A mechanism-based fate model of pesticide solutions on the plant surface under aerial application

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ABSTRACT
Pesticide residues on plant surfaces are a primary source of pesticide bioaccumulation in crops. In this context, we propose a mechanism-based model for understanding the pesticide fate on the plant surface following aerial application, taking into account fate modelling of the pesticide spray solution on the plant surface. Using chlorothalonil as an example, the simulation results revealed that the spray solution dissipated rapidly after aerial application, resulting in the formation of a saturated pesticide solution, which facilitated the diffusion process of the pesticide residue from the plant surface into the peel tissue. The proposed model generated higher simulated residue concentrations in the peel or pulp than the current model, owing to the proposed model’s assumption of rapid dissipation of the spray solution. This indicated that the proposed model specified the influence of the spray solution on the plant’s exposure to residues via the surface deposition pathway, whereas the current modelling approach presented a generic estimate of the residue dissipation on the plant surface that linked to the residue’s fate in the soil.

Introduction
Pesticides are manufactured and synthesized to kill or control insects, illnesses, weeds, and other pests. Globally, pesticides are used widely to protect agricultural crops, and their application can significantly increase crop yield, so contributing to global food security [1–3]. However, the presence of pesticide residues in the environment after their application can pose risks to human and environmental health [4–11]. Among major exposure pathways (such as dermal contact, ingestion, and inhalation), the ingestion of pesticide-contaminated agricultural commodities (such as crops) accounts for a substantial proportion of the total pesticide intake [12,13].

To assist in the prevention and management of population health concerns associated with crop consumption, feasible models have been developed to predict the fate and transport of pesticides in crops from aerial application or soil incorporation (i.e. seed treatment) of pesticides [14–17]. By integrating transformation factors or specific rate constants (i.e. first-order kinetics), these mechanism-based models can be incorporated into numerous lifecycle- or risk-analysis tools to perform high-throughput simulations [7,13]. One of the

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challenges in simulating pesticide residue concentrations in edible crops is how to comprehensively describe the residue fate on the crop surface, as surface deposition of pesticide residues typically accounts for a substantial amount of the residue in crop tissues [18]. This difficulty can be exacerbated when the peel (or periderm) of the crop plays a crucial role in pesticide bioaccumulation in crop tissues [19]. Experimental or modelling investigations have examined the dissipation kinetics of pesticide residues on the plant surface in great detail, which has considerably increased our understanding of the fate of pesticides in the environment-plant system [20, 21]. As the residue fate on the plant surface after aerial application is determined by the interaction between the spray solution [22], periderm (or peel), and pulp, as well as individual transformation pathways (such as photodegradation) [21, 23], a comprehensive process is required, involving the dynamic change of the solution, pesticide penetration through the peel, and pesticide uptake or elimination between the peel and pulp.

Numerous experimental studies showed that the concentrations of pesticide residues between crop peel and pulp differed considerably, which can have a considerable impact on the concentration of pesticide residues on the plant surface due to the concentration gradient-driven diffusion process [24]. In general, the residue levels in peel are higher than those in pulp, which can be attributable to at least two hypotheses: differing chemical compositions between peel and pulp, and the peel’s physical function as a barrier as the crop’s outermost layer. In a previous modelling study, Xiao et al. [19] proposed a diffusion-based model to analyse the fate of pesticides in potatoes by considering the peel dynamics. This model demonstrates a complex mechanism for the peel effect on pesticide uptake by potatoes. However, the method of pesticide uptake by tuber crops can differ greatly from that of above ground crops due to the varied medium of pesticide sources. For instance, the uptake of pesticides by potatoes is primarily driven by the concentration gradient of the pesticide residue between the water phases of soil and potato tissues, which is influenced by the pesticide’s degradability in soil, the ratio of lipid content between soil and potatoes, and the pesticide’s water-octanol partition coefficient, among other factors. However, as there is no solid, stable medium like soil surrounding aboveground crops, the uptake of pesticides by aboveground crops from aerial application is highly dependent on their solution’s fate on the plant surface. Due to the dynamic change of the residue solution on the plant surface, the fate of pesticide residues that land on the plant surface after aerial application is highly complex. Not only can the residue of the active ingredient penetrate plants through peels, but the change in solution mass on the plant surface due to volatilization can also result in a change in the concentration of the residue in the solution, which further complicates the prediction of residue concentrations on the plant surface.

To address this issue, we proposed a mechanism-based model to describe the pesticide fate on the plant surface, with the aim of comprehending the transport process of residue from the crop surface to the pulp tissues. Chlorothalonil and apple, the most widely used pesticide and crop, respectively, were used in a case study to illustrate the model application. Chlorothalonil is frequently detected in crop fields as well as harvested fruits, raising consumer health concerns [25]. Furthermore, chlorothalonil is a broad-spectrum fungicide with a moderate lipophilicity that can represent a large group of agricultural pesticides. Previous modelling studies have also shown that pesticides with moderate lipophilicity have a high bioaccumulation potential in plants [18]; therefore, using chlorothalonil as a modelling demonstration can be representative and
conservative in terms of consumer health risk assessment. Users can modify the model’s input values for specific crops and chemicals. Notably, the aboveground plant can also take up pesticide residues via xylem and phloem transport from the soil and leaf compartments, respectively. The plant uptake of the residue from other exposure pathways (i.e. soil- and leaf-based pathways) was not taken into account in this work because we focused on simulating the pesticide fate on the crop surface. Other plant exposure pathways to pesticide residues have been extensively studied in existing modelling studies [18,26,27].

Materials and methods

General modelling framework

Figure 1 illustrates the information flow of this study’s main focus. The proposed model was compared to the current model, which utilizes the first-order dissipation process of the pesticide on the plant surface regardless of the spray solution. In addition, we elaborated on the differences between the two models’ simulation mechanisms and provided recommendations for future research. Figure 2 depicts the modelling framework for simulating the pesticide fate on the crop surface, taking peel and pulp compartments into consideration. The modelling process is conceptualized in terms of three compartments: the spray solution, the peel, and the pulp compartments. Due to the evaporation process, the spray solution compartment (connected to the crop peel) is not as stable as the soil, so we simulate the pesticide concentration in the spray solution compartment using three phases: (1) the phase of unsaturated spray solution, where the pesticide in the spray solution can diffuse to air and peel, be degraded in water, and its concentration can be affected by water evaporation; (2) the phase of saturated spray solution, where the concentration of the pesticide is equal to its
 Unsaturated spray solution:

![Diagram showing unsaturated spray solution: emission (+) concentration (+) diffusion (±) volatilization (-) degradation (-).](image)

Saturated spray solution:

![Diagram showing saturated spray solution: diffusion (-) volatilization (-) degradation (-).](image)

No spray solution (solid precipitates):

![Diagram showing no spray solution: Peel: diffusion (±) dilution (-) and Pulp: diffusion (±) dilution (-).](image)

**Figure 2.** Schematic of the fate modelling of pesticides in the spray solution, crop peel, and crop pulp (‘+’ denotes the addition process and ‘-’ denotes the subtraction process of the concentration of pesticides in each medium).

...solubility at a certain temperature; (3) the phase of no spray solution, i.e. water has evaporated. In the peel and pulp compartments, the concentration of the pesticide is modelled by the two-directional diffusion process associated with crop growth-induced dilution.

**Spray solution compartment**

After the aerial application, the concentration of the pesticide can be increased by the initial emission (i.e. from zero to an initial level), and it is assumed that the spray solution can adhere evenly to the surface of the crop peel to form a thin layer. The initial concentration of the pesticide in the spray solution attached to the crop peel
\( (C_{\text{Spray}}(0), \text{mg L}^{-1}) \) is equal to that in the original spray solution. The concentration of the pesticide in the spray solution adhered to the peel \((C_{\text{Spray}}(t), \text{mg L}^{-1})\) can then be written as a function of time \((t, \text{d})\) as follows:

\[
\frac{dC_{\text{Spray}}(t)V_{\text{Spray}}(t)}{dt} = \left( \frac{f_{W, \text{Peel}}T_{\text{Peel}}D_{W}}{0.25L_{\text{Peel}}} \right) \left( C_{\text{Spray}}(t) - C_{\text{Peel}}(t) \right) \frac{CF_1A_{\text{Spray}}}{K_{\text{Peel} \rightarrow W}} - g\left( C_{\text{Spray}}(t)K_H - C_{\text{Air}} \right) \frac{CF_1A_{\text{Spray}}}{k_{D, W}} \frac{C_{\text{Spray}}(t)V_{\text{Spray}}(t)}{t} \tag{1}
\]

where \( \left( \frac{f_{W, \text{Peel}}T_{\text{Peel}}D_{W}}{0.25L_{\text{Peel}}} \right) \) denotes the solution-peel conductance (m d\(^{-1}\)) of the pesticide being transported from spray solution to peel, which is determined by the effective diffusion rate of the pesticide in peel that is ‘clogged’ by the tortuosity factor \((T_{\text{Peel}}, \text{unitless})\) (i.e. the labyrinth effect) affecting on the diffusivity of the pesticide in water \((D_W, \text{m}^2 \text{d}^{-1})\). \( f_{W, \text{Peel}} \) (g g\(^{-1}\)) is the water content of the peel. \( CF_1 \) \((1000 \text{ L m}^{-3})\) is the conversion factor \(1\). \( 0.25L_{\text{Peel}} \) denotes the effective diffusion length that is one fourth of the peel thickness \((L_{\text{Peel}}, \text{m})\), because the pesticide in peel can diffuse from (or to) both sides and for each side the equivalent diffusion point should be located at the half point of the half of \( L_{\text{Peel}} \). \( K_{\text{Peel} \rightarrow W} \) \((\text{L kg}^{-1})\) is the peel-water partition coefficient of the pesticide. \( C_{\text{Peel}}(t) \) (mg kg\(^{-1}\)) is the concentration of the pesticide in peel, and thereby \( \frac{C_{\text{Peel}}(t)}{K_{\text{Peel} \rightarrow W}} \) denotes the concentration of the pesticide in the water phase of the peel. As we applied the equivalent diffusion point (i.e. an imaginary point similar to the centre of gravity to simplify the calculation) rather than modelling the concentration gradient of the pesticide in peel or pulp, \( C_{\text{Peel}}(t) \) is not considered to be a function of space. Specifically, in Eq. \((1)\), passive transport through peel tissue via diffusion in the water phase is assumed, which could be suitable for many currently used pesticides with relatively high hydrophilicity (such as systemic pesticides). This water-phase-based diffusion modelling approach is also widely used in current plant uptake models \([19,29,30]\), greatly simplifying pesticide bioaccumulation simulation in plant tissues. Chemical compounds, on the other hand, can be absorbed in peel cuticles \([31–33]\), and their uptake efficiency is determined by their lipophilicity and size \([13,34,35]\). In addition, the epidermis of most plants contains a waxy layer (i.e. the cuticle) that inhibits chemical diffusion in the water phase of plant tissue. As a result, highly lipophilic compounds (such as many historically used pesticides) will enter the peel tissue via the cuticle-based pathway rather than the water-phase diffusion process. This cuticle-based uptake pathway will be discussed further in the following sections (i.e. current models). Due to the assumption that the spray solution is well-mixed, the effective diffusion length of the spray solution was not used in the modelling of pesticide diffusion in the spray solution. Therefore, the solution-peel conductance was calculated based on the peel, which is analogous to the pesticide’s solution-to-air conductance, namely, \( g\left( C_{\text{Spray}}(t)K_H - C_{\text{Air}} \right) \), where \( g \) is the gas conductance (m d\(^{-1}\)) and \( K_H \) is the dimensionless henry’s law constant. To simplify the modelling process, the pesticide concentration in the surrounding air \((C_{\text{Air}})\) is assumed to be zero. \( A_{\text{Spray}} \) \((\text{m}^2)\) is the surface area of the spray solution attached to the crop peel, which is approximately equal to the crop surface area \((A_{\text{Peel}}, \text{m}^2)\). \( k_{D, W} \) \((\text{d}^{-1})\) is the degradation rate of the pesticide in water (i.e. the spray solution). We have omitted the pesticide’s photodegradation rate due to a lack of data and the complexity of sunlight’s penetration from the solution or periderm to pulp tissues. \( V_{\text{Spray}}(t) \) (L) is the volume of the spray solution attached to the crop peel, which
can be expressed as a function of t according to the evaporation process of water [36], if the solute effect can be negligible, as follows:

\[ V_{\text{Spray}}(t) = \begin{cases} V_{\text{Spray}}(0) - \Theta(HR_S - HR_A)A_{\text{Spray}}CF_2 t; & 0 \leq t \leq t_{\text{Dry}} \\ 0; & t \geq t_{\text{Dry}} \end{cases} \]  

(2)

where \( V_{\text{Spray}}(0) \) (L) is the initial volume of the spray solution attached to the peel, which could be estimated based on the assumption that the stable spray solution is generated, i.e. without continuing to form water drops. \( \Theta \) (kg m\(^{-2}\)h\(^{-1}\)) is the evaporation coefficient. \( HR_S \) (kg kg\(^{-1}\)) and \( HR_A \) (kg kg\(^{-1}\)) are the humidity ratios of the saturated air (i.e. the surface of the water) and the atmosphere, respectively. \( CF_2 \) (24 h d\(^{-1}\)) is the unit conversion factor.

Due to the brief duration of the evaporation process, we also assume that there is always pesticide precipitation in the spray solution, namely “\( t \geq t_{\text{Sol}} \)” exists. Notably, we utilize the effective diffusion mechanism (i.e. in the water phase of the plant tissue), which is commonly used in existing plant bioconcentration models [29,30], to simulate the pesticide residue entering the peel tissue from the peel surface. Depending on the size or lipophilicity of the compound, the pesticide residue can also enter the peel or pulp tissues via cuticle penetration [13]. In later sections, we investigate this transport mechanism using the existing modelling approach.

\section*{Crop peel compartment}

When the spray solution is not evaporated, the fate of the pesticide in the crop peel is predicted using the pesticide’s double-direction diffusion mechanism. Therefore, the concentration of the pesticide in peel (\( C_{\text{Peel}}(t) \), mg kg\(^{-1}\)) as a function of t can be expressed as follows:

\[ \frac{dC_{\text{Peel}}(t)}{dt} = -\left( \frac{f_{W,\text{Peel}}T_{\text{Peel}D_W}}{0.25L_{\text{Peel}P_{\text{Peel}}}} \right) \left( \frac{2C_{\text{Peel}}(t)\rho_{\text{Water}}}{K_{\text{Peel}W}} - \frac{C_{\text{Spray}}(t)\rho_{\text{Water}}}{K_{\text{Spray}W}} - C_{\text{Pulp}}(t) \right) - k_G C_{\text{Peel}}(t) \]  

(4)

where \( \rho_{\text{Peel}} \) (kg L\(^{-1}\)) is the density of the peel. \( K_{\text{Pulp}W} \) (L kg\(^{-1}\)) is the pulp-water partition coefficient of the pesticide and \( C_{\text{Pulp}}(t) \) (mg kg\(^{-1}\)) is the concentration of the pesticide in
the crop pulp. The term \(L^2_{\text{Peel}} \rho_{\text{Peel}}\) in the denominator is obtained by dividing the whole equation by the mass of the peel that can be expressed by the product of the surface area, thickness, and density of the crop peel. \(k_G\) (d\(^{-1}\)) is the specific growth rate of the peel.

When \(t \geq t_{\text{Sal}}\), the pesticide in the spray solution will undergo go three phases: 1) the pesticide is saturated in the spray solution, namely \(C_{\text{Spray}}(t) = C_{\text{Sal}}\); 2) the spray solution is evaporated out and the pesticide will be attached to the peel as solid state (i.e. ‘overload’), where it is assumed that the water phase at the outside boundary of the peel has the saturated pesticide solution; and 3) as the diffusion process proceeds, the amount of solid pesticide on the peel surface diminishes until no solid pesticide remains (i.e. \(t_{\text{Non–solid}}\)). Notably, a portion of the pesticide precipitate can be dissolved in the water film or the water phase of the crop peel when the spray solution dries, resulting in a similar fate process for the pesticide residue on the crop surface as when the spray solution does not evaporate. In addition, According to a rough estimate of \(t_{\text{Non–solid}}\) (Table S1), the duration (i.e. \(t_{\text{Non–solid}} – t_{\text{Dry}}\)) is too short to be considered in the piecewise function. In order to simplify the simulation process, we omitted the detailed explanation of the residue fate at \(t_{\text{Non–solid}}\). Therefore, when \(t > t_{\text{Sal}}\):

\[
\frac{dC_{\text{Peel}}(t)}{dt} = -\left(\frac{f_{W,\text{Peel}} T_{\text{Peel}} D_W}{0.25t_{\text{Peel}}^2 \rho_{\text{Peel}} K_{\text{Peel}–W}} \right) \left(2C_{\text{Peel}}(t) - C_{\text{Pulp}}(t) K_{\text{Pulp}–W} \right) - \left(\frac{gC_{\text{F}, A_{\text{Peel}}}}{K_{\text{Peel}–A}} \right) C_{\text{Peel}}(t) - k_G C_{\text{Peel}}(t) \tag{5}
\]

where \(K_{\text{Peel}–A}\) (L kg\(^{-1}\)) is the peel-air partition coefficient of the pesticide that can be estimated by the water and lipid contents of the peel [27,37]. \(M_{\text{Peel}}\) (kg) is the mass of the peel, which can be calculated by \(L^2_{\text{Peel}} \rho_{\text{Peel}}\). The flux of pesticide residues from the peel to the air is simulated based on compartmental concentration but not surface concentration. To simplify the mathematical expressions of the preceding equations, we specify the following specific pesticide rates (or rate constants) in the peel compartment based on existing peel dynamics modelling studies [19,38,39]:

\[
k_{\text{Peel}}^- = \frac{f_{W,\text{Peel}} T_{\text{Peel}} D_W}{0.25t_{\text{Peel}}^2 \rho_{\text{Peel}} K_{\text{Peel}–W}} \tag{6a}
\]

\[
k_{\text{Peel}}^+ = \frac{f_{W,\text{Peel}} T_{\text{Peel}} D_W \rho_{\text{Water}}}{0.25t_{\text{Peel}}^2 \rho_{\text{Peel}}} \tag{6b}
\]

\[
k_{\text{Peel}}^+ = \frac{f_{W,\text{Peel}} T_{\text{Peel}} D_W}{0.25t_{\text{Peel}}^2 \rho_{\text{Peel}} K_{\text{Pulp}–W}} \tag{6c}
\]

\[
k_{\text{Peel}}^- = gC_{\text{F}, 1} \frac{K_{\text{Peel}–A}}{L_{\text{Peel}}} \tag{6d}
\]

where \(k_{\text{Peel}}^-\) (d\(^{-1}\)) is the elimination rate constant of pesticide in crop peel via diffusion to the spray solution and pulp. \(k_{\text{Peel}}^+\) (d\(^{-1}\)) and \(k_{\text{Peel}}^+\) (d\(^{-1}\)) are the uptake rate constants of the pesticide in the peel via diffusion from the spray solution and pulp, respectively. \(k_{\text{Peel}}^-\) (d\(^{-1}\)) is the elimination rate constant of the pesticide in peel to the air. Consequently, the pesticide fate in the peel compartment described in Eq. (4)–(5) can be further expressed as follows:
Crop pulp compartment

The fate of the pesticide in the pulp compartment is characterized by radial diffusion [29,30] and dilution processes, because many aboveground crops (such as apple and orange) have a spherical shape:

\[
\frac{dC_{\text{Pulp}}(t)}{dt} = - \left( \frac{23\varphi_{\text{W}}T_{\text{Pulp}}D_{\text{W}}}{r^2\rho_{\text{Pulp}}} \right) \left( \frac{C_{\text{Pulp}}(t)}{K_{\text{Pulp--W}}} - \frac{C_{\text{Pulp}}(t)}{K_{\text{Pulp--W}}} \right) - k_G C_{\text{Pulp}}(t)
\]

where \( r \) (m) is the radius of the crop pulp, and \( \rho_{\text{Pulp}} \) (kg L\(^{-1}\)) is the pulp density. The product of the term \( \frac{23\varphi_{\text{W}}T_{\text{Pulp}}D_{\text{W}}}{r^2\rho_{\text{Pulp}}} \) and \( \frac{1}{K_{\text{Pulp--W}}} \) denotes the effective diffusivity of the pesticide in the pulp tissue. As \( C_{\text{Pulp}}(t) \) is independent on space, \( \frac{C_{\text{Pulp}}(t)}{K_{\text{Pulp--W}}} \) denotes the concentration of the pesticide in the water phase of the pulp at the peel-pulp boundary. Then, by substituting the uptake and elimination rate constants of pesticides in crop pulp as follows:

\[
k_-^{\text{Pulp}} = \frac{23\varphi_{\text{W}}T_{\text{Pulp}}D_{\text{W}}}{r^2\rho_{\text{Pulp}}} \frac{1}{K_{\text{Pulp--W}}}
\]

\[
k_+^{\text{Pulp}} = \frac{23\varphi_{\text{W}}T_{\text{Pulp}}D_{\text{W}}}{r^2\rho_{\text{Pulp}}} \frac{1}{K_{\text{Pulp--W}}}
\]

we can further express Eq. (8) as follows:

\[
\frac{dC_{\text{Pulp}}(t)}{dt} = k_+^{\text{Pulp}} C_{\text{Pulp}}(t) - \left( k_+^{\text{Pulp}} + k_G \right) C_{\text{Pulp}}(t); \ t \geq 0
\]

Crop uptake of pesticides via the surface deposition pathway

The fate model of pesticides on plant surfaces can be used to examine crop pesticide uptake via the surface deposition pathway. Current plant uptake modelling studies simulated pesticide bioaccumulation in crops using an empirical estimation of pesticide dissipation kinetics on plant surfaces [18,40]. Here, we use the proposed fate model of pesticides on crop surfaces to improve the bioaccumulation modelling via the surface deposition pathway, as the proposed mechanism-based model takes into account the dynamic change of the spray solution, thereby more accurately representing the actual scenario of aerial application.

Due to the rapid evaporation of the thin film of pesticide spray solution that adheres to the peel surface, we eliminate the spray solution compartment and ‘extract’ the amount of pesticide residues from the spray solution to the surface of the crop peel before the pesticide precipitates disappear, such that the pesticide concentration in the water phase
of the peel surface is equal to its solubility. Consequently, the approximate two-compartment model is as follows:

In the peel compartment:

$$\frac{dC_{\text{Peel}}^{AP}(t)}{dt} = \begin{cases} k_{\text{Spray}}^{+} C_{\text{Sol}}^{AP} + k_{\text{Pulp}}^{+} C_{\text{Pulp}}^{AP}(t) - (k_{\text{Peel}} + k_{\text{Air}}^{+} + k_{G}) C_{\text{Peel}}^{AP}(t); 0 \leq t < t_{\text{Dry}} \\ k_{\text{Pulp}}^{-} C_{\text{Pulp}}^{AP}(t) - (k_{\text{Peel}} + k_{\text{Air}}^{+} + k_{G}) C_{\text{Peel}}^{AP}(t); t \geq t_{\text{Dry}} \end{cases}$$

(11)

and in the pulp compartment:

$$\frac{dC_{\text{Pulp}}^{AP}(t)}{dt} = k_{\text{Pulp}}^{+} C_{\text{Peel}}^{AP}(t) - (k_{\text{Pulp}} + k_{G}) C_{\text{Pulp}}^{AP}(t)$$

(12)

where ‘AP’ represents the variables simulated using the approximate approach. In the supplementary file, the analytical solution to the approximate model is provided.

**Model application and evaluation**

In this study, we applied apples to perform the modelling exercise. Due to its great nutritional content and wonderful flavour, apple is one of the most important and popular economic crops. In addition to being consumed directly, apples have been processed into a variety of commercial food products, such as juice, sources, vinegar, and chips. On a regular basis, pesticide residues have been identified in apple products, and some of the samples potentially pose severe health risks. We selected chlorothalonil as an example because it is one of the most commonly used and detectable pesticides on crops [41]. Users can conduct chemical- and plant-specific calculations by following the proposed simulation procedure, which is provided in the Supplementary File.

To evaluate the model, sensitivity test were conducted to assess the impact of input variables on simulation outcomes. Due to the lack of data regarding the fate of the pesticide spray solution on plant surfaces, we tested the model using an empirical method. Juraske et al. [42] investigated the overall dissipation kinetics of pesticides on the plant surface and gave empirical estimations of the dissipation rate constant using soil data. In order to further evaluate the mechanism-based fate model, we compared simulation results with estimates of Juraske et al. [42]. On the basis of Juraske et al.'s [42] approximation of the dissipation rate estimate for pesticide residues on plant surfaces, current modelling studies have included a plant surface compartment in plant uptake models to simulate the pesticide bioaccumulation process in plant tissues [18,40,43], which can be expressed in the following equations.

In the peel surface compartment, a first-order kinetics-based dissipation process is assumed [42] as follows:

$$\frac{dC_{\text{PS}}^{CM}(t)}{dt} = -k_{\text{Diss,PS}} C_{\text{PS}}^{CM}(t); t \geq 0$$

(13)

where the superscript ‘CM’ represents the current modelling approach. $C_{\text{PS}}^{CM}(t)$ (mg kg$^{-1}$) denotes the pesticide concentration on the peel surface using the current modelling approach. $k_{\text{Diss,PS}}$ (d$^{-1}$) is the dissipation rate constant of the pesticide on the peel surface, which can be estimated using the soil value (primarily by degradation) [42]. The
calculation of $C_{PS}^{CM}(0)$, namely the initial condition of $C_{PS}^{CM}(t)$, is provided in the Supplementary File.

In the peel and pulp compartments, similar to the approximate model, but with an additional uptake pathway via penetration [13], the following processes can be described:

$$\frac{dC_{peel}^{CM}(t)}{dt} = k_{penel}C_{ps}^{CM}(t) + k_{pulp}^{+}C_{pulp}^{CM}(t) - (k_{penel}^{-} + k_{pulp}^{Air} + k_{G})C_{peel}^{CM}(t); t \geq 0$$

$$\frac{dC_{pulp}^{CM}(t)}{dt} = k_{pulp}^{+}C_{peel}^{CM}(t) - (k_{pulp}^{-} + k_{G})C_{pulp}^{CM}(t); t \geq 0$$

where $k_{penel}$ (d$^{-1}$) represents the uptake rate constant of the pesticide in the peel via penetration of cuticle tissues, which can be approximated using the molecular weight and lipophilicity of the residue (Table S1) [13,44,45]. As the spray solution is not considered in the current modelling approach, the model is not constructed as a piecewise function [13,40]. Thus, we can compare input values for the model are provided in the Supplementary File.

**Results and discussion**

**Simulation of pesticide fate considering spray solution dynamics**

In this section, we demonstrate the simulation results (i.e. pesticide levels in plant tissues) of the mechanism-based fate model (Figure 3), taking into consideration the spray solution dynamics. The Supplemental File contains essential data, functions, and R codes for solving the mechanism-based model. Users can then modify model inputs for chemical-specific outcomes. Due to the quick evaporation of the spray solution on the apple surface, the simulated chlorothalonil concentration in the spray solution increased rapidly from the initial concentration (i.e. 0.2 mg L$^{-1}$) to the saturated concentration (i.e. 0.81 mg L$^{-1}$) within 0.0193 d (28 min). As shown by the red line in Figure 3(b), the saturated chlorothalonil solution accelerated the diffusion process of the residue from the apple surface into the peel tissue. This observation is a result of the fact that, in the proposed model, the diffusion process of the pesticide residue in the water phases of the plant tissues was used to simulate the plant uptake of the residue via the surface deposition exposure pathway. Consequently, high residue concentrations in the spray solution can enhance the peel’s capacity to take up residues. The simulated chlorothalonil concentration in the peel began to decrease after 0.026 d (37 min), as depicted by the green dot line in Figure 3(b), since after 0.026 d there were no residues on the peel surface and the residue dissipated rapidly in the peel compartment due to the thin layer of apple peel. Consequently, the simulated chlorothalonil concentration in the peel reached nearly zero after approximately 0.03 d (43 min). As shown in Figure 3(c), the simulated chlorothalonil concentration in the pulp compartment displayed a distinct pattern than in the peel compartment. Even though there were no chlorothalonil residues on the apple surface after 0.026 d (37 min), the concentration of chlorothalonil in the apple pulp continued to increase. The diffusion mechanism from the peel residue was responsible for the pulp’s continuously increasing concentration. The overall chlorothalonil dissipation rate in the pulp was lower than in the peel compartment because the peel acted as a barrier to prevent the residue in the pulp...
from evaporating into the air. In addition, the pulp had a greater effective diffusion distance than the peel, resulting in a lower simulated elimination rate constant via the diffusion process (Supplementary File). Consequently, the mechanism-based fate model indicated that the rapid evaporation of the spray solution increased the peel’s uptake of the pesticide residue, but that the residue rapidly dissipated from the peel tissue as the residue precipitate disappeared soon from the peel surface.

**Different simulation mechanisms between the proposed and current models**

In this section, we illustrate and compare the simulation mechanisms between the proposed and current models for the plant uptake of the pesticide residue via the surface deposition pathway. The proposed model takes into account the spray solution and
pesticide precipitate on the plant surface as the source of the plant’s exposure to the residue, whereas the current model adopts the empirical dissipation kinetics of the pesticide residue on the plant surface, rather than specifying the dynamic change of the spray solution [18,42]. Using the aerial application of chlorothalonil solution to apple fruits, the simulation results of these two models can be compared, as shown in Figure 4. Details regarding the derivation process of the two models are provided in S3 and S4 of the Supplementary File. There were inconsistencies in the levels of simulated residues in the peel and pulp of the apple, which can be attributable to distinct modelling mechanisms.

First, it was observed that the simulated residue levels in the peel or pulp using the proposed model were much higher than those simulated using the current model. This is because the proposed model assumes rapid evaporation of the spray solution, resulting in a chlorothalonil-saturated solution on the plant surface, which considerably accelerates the diffusion process of the residue from the apple surface into the peel via the water phase. For instance, the initial chlorothalonil concentration in the spray solution was estimated to be 0.2 mg L\(^{-1}\) (Table S1), and shortly after aerial application (i.e. the spray solution dissipated rapidly from the plant surface), the concentration of the saturated solution on the apple surface was estimated to be 0.8 mg L\(^{-1}\) (based on its solubility at 25°C) [46], which enhanced the diffusion process of the residue from the apple surface into the peel tissue. In contrast, the current model does not account for the fate of the spray solution and instead takes an empirical estimate of the pesticide’s overall dissipation rate on the plant surface derived from soil dissipation data (i.e. primarily through the degradation process). Due to the absence of the concentration process of the pesticide residue in the spray solution in the current model, the simulated efficiency of residue uptake by apple fruit via the surface deposition exposure pathway was lower than that predicted by the proposed model. Second, using the proposed model, we observed that the peel had higher residue levels than the pulp, contrary to the simulation results using the current model. This discrepancy between the two models can be explained by the fact that the proposed model includes critical points of time when the spray solution or pesticide precipitate vanishes from the plant surface. In the proposed model, there are no pesticide residues on the plant surface after the critical time. Without the residue source (residues on the plant surface) for the peel compartment, the simulated residue level in the peel compartment decreased more rapidly than in the pulp because pesticide residue dissipates more quickly in the peel compartment than in the pulp compartment. However, the current model employs a first-order kinetics-based process to define the dissipation behaviour of pesticide residue on the plant surface, regardless of the disappearance of the spray solution or pesticide precipitate. Consequently, there are always residues left on the plant surface, which serve as a constant source of the residue in the peel compartment, leading to higher simulated residue levels in the peel compared to the pulp.

The simulation outcome of the proposed model (e.g. pesticide residue levels in plants) is significantly affected by the duration of the spray solution’s drying time as well as the existing residue precipitate on the plant surface. In this study, we defined a short drying time (i.e. \(t_{Dry}\)) for the spray solution and pesticide precipitate on the plant surface, resulting in higher chlorothalonil residual levels in apple pulps than peels. This is owing to the fact that after \(t_{Dry}\), the net residue amount on the plant surface is not taken into
account, and so there is no residual source of the plant’s exposure to pesticides via the surface deposition exposure pathway. As a result, the residue dissipates far rapidly in the peel tissue than in the pulp tissue. In contrast, the current modelling approach utilizes the first-order dissipation kinetics of the pesticide residue on the plant surface, irrespective of the fate of the spray solution or residue precipitate [18,42]; thus, the pesticide is always present on the plant surface, constituting a continuous source of plant exposure to the residue via the surface deposition pathway. As a result, the peel has a continual flux of residues from the plant surface, resulting in higher levels of simulated residues in the peel than in the pulp.

Figure 4. Chlorothalonil residue levels simulated in the apple peel and pulp using the proposed (a) and current (b) models. The simulation is based on the plant’s exposure to the residue via the surface deposition pathway. Input values and numerical equations for the model are provided in the Supplemental File. The current model is based on the empirical approach of Juraske et al.
Therefore, the model provided in this work gives a specific perspective that concentrates on the dynamics of the spray solution, and its simulation outcome is greatly influenced by the specified drying or disappearing time of the spray solution or pesticide precipitate. This mechanism-based model has the advantage of incorporating the spray solution into the pesticide fate or plant uptake models, which would more accurately describes the real-world scenario in which pesticides are delivered to crops via sprays. As the drying or disappearing process of the spray solution or pesticide precipitate on the plant surface is influenced by numerous dynamic factors (such as weather conditions, solution compositions, and crop morphologies), it is difficult to present a simple model. As a result, the proposed model may produce simulation results with a high degree of variability or uncertainty, which may restrict the model’s performance. In contrast, the current model simplifies the pesticide fate on the plant surface by employing the first-order dissipation kinetics, which is empirically derived using soil dissipation data (primarily via the degradation process). This approach empirically includes major elimination pathways (such as precipitation, photodegradation, and volatilization) and estimates residue levels on the plant surface. Due to the absence of the spray solution compartment in the current model, the simulation outcome is independent of many dynamic factors like plant morphologies, surface tension, wind speed, and solution compositions. As a result, the uncertainty or variability of the simulated residue concentrations in plant tissues is rather low. Due to the fact that the spray solution is not taken into account, the current modelling approach has trouble characterizing the level of residue on the plant surface. Several modelling studies, for instance, determined the level of residue by dividing the residue mass on the leaf surface by the leaf mass [18,47]. This definition is inadequate because, when the spray solution evaporates, the concentration of residue in the solution increases, which cannot be accounted for by the current modelling approach.

**Limitations and recommendations**

The proposed mechanism-based model emphasizes the effect of spray solution dynamics on the plant’s exposure to pesticide residues through the surface deposition pathway. Incorporating the spray solution as one of the modelling compartments aids in understanding the pesticide fate on the plant surface; however the model can only be implemented during stable environmental conditions (i.e. no precipitations). Due to the rapid evaporation of the spray solution following pesticide application, the spray-solution-based fate model can be applied by assuming no precipitation during this brief period. In spite of this, we recommend that the proposed model be incorporated into the current modelling approach to account for the scenarios before and after the complete dissipation of the spray solution, as the current modelling approach uses the overall dissipation kinetics of the pesticide on the plant surface, which accounts for other elimination pathways (such as precipitation) in a generic manner.

A number of assumptions made to simplify the simulation process may reduce the model’s accuracy. For instance, the formation of the spray solution film on the plant surface is a physically complex process involving crop morphologies, surface tension, and the viscosity of the spray solution. These physical factors can also be a function of time due to the plant’s growth and the change of the spray solution. Due to a lack of advanced
mathematical tools, it was assumed that the spray solution formed a uniform layer on the
crop surface. However, gravity can significantly impact the distribution of the spray
solution on the surface of the crop, resulting in an uneven distribution. For instance,
the spray solution film could be thinner on the bottom side of the crop than on the top
side. Therefore, the diffusion mechanism of pesticide residues from the plant surface into
peel or pulp tissues cannot be simply modelled under the assumption of homogeneity.
Consequently, sophisticated mathematical tools are expected to aid in understanding the
dynamics of the spray solution on the plant surface in real-world scenarios, taking into
account the crop’s dynamic morphologies. In this study, the spray solution is simplified as
a mixture of water and pesticide residues, whereas in reality, spray solutions (i.e. pesticide
formulations) typically include emulsifiers, wettable powders, and other solvents.
Consequently, the composition of the spray solution could influence the fate of the
solution on the plant surface as well as plant uptake of pesticide residues. For instance,
the rate of volatilization of a spray solution depends on its chemical components and
solute concentrations. The emulsifiers in the spray solution may also influence the overall
lipophilicity of the pesticide solution, which regulates the pesticide residue penetration
process through the peel. Therefore, formulations of pesticides and the effect of chemical
components on the fate of the spray solution must be investigated. Experiment data on
the fate of pesticides and their solutions on plant surfaces are currently lacking due to the
complicated interaction between pesticide formulations and plant surfaces. As a result,
we put the model to the test by comparing simulation results to a current modelling
approach. Although this can aid in evaluating the proposed approach from a modelling
standpoint and investigating the differences in the underlying mechanisms for the two
modelling approaches, field data are still required to validate the proposed model in order
to understand the fate of pesticides and their solutions on plant surfaces.

Furthermore, to illustrate the modelling experiment, we used generic or default values for
several model inputs, assuming constant environmental circumstances. However, some
environmental conditions (such as wind speed, sunlight intensity, humidity, and temperature)
have a significant effect on the evaporation of the spray solution, which could result in a wide
range of estimations for plant exposure to pesticide residues via the surface deposition
pathway. As these environmental factors often exhibit seasonal or regional patterns, the
fate of pesticides on the surface of plants may likewise exhibit spatiotemporal patterns. Using
temperature and relative humidity, several modelling studies have studied the spatiotem-
poral pattern of pesticide bioaccumulation in the food chain [48,49]. As the dissipation kinetics
of the spray solution can be considerably affected by numerous weather factors, it would be
beneficial to explore the spatiotemporal pattern of the residue fate on the plant surface to
improve the region-specific pesticide exposure assessment. Users can adjust weather-
dependent model inputs to generate region-specific results. Additionally, crop variety can
considerably impact the process of residue uptake. For instance, the sensitivity analysis
revealed that peel properties (e.g. thickness) played a significant role in simulating the uptake
or elimination rate constants of the pesticide residue (Figure S1), resulting in a wide range of
simulated residue concentrations in apples. Therefore, we advise recalculating the input rate
constants of the pesticide residue depending on the particular crop varieties.

As the proposed model focused on the surface deposition pathway of the plant’s exposure
to pesticides, the simulated results for pesticide residue levels in plants did not account for
other possible pathways, including transport from the soil (via the xylem-transport-based
route) and leaf surface (via the phloem-transport based route) [13,14,26,27]. These omitted exposure pathways to pesticide residues have been extensively evaluated by current modelling studies [13,14,18,26,27]; therefore, users can incorporate the soil or leaf surface into the proposed model as additional modelling compartments; specifically, these additional residue sources will present additive effects on pesticide residue levels in plants if the first-order kinetics-based fate model is used [18]. Therefore, the model proposed by this study provided users with a new perspective on the plant’s exposure to pesticides via the surface deposition pathway, taking into account the dissipation dynamics of the spray solution, which can be further improved by the addition of other possible exposure pathways to comprehend pesticide bioaccumulation in plants. In addition, the epidermis of most plants is covered by a waxy layer (i.e. the cuticle), which could hinder the diffusion of pesticide residues through the water phase of plant tissue but promote the diffusion pathway through cuticles [32,34,35]. Therefore, the cuticle-based uptake process must be considered, especially for highly lipophilic substances or plants with thick periderms. Consequently, it is anticipated that the fate modelling of spray solutions proposed by this work will be incorporated into existing modelling approaches that utilize the cuticle-related penetration process.

Another shortcoming is that contrary to the current model, there are no pesticide residues remained on the plant surface after the critical time in the proposed model. Instead of assuming that pesticide residues disappear immediately after the spray solution dries, the residue precipitate should have a complicated interaction with the liquid or solid phase of the plant surface in real-world circumstances. From this perspective, the current model could more accurately reflect the fate of residues on the plant surface over a long period of time, although without accounting for the fate of the spray solution. Thus, we recommend integrating the proposed and current models to thoroughly simulate the residue fate on the plant surface, taking into account not only the spray solution dynamics over a short time period, but also guaranteeing the residue remains on the plant surface over a long time period.

**Conclusions**

To aid in understanding the fate of pesticides on plant surfaces, we present a mechanism-based model to simulate the plant uptake of pesticide residues via the exposure pathway of surface deposition, taking into account the dynamic change of the spray solution following aerial application. The proposed modelling procedures permit users to perform chemical and plant-specific calculations by modifying the model’s input values. Using apple and chlorothalonil as an example, the simulation results revealed that the change in the spray solution (rapid dissipation) plays a critical role in regulating the pesticide diffusion process from the plant surface into the tissues. The proposed model gives a simulation mechanism that differs from current modelling approaches for the pesticide fate on the plant surface and the plant’s exposure to the residue via the surface deposition pathway. The findings of the comparison between the proposed and current models distinguished between the specific (i.e. focused on the spray solution) and generic (i.e. estimating from soil data) perspectives of the residue fate on the plant surface. The proposed model with a specific emphasis on the influence of the spray solution on the pesticide fate can illustrate the residue’s plant uptake process within a relatively short time period, whereas the current modelling approach, which utilizes the overall dissipation kinetics, can better predict the
pesticide bioaccumulation in plants over a long time period. As the proposed model focuses on the change of the pesticide spray solution and utilizes the effective diffusion process to characterize the residue’s uptake by plants, additional factors, such as precipitation, sunlight intensity, surface tension, pesticide formulations, other penetration mechanisms (e.g. through cuticles), and other plant’s exposure pathways to residues (e.g. uptake from the soil and leaf surface), must be accounted for in future studies. Furthermore, field data on the fate of pesticide residues and their formulations on plant surfaces are required in future studies to understand the residue uptake process and validate the mechanism-based model. Nevertheless, the proposed model will improve the understanding of the pesticide fate on plant surfaces, particularly in the case of aerial applications. It is anticipated that the proposed model will be integrated with the current model to comprehensively describe both the pesticide fate on plant surfaces and plant exposure to pesticide residues.

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