Improved plant bioconcentration modeling of pesticides: The role of periderm dynamics

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Abstract

BACKGROUND: There is a continuous need to advance pesticide plant uptake models in support of improving pest control and reducing human exposure to pesticide residues. The periderm of harvested root and tuber crops may affect pesticide uptake, but is usually not considered in plant uptake models. To quantify the influence of the periderm on pesticide uptake from soil into potatoes, we propose a model that includes an explicit periderm compartment in the soil–plant mass balance for pesticides.

RESULTS: Our model shows that the potato periderm acts as an active barrier to the uptake of lipophilic pesticides with high $K_{ow}$, while it lets more lipophobic pesticides accumulate in the medulla (pulp). We estimated bioconcentration factors (BCFs) for over 700 pesticides and proposed parameterizations for including the effects of the periderm into a full plant uptake modeling framework. A sensitivity analysis shows that both the degradation half-life inside the tuber and the lipophilicity drive the contributions of other aspects to the variability of BCFs, while highlighting distinct dynamics in the periderm and medulla compartments. Finally, we compare model estimates with measured data, showing that predictions agree with field observations for current-use pesticides and some legacy pesticides frequently found in potatoes.

CONCLUSION: Considering the periderm improves the accuracy of quantifying pesticide uptake and bioconcentration in potatoes as input for optimizing pest control and minimizing human exposure to pesticide residues in edible crops.

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Keywords: environmental modeling; food crops; food safety; health risk assessment; dynamiCROP

1 INTRODUCTION

To achieve a sustainable crop production, optimized pest control and minimized related risk for humans and the environment are crucial. Pesticides are widely applied to enhance the productivity of agricultural crops and to fight unwanted pests. After field application, pesticides can enter crops through multiple pathways, such as absorption and plant uptake, which can lead to negative health impacts for humans.\(^1\text{–}^8\) Potato, as one of the most consumed crops worldwide, plays a significant role in the global food supply.\(^9\) Pesticide residues are frequently detected in harvested potato tubers around the world, with research indicating that diffusion from the soil is a major contributor.\(^10\text{–}^12\) To control pests and manage the pesticide application in potato fields, it is necessary to evaluate the potato uptake of pesticides and accurately predict the pesticide concentrations in edible tubers. Several experimental and modeling studies have attempted to improve our understanding of the fate of pesticides in the soil–potato environment, with significant contributions to predicting pesticide residues and estimating related human exposures and risks.\(^10\text{–}^18\)

The potato periderm, which is the outer layer of the tuber that replaces the epidermis during early growth, plays a significant role in protecting the inner tuber tissues against pathogens, dehydration, and physical injury.\(^19,20\) The periderm consists of three layers, the phellem, phellogen, and phelloderm, each of which is composed of unique cells. Although some studies define the outer component of the periderm, i.e. suberized phellem cells, as the potato skin,\(^19,20\) the outer layer of tissue that separates the inside tuber (or medulla) from the environment is frequently referred to as the potato peel (or periderm), which can conceptually simplify the analysis of pesticide transfer from soil into potato tubers. Experimental studies have shown that potato periderm and potato medulla accumulate very different levels of pesticide residue,\(^13,21\) and that removing or washing the periderm before cooking can reduce the exposure to pesticide residues.\(^22,23\) This is because of the different chemical components (e.g. lipids) and micro physical structures (e.g. porosity) of periderm and medulla. Numerous studies have assessed the penetration of chemicals in crop skins at the micro scale, which is generalized as the sorption-diffusion-desorption process.\(^24\text{–}^26\) The aqueous-pore
and lipophilic pathways governing the penetration of chemicals in crop cuticles have also been investigated. These experimental and modeling studies have significantly contributed to our understanding of chemical penetration mechanisms in crop cuticles. However, due to its complexity, the influence of the potato periderm is usually not considered in residue estimates of applied field pesticides in edible crop components after harvest and potential food processing as input for human exposure and related health impact assessments. Hence, a simplified tool that can treat the complex structure of the potato periderm as a single compartment is required to evaluate the influence of the periderm on the transport of pesticides from soil into potato tubers. Such a tool could be further incorporated into existing plant uptake models to help reduce human exposure to pesticide residues in edible crop components as well as to evaluate the influence of food processing (e.g. peeling) on the magnitude of residue-related exposure.

To address this gap, it is the aim of the present study to propose a modeling approach that treats the potato periderm as a separate compartment to quantify the influence of the periderm on the uptake of pesticides into edible potato tubers and related residues. To achieve this aim, we defined three specific objectives: (i) to develop a model for pesticide uptake into potato tubers that explicitly considers the periderm (periderm model) and compare results with uptake without considering the periderm (nonperiderm model); (ii) to parameterize the periderm model for inclusion into existing plant uptake models for human exposure and health impact assessments; and (iii) to identify the key input variables that drive modeled pesticide uptake into potato tubers as input for further refining the model.

2 METHODS AND MATERIALS

2.1 General framework

2.1.1 General process of pesticide uptake into potato tubers

Figure 1 illustrates the conceptual framework of pesticide transport from the soil to the potato medulla through the potato periderm. The entire transport process is modeled based on three compartments: (i) the soil compartment where pesticide transport is predominantly affected by pesticide emission, degradation in soil, and diffusion to (or from) potato tubers; (ii) the tuber periderm compartment, where pesticide transport is determined by diffusion to (or from) both the soil and medulla, dilution by growth of the potato, and degradation; and (iii) the medulla compartment, where pesticide transport is also determined by diffusion, growth dilution, and degradation processes. Other possible pesticide fate processes, such as volatilization from soil surfaces to air and leaching to deeper soil layers, which are affected by weather and soil conditions, are not discussed in more detail due to our focus on the influence of the potato periderm on pesticide residue dynamics in edible potato tubers. When incorporating processes between soil, potato periderm, and medulla into more complex plant uptake frameworks, additional relevant processes are usually already considered.

2.1.2 General derivation process of pesticide uptake models

Our periderm model of pesticide uptake into potato tubers was developed based on a classic nonperiderm model where the periderm compartment was not considered. For the nonperiderm model in Section 2.3, two compartments (i.e. soil and medulla) were considered, for which the ordinary differential equation can be directly solved by eliminating the pesticide fate in the soil compartment according to the first-order kinetics degradation process. For the periderm model, three compartments (i.e. soil, periderm, and medulla) were considered, for which the pesticide fate models for periderm and medulla compartments are expressed in sections 2.4 and 2.5, respectively. In section 2.6 we combine the pesticide fate models into a set of two differential equations with two variables, which are solved using the technique of the nonhomogeneous linear differential equation (Supporting Information Appendix S1).

2.2 Soil compartment

For the soil compartment, we assume that the soil application of pesticides is the major source of pesticides in soil, therefore first-order degradation kinetics are used to determine the concentration of pesticides in soil \( C_S(t) \) (mg kg\(^{-1}\)) as a function of time \( t \) (day), using a degradation rate \( k_g \) (days\(^{-1}\)). We assume that \( C_S(t) \) is not affected by diffusion into the potato, since this loss of pesticides can be quickly balanced by the pesticide available in the surrounding soil. Therefore, the following equation is used for the soil compartment:

\[
C_S(t) = C_S(0) \exp(-k_g t)
\]

where \( C_S(0) \) (mg kg\(^{-1}\)) is the initial concentration of pesticides in the soil.

2.3 Classic ‘nonperiderm’ model

A nonperiderm modeling approach to estimate pesticide uptake into potato tubers has been widely employed and can be expressed by a simple two-compartment model (i.e. soil and potato medulla), where the potato grows until it reaches its maximum mass (i.e. when \( 0 \leq t \leq t_g \), where \( t_g \) is the time when the potato stops growing):

\[
\frac{dC_{PM}^{NP}(t)}{dt} = -\left( \frac{2f_{W,M}T_mD_W}{\rho M r^2} \right) \left( \frac{C_{PM}(t) - C_{PM}^{NP}(t)}{K_{MW}} \right) + \left( k_g + k_m \right) C_{PM}^{NP}(t)
\]

where \( C_{PM}^{NP}(t) \) (mg kg\(^{-1}\)) denotes the pesticide concentration in the potato medulla expressed in the nonperiderm model (superscript NP denotes the nonperiderm model), \( f_{W,M} \) (g kg\(^{-1}\)) and \( T_m \) (unitless) are the water content and tortuosity factor of the medulla, respectively, and \( D_W \) (m\(^2\) day\(^{-1}\)) is the diffusivity of the pesticide in water. \( \rho M \) (kg L\(^{-1}\)) and \( r \) (m) are the density and radius of an assumed perfect-sphere medulla. \( K_{MW} \) (L kg\(^{-1}\) or
L L\(^{-1}\)) and \(K_{MW}\) (L kg\(^{-1}\)) are the bulk soil-water and medulla-water partition coefficients, respectively. \(k_g\) (days\(^{-1}\)) is the growth rate of the potato medulla and \(k_m\) (days\(^{-1}\)) is the degradation rate of the pesticide in the potato medulla, which is approximated using \(k_d\)\(^{38}\). By replacing \(C_S(t)\) by \(C_S(0)\exp(-k_d t)\) according to Eqn (1), Eqn (2) can be solved with the initial condition of \(C_S^{NP}(t) = 0\) as:

\[
C^{NP}(t) = C_S(0) \left( \frac{k_m^+}{k_m^+ + k_g + k_m - k_d} \right) \exp(-k_g t) \exp\left(-\left(k_m^+ + k_g + k_m\right)t\right)
\]

\[\text{(3)}\]

\[
BCF^{NP}(t) = \frac{C^{NP}(t)}{C_S(0)} = \left( \frac{k_m^+}{k_m^+ + k_g + k_m - k_d} \right) \left[1 - \exp\left(\left(k_d - k_m^+ - k_g - k_m\right)t\right)\right]
\]

\[\text{(4a)}\]

\[
\left\{ \begin{array}{l}
k^+ = \frac{2\lambda f_{W,M} T_M D_W}{r^2 \rho_M K_{SW}} \\
C^+ = \frac{2\lambda f_{W,M} T_M D_W}{r^2 \rho_M K_{MW}}
\end{array} \right.
\]

\[\text{(4b)}\]

where BCF\(^{NP}\)(t) is the bioconcentration factor of the pesticide in potato medulla (BCF\(^{NP}\)(t)) for the nonperiderm model, which is defined as the ratio of \(C^{NP}\)(t) to \(C_S(0)\) at a given time step. We note that the term BCF describes the bioaccumulation of pesticide in organisms (e.g. terrestrial plants and aquatic life) in a general way, and some other terms such as biota-soil accumulation factor can be more specifically for the soil-based bioaccumulation process. In this study, we use the term BCF to be consistent with current studies on plant uptake of pesticides, acknowledging that it refers to the soil-potato system. \(k_m^+\) (days\(^{-1}\)) and \(k_m^-\) (days\(^{-1}\)) are the pesticide uptake and elimination rates by the potato without considering the periderm, respectively. In this study, the shape of the potato (i.e. radius, mass, and surface area) does not change over time in the model, even though the growth dilution of pesticides in potatoes is included in the model\(^{10,14}\). We tested the dynamic solution against more simplified solutions assuming constant coefficients based on fixed tuber characteristics and found that pesticide dynamics are not very sensitive to differences in tuber characteristics over time\(^{38}\), particularly for the periderm compartment (i.e. the thin layer) at harvest.

### 2.4 Potato periderm compartment

In the periderm model, we introduced a separate periderm compartment between soil and potato medulla. Although a spherical shape is assumed for the potato tuber, we modeled the diffusion process of a particular pesticide through the periderm on a planar basis because the layer is very thin, thus the top and bottom sides of the periderm are approximately equal. As the pesticide can diffuse through both sides of the periderm, we modeled this diffusive process by treating the periderm as a thin disc that has an equivalent diffusion length on both sides to 0.25 times the thickness of the periderm, i.e. 0.25\(L_p\) (m)\(^{30}\). With that, the concentration of the pesticide in the periderm can be expressed as follows:

\[
\frac{dC_P(t)M_p}{dt} = -A_p \left( \frac{f_{W,P} T_P D_W C_F}{0.25 L_p} \right) \left( \frac{C_P(t)}{K_{PW}} - \frac{C_S(t)}{K_{SW}} \right) C_P(t)M_p
\]

\[\text{(5)}\]

where \(C_P(t)\) (mg kg\(^{-1}\)) and \(C_M(t)\) (mg kg\(^{-1}\)) are the concentrations of the pesticide in the periderm and medulla, respectively. \(M_p\) (kg) is the mass of the potato periderm, and \(A_p\) (m\(^2\)) and \(L_p\) (m) are the area, i.e. the surface area of the potato, and the thickness of the periderm, respectively, thus \(M_p\) can be expressed by \(A_p L_p \rho_p\), where \(\rho_p\) (kg L\(^{-1}\)) is the density of the periderm. \(C_F(10^3\text{L m}^{-3})\) is a unit conversion factor. \(K_{PW}\) (L kg\(^{-1}\)) is the periderm–water partition coefficient. \(k_g\) and \(k_m\) are assumed to be the same for the periderm and medulla. In Eqn (5), we describe \(C_P(t)\) as a function of time, based on the passive diffusive process of the pesticide through the water phase of the periderm\(^{10,14}\) therefore \(C_S(t)\) and \(C_M(t)\) denote the concentrations of the pesticide in the water phase of the periderm–soil and periderm–medulla interfaces, respectively. Thus, the term \(f_{W,P} T_P D_W\) multiplied by \(\frac{1}{M_p \rho_p}\) denotes the effective diffusivity of the pesticide in the periderm tissue (the labyrinth factor), where \(f_{W,P}\) (g g\(^{-1}\)) and \(T_P\) (unitless) are the water content and tortuosity factor of the periderm, respectively. By substituting \(M_p\) with \(A_p L_p \rho_p C_F\), Eqn (5) can be expressed as:

\[
\frac{dC_P(t)}{dt} = -\left( \frac{f_{W,P} T_P D_W}{0.25 L_p \rho_p} \right) \left( \frac{C_F(t) - C_S(t)}{K_{PW}} - \frac{C_M(t)}{K_{MW}} \right) - (k_g + k_m) C_P(t)
\]

\[\text{(6)}\]

As \(k_g\) is applied instead of the logistic function of potato growth, when the potato stops growing (i.e. \(t > t_g\)), Eqn (5) can be further simplified by setting \(k_g = 0\). It is assumed that the potato is harvested when it reaches its maximum mass (i.e. \(t = t_g\)), therefore we only consider the situation when \(0 \leq t \leq t_g\).

### 2.5 Potato medulla compartment

For the potato medulla compartment, we describe \(C_M(t)\) as a function of time as a radial diffusion process by assuming a spherical shape for the potato\(^{10,14}\) which can be expressed as:

\[
\frac{dC_M(t)}{dt} = \left( \frac{23 f_{W,M} T_M D_W}{r^2 \rho_M} \right) \left( \frac{C_M(t) - C_S(t)}{K_{MW}} - \frac{C_P(t)}{K_{PW}} \right) -(k_g + k_m) C_M(t)
\]

\[\text{(7)}\]

Like the periderm compartment, when \(t > t_g\), the situation can be expressed by setting \(k_g\) in Eqn (7) to zero.

### 2.6 Solutions for nonhomogeneous linear differential equations

To solve the differential equations Eqn (6) (i.e. residue concentrations in the periderm compartment) and Eqn (7) (i.e. residue concentrations in the medulla compartment), we first replaced \(C_S(t)\) by \(C_S(0)\exp(-k_d t)\) in Eqn (6) to eliminate the variable \(C_S(t)\) (i.e. residue concentrations in the soil compartment). Thus, Eqns (6) and (7) make up a set of two differential equations with two variables, namely \(C_P(t)\) and \(C_M(t)\). Then, we simplified the expression of Eqns (6) and (7) by making the following substitutions:

\[
k_p^+ = \frac{f_{W,P} T_P D_W}{0.25 L_p \rho_p K_{PW}}
\]

\[\text{(8a)}\]

\[
k_p^- = \frac{f_{W,M} T_M D_W}{0.25 L_p \rho_p K_{MW}}
\]

\[\text{(8b)}\]
3 RESULTS AND DISCUSSION

3.1 Pesticide uptake into potato periderm and medulla

To illustrate the influence of the periderm on pesticide uptake into potato tubers, we use chlorpyrifos (CAS: 2921-88-2) as a widely used organophosphate insecticide applied in potato fields that has been frequently evaluated in modeling studies using nonperiderm models. For potatoes, dynamiCROP currently relies on a nonperiderm model, which we refine by introducing a periderm-adjusted factor (PAF), which is defined as the ratio of the simulated BCFs of the periderm model to the nonperiderm model.

\[
\begin{align}
C_p(t) &= \frac{dC_p(t)}{dt} = k_p^{w}C_s(0)e^{-k_p^{w}t} + k_p^{M}C_m(t) - (2k_p^{w} + k_g + k_m)C_p(t) \\
C_M(t) &= \frac{dC_M(t)}{dt} = k_p^{M}C_p(t) - (k_g + k + k_m)C_M(t)
\end{align}
\]

Eqn (9) can be solved as the nonhomogeneous linear differential equation (Supporting Information) with the initial conditions of \(C_p(t) = 0\) and \(C_M(t) = 0\) as follows:

For the medulla compartment:

\[
C_M(t) = \delta_1 C_s(0) \left( \frac{k_d + \lambda_2}{\lambda_1 - \lambda_2} \right) e^{(\lambda_2 - \lambda_1)t} \quad (10a)
\]

\[
BCF_M(t) = \frac{C_M(t)}{C_s(t)} = \delta_1 \left( \frac{k_d + \lambda_2}{\lambda_1 - \lambda_2} \right) e^{(\lambda_2 - \lambda_1)t} + 1 \quad (10b)
\]

where \(\delta_1, \lambda_1\), and \(\lambda_2\) are equation coefficients that are expressed by the specific rates of pesticides. \(BCF_M(t)\) is the bioconcentration factor of the pesticide in potato medulla.

For the periderm compartment:

\[
C_p(t) = \frac{\delta_1 C_s(0)}{k_p} \left( \frac{k_m + k_g + k_m + \lambda_1}{\lambda_1 - \lambda_2} \right) e^{(\lambda_2 - \lambda_1)t} - \left( \frac{k_m + k_g + k_m + \lambda_2}{\lambda_1 - \lambda_2} \right) e^{(\lambda_2 - \lambda_1)t} \quad (11a)
\]

\[
BCF_P(t) = \frac{C_p(t)}{C_s(t)} = \frac{\delta_1}{k_p} \left( \frac{k_m + k_g + k_m + \lambda_1}{\lambda_1 - \lambda_2} \right) e^{(\lambda_2 + k_d)t} - \left( \frac{k_m + k_g + k_m + \lambda_2}{\lambda_1 - \lambda_2} \right) e^{(\lambda_2 + k_d)t} + \left( k_m + k_g + k_m - k_d \right) e^{-k_d t} \quad (11b)
\]

where \(BCF_M(t)\) is the bioconcentration factor of the pesticide in potato periderm.

2.7 Periderm model application

To practically evaluate pesticide uptake into potato medulla through an effective periderm compartment, we propose the following methods: (i) the direct application of \(BCF_M(t)\) derived by the periderm model, for which the simulated results are summarized in the Supporting Information; (ii) the parameterized comparison between \(BCF_M(t)\) derived by the periderm model and \(BCF_M^{(w)}(t)\) derived by a nonperiderm model; (iii) the incorporation of the periderm effect into pesticide uptake and elimination rates from the nonpeel model; and (iv) the integration of our results into dynamiCROP as a dynamic multicrop plant uptake model that is applied for estimating the human exposure and health impacts associated with pesticide residues in food crops. For potatoes, dynamiCROP currently relies on a nonperiderm model, which we refine by introducing a periderm-adjusted factor (PAF), which is defined as the ratio of the simulated BCFs of the periderm model to the nonperiderm model.
application, $C_M(t)$ reaches its maximum value of $1.86 \times 10^{-3}$ mg kg$^{-1}$ per unit level of $C_S(0)$.

To better reflect the uptake efficiency of chlorpyrifos by potato periderm and medulla from the soil, we also depict $BCF_M(t)$ and $BCF_P(t)$ as a function of time in Fig. 2(A). The results show that both $BCF_M(t)$ and $BCF_P(t)$ increase as time increases within its interval, i.e. between pesticide application and potato harvest, if we assume that the harvest is 60 days after pesticide application, as shown in Fig. 2. In general, $BCF_P(t)$ is much larger than $BCF_M(t)$ for chlorpyrifos, which corresponds to the results of $C_P(t)$ and $C_M(t)$ discussed above. For example, 5 days after application, the estimated $BCF_P(t)$, which is $5.41 \times 10^{-3}$, is approximately 26 times higher than $BCF_M(t)$ (i.e. $2.05 \times 10^{-4}$). When time increases, both $BCF_M(t)$ and $BCF_P(t)$ approach their asymptotes, for which the limit values are approximately $2.69 \times 10^{-3}$ and $5.49 \times 10^{-2}$ for $BCF_M(t)$ and $BCF_P(t)$, respectively, indicating that both the potato periderm and medulla can theoretically take up chlorpyrifos at harvest time (assumed as 60 days after application), where the concentrations are approximately 5.5% and 0.27% of the unit concentration in soil. Therefore, measuring the $C_S(t)$ value of chlorpyrifos at harvest can help predict how much chlorpyrifos is accumulated in the potato periderm and medulla. The simulated $BCF_M(t)$ is lower than $BCF_P(t)$ for chlorpyrifos for the following reasons. Thermodynamically, potato periderm has a larger lipid content (0.003 g g$^{-1}$) than medulla (0.001 g g$^{-1}$), which can store more chlorpyrifos in the periderm than the medulla per mass unit due to its lipophilic property (i.e. log $K_{OW}$ = 4.96). Kinetically, the periderm acts as a barrier that separates the soil and potato medulla, which limits the transfer flux of chlorpyrifos from soil to medulla by mediating the effective concentration gradients between soil and periderm, and further between periderm and medulla.

Furthermore, we compare the simulated results of chlorpyrifos uptake by potato medulla between our periderm model (i.e. $BCF_M(t)$) and a nonperiderm model (i.e. $BCF_{NP}(t)$), as illustrated in Fig. 2(B). Compared to the nonperiderm model, $BCF_M(t)$ simulated from the periderm model exhibits both a time lag and a degree reduction of chlorpyrifos uptake in potato medulla. For example, only 2 days after chlorpyrifos application, $BCF_{NP}(t)$ exceeds 0.002 (i.e. $2.31 \times 10^{-3}$), which occurs 7 days after application for the periderm model (i.e. $BCF_M(t) = 2.33 \times 10^{-3}$). Also, 30 days after chlorpyrifos application, $BCF_{NP}(t)$ is $5.03 \times 10^{-3}$, whereas $BCF_M(t)$ is $2.69 \times 10^{-3}$. This is because the barrier compartment is not applied in the nonperiderm model, therefore chlorpyrifos is assumed to directly diffuse to the potato medulla from the soil without a rate-limiting step, which might overestimate pesticide uptake into edible potato parts. Also, due to the higher organic matter content of soil, the $K_{SW}$ (i.e. 247.6 kg kg$^{-1}$) of chlorpyrifos is much higher than the $K_{Peel-W}$ of 25.4 kg kg$^{-1}$, which leads to a larger concentration gradient in the water phase between soil and medulla in the nonperiderm model than that between periderm and medulla in the periderm model.

The periderm model predicts that $C_M(t)$ reaches the maximum value (8 days after chlorpyrifos application) at the earlier time as previous modeling studies, i.e. 13 days reported by Paraiba and Kataguri$^{14}$ and 11 days reported by Jurasek et al.$^{12}$ which is

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### Table 1. Input variables of the periderm model

| Model input variables               | Symbol | Unit     | Value     | Note                                                                 | References |
|-------------------------------------|--------|----------|-----------|----------------------------------------------------------------------|------------|
| Periderm water content              | $f_{WP}$ | g g$^{-1}$ | 0.842     | Estimated from water content and air pores                           | 42, 43     |
| Medulla water content               | $f_{WM}$ | g g$^{-1}$ | 0.778     | Estimated from water content and air pores                           | 10         |
| Periderm tortuosity factor          | $T_P$  | —        | 0.80      |                                                                      | 10         |
| Medulla tortuosity factor           | $T_M$  | —        | 0.72      |                                                                      | 10         |
| Periderm thickness                  | $L_P$  | m        | 0.0003    |                                                                      | 45         |
| Medulla radius                      | $r$    | m        | 0.04      |                                                                      | 10         |
| Periderm density                    | $\rho_P$ | kg L$^{-1}$ | 1.1      | Approximated from the density of medulla                             | 30         |
| Medulla density                     | $\rho_M$ | kg L$^{-1}$ | 1.1      |                                                                      | 10         |
| Growth rate                         | $k_d$  | d$^{-1}$ | 0.139     |                                                                      | 10         |
| Periderm lipid content              | —      | g g$^{-1}$ | 0.003     |                                                                      | 42         |
| Medulla lipid content               | —      | g g$^{-1}$ | 0.001     |                                                                      | 10         |
| Periderm carbohydrate content      | —      | g g$^{-1}$ | 0.155     | Estimated (including fiber and starch)                              | 42         |
| Medulla carbohydrate content       | —      | g g$^{-1}$ | 0.154     |                                                                      | 10         |
| Pesticide-specific variables        |        |          |           |                                                                      |            |
| Periderm-water partition coefficient | $K_{PW}$ | L kg$^{-1}$ | Vary     | Estimated by the nutrition composition and the carbohydrate–water partition coefficient | 10, 46 |
| Medulla-water partition coefficient | $K_{MW}$ | L kg$^{-1}$ | Vary     | Estimated by the nutrition composition and the carbohydrate–water partition coefficient | 10, 46 |
| Soil-water partition coefficient   | $K_{SW}$ | L kg$^{-1}$ | Vary     | Estimated by soil properties and the octanol–water partition coefficient | 10, 14 |
| Diffusivity in water               | $D_W$  | m$^2$ days$^{-1}$ | Vary |                                                                      |            |
| Degradation rate in soil           | $k_d$  | days$^{-1}$ | Vary     |                                                                      |            |
| Degradation rate in periderm and medulla | $k_m$ | days$^{-1}$ | Vary     |                                                                      |            |

*Pesticide-specific values are taken from or calculated based on the Pesticide Properties Database (PPDB)$^{17}$ and summarized in the Supporting Information.
because previous modeling studies did not consider the degradation process of chlorpyrifos in potato for which the rate is significantly larger than that in soil (i.e. $k_m = 0.16 \text{day}^{-1}$ and $k_d = 0.033 \text{day}^{-1}$). Juraske et al.\textsuperscript{12} reported a simulated BCF value of $7.40 \times 10^{-3}$ for chlorpyrifos in potato, which is based on a ratio of the maximum concentration in potato and the maximum concentration in soil. Juraske et al.\textsuperscript{12} simulated a value approximately 2.75 times higher than our simulated BCF\textsubscript{M}($t=30$) ($2.69 \times 10^{-3}$ at 30 days after chlorpyrifos application). Paraiba and Katagiri\textsuperscript{13} simulated the BCF of pesticides by setting $t$ to infinity, which denotes the asymptote illustrated in Fig. 2(B). However, it must be noted that when setting $t$ to infinity, the model (including both periderm and nonperiderm models) should eliminate $k_g$, as described in Section 2.3, because the potato has reached its maximum time at $t_f$, unless $k_g$ is negligible compared to other uptake or elimination rates shown in Eqs (8a)–(8e) and Eqs (4b)–(4c). Paraiba and Katagiri\textsuperscript{13} reported a simulated BCF value of $1.10 \times 10^{-3}$ for chlorpyrifos in potato, which is approximately four times higher than the result obtained by the periderm model and approximately two times higher than that from the nonperiderm model (i.e. $5.03 \times 10^{-3}$). Overall, the BCF values of chlorpyrifos in potato reported by previous modeling studies are higher than the results simulated by the periderm model because previous studies did not add the rate-limiting periderm compartment, and higher than the results simulated by the nonperiderm model because they did not consider the degradation process of the pesticide inside the potato. According to the experimental data of Juraske et al.\textsuperscript{12} the average concentration of chlorpyrifos in potato is $0.013 \text{mg kg}^{-1}$, the average concentration in soil is $2.21 \text{mg kg}^{-1}$, and the estimated BCF of chlorpyrifos in potato is $5.88 \times 10^{-3}$, which matches well with our nonperiderm model predictions (i.e. BCF\textsubscript{NP}($t=30$) = $5.03 \times 10^{-3}$). Approximately, our periderm model predicts a result (i.e. BCF\textsubscript{M}($t=30$) = $2.69 \times 10^{-3}$) that is 54% lower than the estimated BCF of chlorpyrifos in potato, and previous modeling studies have a simulated result (i.e. $1.10 \times 10^{-3}$) that is 87% higher than the estimated value. It is noted that, although our model simulates one application of chlorpyrifos and Juraske et al.\textsuperscript{12} applied chlorpyrifos three times in a potato field, the BCF\textsubscript{M}($t$) in both the periderm and nonperiderm models is independent of $C_S(0)$, therefore the results predicted by our periderm model match better than current models with the limited field data.

### 3.2 Application contexts of the periderm model

#### 3.2.1 Direct application of the periderm model

For the direct application of BCF\textsubscript{M}($t$) derived from the periderm model, we parameterize the quantitative relationship of BCF in the periderm and nonperiderm models. This will enable exposure and risk assessors to compare their data of interest when their results are based on a nonperiderm model, which is widely applied and the analytical solution is easy to determine. Figure 3(A) illustrates the logarithm (base 10) of BCF\textsubscript{M}($t$) and BCF\textsubscript{NP}($t$) for 740 pesticides at harvest ($t_h = 30$ days, 45 days, and 60 days), which indicates a good linear relationship ($R^2 > 0.99$). However, it is observed that several pesticides have extremely high values that could affect the regression curves, which are caused by large $k_m$ values. Although these pesticides have large simulated BCF values in potatoes, their concentrations in potatoes are extremely low due to their large $k_d$ values in soils, thus it is not so meaningful to consider high-degradability pesticides with respect to pesticide contamination in potatoes. Therefore, in Fig. 3(B) we also plot the logBCF\textsubscript{M}($t$) and logBCF\textsubscript{NP}($t$) values for pesticides with a $k_m$ value less than 0.4 day$^{-1}$. These three groups of plots at different harvest times (i.e. 30 days, 45 days, and 60 days) are almost the same because, for most pesticides, BCF\textsubscript{M}($t$) and BCF\textsubscript{NP}($t$) at 30 days after pesticide application are already close to their asymptotes. Based on the fitted regression equations, we obtain the following quantitative relationship of pesticide BCFs in potato between the periderm and nonperiderm models at harvest ($t_h = 45$ days):

$$
\text{BCF}_{\text{M}} \approx \begin{cases} 
0.81(\text{BCF}_{\text{NP}})^{1.03}, & \text{whole dataset} \\
0.89(\text{BCF}_{\text{NP}})^{1.12}, & \text{selected dataset} 
\end{cases}
$$

Thus, Eqn (12) can be used to convert the pesticide BCF in potatoes at harvest simulated by a nonperiderm model into a predicted BCF interval where the effective influence of the peel is considered. For example, the simulation of BCF\textsubscript{M}($t$) value at harvest (i.e. $t_h \geq 30$ days) for chlorpyrifos using the periderm model

![Figure 2. (A) Modeling concentration (based on a unit initial concentration of the chemical in the soil, i.e. $C_z(0) = 1.0 \text{mg kg}^{-1}$) and bioconcentration factor (BCF) of chlorpyrifos in potato periderm and medulla based on the periderm model. (B) Modeling concentration and BCF of chlorpyrifos in potato medulla based on the periderm and nonperiderm models.](image-url)
than medulla (0.778) makes the periderm layer act as a rate-accelerating compartment, which does not occur with nonperiderm models at different assumed harvest times (30 days, 45 days, and 60 days after pesticide application) for 740 pesticides. (B) Log BCF of pesticides in potato medulla simulated from periderm and nonperiderm models at different assumed harvest times for 726 pesticides with \( k_m \) less than 0.4 days\(^{-1}\).

is \(2.69 \times 10^{-3}\). The uncertainty interval of BCF\(_M\) from the BCF\(_M\) value of the nonperiderm model (i.e. 5.03 \( \times 10^{-5}\)) according to Eqn (12) is \([2.38 \times 10^{-3}, 3.48 \times 10^{-3}]\). As the pesticide diffusion process by potatoes from or to soil via the water phase can be facilitated for pesticides with low \( K_{OW} \) values (e.g. many lipophilic pesticides), a higher water content in potato periderm (0.842)\(^{32,43}\) than medulla (0.778)\(^{19}\) makes the periderm layer act as a rate-accelerating compartment, which does not occur with rather lipophilic pesticides like chlorpyrifos, as shown in Fig. 2. In addition, after the \( C_M(t) \) value of a lipophilic pesticide reaches the maximum value, i.e. the uptake rate is equal to the depuration rate, the periderm acts as a barrier that weakens the pesticide diffusion process from potato to soil, which is due to the relatively higher water content ratio in periderm and soil than that in medulla and soil in the nonperiderm model. For example, Fig. 4 (A) illustrates the simulated log BCF\(_M\) after 60 days without pesticide application plotted vs log \( K_{OW} \) values, which does not include 10 pesticides of the selected 740 pesticides with \( k_d \) values greater than 1.39 day\(^{-1}\) (i.e. half-life less than 0.5 day) due to their extremely high log BCF\(_M\) values. The Fig. 4(A) shows that lipophilic pesticides, such as a systemic organic chemical with log \( K_{OW} \) less than 2.0,\(^{48}\) typically have simulated log BCF\(_M\) values greater than zero (i.e. BCF\(_M\)>1). Conversely, for lipophilic pesticides, as log \( K_{OW} \) increases, log BCF\(_M\) decreases with a significant slope. This is because lipophilic pesticides are thermodynamically favorable for storage in lipids, and the lipid content ratio of soil and medulla is much larger than the water content ratio, which results in a significant reduction in BCF\(_M\) for pesticides with high log \( K_{OW} \). In the yellow circle area of Fig. 4(A), some lipophilic pesticides with high log \( K_{OW} \) exhibit high simulated log BCF\(_M\) values, which is due to their relatively high degradability in soil as compared to the degradability in potato, resulting in their \( C_S(t) \) values approaching zero at harvest, resulting in high estimated BCF\(_M\). This modeling phenomenon can be further evaluated by comparing the log BCF\(_M\) values of pesticides at harvest to their \( k_d \) values (see Fig. 4 (B)). That is, when pesticide \( k_d \) values are small, their simulated log BCF\(_M\) values are widely distributed; however, when their \( k_d \) values become large, the simulated log BCF\(_M\) values exhibit minimal variability. This preliminary comparison may indicate that when a pesticide has low degradability in soil, its simulated BCF\(_M\) at harvest is more dependent on other physiochemical parameters (e.g. log \( K_{OW} \)), which is consistent with previous studies.\(^{49,50}\) Conversely, when a pesticide has high degradability in soil, the simulated BCF\(_M\) at harvest becomes very large and is almost unaffected by other parameters due to its extremely low \( C_S\).

3.2.3 Integration of the periderm effect into uptake and elimination rates

We can further use the pesticide uptake and elimination rates derived from the nonperiderm model, i.e. in Eqns (4a)–(4c), to integrate the BCF\(_M(t)\) of the periderm model at harvest. However, this approach is determined by a quantitative comparison between the sum of the elimination rates by pesticide (i.e. \( k_d^g + k_d^m \)) and the soil degradability of potato (i.e. \( k_d \)). Paráiba and Katanuki\(^{14}\) explored the expression of BCF by setting \( t \) to infinity and proposed two cases by comparing \((k_m^S+k_g)\) and \( k_d \).
It is noted that their model does not consider the degradation process of the pesticide inside the potato. Although the mathematical expression was well derived, discussing the BCF of pesticides in potato by setting $t$ to infinity is not practical because the derived BCF values become meaningless when $t$ is large enough where $C_S(t)$ approaches zero. Also, potatoes are harvested within a finite time after pesticide application (e.g., 30–60 days), therefore BCF should be discussed for actual field conditions.

We find that, when $k_a$ is relatively small compared to $(k_M^{-5} + k_9 + k_m)$, both $BCF_M(t)$ in the periderm model and $BCF_M^P(t)$ in the nonperiderm model can be very close to their limits (i.e., asymptotes) at harvest. For example, 30 or more days after pesticide application, when $k_M^{-5} + k_9 + k_m \geq k_d + 0.1$, i.e. $1-\exp((k_a-k_M^{-5}-k_g-k_m)t) \geq 0.95$, according to Eqn (4a) we have:

$$BCF_{NP}^{M}(t) = \left(\frac{k_M^{-5}}{k_M^{-5} + k_9 + k_m - k_d}\right) \left[1-\exp((k_a-k_M^{-5}-k_g-k_m)t)\right]$$

$$\approx \frac{k_M^{-5}}{k_M^{-5} + k_9 + k_m - k_d}$$

(13)

Then, combining Eqns (12) and (13), we have

$$BCF_M(\tau_0) \approx 0.81 \left(\frac{k_M^{-5}}{k_M^{-5} + k_9 + k_m - k_d}\right)^{1.03} \forall \text{pesticides with}$$

$$k_M^{-5} + k_9 + k_m \geq k_d + 0.1$$

(14)

The uptake and elimination rates of pesticides derived from the nonperiderm model are provided in the Supporting Information. To summarize, we can estimate the BCFs of pesticides in potatoes by considering the periderm effect by three approaches, as follows: at harvest ($\tau_0 = 30$ days):

$$BCF_M = \begin{cases} 
BCF_{M}(\tau_0), \text{applying the peel model} \\
0.81 \left(BCF_{M}^{NP}(\tau_0)\right)^{1.03}, \text{applying the non-peel model} \\
0.81 \left(\frac{k_M^{-5}}{k_9 + k_9 + k_m - k_d}\right)^{1.03}, \text{conditionally applying ‘rates’}
\end{cases}$$

(15)

3.2.4 Implementation into the dynamiCROP plant uptake model

In addition to the parameterized approaches for $BCF_M$, the results of our periderm model can also be directly incorporated into dynamic plant uptake models, such as dynamiCROP.11,39 For that, we define a periderm-adjusted factor (PAF), which is based on an approximate assumption that potatoes are harvested 30 days after pesticide application, as follows:

$$PAF = \frac{C_M(\tau_0)}{BCF_M(\tau_0)} = \frac{BCF_{M}(\tau_0)}{BCF_{NP}^{M}(\tau_0)}$$

$$\approx \begin{cases} 
0.81 \left(BCF_{M}^{NP}(\tau_0)\right)^{0.03}, \text{applying the non-peel model} \\
0.81 \left(\frac{k_M^{-5}}{k_9 + k_9 + k_m - k_d}\right)^{0.03}, \text{conditionally applying ‘rates’}
\end{cases}$$

(16)

PAF can be used as a multiplicative factor modifying pesticide residue estimates in potato tubers. The PAFs for 740 pesticides are provided in the Supporting Information. It is noted that the specific rates in Eqn (16) under conditionally applying ‘rates’ may be different to the rate constants used in dynamiCROP due to different sources of the pesticide physicochemical parameters. It is also noted that for other times between pesticide application and potato harvest, Eqn (16) can be adapted using different $\tau_0$ values, but the condition of $1-\exp((k_a-k_M^{-5} - k_g-k_m)t) \geq 0.95$ must in such cases be adapted using the method under conditionally applying ‘rates’.

Generally, limiting components or aspects strongly influencing pesticide dynamics in crops should be considered based on our findings for how periderm influences BCFs for many pesticides to allow a more accurate estimation of pesticide residues and BCFs for the wider range of pesticide–crop combinations.

3.3 Model evaluations, limitations, and recommendations

We evaluated our model by comparing the simulated results with field measurements, which included current-use pesticides (some of which are used around the world and some of which are used in some top agricultural producing countries), and other organic pollutants that are frequently found in crop fields.

3.3.1 Model evaluation with current-use pesticides

For some pesticides that are currently being widely used, the uptake mechanism by our periderm model can better explain some field observations as compared to the nonperiderm model. For example, Antonious et al.31 conducted a field study to evaluate the residues of pyrethrins in potato tubers and leaves. It was observed that there were significant residue levels of pyrethrins in the potato leaf surface, but no residue was detected inside the tuber (i.e. below the limit of detection). This phenomenon can be explained by the periderm model, which predicts that $BCF_{M}$ and $BCF_{P}$ at harvest (i.e. $\tau_0 = 30$ days) are $3.40 \times 10^{-4}$ and $4.38 \times 10^{-2}$, respectively, whereas the nonperiderm model overestimates the $BCF_{NP}$ of pyrethrins. Our prediction indicates that the periderm can act as a barrier to impede the uptake process of pyrethrins into the tuber due to the high lipophilicity of pyrethrins (i.e. $\log K_{OW} = 6.15$). The uptake mechanism by potato tubers illustrated by the periderm model can further explain Roy et al.’s32 field observation, where relatively more residues of mancozeb were accumulated inside the tuber (i.e. 17.90–20.80 mg g$^{-1}$) due to its low $K_{OW}$ value of 0.62, as compared to pyridoxin, for which fewer residues were found inside the tuber (i.e. 0.16–0.36 mg g$^{-1}$) because of its high lipophilicity (i.e. $\log K_{OW} = 4.24$), which is again explained by the periderm effect.

Although some organophosphorus pesticides have been evaluated and banned in recent years in North America and Europe, they are still approved for use in some top agricultural-producing countries such as Australia, Brazil, China, and India. For example, ethoprophos had been banned by the European Union but is still registered and approved for use in Australia and China. Therefore, we further evaluated our model for such pesticides because they could still pose a risk to parts of the world population that receive food crops from these countries. Witczak et al.25 evaluated a total of seven organophosphorus pesticides in fruits and vegetables and compared the measured residue levels to the European Union’s maximum residue levels for population health risk assessment, where the distributions of the residue levels in the periderm
and medulla (pulps) of two types of potatoes (i.e. potato and early potato) were measured. These organophosphorus pesticides are ethoprophos, diazinon, chlorpyrifos-methyl, parathion-methyl, fenchlorphos, chlorpyrifos, and merfos. Among them, chlorpyrifos-methyl and fenchlorphos were not detected, and merfos lacked data in the periderm of the early potato. We compared our simulated \( \text{CP}\text{C}_\text{M} \) values to the available measured data by Witczak et al.\(^{21} \) (Table 2), showing that all model estimates are within the range of measured data. The mean absolute error (MAE) between the simulated log \( \text{CP}\text{C}_\text{M} \) values and the measured log \( \text{CP}\text{C}_\text{M} \) values (i.e. the average of the minimum and maximum values of the measured log \( \text{CP}\text{C}_\text{M} \)) is 0.3, which is much less than the average range of the measured log \( \text{CP}\text{C}_\text{M} \) values (i.e. 1.2). This further indicates that the simulated log \( \text{CP}\text{C}_\text{M} \) values using the proposed periderm model fall within the range of the experimental data. In addition, the simulated results have a similar trend to the measured data for early potato. For example, chlorpyrifos has the highest measured \( \text{CP}\text{C}_\text{M} \) value for early potatoes compared to other three pesticides, which is due to its high lipophilicity. This phenomenon can also be observed by the dynamic modeling process (Fig. 2(A)), the input variable analysis (Fig. 4(A)), and the sensitivity analysis (Fig. S2), indicating that the periderm can act as a barrier for the uptake of highly lipophilic pesticides, which agrees with field studies.\(^{39} \) The reason for relatively wide measurement ranges could be due to different compositions (e.g. lipid and water contents) of the periderm for different types of potatoes.\(^{38} \) As this study aimed to introduce a periderm-based modeling framework for the plant uptake of pesticides, some input variables such as periderm and medulla compositions were taken from current literature as default values,\(^{42,43} \) which should be adjusted according to different types or varieties of potatoes when comparing model results to specific potato varieties.

### 3.3.2 Model evaluations with historical-use pesticides

The parameterization of the periderm model can be applied to legacy pesticides and other organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) that are frequently found in potato fields.\(^{10} \) Figure 5(A) illustrates the relationship between log \( K_{\text{OW}} \) and log BCF of

| Pesticide       | Pulp (medulla) | Periderm | Pulp (medulla) | Periderm | Pulp (medulla) | Periderm | Pulp (medulla) | Periderm | Pulp (medulla) |
|-----------------|----------------|----------|----------------|----------|----------------|----------|----------------|----------|----------------|
| Ethoprophos     | 0.11           | 0.07     | 0.91           | 0.02     | 1.62           | 56.88    | 3.74           |          |                |
| Diazinon        | 0.19           | 0.48     | 1.89           | 0.09     | 0.40           | 21.00    | 4.76           |          |                |
| Parathion-methyl| 0.70           | 0.35     | 1.41           | 0.07     | 2.01           | 20.74    | 2.26           |          |                |
| Chlorpyrifos    | 13.10          | 1.14     | 31.00          | 0.73     | 11.49          | 42.58    | 20.42          |          |                |

Note: Measured \( \text{CP}\text{C}_\text{M} \) values are calculated using the average values of pesticide concentrations in potato periderm and medulla.

Figure 5. (A) Simulated (periderm model) and measured (underground parts of plants) bioconcentration factors (log BCF) plotted with octanol–water partition coefficients (log \( K_{\text{OW}} \)) of organic chemicals (e.g. pesticides, PCBs, etc.). (B) The difference of the simulated log BCF values of 708 pesticides using the periderm model between the periderm and medulla (i.e. \( \Delta \text{log}_{\text{BCF}} \) (periderm – medulla)) compared to the difference of the simulated log BCF values between the first equilibrium partitioning (EqP) and the second equilibrium partitioning (EqP\text{Kin}) models (i.e. \( \Delta \log_{\text{BCF}} \) (EqP – EqP\text{Kin})). The EqP model uses a lipid content of 0.003 (i.e. the lipid content of potato periderms) and the EqP\text{Kin} model uses a lipid content of 0.001 (i.e. the lipid content of potato medulla).
pesticides predicted by the periderm model, which is compared with the measured relationship of legacy pesticides and other organic pollutants collected from existing literature. The predicted and measured curves of both tuber and periderm compartments present a high degree of consistency of the trend, indicating that the peel compartment can impede the tuber uptake of high-lipophilic organic compounds. This consistency can extend the use of the periderm model to other chemicals and tuber plants. We note that some pesticides with high degradability in soil are omitted in Fig. 5 (discussed in Fig. 4). In addition, we compared the difference of the simulated log BCF values between the periderm and medulla compartments of 708 pesticides [i.e. $\Delta \log_{BCF}$ (periderm – medulla)] to the difference of the simulated log BCF values between the first equilibrium partitioning (EqP) and the second equilibrium partitioning (EqP_Kin) models [i.e. $\Delta \log_{BCF}$ (EqP – EqP_Kin)] in Fig. 5(B). The EqP and EqP_Kin models were proposed by Briggs et al. to estimate the log BCF values of chemicals in roots for the equilibrium and nonequilibrium (i.e. adjustment by a kinetic factor) scenarios, respectively. Thus, the EqP model describes a scenario where the root uptake process of chemical residues from the soil is fast and an equilibrium can be soon reached (e.g. the periderm compartment), whereas the EqP_Kin model describes a scenario where the net residue uptake process is relatively slow (e.g. dilution process due to the plant growth) and the ‘equilibrium’ should be adjusted by a kinetic factor (i.e. a nonequilibrium state) (e.g. the medulla compartment). The correlation coefficient between $\Delta \log_{BCF}$ (periderm – medulla) and $\Delta \log_{BCF}$ (EqP – EqP_Kin) for the selected log $K_{OW}$ values is approximately 0.99. This indicates that the equilibrium of pesticide concentrations between periderm and soil compartments is quickly reached, and the tuber uptake of hydrophobic pesticides (large log $K_{OW}$ values) can be significantly impeded, which is consistent with Briggs’ proposed models.

Although some historical legacy pesticides had been banned for use in some countries, their environmental ubiquity and persistence mean they are frequently found in potato and other crop tissues, which can still pose a risk to human health. Thus, we further evaluated our model with some legacy pesticides. Zohair et al. conducted a comprehensive investigation of the concentrations of organic contaminants in potato periderm and medulla (cores) and in farmland soil for four potato varieties, which included 16 organochlorine pesticides (OCPs). Taking the concentrations of OCPs in periderm, medulla, and soil from Zohair et al., we calculated the measured BCFs of pesticides in potato medulla and the measured $C_{soil}$ values, which are summarized in Table 3 and compared to the simulated BCFs using the periderm and nonperiderm models and the simulated $C_{soil}$ values using the periderm model. Furthermore, Fig. S3A compares the ranges of measured BCF$_{soil}$ values, which are derived from the average values for four potato varieties, to the ranges of simulated BCF$_{soil}$ values using the periderm model, which are derived from the values obtained using the three approaches based on Eqn (15). Of these 16 OCPs, the BCF$_{soil}$ values for 10 pesticides simulated using the periderm model fall in the range of the measured values. The BCF$_{soil}$ values of alpha-hexachlorocyclohexane (alpha-HCH), beta-HCH, and beta-endosulfan simulated using the periderm model are higher than the measured values, and for hexachlorobenzene and 4,4′-dichlorophenyl dichloroethylene (DDE) the simulated values are lower than the measured values. The MAE between the measured log BCF$_{soil}$ values (i.e. the average of minimum and maximum values of the measured log BCF$_{soil}$) and simulated log BCF$_{soil}$ values using the periderm model was 0.94, which is approximately half of the average range of the measured log BCF$_{soil}$ values of these 16 OCPs. This indicates that for many of the selected OCPs there are large overlaps between the measured and simulated ranges of the BCF$_{soil}$ values. In addition, the MAE between the measured $C_{soil}$ values (i.e. the average of the minimum and maximum values of the measured $C_{soil}$) and simulated $C_{soil}$ values using the periderm model for the selected 15 OCPs (except for alpha-HCH whose field data are not available) is 0.79, which is approximately half of the average range of the measured $C_{soil}$ values (i.e. 1.54). This also indicates that, in general, the simulated $C_{soil}$ values fall within the range of the measured $C_{soil}$ values.

However, the simulated $C_{soil}$ values of six pesticides (beta-HCH, aldrin, heptachlor, beta-endosulfan, 4,4′-dichlorophenyl dichloroethylene (DDD), and 4,4′-dichlorodiphenyltrichloroethane (DDT)) are inconsistent with the field data (Fig. S3B). This inconsistency for selected pesticides should be addressed in future studies.

### 3.3.3 Limitations and recommendations

First, we treat the potato as a spherical shape, whereas some varieties of potato are similar to an elliptical shape (e.g. egg), which has a different within-medulla distribution of the pesticide. We also model pesticide uptake by potatoes based on the steady-state growth stage of the tuber, whereas the actual formation and growth of the potato periderm during the transition state of the potato tuber from seeds may involve different mechanisms of pesticide uptake, especially during the development of the periderm. It is not clear what growth stage of the tubers and the pre-harvest interval (PHI) of pesticides were used in the experiment. More importantly, due to the data limitation, the $k_m$ values of pesticides were approximated using the available information, for which the microbial and chemical degradation mechanisms of pesticides in potato tissues are not fully understood yet. These potato-related factors are expected to be solved by developing new mathematical tools and conducting experiments. Second, the weather and soil conditions are not considered in our model and may differ from those in the experimental study, which could significantly affect the fate of pesticides in soil and further impact the uptake of pesticides by potatoes. Weather conditions such as temperature and humidity in the soil and air can affect the transpiration rate of plants, which determines the pesticide uptake rate by plants. Moreover, different geographical regions always form different soil characteristics, including mineral contents, microorganisms, and physical properties, which can affect the horizontal or vertical distribution of pesticide residues in soil. Thus, a comprehensive fate model that incorporates the distribution of pesticides in soil is required to obtain better estimates of BCFs, especially for some tubers that grow deeply underground the soil. Third, different groups may develop different potato farming practices, such as timing, pesticide application patterns, and fertilizer applications, thus pesticide uptake by potatoes can be affected by the mixture of chemicals in soil solutions, which may further impact the diffusion behavior of pesticides to potatoes. In this regard, integrating the pattern of pesticide emission into the periderm model can be helpful for predicting the BCF of pesticides in potatoes at harvest. Moreover, although we propose a simple PAF as a multiplication factor for integrating...
Table 3. Summary of measured BCF<sub>M</sub> and C<sub>SP</sub>/C<sub>SM</sub> values for four potato varieties compared to simulated BCF<sub>M</sub> and C<sub>SP</sub>/C<sub>SM</sub> values using periderm and nonperiderm models at harvest (30 days after pesticide application)

| Pesticides       | Measured BCF<sub>M</sub> | Measured C<sub>SP</sub>/C<sub>SM</sub> | Simulated BCF<sub>M</sub> by periderm model | Simulated BCF<sub>M</sub> by nonperiderm model | Simulated C<sub>SP</sub>/C<sub>SM</sub> |
|------------------|--------------------------|--------------------------------------|---------------------------------------------|-----------------------------------------------|-------------------------------------|
| Cara Valour      | 7.7E-03*                 | 7.7E-03*                             | 6.0E-03*                                    | 3.3E+01**                                    | 6.8E-04                            |
| Kestrel          | 6.7E-03*                 | 1.2E+04*                             | NA                                          | 1.9E-02                                      | 2.3E+01**                           |
| Desiree          | 6.0E-03*                 | 3.3E-03*                             | NA                                          | 3.1E-02                                      | 4.9E+00                            |
| Approach 1       | 1.4E-04*                 | 4.3E-04*                             | NA                                          | 2.0E-02                                      | 4.8E+00                            |
| Approach 2       | 8.7E-04*                 | 3.3E-03*                             | 1.3E-04*                                    | 2.3E-02                                      | 4.5E+00                            |
| Approach 3       | 1.6E+02                  | 8.7E-04*                             | NA                                          | 3.4E-02                                      | 4.5E+00                            |
| Heptachlor       | 3.8E-03*                 | 1.9E-01*                             | 5.0E-03*                                    | 1.5E-02                                      | 1.5E+02                            |
| Aldrin           | 9.7E-05*                 | 5.5E-02*                             | 7.7E-03*                                    | 1.4E-02                                      | 2.9E+02                            |
| Heptachlor epoxide | 3.0E-04*               | 2.5E-04*                             | 1.6E-01*                                    | 2.3E-03                                      | 4.3E-03                            |
| alpha-Endosulfan | 2.9E-01                  | 1.2E+04*                             | 3.6E-03*                                    | 2.2E-03                                      | 4.9E+01                            |
| Dieldrin         | 4.5E-05*                 | 8.4E-02*                             | 3.5E-02*                                    | 1.6E-02                                      | 4.5E+01                            |
| Endrin           | 3.0E-03*                 | 3.4E-01*                             | 1.6E-01*                                    | 1.1E-03                                      | 1.4E-03                            |
| beta-Endosulfan  | 1.8E-04*                 | 7.7E-05*                             | 8.1E-04*                                    | 1.6E-02                                      | 1.9E-02                            |
| 4,4'-DDD         | 2.6E-04*                 | 9.4E-04*                             | 2.2E-03*                                    | 1.6E-02                                      | 5.6E+00                            |
| 4,4'-DDT         | 4.2E-04*                 | 4.3E-04*                             | 8.3E-04*                                    | 1.6E-02                                      | 2.6E-02                            |
| 4,4'-DDD         | 4.4E-05*                 | 9.7E-03*                             | 1.3E-02*                                    | 1.6E-02                                      | 5.9E+02                            |
| Methoxychlor     | 1.9E-04*                 | 3.8E-01*                             | 5.5E-04*                                    | 2.1E-01                                      | 5.9E+02                            |

HCH, hexachlorocyclohexane. Measured BCF<sub>M</sub> and C<sub>SP</sub>/C<sub>SM</sub> values are calculated using the average values of pesticide concentrations in potato periderm, medulla, and soil.13

*Pesticide levels in potato medulla (core) are lower than the detection limit of 0.001 ppb (μg kg<sup>-1</sup>), therefore the measured BCFs should be lower than values indicated by *. **Pesticide levels in medulla are lower than the detection limit, therefore the measured ratios should be larger than estimated values indicated by **. NA, pesticide levels in both soil and medulla are lower than the detection limit, therefore the measured BCFs are not available. Heptachlor epoxide is used to model the BCF because heptachlor-endo-epoxide is not in our database. For the simulated BCF<sub>M</sub> (periderm model), approaches 1, 2, and 3 refer to BCF<sub>M</sub><sub>t<sub>0</sub></sub>: <sup>12</sup> BCF<sub>NP</sub><sub>M</sub>/C<sub>0</sub>/C<sub>1</sub>, and <sup>13</sup> BCF<sub>M</sub><sub>k<sub>−S<sub>M</sub> + k<sub>g</sub> + k<sub>m</sub> − k<sub>d</sub></sub>/C<sub>16</sub>/C<sub>17</sub> in Eqn (15), respectively.
our results into more complex plant uptake models, this approach can only be used when pesticide diffusion to the tuber dominates the overall uptake process. Otherwise, other uptake routes such as the stem and leaf must be considered before incorporating the PAF.\textsuperscript{39} Experimental data on BCFs are missing for many combinations of current-use pesticides applied to food crops and further research is needed to test a wider range of pesticides applied across crops. Even though a comprehensive uptake model incorporated with soil factors, weather conditions, and pesticide application patterns is needed in future studies, to the best of our knowledge this is the first modeling study to treat the complex structure of the potato periderm as a single compartment, which illustrates a more thorough understanding of the uptake mechanism of the pesticide by the potato than the nonperiderm model and yields some degree of consistency with the field data.

4 CONCLUSION

We proposed a model for evaluating the effect of periderm on pesticide uptake from soil into potato tubers by introducing an explicit tuber periderm compartment. Compared to a nonperiderm model, the results indicate that the periderm acts as a barrier, reducing the BCF in medulla for lipophilic pesticides but increasing the BCF for systemic pesticides as a result of different lipid contents in the periderm and medulla. Sensitivity analysis indicated that both the degradability of pesticides inside the potato and the lipophilicity play a key role in determining the contributions of other variables (i.e. uptake and elimination rates) to the simulated BCFs. In addition, we propose several methods for application of the periderm model by parameterizing the relationship of the simulated results between the periderm and nonperiderm models, and incorporation of a periderm-adjustment factor into dynamic plant uptake models as a multiplicative residue correction factor. Although a comparison of model estimates with measured data shows some degree of consistency, the inclusion of other key factors such as weather conditions and tuber plant physiology in future studies can further improve the accuracy of the model. Considering the periderm improves the accuracy of quantifying pesticide uptake and bioconcentration in potato tubers as input for optimizing pest control and minimizing human exposure to pesticide residues in edible food crops.

ACKNOWLEDGEMENTS

This work was financially supported by the Sun Yat-sen University (grants 580000–18841211 and 580000–18841290), as well as by the SPRINT project (grant agreement no. 862568) and by the FNS-Cloud project (grant agreement no. 863059), both funded under the European Union’s Horizon 2020 Research and Innovation program.

SUPPORTING INFORMATION

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

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