed to backward estimate degradation rate constants of pesticides

© 2022 The Authors.
Pest Management Science published by John Wiley & Sons Ltd on behalf of Society of Chemical Industry.

15264998, 2023, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/ps.7288 by Danish Technical Knowledge, Wiley Online Library on [16/02/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

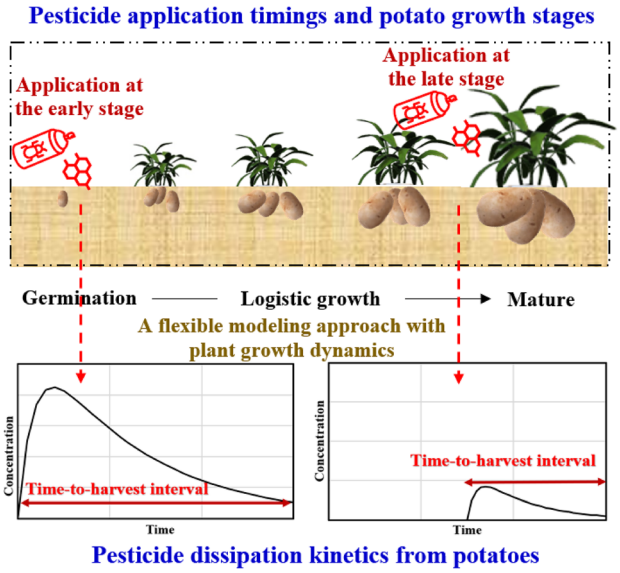

Figure 2. Schematic of the dissipation kinetics of pesticide residues from potatoes affected by pesticide application timings (preharvest interval) and potato growth dynamics.

in potatoes, for which the underlying mechanism (more information is available in Section 2.6) can be expressed as follows:

$$\underbrace{\mathrm{MAE}\left[\text{experimental data},\ \overbrace{\text{simulated data}}^{\text{Input (degradation kinetics)}}\right]}_{\text{Curve fitting using the operational tool}} \rightarrow \underbrace{\min(\mathrm{MAE})}_{\text{Target output}} \tag{1}$$

where MAE(.) denotes the mean absolute error function, which fits the experimental and simulated data (by setting degradation rate constants) to determine the minimal value, min(MAE). Given that pesticide degradation in plant tissues is mainly an enzymatic process that is limited by the number of enzymes produced by plant cells,[36] first-order degradation kinetics can be assumed when the residue concentration in plant tissues is lower than the respective enzyme concentration. Since residual pesticide concentrations in plant tissues are typically lower than plant enzyme concentrations, the related Michaelis–Menten enzymatic kinetics of pesticide residue in plant tissues can be approximated using first-order rate constants. This approximation has been widely utilized in pesticide fate modeling, such as biotransformation in mammalian livers,[37,38] biodegradation in crops,[8,28] and dissipation in soils.[39] In addition, the use of first-order kinetics can simplify the modeling procedure, allowing for high-throughput simulations of chemical fate for risk or life-cycle impact assessment.[40–42] In the rather rare case when pesticide residue concentrations are relatively high or plant tissues cannot supply enough enzymes to metabolize certain chemicals, other types of degradation kinetics, such as biphasic and zero-order processes,[43] might be considered.

2.2 Potato uptake model with plant growth dynamics

The dissipation process of the pesticide in potatoes (including uptake and elimination processes) can be expressed by the following governing equation, which was developed based on well-established mass-balance-based plant uptake models of pesticides:[8,35]

$$\frac{dC_p(t)}{dt} = \overbrace{\underbrace{\overbrace{\underbrace{k_{s\rightarrow p}(t)}_{\text{Modeling}}\ \underbrace{C_s(t)}_{\text{Experiment}}}^{\text{Uptake from soil}}}_{\text{Dissipation from potato}} - \overbrace{\left[\underbrace{k_{p\rightarrow s}(t)+k_{\text{grow},p}}_{\text{Modeling}}+\underbrace{k_{\text{deg},p}}_{\text{Unknown}}\right]\underbrace{C_p(t)}_{\text{Experiment}}}^{\text{Elimination from potato}}}^{\in[0t_{\text{harv}}]}\ \forall t \tag{2}$$

where $C_p(t)$ (in mg kg^{-1}) and $C_s(t)$ (in mg kg^{-1}) are pesticide concentrations in the potato and soil, respectively as a function of time (t, day) from planting ($t = 0$) to harvest ($t = t_{\text{harv}}$); $k_{s\rightarrow p}(t)$ (d^{-1}) and $k_{p\rightarrow s}(t)$ (d^{-1}) are the soil-to-potato uptake and potato-to-soil elimination rate constants of the pesticide via diffusion, respectively, considering potato growth dynamics; $k_{\text{grow},p}$ (d^{-1}) is the dilution rate constant, which is equal to the specific growth rate of the potato;[33,35] and $k_{\text{deg},p}$ (d^{-1}) is the degradation rate constant of the pesticide in the potato. The latter is considered to be independent of t, since the biodegradation process is active throughout the growth cycle of the potato.

Therefore, $C_s(t)$ can be expressed using the residue's first-order kinetic dissipation rate in the soil ($k_{\text{diss},s}$, d^{-1}) as follows

$$C_s(t) = \begin{cases} 0\ \forall t \in [0,\ t_E) \\ C_s(t_{\text{appl}})\exp\left[-k_{\text{diss},s}(t-t_{\text{appl}})\right]\forall t \in [t_{\text{appl}},\ t_{\text{harv}}] \end{cases} \tag{3}$$

where t_{appl} (in days) is the time when the pesticide application occurs; thus, THI equals '$t_H - t_E$'. $C_s(t_{\text{appl}})$ (in mg kg^{-1}) is the residue concentration in the soil immediately after pesticide application. $C_s(t_{\text{appl}})$ and $k_{\text{diss},s}$ can be obtained from field studies.

Thus, $k_{s\rightarrow p}(t)$ and $k_{p\rightarrow s}(t)$ can be estimated based on the diffusion process of the pesticide through water phases of the potato and soil[31,35] as follows:

$$k_{s\rightarrow p}(t) = \frac{23D_{\text{effe}}}{[r_p(t)]^2 K_{sw}\rho_p}\forall t \in [0,\ t_{\text{harv}}] \tag{4a}$$

$$k_{p\rightarrow s}(t) = \frac{23D_{\text{effe}}}{[r_p(t)]^2 K_{pw}\rho_p}\forall t \in [0,\ t_{\text{harv}}] \tag{4b}$$

where D_{effe} (m^2 d^{-1}) is the effective diffusivity of the pesticide in potato tissues; K_{sw} (in L kg^{-1}) and K_{pw} (in L kg^{-1}) are the soil–water and potato–water partition coefficients of the pesticide, respectively; ρ_p (kg L^{-1}) is the density of the potato; and $r_p(t)$ (in meters) is the radius of the potato, assuming the spherical shape,[35] as a function of t, which can be expressed using the logistic growth function[8,33] as follows:

$$r_p(t) = \left(\frac{3M_p^{Max}}{4\pi\rho_p CF}\right)^{\frac{1}{3}}\left[1+\left(\frac{M_p^{Max}-M_p^0}{M_p^0}\right)exp\left(-k_{\text{grow},p}t\right)\right]^{-\frac{1}{3}}\forall t \in [0,\ t_{\text{harv}}] \tag{5}$$

where M_p^{Max} (in kilograms) and M_p^0 (in kilograms) are the maximum and initial masses of the potato, respectively; and CF (1000 L m^3) is the unit conversion factor.

 © 2022 The Authors.
Pest Management Science published by John Wiley & Sons Ltd on behalf of Society of Chemical Industry.

15264998, 2023, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/ps.7288 by Danish Technical Knowledge, Wiley Online Library on [16/02/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

2.3 Experimental kinetics of pesticide dissipation in potatoes

Based on the measured dissipation half-life ($HL^{exp}_{diss,p}$, in days) from field studies, first-order kinetics was used to describe the process of pesticide residue dissipation in potatoes. The residue concentration in the potato ($C^{exp}_p(t)$, in mg kg^{-1}) can then be expressed as follows:

$$C^{exp}_p(t) = 0 \forall t \in [0, t_{appl}) \tag{6a}$$

$$C^{exp}_p(t) = \underbrace{C^{exp}_p(t_{appl})}_{\text{Experiment}} \exp\left[-\underbrace{k^{exp}_{diss,p}}_{\text{Experiment}}(t - t_{appl})\right] \forall t \in [t_{appl}, t_{harv}] \tag{6b}$$

where $k^{exp}_{diss,p}$ (d^{-1}) is the pesticide's dissipation rate constant and $C^{exp}_p(t_{appl})$ (in mg kg^{-1}) is the pesticide concentration in the potato immediately after pesticide emission. Both values can be determined through field experiments.[25,44–46]

2.4 Estimating degradation rate constants via curve fitting

Incorporating Eqn (3) into Eqn (2), the model can be expressed as follows:

$$C_p(t) = 0 \forall t \in [0, t_{appl}) \tag{7a}$$

$$\frac{dC_p(t)}{dt} = k_{s\longrightarrow p}(t) C_s(t_{appl}) \exp\left[-k_{diss,s}(t - t_{appl})\right] - \left[k_{p\longrightarrow s}(t) + k_{grow,p} + \underbrace{k_{deg,p}}_{\text{Unknown}}\right] C_p(t) \forall t \in [t_{appl} t_{harv}] \tag{7b}$$

The $k_{deg,p}$ value of the pesticide can then be estimated by comparing $C_P(t)$ in Eqn (7b) with $C^{exp}_p(t)$ in Eqn (6b). As shown in Fig. 2, $C_p(t)$ will increase after pesticide application from zero to positive values (the period of zero value is contingent on application patterns such as foliar spraying and soil incorporation). Nevertheless, the first-order dissipation kinetics curve obtained from the experimental data, i.e. $C^{exp}_p(t)$ expressed in Eqn (6b), indicates that $C^{exp}_p(t)$ decreases throughout the entire interval of t (i.e. from pesticide application to crop harvest). In order to conduct the curve fitting between the proposed model and the experimental curve, unless the maximum value of $C_p(t)$ can be reached very quickly after pesticide application, $C_p(t)$ must be adjusted to a monotonic function.

2.5 Time-independent diffusion rate constants (non-dynamic models)

As depicted in Fig. 1, when the THI is less than or equal to half of the potato's growth cycle (i.e. 40 days), the pesticide diffusion rate constants can be considered as time-independent values. Then, Eqn (2) can be rewritten as follows:

$$\frac{dC^{ND}_p(t)}{dt} = k^{ND}_{s\longrightarrow p} C_s(t) - \left(k^{ND}_{p\longrightarrow s} + k_{grow,p} + k^{ND}_{deg,p}\right) C^{ND}_p(t) \forall t \in [0, t_{harv}] \tag{8}$$

where $C^{ND}_p(t)$ (in mg kg^{-1}) denotes the pesticide concentration in the potato for the non-dynamic model; $k^{ND}_{S\longrightarrow P}$ (d^{-1}) and $k^{ND}_{p\longrightarrow s}$ (d^{-1}) are the time-independent soil-to-potato uptake and potato-to-soil elimination rate constants via diffusion, respectively; and $k^{ND}_{deg,p}$ (d^{-1}) is the degradation rate constant estimated using the non-dynamic model. Combining with the $C_s(t)$ in Eqn (3), $C^{ND}_p(t)$ can be solved as shown in Methods S2 of the Supporting Information. Then, $k^{ND}_{deg,p}$ can be resolved by fitting the curves of Eqns (6b) and (s2b).

Some pesticides are applied multiple times during the potato's growth cycle, and the experimental dissipation kinetics curves of pesticides in potatoes and soil are typically determined after the final application (i.e. between the last pesticide application and the potato harvest). In addition, most experiment curves typically begin at the highest pesticide concentration in potatoes to determine the first-order dissipation curve, ignoring the pesticide's net uptake process. With this, $C^{ND}_p(t)$ in Eqn (8) can be refined as follows:

$$\frac{dC^{ND,last}_p(t)}{dt} = k^{ND}_{s\longrightarrow p} \underbrace{C^{last}_s(t)}_{\text{Experiment}} - \left(k^{ND}_{p\longrightarrow s} + k_{grow,p} + \underbrace{k^{ND,last}_{deg,p}}_{\text{Unknown}}\right) C^{ND,Last}_p(t) \forall t \in [t_{appl,last} t_{harv}] \tag{9a}$$

$$C^{last}_s(t) = C^{last}_s(t_{appl,last}) \exp\left[-k_{diss,s}(t - t_{appl,last})\right] \forall t \in [t_{appl,last}, t_{harv}] \tag{9b}$$

where $C^{ND,last}_p(t)$ (in mg kg^{-1}) and $C^{last}_s(t)$ (mg kg^{-1}) denote pesticide concentrations in the potato and soil as functions of t, respectively, in the non-dynamic model for the most recent pesticide application; $k^{ND,last}_{deg,p}$ (d^{-1}) is the degradation rate constant of the pesticide in the potato for the last pesticide application. Then, $C^{ND,last}_p(t)$ in Methods S2, Eqn (s2a) can be solved with initial conditions "$C^{last}_s(t_{appl,last})$ and $C^{ND,last}_p(t_{appl,last})$" at the time of the last pesticide application ($t_{appl,last}$, day), as determined by field studies, as shown in Methods S2.

Then, the $k^{ND,last}_{deg,p}$ value of the pesticide residue can be estimated by fitting $C^{ND,last}_p(t)$ in Methods S2, Eqn (s3) as follows:

$$C^{exp,last}_p(t) = \overbrace{C^{exp,last}_p(t_{appl,last})}^{\text{Earlier applications}} \exp\left[-k^{exp,last}_{diss,p}(t - t_{appl,last})\right] \forall t \in [t_{appl,last} t_{harv}] \tag{10}$$

where $C^{exp,last}_p(t)$ (in mg kg^{-1}) is the pesticide concentration in the potato as a function of t, described by the first-order dissipation kinetic rate constant ($k^{exp,last}_{diss,p}$, d^{-1}) determined from the experimental data during the time between the last pesticide application and harvest (i.e. $t \in [t_{appl,last}, t_{harv}]$). Notably, the majority of experimental studies assessing the first-order dissipation kinetics of pesticide residues in potatoes collected potato samples between the last pesticide application and harvest, which corresponds to the scenario given in Eqn (10).

© 2022 The Authors.

15264998, 2023, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/ps.7288 by Danish Technical Knowledge, Wiley Online Library on [16/02/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

2.6 Operationalization

According to Eqn (1), the underlying mechanism of the operational tool can be expressed as follows:

$$\mathrm{MAE}\left[\underbrace{C_p^{\exp}(t)}_{\text{Experiment}}, \underbrace{C_p^{\text{model}}\left(t,\ \underbrace{k_{\deg,p}}_{\text{Input}}\right)}_{\text{Modeling}}\right] \rightarrow \underbrace{\min(\mathrm{MAE})}_{\text{Output}} \tag{11}$$

where $C_p^{\text{model}}(t, k_{\deg,p})$ (in mg kg^{-1}) is the modeled pesticide concentration in potatoes, which includes the dynamic (i.e. using the time-dependent radius of potatoes) and non-dynamic (using the time-independent radius of potatoes) models. In the operational tool, $k_{\deg,p}$ (the unknown degradation rate constant) is the input value that users can arbitrarily set to generate MAE values; $\mathrm{MAE}\left[C_p^{\exp}(t), C_p^{\text{model}}(t,\ k_{\deg,p})\right]$ is the output result, of which the minimum value (or values close to the minimum value), namely $\min(\mathrm{MAE})$, is the target output. Therefore, $\min(\mathrm{MAE})$ indicates that the experimental and modeled curves are very similar, with the input $k_{\deg,p}$ being the pesticide's estimated degradation rate constant in potatoes.

The operational tool is provided in the Supporting Information Spreadsheets S1–S3, and inputs can be adapted upon availability of refined data such as own experimental data. As there are currently no analytical solutions for the dynamic model,[33] a finite-approximation approach was proposed to calculate the time-dependent rate constants sheet-by-sheet in order to perform the modeling exercise. Analytical solutions were inserted into the operational tool to simulate pesticide concentrations in potatoes for non-dynamic models. We note that experimental curves of the pesticide dissipation kinetics in potatoes do not typically include the net uptake stage that is included in the simulated curves (i.e. dynamic and non-dynamic models). Therefore, when calculating the MAE between experimental and simulated curves, the adjustment was made to calibrate the time based on the highest simulated values of the proposed models, as follows:

$$\mathrm{MAE}'\left[\underbrace{C_p^{\exp}(t)}_{\text{Experiment}}, \underbrace{C_p^{\text{model}}\left(\underbrace{t+\overbrace{\Delta t}^{\text{Net uptake stage}}}_{\text{Calibration}},\ \underbrace{k_{\deg,p}}_{\text{Input}}\right)}_{\text{Modeling}}\right] \rightarrow \underbrace{\min(\mathrm{MAE}')}_{\text{Output}} \tag{12}$$

where MAE′ denotes the adjusted MAE, and Δt (in days) is the period of the net uptake stage of the pesticide in potatoes for the proposed models. Thus, '$t+\Delta t$' eliminates the net uptake stage of the proposed models in order to match the experimental curve (i.e. a monotonically decreasing function).

2.7 Case study

We matched the curves between the proposed and the first-order dissipation kinetic models in an illustrative case study for a neonicotinoid insecticide, a plant growth regulator, and an organophosphate insecticide as example pesticides, using data from existing field studies. Abd-Alrahman[45] evaluated the dissipation kinetics of thiamethoxam (a broad-spectrum neonicotinoid insecticide) in potatoes and soil. Due to the lack of clarity on the THI of thiamethoxam, both dynamic and non-dynamic models were used to evaluate the degradation kinetics of thiamethoxam in potatoes. Zhang *et al.*[44] examined the dissipation behaviors of mepiquat (a plant growth regulator) in potatoes and soil, and their field studies were conducted in various regions with THIs of less than 40 days. Thus, the non-dynamic model was utilized to discuss the estimated degradation kinetics of mepiquat in potatoes with geographical variations.

Chlorpyrifos, a commonly used organophosphate in potato fields, was also selected for the modeling exercise due to its high lipophilicity, which represents a different bioconcentration behavior in potatoes compared to chemicals with low lipophilicity (e.g. thiamethoxam and mepiquat).[32] Narenderan *et al.*[46] conducted a series of field experiments to evaluate the dissipation kinetics of commonly used organophosphate insecticides (including chlorpyrifos) in potatoes and soil with 21-days THIs. In addition, Juraske *et al.*[25] proposed a dynamic uptake model to simulate pesticide concentrations in potatoes with multiple application events (the final application event 13 days prior to harvest), which was evaluated in an experimental study. Consequently, the improved non-dynamic model was used to estimate the degradation rate constant of chlorpyrifos in potatoes. Noting that Juraske *et al.*[25] also measured the growth dynamics of the potato, the value of 0.06 d^{-1} was used when simulating their study. Inputs specific to chemicals and plants are provided in the Methods S3–S5.

2.8 Model improvement

As environmental factors (e.g. weather conditions) can have a substantial effect on pesticide degradation kinetics in the soil, pesticide bioconcentration in plants, and plant growth,[39,47–52] it is necessary to increase the model's flexibility in order to conduct region-specific evaluation. In this study, rate constants of pesticides in soil and plant tissues were obtained from existing field research, whose values were climate- and region-specific. Thus, we modified the uptake or elimination rate constants to achieve region-specific simulation results. Diffusion-based uptake rate constants of pesticides in potatoes can be significantly affected by soil properties, similar to other plants with soil-based exposure pathways (e.g. foliar vegetation, carrot, and wheat).[8,27,53] As a result, elimination processes representing diffusion as well as dilution need to be addressed in site-specific assessment of pesticide degradation rates for potatoes. Potato growth rates are affected by seasons, locations, soil fertility, and planting methods; hence, the dilution rate constant of the pesticide in potatoes can exhibit spatiotemporal patterns. In order to demonstrate the feasibility of the enhanced model, we estimated the variability interval of dilution rate constants, which were then incorporated into the proposed operational tool to provide corresponding outputs. Even though experimental results on pesticide dissipation kinetics in the soil are already site-specific, dissipation processes in the soil can be significantly influenced by dynamic environmental factors (e.g. temperature, humidity, and rainfall events).[39] Thus, we also conducted the variability analysis of the proposed modeling approach by taking into consideration the variation in pesticide dissipation rate constants in the soil, which can help improve the operational tool proposed for site-specific applications. In addition, field research has revealed that the potato's growth rate constant (or relative growth rate) can vary over its life cycle,[54] contrary to existing modeling approaches that assume constant values.[25 33,35] Using time-dependent rate constants as stated in

© 2022 The Authors.

15264998, 2023, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/ps.7288 by Danish Technical Knowledge, Wiley Online Library on [16/02/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Eqn (7b), this issue can also be resolved by the operational tool proposed. In Methods S6, a stepwise procedure is provided for improving the application of the model by considering dynamic environmental factors. Where feasible, users are able to modify rate constants (e.g. based on local measurements) to get outputs that are region-, plant-, and chemical-specific.

3 RESULTS AND DISCUSSION

3.1 Degradation kinetics of thiamethoxam in potatoes

In the proposed operational tool, we utilized the experimental data of Abd-Alrahman[45] to evaluate the degradation kinetics of thiamethoxam in potatoes. Due to the lack of THI data, we varied the THI values of thiamethoxam in the proposed dynamic and non-dynamic models in order to discuss the simulated degradation kinetics of potatoes. Figure 3 depicts the simulated thiamethoxam concentrations in potatoes using the dynamic and non-dynamic models, generated by the proposed operational tool with a default THI of 21 days, which is commonly used for some insecticides applied to potato fields.[55] The simulation results demonstrated that dynamic and non-dynamic models generated nearly identical concentration curves for thiamethoxam in potatoes. When the degradation rate constant was set to 4 d^{-1}, the MAEs for the dynamic and non-dynamic models with respect to the experimental curve were 0.01 and 0.03, respectively. When the THI is 21 days, the potato is already in the maturation stage and has reached a stable size (assuming that the duration of the potato's growth cycle is 80 days). This explains why these two models produce similar results (e.g. radius). Consequently, both dynamic and non-dynamic models can be used to estimate the degradation rate constant of thiamethoxam in potatoes. Setting the degradation rate constants to 3 d^{-1} and 5 d^{-1} for the non-dynamic model resulted in MAEs of 0.09 and 0.10, respectively, indicating that setting the degradation rate constant to 4 d^{-1} resulted in a more accurate curve fitting between the simulated and experimental curves. Therefore, 4 d^{-1} could be used as the degradation rate constant of thiamethoxam in plant tissues in this instance.

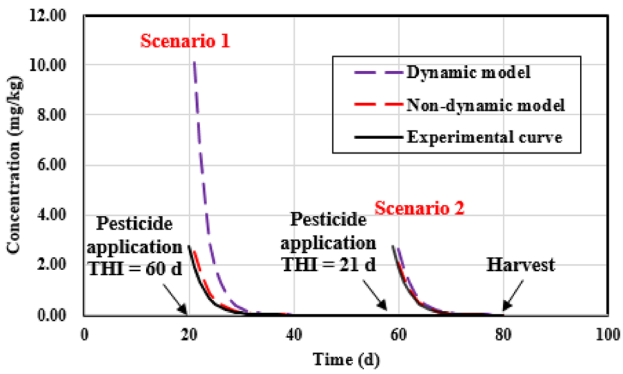

Figure 3. Simulated concentrations of thiamethoxam in potatoes by the dynamic and non-dynamic models, plotted against time and compared to the experimental concentrations. The proposed operational tool was used to generate figures. Scenario 1: The time-to-harvest interval (THI, in days) was determined to be 60 days. The input degradation rate constants were 4 d^{-1} and 20 d^{-1}, resulting in mean absolute errors (MAEs) (output) of 0.35 and 0.02, respectively. Scenario 2: the time-to-harvest interval (THI) was determined to be 21 days. For the dynamic and non-dynamic models, the input degradation rate constant was 4 d^{-1}, resulting in MAEs (output) of 0.01 and 0.03, respectively.

Inconsistency was observed in the estimated degradation rate constants between the dynamic and non-dynamic models when the THI reached 60 days. Figure 3 depicts the simulated thiamethoxam concentrations in potatoes generated by the dynamic model with a degradation rate constant of 4 d^{-1}, resulting in an MAE of 0.35. However, when the degradation rate constant for the dynamic model was set to 20 d^{-1}, the corresponding MAE was 0.02 (Fig. 3). The simulation results indicated that a high input value (i.e. the degradation rate constant of thiamethoxam in potatoes) was required if the pesticide was emitted during the early stage of potato growth (e.g. THI = 60 days) in order to match the environmental curve. This high input value is linked to the fact that when the potato is relatively small (i.e. has a small radius), the uptake process of thiamethoxam from the soil is significantly enhanced (Fig. 4); consequently, a high degradation rate constant of thiamethoxam in the potato is expected to match the experimental curve. Even though the rate constant of 20 d^{-1} existed mathematically, it was much higher than observed or estimated dissipation rate constants in plant tissues,[56] indicating that Abd-Alrahman's field study[45] was unlikely to have been conducted under the THI of 60 days. When the THI was set to 40 days, both dynamic and non-dynamic models yielded similar results (Supporting Information, Fig. S1) to the scenario where the THI was 21 days. This is because, at the time of the pesticide application (40 days after planting the potato), the potato was very close to maturity, resulting in a relatively stable size as well as the simulated diffusion rate constants (Fig. 4). Therefore, we infer that Abd-Alrahman[45] applied thiamethoxam when the potato was at or near maturity, and the degradation rate constant of 4 d^{-1} in potatoes could be used as a preliminary value for simulating thiamethoxam concentrations in plants.

3.2 Degradation kinetics of mepiquat in potatoes

We observed geological variations in the estimated degradation kinetics of potatoes for mepiquat. Zhang *et al.*[44] evaluated the dissipation kinetics of mepiquat in potatoes and soil by conducting field studies in three Chinese regions (Methods S5.2). Based on experimental data collected in Beijing, the simulation results (Fig. S2) indicated that the estimated degradation rate constants of mepiquat in potatoes were extremely high (e.g. 15 d^{-1}). Nonetheless, the simulation results (Figs S3 and S4), which were based on experimental data collected in Hunan and Jiangsu, showed contradictory outcomes. According to Hunan and Jiangsu field studies, the estimated degradation rate constants of mepiquat in potatoes were 1.5 d^{-1} and 0 d^{-1}, respectively. Notably, the fitted dissipation kinetics of mepiquat in potatoes (i.e. the experimental curve used in the proposed operational tool) had a relatively low R^2 (0.62) compared to those of Hunan and Jiangsu (0.95). The relatively low R^2 value of the experimental curve may propagate uncertainty in the estimated value of the degradation rate constant of mepiquat in potatoes. Nonetheless, between Hunan and Jiangsu, a substantial variation in the estimated degradation rate constant was also observed.

Intriguingly, we discovered some inconsistencies in the experimental data. For instance, the estimated dissipation half-life of mepiquat in the soil of Beijing (i.e. 4.6 days) was twice that in the soil of Jiangsu (i.e. 2.2 days),[44] indicating that the residue of mepiquat dissipated more quickly in the soil of Jiangsu. Consequently, after pesticide application, the concentration of mepiquat in the soil of Jiangsu decreased more rapidly than in the soil of Beijing, resulting in a large driving force (i.e. the potato-to-soil diffusion flux of mepiquat) that 'pulled' the mepiquat

15264998, 2023, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/ps.7288 by Danish Technical Knowledge, Wiley Online Library on [16/02/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

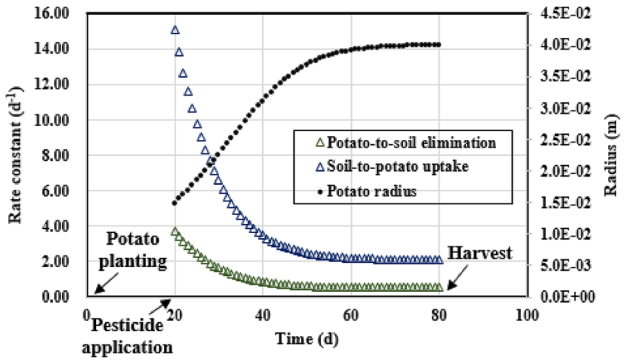

Figure 4. Simulated time-dependent uptake (soil-to-potato diffusion) and elimination (potato-to-soil diffusion) rate constants of thiamethoxam in potatoes and potato radii, plotted against time. The plots were generated by the proposed tool based on spreadsheets. The simulation began at 20 days (immediately after pesticide application) and ended at 80 days (at harvest), which corresponds to the scenario in which the preharvest interval of 60 days was utilized.

residue out of the potatoes in Jiangsu. If the degradation kinetics of mepiquat in potato tissues of these regions were identical, the mepiquat dissipation rate measured in Beijing would be lower than that measured in Jiangsu. However, the field study revealed that the rate of mepiquat dissipation in Beijing-measured potatoes (i.e. the half-life of 2.4 days) was greater than that in Jiangsu (i.e. the half-life of 3.4 days).[44] In addition, regional temperature differences could account for the geographical variation in reported half-lives of mepiquat in the soil. Beijing is in northern China, and the annual average temperature was lower than that of Jiangsu and Hubei, which are located in southern China, indicating that the half-life of mepiquat in the soil of Beijing should be longer than that of Hunan and Jiangsu, which is consistent with the experimental data.[44] Nonetheless, if temperature plays a significant role in the degradation and diffusion kinetics of the pesticide, then the dissipation kinetics of mepiquat in Beijing potatoes should be greater than in Hunan and Jiangsu, which is not supported by the experimental data. Consequently, we inferred from the experimental data that weather conditions, soil properties, and potato varieties caused these contradictions. For instance, mepiquat has a very low lipophilicity ($\log K_{OW} = -3.6$), so the water content of the soil can have a substantial effect on the partition coefficient between soil and water, which in turn influences the uptake and elimination rate constants of mepiquat via diffusion. Consequently, the geological variation in weather conditions (e.g. precipitation and humidity) and soil properties (e.g. water content) can result in a substantial variation in the measured dissipation kinetics of mepiquat in potatoes and soil. In addition, weather conditions and soil properties may influence the growth dynamics (e.g. growth rate) or physiological traits (e.g. periderm) of plants,[57] thereby modifying the uptake or elimination rate constants of the pesticide in plants.[32] In addition to plant growth dynamics, the simulation results of the proposed model suggested that dynamic factors, such as weather conditions, soil properties, and plant physiology, should be considered.

3.3 Degradation kinetics of chlorpyrifos in potatoes

For the degradation kinetics of chlorpyrifos in potatoes, different field studies produced inconsistent simulation results. Figure S5 (A)) compares the simulated chlorpyrifos concentrations in potatoes over time to the experimental concentration curve (the dissipation kinetics of chlorpyrifos in potatoes). As the simulated concentrations were significantly lower than the experimental data,[46] the degradation rate constant could not be inputted into the operational tool. The simulation results indicated that the non-dynamic model proposed by Narenderan *et al.*[46] could not adequately describe the uptake and elimination behaviors of chlorpyrifos. This discrepancy between simulation and experiment may be because the high lipophilicity of chlorpyrifos hindered the simulated uptake kinetics (i.e. potato-to-soil uptake rate constant via diffusion).[32] Consequently, using the current uptake model, the simulated chlorpyrifos concentrations in potatoes could not exceed 5 mg kg^{-1}, as measured in a field study (Fig. S5(A)). Using the improved non-dynamic model (i.e. assuming an accumulated concentration of chlorpyrifos in potatoes prior to pesticide application resulting from previous chlorpyrifos applications) (Fig. S5(B)), the simulated chlorpyrifos concentrations in potatoes matched the experimental curve more closely than the non-dynamic model. In the enhanced non-dynamic model, the initial concentration of the pesticide in the potato was set to match experimental data instead of assuming a zero initial concentration. The calculated degradation rate constant was zero despite the fact that the simulated chlorpyrifos concentrations were lower than the experimental data. This was because the simulated chlorpyrifos uptake kinetics in potatoes were inhibited.

Nevertheless, the simulation results based on the study by Juraske *et al.*[25] were more in line with the experimental data. Figure 5 depicts the estimated lower and upper limits of the degradation rate constant of chlorpyrifos in potatoes based on the improved non-dynamic model. The simulation outcomes closely matched the experimental curves. The MAE is 0.001 when the degradation rate constant is set to 0.2 d^{-1}. This indicates that the proposed modeling approach based on current plant uptake models agrees with the experimental data from Juraske *et al.*[25] Notably, in the study conducted by Juraske *et al.*,[25] pesticide concentrations in the soil were simulated as a function of vertical distance rather than as a homogenous distribution. Since pesticide residues in the soil are the only source of residues absorbed by potatoes, accurate measurement or simulation of the pesticide concentration in the soil matrix is desired. In real-world scenarios, the pesticide concentration in the soil is vertically distributed after pesticide application; therefore, homogeneous distribution cannot be assumed to provide the most accurate estimation of the pesticide concentration in the soil surrounding potatoes. Most current field or modeling studies adopted the first-order dissipation kinetics of the pesticide in the soil, assuming homogeneous distribution to simplify the calculation process; this should be improved by adjusting the soil residue concentration based on the planting depth of tubers. Notably, in order to preserve simplicity, the suggested operational tool intended to fit pesticide uptake models to experimental studies evaluating the first-order kinetics of pesticide residues in potatoes. Thus, the simulation focused on the period between the last pesticide application and crop harvest. If the experimental study collected samples during the whole life cycle of the potato growth, curve fitting can be extended to include additional pesticide application events in addition to the final one.

3.4 Model improvement and recommendations

Due to their generally stable environment (i.e. underground environment) and well-established uptake models that have been validated by extensive field studies, potatoes were used as an initial

© 2022 The Authors.

15264998, 2023, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/ps.7288 by Danish Technical Knowledge, Wiley Online Library on [16/02/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

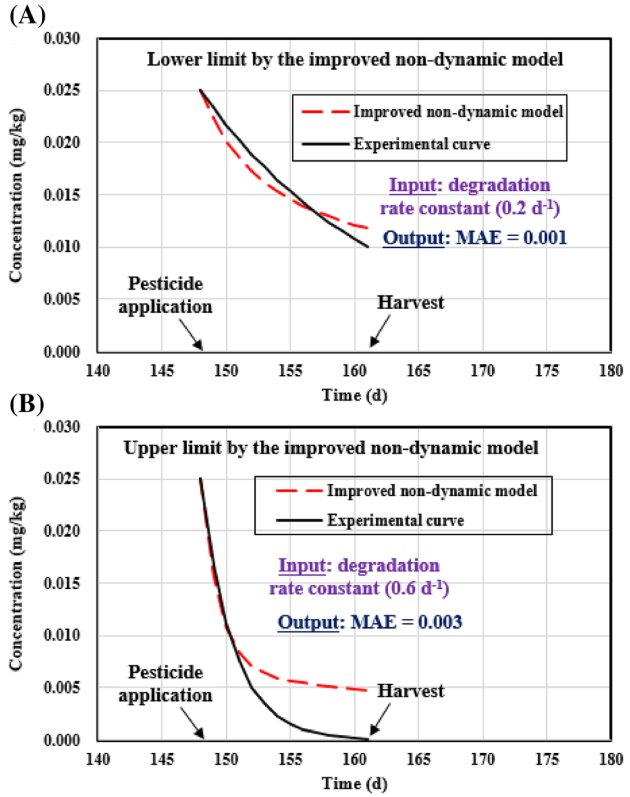

Figure 5. Simulated chlorpyrifos concentrations in potatoes by the improved non-dynamic model plotted against time, compared to the experimental concentration curve. The proposed operational tool was used to generate figures. The time-to-harvest interval (THI, in days) was determined to be 13 days. The lower (A) and upper (B) limits for the input degradation rate constants were 0.2 d^{-1} and 0.6 d^{-1}, resulting in mean absolute errors (MAEs) (output) of 0.001 and 0.003, respectively. The experimental data were obtained from Juraske *et al.*[25]

model plant in the proposed modeling approach.[25,31,35] Other types of plant uptake or dissipation models should be tested for their reliability in estimating plant-specific degradation kinetics in future efforts, notwithstanding the possibility of a high degree of uncertainty. Root crops (e.g. carrot, beet, and sweet potato) have more uptake or elimination routes of pesticide residues (e.g. xylem or phloem transport) than tuber plants, resulting in a buildup of uncertainty in simulation outputs.[53,58] Other underground plants (e.g. groundnuts) have distinctive development patterns (e.g. geocarpic fruit growth) that complicate the simulation of pesticide degradation kinetics.[59] Many aboveground plants (e.g. wheat, apple, and banana) have multiple exposure pathways to pesticides, including leaf surface, fruit surface, and soil, resulting in greater uncertainty in simulation results compared to tuber plants.[8,15,18,60–64] However, once well-controlled experimental data are available, users can add degradation rate constants as an unknown variable into current plant uptake models to back-estimate plant-specific pesticide degradation kinetics for crops other than potato.

Some model input variables are site-specific. For instance, the growth rate constant of a plant can vary greatly based on plant variety, environmental conditions, soil fertility, and planting method.[50,52,54,65] During the growth cycle of a plant, even the relative growth rate can be time-dependent.[54] Numerous modeling studies have assumed constant specific growth rates of plants to simplify the simulation process, which can be for dietary risk assessment, especially when high dilution rate constants are included.[8,35,53] Nevertheless, this simplified method may overestimate pesticide residue levels in harvested plants. In this study, time-dependent model inputs can be included into the operational tool (Methods S6), hence facilitating simulations of real-world scenarios. Users are able to determine their own model inputs (e.g. rate constants for plant growth) and generate site-specific results.

4 CONCLUSIONS

In the present study, a modeling approach to estimating degradation rate constants in plant tissues was proposed. Based on several available plant uptake models for this crop, we utilized potato as a model plant. By fitting simulation results with experimental data, an operational tool was developed to backward-estimate the degradation rate constants of pesticides in potatoes. We conducted case studies for three pesticides that can accommodate a variety of experimental conditions (i.e. THI and multiple application events). Using reported data to perform the modeling exercise, we suggest that future research should focus on the following aspects in order to improve the degradation kinetics estimate of pesticides in plants:

(i) the growth dynamics of potatoes during the growth stage can significantly affect the uptake and elimination kinetics of the pesticide in potatoes, indicating that the pesticide's THI must be taken into account when evaluating the degradation kinetics of the pesticide in plant tissues;
(ii) geological variations in weather conditions and soil properties are essential for determining the degradation kinetics of the pesticide in potatoes, which cannot be ignored in field or modeling studies;
(iii) the dissipation kinetics of the pesticide in the soil has a significant effect on the dissipation kinetics of the pesticide in potatoes; therefore, a comprehensive investigation of the residue concentration in the soil, particularly at planting depths of tubers, is strongly suggested;
(iv) conceiving experimental/modeling studies to directly measure/predict degradation kinetics of pesticides in plant tissues, such as *in vitro* culture of plant cells[66] and *in silico* analysis of the chemical–plant interaction;[67]
(v) implementing the proposed modeling approach into other software with specialized functional packages to conduct more robust parameter evaluation and calibration (e.g. PEST).

With the earlier-mentioned recommendations, the proposed modeling approach can be further enhanced to be more adaptable to environmental conditions (weather and soil properties) and plant species (aboveground and belowground crops). We anticipate that plant uptake models for other crops (such as apple and wheat) will in the future be added into the operational tool utilizing the simulation mechanism depicted in Eqn (1) in order to derive degradation rate constants of pesticide residues in other crops. With the computed degradation rate constants, it is then possible to determine the simulated dissipation rate constants of pesticide residues in plants. Consequently, existing modeling tools can be equipped with the curve-fitting function to simulate dissipation or degradation rate constants of pesticide residues in various plant species, which will aid both health risk and life cycle impact assessments of pesticides.

© 2022 The Authors.

15264998, 2023, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/ps.7288 by Danish Technical Knowledge, Wiley Online Library on [16/02/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

AUTHOR CONTRIBUTIONS

Zijian Li: conceptualization, methodology, data curation, discussion, writing – original draft, writing – review and editing. Peter Fantke: conceptualization, methodology, data curation, discussion, writing – review and editing, funding acquisition.

CONFLICTS OF INTEREST

There are no conflicts to declare.

ACKNOWLEDGEMENTS

This study was financially supported by the SPRINT project (grant agreement no. 862568) funded under the European Union's Horizon 2020 Research and Innovation program, by the 'Safe and Efficient Chemistry by Design (SafeChem)' project funded by the Swedish Foundation for Strategic Environmental Research (grant agreement no. DIA 2018/11), and by the PARC project (grant agreement no. 101057014) funded under the European Union's Horizon Europe Research and Innovation program. Microsoft Office 3D Models and Icons assisted in the design of figures.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

REFERENCES

1 Maggi F, la Cecilia D, Tang FHM and McBratney A, The global environmental hazard of glyphosate use. *Sci Total Environ* **717**:137167 (2020).
2 Sharma A, Kumar V, Shahzad B, Tanveer M, Sidhu GPS, Handa N *et al.*, Worldwide pesticide usage and its impacts on ecosystem. *SN Appl Sci* **1**:1446 (2019).
3 Topping CJ, Aldrich A and Berny P, Overhaul environmental risk assessment for pesticides. *Science* **1979**:360–363 (2020).
4 Fantke P, Friedrich R and Jolliet O, Health impact and damage cost assessment of pesticides in Europe. *Environ Int* **49**:9–17 (2012).
5 Tang FHM, Lenzen M, McBratney A and Maggi F, Risk of pesticide pollution at the global scale. *Nat Geosci* **14**:206–210 (2021).
6 Maggi F, Tang FHM, Black AJ, Marks GB and McBratney A, The pesticide health risk index—An application to the world's countries. *Sci Total Environ* **801**:149731 (2021).
7 Raherison C, Baldi I, Pouquet M, Berteaud E, Moesch C, Bouvier G *et al.*, Pesticides exposure by air in vineyard rural area and respiratory health in children: a pilot study. *Environ Res* **169**:189–195 (2019).
8 Fantke P, Charles R, de Alencastro LF, Friedrich R and Jolliet O, Plant uptake of pesticides and human health: dynamic modeling of residues in wheat and ingestion intake. *Chemosphere* **85**:1639–1647 (2011).
9 Dorca-Preda T, Fantke P, Mogensen L and Knudsen MT, Towards a more comprehensive life cycle assessment framework for assessing toxicity-related impacts for livestock products: the case of Danish pork. *Sci Total Environ* **815**:152811 (2022).
10 Romero-González R and Garrido Frenich A, Application of HRMS in pesticide residue analysis in food from animal origin, in *Applications in High Resolution Mass Spectrometry: Food Safety and Pesticide Residue Analysis*. Elsevier, Amsterdam, Netherlands (2017).
11 Ramón F and Lull C, Legal measures to prevent and manage soil contamination and to increase food safety for consumer health: the case of Spain. *Environ Pollut* **250**:883–891 (2019).
12 Li Z and Fantke P, Framework for defining pesticide maximum residue levels in feed: applications to cattle and sheep. *Pest Manage Sci* (2022). https://doi.org/10.1002/ps.7241
13 Fantke P and Jolliet O, Life cycle human health impacts of 875 pesticides. *Int J Life Cycle Assess* **21**:722–733 (2016).
14 Gentil C, Basset-Mens C, Manteaux S, Mottes C, Maillard E, Biard Y *et al.*, Coupling pesticide emission and toxicity characterization models for LCA: application to open-field tomato production in Martinique. *J Cleaner Prod* **277**:124099 (2020).
15 Pang N, Fan X, Fantke P, Zhao S and Hu J, Dynamics and dietary risk assessment of thiamethoxam in wheat, lettuce and tomato using field experiments and computational simulation. *Environ Pollut* **256**:113285 (2020).
16 Rein A, Legind CN and Trapp S, New concepts for dynamic plant uptake models. *SAR QSAR Environ Res* **22**:191–215 (2011).
17 Rein A, Bauer-Gottwein P and Trapp S, New model concepts for dynamic plant uptake and mass flux estimates in the soil-plant-air system, in *Groundwater Quality Management in a Rapidly Changing World: 7th International Groundwater Quality Conference*. IAHS Press, Zurich, Switzerland (2010).
18 An Q, Wu Y, Li D, Hao X, Pan C and Rein A, Development and application of a numerical dynamic model for pesticide residues in apple orchards. *Pest Manage Sci* **78**:2679–2692 (2022).
19 Burken JG and Schnoor JL, Uptake and metabolism of atrazine by poplar trees. *Environ Sci Technol* **31**:1399–1406 (1997).
20 Burken JG and Schnoor JL, Predictive relationships for uptake of organic contaminants by hybrid poplar trees. *Environ Sci Technol* **32**:3379–3385 (1998).
21 Burken JG and Schnoor JL, Phytoremediation: plant uptake of atrazine and role of root exudates. *J Environ Eng* **122**:958–963 (1996).
22 Fantke P, Wieland P, Juraske R, Shaddick G, Itoiz ES, Friedrich R *et al.*, Parameterization models for pesticide exposure via crop consumption. *Environ Sci Technol* **46**:12864–12872 (2012).
23 Fantke P, Juraske R, Antón A, Friedrich R and Jolliet O, Dynamic multicrop model to characterize impacts of pesticides in food. *Environ Sci Technol* **45**:8842–8849 (2011).
24 Juraske R, Fantke P, Ramírez ACR and González A, Pesticide residue dynamics in passion fruits: comparing field trial and modelling results. *Chemosphere* **89**:850–855 (2012).
25 Juraske R, Mosquera Vivas CS, Erazo Velásquez A, García Santos G, Berdugo Moreno MB, Diaz Gomez J *et al.*, Pesticide uptake in potatoes: model and field experiments. *Environ Sci Technol* **45**:651–657 (2011).
26 Trapp S, Fruit tree model for uptake of organic compounds from soil and air. *SAR QSAR Environ Res* **18**:367–387 (2007).
27 Trapp S and Matthies M, Generic one-compartment model for uptake of organic chemicals by foliar vegetation. *Environ Sci Technol* **29**: 2333–2338 (1995).
28 Jacobsen RE, Fantke P and Trapp S, Analysing half-lives for pesticide dissipation in plants. *SAR QSAR Environ Res* **26**:325–342 (2015).
29 Fantke P, Gillespie BW, Juraske R and Jolliet O, Estimating half-lives for pesticide dissipation from plants. *Environ Sci Technol* **48**:8588–8602 (2014).
30 Aliferis KA and Chrysayi-Tokousbalides M, Metabolomics in pesticide research and development: review and future perspectives. *Metabolomics* **7**:35–53 (2011).
31 Paraíba LC and Kataguiri K, Model approach for estimating potato pesticide bioconcentration factor. *Chemosphere* **73**:1247–1252 (2008).
32 Xiao S, Li Z and Fantke P, Improved plant bioconcentration modeling of pesticides: the role of peel dynamics. *Pest Manage Sci* **77**:5096–5108 (2021).
33 Xiao S, Gong Y, Li Z and Fantke P, Improving pesticide uptake modeling into potatoes: considering tuber growth dynamics. *J Agric Food Chem* **69**:3607–3616 (2021).
34 Itoiz ES, Fantke P, Juraske R, Kounina A and Vallejo AA, Deposition and residues of azoxystrobin and imidacloprid on greenhouse lettuce with implications for human consumption. *Chemosphere* **89**: 1034–1041 (2012).
35 Trapp S, Cammarano A, Capri E, Reichenberg F and Mayer P, Diffusion of PAH in potato and carrot slices and application for a potato model. *Environ Sci Technol* **41**:3103–3108 (2007).
36 van Eerd LL, Hoagland RE, Zablotowicz RM and Hall JC, Pesticide metabolism in plants and microorganisms. *Weed Sci* **51**:472–495 (2003).
37 Dong Z, Li T, Wan Y, Sun Y and Hu J, Physiologically based pharmacokinetic modeling for chlorinated Paraffins in rats and humans: importance of biliary excretion. *Environ Sci Technol* **54**:938–946 (2020).

© 2022 The Authors.

15264998, 2023, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/ps.7288 by Danish Technical Knowledge, Wiley Online Library on [16/02/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

38 Li Z, Xiong J and Fantke P, Screening of pesticide distributions in foods of animal origin: a matrix-based approach for biotransfer factor modeling of grazing mammals. *Environ Sci: Processes Impacts* **24**: 609–624 (2022).
39 Li Z and Niu S, Modeling pesticides in global surface soils: evaluating spatiotemporal patterns for USEtox-based steady-state concentrations. *Sci Total Environ* **791**:148412 (2021).
40 Xiao S, Li Z and Fantke P, Improved plant bioconcentration modeling of pesticides: the role of periderm dynamics. *Pest Manage Sci* **77**: 5096–5108 (2021).
41 Fantke P, Wieland P, Wannaz C, Friedrich R and Jolliet O, Dynamics of pesticide uptake into plants: from system functioning to parsimonious modeling. *Environ Model Softw* **40**:316–324 (2013).
42 Rosenbaum RK, Margni M and Jolliet O, A flexible matrix algebra framework for the multimedia multipathway modeling of emission to impacts. *Environ Int* **33**:624–634 (2007).
43 Zhao J and Wilkins RM, Low molecular weight polylactic acid as a matrix for the delayed release of pesticides. *J Agric Food Chem* **53**: 4076–4082 (2005).
44 Zhang F, Fan S, Liu S, Li X and Pan C, Dissipation and residue behavior of mepiquat on wheat and potato field application. *Environ Monit Assess* **185**:9101–9109 (2013).
45 Abd-Alrahman SH, Residue and dissipation kinetics of thiamethoxam in a vegetable-field ecosystem using QuEChERS methodology combined with HPLC-DAD. *Food Chem* **159**:1–4 (2014).
46 Narenderan ST, Meyyanathan SN, Karri VVSR, Babu B and Chintamaneni P, Chemometrics assisted QuEChERS extraction method for the residual analysis of organophosphate insecticides: application to their dissipation kinetics in open field ecosystem. *Anal Chem Lett* **10**:798–810 (2020).
47 Li Z, Modeling pesticide residues in nectar and pollen in support of pesticide exposure assessment for honeybees: a generic modeling approach. *Ecotoxicol Environ Saf* **236**:113507 (2022).
48 Ingram KT and McCloud DE, Simulation of potato crop growth and development 1. *Crop Sci* **24**:21–27 (1984).
49 Puertas JM, Ruiz J, de la Vega MR, Lorenzo J, Caminal G and González G, Influence of specific growth rate over the secretory expression of recombinant potato carboxypeptidase inhibitor in fed-batch cultures of Escherichia coli. *Process Biochem* **45**:1334–1341 (2010).
50 Dubenok NN, Melikhov V v, Novikov AA, Bolotin DA and Vasilyuk DI, Processing of specific growth of various potato varieties under drip irrigation in lower Volga region. *IOP Conf Ser: Earth Environ Sci* **624**: 012014 (2021).
51 Li Z, Spatiotemporal pattern models for bioaccumulation of pesticides in common herbaceous and woody plants. *J Environ Manage* **276**: 111334 (2020).
52 Worthington CM and Hutchinson CM, Accumulated growing degree days as a model to determine key developmental stages and evaluate yield and quality of potato in Northeast Florida. *Proc Fla State Hortic Soc* **118**:98–101 (2005).
53 Li Z, Modeling plant uptake of organic contaminants by root vegetables: the role of diffusion, xylem, and phloem uptake routes. *J Hazard Mater* **434**:128911 (2022).
54 Howlader O and Hoque M, Growth analysis and yield performance of four potato (Solanum tuberosum L.) varieties, *Bangladesh*. *J Agric Res* **43**:267–280 (2018).
55 Chen L, Jia C, Li F, Jing J, Yu P, He M *et al*., Dissipation and residues of fluazinam and dimethomorph in potatoes, potato plants, and soil, determined by QuEChERS ultra-performance liquid chromatography tandem mass spectrometry. *Environ Sci Pollut Res* **25**:32783–32790 (2018).
56 Lewis KA, Tzilivakis J, Warner DJ and Green A, An international database for pesticide risk assessments and management. *Hum Ecol Risk Assess* **22**:1050–1064 (2016).
57 Ramos TB, Simionesei L, Jauch E, Almeida C and Neves R, Modelling soil water and maize growth dynamics influenced by shallow groundwater conditions in the Sorraia Valley region, Portugal. *Agric Water Manage* **185**:27–42 (2017).
58 Trapp S, Dynamic root uptake model for neutral lipophilic organics. *Environ Toxicol Chem* **21**:203–206 (2002).
59 Li Z, Modeling pesticide residue uptake by leguminous plants: a geocarpic fruit model for peanuts. *Pest Manage Sci* (2022). https://doi.org/10.1002/ps.7184
60 Juraske R, Antón A, Castells F and MAJ H, Human intake fractions of pesticides via greenhouse tomato consumption: comparing model estimates with measurements for Captan. *Chemosphere* **67**:1102–1107 (2007).
61 Fantke P and Juraske R, Variability of pesticide dissipation half-lives in plants. *Environ Sci Technol* **47**:3548–3562 (2013).
62 Juraske R, Antón A and Castells F, Estimating half-lives of pesticides in/on vegetation for use in multimedia fate and exposure models. *Chemosphere* **70**:1748–1755 (2008).
63 Paraíba LC, Pesticide bioconcentration modelling for fruit trees. *Chemosphere* **66**:1468–1475 (2007).
64 Trapp S, Rasmussen D and Samsøe-Petersen L, Fruit tree model for uptake of organic compounds from soil. *SAR QSAR Environ Res* **14**: 17–26 (2003).
65 Balemi T and Schenk MK, Genotypic variation of potato for phosphorus efficiency and quantification of phosphorus uptake with respect to root characteristics. *J Plant Nutr Soil Sci* **172**:669–677 (2009).
66 Harms HH, In-vitro systems for studying phytotoxicity and metabolic fate of pesticides and xenobiotics in plants. *Pestic Sci* **35**:277–281 (1992).
67 Liu N, Li M, Gong Y, Liu F and Li T, Cytochrome P450s—their expression, regulation, and role in insecticide resistance. *Pestic Biochem Physiol* **120**:77–81 (2015).

 © 2022 The Authors.
Pest Management Science published by John Wiley & Sons Ltd on behalf of Society of Chemical Industry.

15264998, 2023, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/ps.7288 by Danish Technical Knowledge, Wiley Online Library on [16/02/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License