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Modeling pesticide removal efficiency by vegetative filter strip under PWC scenarios

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10/26/2020

1 Introduction

Vegetative filter strip (VFS) is an agricultural best management practice (BMP) recommended by U.S. Natural Resources Conservation Service to reduce pesticide pollution to surface water (USDA, 2000). VFS has been required or recommended for agricultural applications of some pesticide products including pyrethroids and neonicotinoids. For example, many bifenthrin product labels required a 10-ft VFS between the field edges and down gradient aquatic habitat (USEPA, 2008). For imidacloprid, applications within 10 ft of aquatic areas are prohibited to allow growth of a VFS. There is no standard procedure to evaluate pesticide fate and transport in a VFS under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) modeling framework. Therefore, the mitigation effectiveness of a VFS has not been considered in the recent ecological risk assessments (ERAs) on pyrethroids and imidacloprid by U.S. Environmental Protection Agency (USEPA, 2016b, a). For research and development purpose, quantitative assessment of VFS is usually implemented with the Vegetative Filter Strip Model (VFSMOD) (Muñoz-Carpena et al., 1999; Muñoz-Carpena and Parsons, 2004) for hydrological simulations and customized procedures for pesticide trapping effects (including adsorption, infiltration, and dissipation).

Surface Water Protection Program (SWPP) of California Department of Pesticide Regulation (DPR) uses the Pesticide in Water Calculator (PWC) scenarios (USEPA, 2016d) for pesticide exposure assessment in agricultural areas of California (Luo, 2017a). In 2017, a semi-mechanistic modeling approach for pesticide removal in a VFS was developed by SWPP, and integrated with PWC to build the first-generation PWC-VFS modeling system (Luo, 2017b). While the hydrology is mechanistically simulated by VFSMOD, pesticide fate and transport processes in a VFS were modeled with a semi-mechanistic method with conservative assumptions. As a part of the modeling efforts for conservation practices in agricultural areas of California, the approach was evaluated with bifenthrin as a test agent (Luo, 2019). The limitations were also reported, mainly related to the separate and sequential simulations of the actually simultaneous processes of pesticide trapping and extraction. In this study, a fully mechanistic approach is developed with physically-based modeling on the runoff-soil exchange of pesticide in a VFS. The PWC-VFS modeling system is updated with the new approach and

expected to predict pesticide removal efficiencies by a VFS with a wide range of chemical and soil properties, and facilitate continuous modeling for long-term mitigation effects under the PWC scenarios.

The next section reviews the modeling studies in the literature on hydrological and pesticide simulations in a VFS, and briefly summarizes the previous development by SWPP. Section 3 presents the new model development. Case studies with the new approach are demonstrated in Section 4 with selected pesticides (bifenthrin, chlorpyrifos, imidacloprid, and permethrin) under 14 PWC scenarios in California.

2 Literature review

2.1 Single-event pesticide trapping in a VFS

VFSMOD was originally developed to quantify the trapping effects for water flow (ΔQ) and suspended sediment (ΔE) during a single runoff event through a VFS (Muñoz-Carpena et al., 1999; Muñoz-Carpena and Parsons, 2004). The most influencing input variables are incoming runoff (Q_i, m^3), incoming sediment load (E_i, kg), and saturated hydraulic conductivity (K_{sat}, m/s). The three variables together explain the majority of the variability (R^2= 0.76 for runoff and 0.64 for sediment, N= 1650) on the measured VFS performance (White and Arnold, 2009). In addition to field measurements, soil models for runoff generation and soil erosion are used to simulate the drainage area (an agricultural field) upstream to the VFS, and generate the incoming loads of water, sediment, and chemicals (e.g., nutrients and pesticides) for VFSMOD. For example, the distribution package of VFSMOD includes a companion utility, Unit Hydrograph (UH), that creates synthetic model inputs for the upslope source area based on the National Resource Conservation Service design storm for a given location and soil type. Previous studies have demonstrated the successful coupling with other models, such as Soil Water Assessment Tool (SWAT) and Pesticide Root-Zone Model (PRZM).

Early prediction of pesticide trapping by a VFS was based on regression relationships derived from experimental data. The simplest relationship only uses one independent variable of VFS width (W_B, m, in the flow direction through the filter) to predict the pesticide reduction (ΔP) through a VFS (Webster and Shaw, 1996; Cole et al., 1997). This equation was incorporated into SWAT version 2005 (Neitsch et al., 2005),

$$\Delta P = 0.367 \times W_B^{0.2967} \quad (1)$$

Taking a 10-ft VFS as an example, the removal efficiency is calculated as 51% for any pesticide regardless of physicochemical properties and field conditions. Therefore, it's more appropriate for relative comparison on the mitigation effects with various proposed filter sizes. This equation was used to model VFS effectiveness to reduce organophosphate pesticides in the Central Valley (Luo and Zhang, 2009; Zhang and Zhang, 2011).

Pesticide reduction through a VFS is related to the reductions of runoff and sediment. Therefore, the prediction of ΔP is refined by introducing ΔQ and ΔE as independent variables and considering the physicochemical properties of the pesticide of interest. For example, the

following regression equation was developed by Sabbagh et al. (2009) with 47 field measurements,

$$\Delta P = f(\Delta Q, \Delta E, F_{ph}, \%C)$$

$$= 24.79 + 0.54\Delta Q + 0.52\Delta E - 2.42 \ln(F_{ph} + 1) - 0.89\%C \quad (2)$$

where F_{ph} (-) is the ratio of incoming pesticide mass in the dissolved phase relative to that sorbed to sediment, and %C (-) is the percent clay content. Coupled modeling by VFSMOD and Eq. (2) were compared with three other models (APEX, PRZM_BUFF, and PEMM) and determined to best match the observed pesticide reductions for four chemicals with K_{OC} ranging from 54 to 12,500 L/kg (Winchell et al., 2011). In 2019, the regression equation was re-calibrated with an enlarged experimental dataset (N=244) (Reichenberger et al., 2019),

$$\Delta P = -11.5142 + 0.5949\Delta Q + 0.4892\Delta E - 0.3753 \ln(F_{ph} + 1) + 0.2039\%C \quad (3)$$

With a similar formulation, another regression equation was proposed by Chen et al. (2016),

$$\Delta P = f(\Delta Q, \Delta E, Cat, \%C) \quad (4)$$

where "Cat" is a categorical variable (Cat= 1 for K_{OC}> 9000 L/kg or Cat= 0 otherwise). Both "F_{ph}" in Eq. (2) and "Cat" in Eq. (4) represent the effects of pesticide phase distribution on the prediction of removal efficiency by a VFS. Limitations are observed in both regression equations. First, K_d would be a better parameter than K_{OC} in Eq. (4) for indicating pesticide adsorption, given the wide range of organic carbon contents in the soil: 0.008-0.0406 in the experimental data or 0.0029-0.0348 in the PWC scenarios for California. For the same pesticide, its K_d value may vary up to 12X (=0.0348/0.0029) over different soil settings. Second, since the field measurements only reported "total" masses of pesticide (in dissolved and sorbed phases) in the influent and effluent flows, the instantaneous equilibrium was assumed for calculating F_{ph} value in in Eq. (2). Consequently, F_{ph} is estimated as a function of incoming sediment concentration (E_{in}/Q_{in}, with E_{in} and Q_{in} denoting the incoming sediment loading and runoff volume, respectively) (Sabbagh et al., 2009), not necessarily reflecting the actual phase distribution of the incoming pesticide masses,

$$F_{ph} = \frac{Q_{\text{in}}}{K_d E_{\text{in}}} \quad (5)$$

Most of the soil models separately predict pesticide yields in dissolved and sorbed phases, which can be used to build a physically based modeling approach for pesticide trapping in a VFS. Since SWAT version 2009 (Neitsch et al., 2009), a semi-mechanistic method was developed to predict the reduction of pesticide in water runoff or suspended sediment. In this method, infiltration and sedimentation are assumed the only relevant mechanisms of pesticide trapping in a VFS,

$$\begin{cases} \Delta P_d = \Delta Q \\ \Delta P_{\text{p}} = \Delta E \end{cases} \quad (6)$$

where ΔP_d and ΔP_p are the removal efficiency for pesticides in dissolved and sorbed phases, respectively. The same assumption and equations were adopted in SWPP's previous study (Luo, 2017b). Compared to regression equations (2)-(4), the semi-mechanistic method is independent on field measurements, and thus can be applied to the field conditions not covered by available experimental data. The empirical, Eqs. (2)-(4), and mechanistic, Eq. (6), approaches were evaluated with an extended single-event field database (Reichenberger et al., 2019). The authors confirmed the general performance ranking for ΔP prediction: Eq. (6) > (4) > (2), and recommended the mechanistic approach as a viable alternative to the regression equations for regulatory modeling.

Another advantage for the mechanistic approach is its convenience for further model development such as the long-term exposure analysis (see the next Section). The mechanistic approach considers individual physical processes of infiltration and sedimentation, and can be incorporated with equations for other processes such as extraction of previously trapped pesticide in a VFS. Pesticide extraction (also called uptake or pickup in the literature) includes runoff extraction for dissolved mass in the soil pore water and erosion extraction for sorbed mass by particle resuspension. The regression equations represent the aggregated mitigation effects by comparing the measured pesticide loads in influent and effluent flows. Since pesticide extraction in a VFS is not measurable, regression approaches are essentially not appropriate for continuous modeling of pesticide in a VFS.

2.2 Continuous modeling of pesticide in a VFS

Continuous modeling of pesticide simulates long-term mitigation effects on pesticide in multiple, consecutive runoff events through a VFS. Continuous modeling of VFS is usually implemented by coupling VFSMOD (for a VFS) with PRZM (for an agricultural field). Daily results of edge-of-field loads (Q_i for water, E_i for sediment, and P_i for pesticide) predicted by PRZM are used to drive the hydrological and pesticide simulations in a VFS. Early studies simply adjusted PRZM-predicted fluxes with VFSMOD modeling (for water and sediment) and the regression model in Eq. (2) (for pesticide) (Sabbagh et al., 2010; Sabbagh et al., 2013) (Figure 1). These studies assumed that pesticide trapped in a VFS was immediately removed from the simulation domain. In other words, the vegetative filter is always new, uncontaminated for each runoff event.

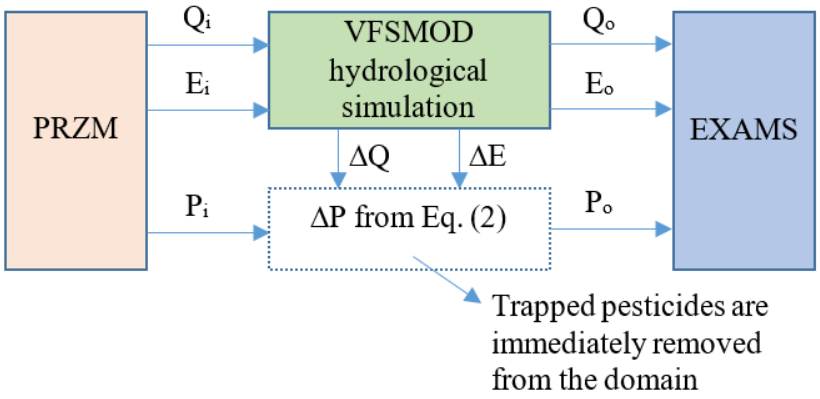

Figure 1. Early modeling efforts to link VFSMOD and PRZM for pesticide mitigation in a VFS (Q_i, E_i, and P_i are incoming loads to a VFS predicted by PRZM for runoff, suspended sediment, and pesticides, respectively. Q_o, E_o, and P_o are the effluent loads)

Once trapped in a VFS, pesticides are subject to fate and transport processes including partitioning, degradation, and percolation. In addition, the pesticide residues may re-enter the overland flow in the next runoff event by runoff extraction and sediment resuspension. Modeling approaches for mass balance and degradation processes for pesticide in a VFS were first developed by the VFSMOD team (Muñoz-Carpena, 2014; Muñoz-Carpena et al., 2015). The key variable is pesticide mass retained in the mixing soil layer of a VFS. The mixing layer depth is recommended to be 2 cm for consistency with that in PRZM (USEPA, 2006a; Muñoz-Carpena, 2014). During a dry period between two runoff events, retained pesticide in the mixing layer may be lost by degradation and percolation. In the next runoff event, it's assumed that all retained pesticide masses will be transported from the mixing layer, and added to the incoming pesticide mass (highlighted as a red arrow connector in Figure 2) (Muñoz-Carpena et al., 2015). This is essentially an empirical method by prescribing the extracted pesticide masses without simulating the associated physical processes.

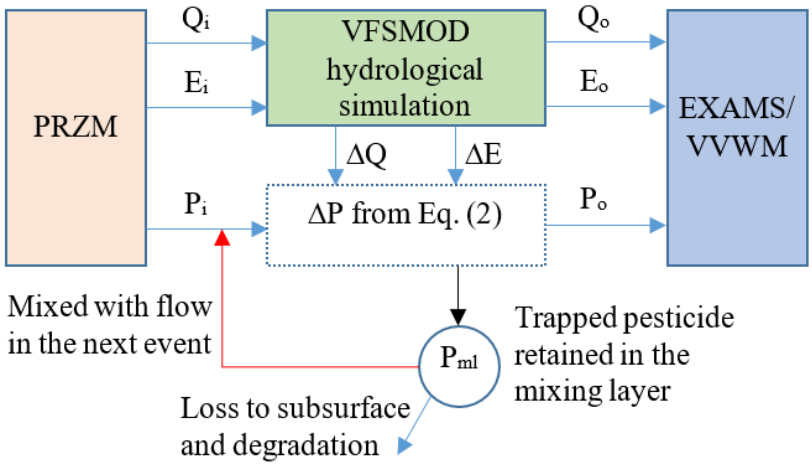

Figure 2. Current modeling approach for continuous modeling of pesticide in a VFS

The modeling approach in Figure 2 was implemented in SWPP's previous work (Luo, 2017b), but with the pesticide trapping estimation by the semi-mechanistic method, Eq. (6), and upgrade of USEPA modeling framework from PRZM3-EXAMS to PWC (PRZM5-VVWM). Later, the semi-mechanistic trapping equation and the PWC framework were also evaluated by the VFSMOD team (Muñoz-Carpena et al., 2019). The differences between the two studies (Luo, 2017b; Muñoz-Carpena et al., 2019) are mainly observed for the pre-processing of PRZM-predicted pesticide load (P_i) and the assumption on the extraction of retained pesticides to the incoming flow in the next runoff event (Figure 2). Specifically, In Muñoz-Carpena et al. (2019), Eq. (6) was modified by assuming instantaneous equilibrium for pesticide in the incoming flow between dissolved and sorbed phases before trapping by a VFS,

$$\Delta P = \frac{Q_i \Delta Q + K_d E_i \Delta E}{Q_i + K_d E_i} \quad (7)$$

In addition, both approaches used an empirical method for pesticide extraction, but with different assumed pesticide amounts from the mixing layer: "100% [dissolved]" (Luo, 2017b) vs. "100% [dissolved] + 100% [sorbed]" (Muñoz-Carpena et al., 2019).

2.3 Summary of previous modeling approaches for VFS

A modeling approach for pesticide removal in a VFS consists of two modeling components: hydrological (water and sediment) and pesticide simulations. When developing and presenting a VFS model, therefore, it's important to specify each of the components. Summarized in Table 1 are existing modeling studies for continuous simulation with their corresponding approaches for hydrology and pesticide. For comparison, the proposed approach in this study is also listed. Even with the same mechanistic hydrological simulation by VFSMOD, different modeling approaches can be implemented for pesticide.

Table 1. Modeling approaches for pesticide removal in a VFS

VFS modeling approach in…	Hydrological simulation	Pesticide simulation
Early version SWAT [1]	NA	Empirical method, Eq. (1)
SWAT 2009 and after	Empirical	Semi-mechanistic, Eq. (6)
Sabbagh et al. (2009) [2]	Mechanistic (VFSMOD)	Empirical, Eq. (2)
Luo (2017b)	Mechanistic (VFSMOD)	Semi-mechanistic, Eq. (6)
Muñoz-Carpena et al. (2019)	Mechanistic (VFSMOD)	Empirical, Eqs. (2)-(4), and semi-mechanistic, Eq. (7)
This study	Mechanistic (VFSMOD)	Mechanistic (this report)

Notes: [1] SWAT = Soil Water Assessment Tool. [2] The regression equation in (2) has been incorporated in the current VFSMOD. Therefore, the modeling approach with "VFSMOD for hydrology) and Eq. (2) for pesticide" has been widely used in VFS modeling studies during the last decade. Here only shows the initial development by Sabbagh et al. (2009). See a full citation list in the VFSMOD website (https://abe.ufl.edu/faculty/carpena/vfsmod/citations.shtml).

There are limitations in the existing approaches for pesticide (i.e., regression equations and semi-mechanistic method). First, the field data used to build a regression equation are generally measured for water soluble pesticides. Taking the extended field database (Reichenberger et al., 2019) as an example, the median K_d is 5.2 L/kg and the 90th percentile is 110 L/kg over the 244 data points (Figure 3). There are only 17 data points, or 7% of the database, associated with K_d > 200 L/kg, and 2 data points with K_d > 1000 L/kg (2%). Therefore, the resulting regression equation would be more appropriate to pesticides with low or moderate adsorption with K_d< 200 L/kg, but not suitable to hydrophobic compounds such as pyrethroids.

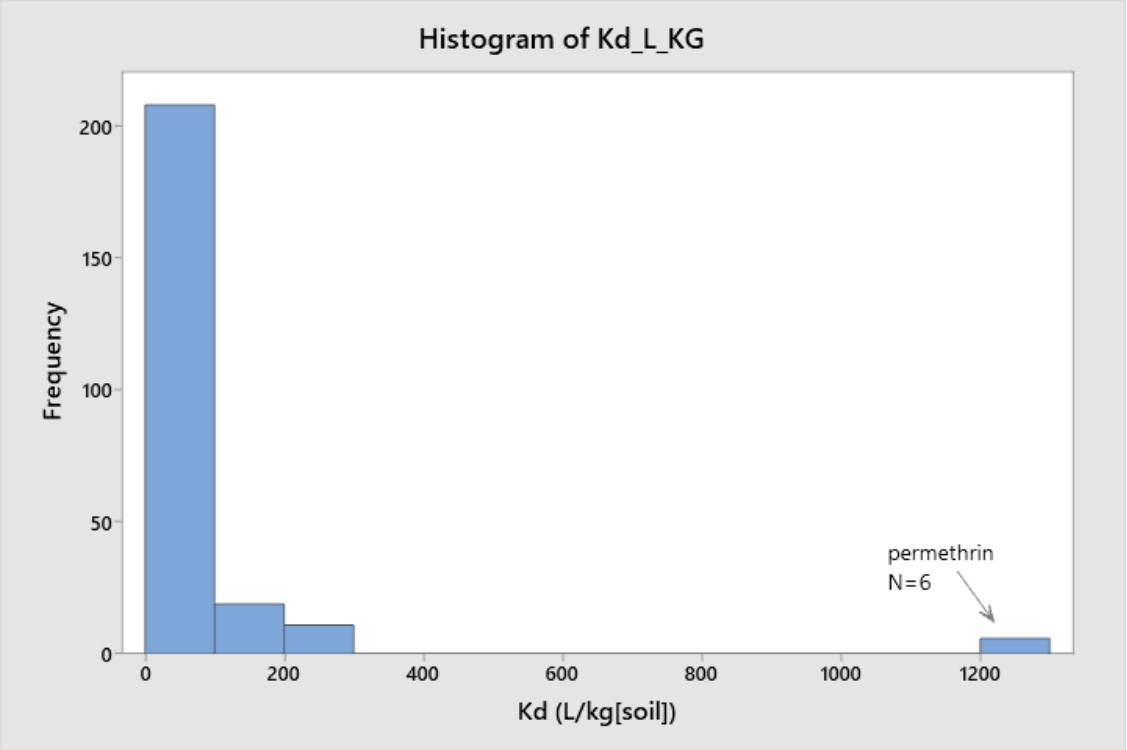

Figure 3. Histogram of pesticide K_d values in the field measurements used to build the regression equation for pesticide removal efficiency in a VFS, total N= 244

Secondly, in all studies with regression equation and some studies with semi-mechanistic method, instantaneous equilibrium was assumed for incoming pesticide masses (i.e., edge-of-field pesticide fluxes) in dissolved and sorbed phases. For example, with equilibrium assumption, Eq. (5) is used to estimate pesticide mass ratio between dissolved and sorbed phases. Otherwise, without this assumption, the phase distribution factor would be expressed as,

$$F_{ph} = \frac{RFLX}{EFLX} \tag{8}$$

where RFLX and EFLX are edge-of-field pesticides fluxes in dissolved and sorbed phases, respectively, by following the PRZM terminology. Similarly, Eq. (7) is an equilibrium version of the semi-mechanistic method, Eq. (6), used by Reichenberger et al. (2019). With equilibrium assumption, pesticide removal efficiency would be reported as the aggregated reduction (ΔP) as in Eqs. (2) and (5), rather than the reductions for individual phases (ΔP_d and ΔP_p). Note that the VFS modeling in SWAT 2009 (and later versions) and in Luo (2017b, 2019) (Table 1), instantaneous equilibrium for incoming pesticide was not assumed, so pesticide reduction was calculated for each phase as an intermediate modeling result.

Results of field measurements and PRZM model predictions indicate that the edge-of-field pesticide masses are not necessarily in equilibrium. The prediction of pesticide removal through a VFS is sensitive to the phase distribution of the incoming pesticide runoff. A case study is developed to demonstrate the effects of the equilibrium assumption on the predicted phase distribution. Bifenthrin and the PWC scenario for "CA almond" are used in the case study, and

all input data are taken from the ecological risk assessment by USEPA for pyrethroids (USEPA, 2016a). PRZM results are extracted for edge-of-field fluxes of water, suspended solids, and pesticide in each phase. By assuming equilibrium, the phase distribution factor (F_{ph}) is calculated as 4.4 with Eq. (5). Since F_{ph} is the ratio of pesticide masses between dissolved and sorbed phase, the resulting value suggests that majority (4.4/(4.4+1)=81%) of the edge-of-field pesticide masses are associated with water runoff. For a hydrophobic chemical such as bifenthrin, this F_{ph} value may not be realistic. If an instantaneous equilibrium is not assumed, F_{ph} is calculated as 0.22 with Eq. (8), indicating 18% (=0.22/(0.2+1)) of the incoming pesticide in dissolved phase and 82% particle-bound.

Finally, the existing modeling approaches for pesticide removal in a VFS are irrelevant to the incoming pesticide loadings. Specifically, regression equations, see Eqs. (2) and (4), are only established as a function of incoming flow (Qi), sediment (Ei), and their reductions (ΔQ and ΔE) , while the semi-mechanistic method is only sensitive to ΔQ and ΔE in Eq. (6). None of the equations considered incoming pesticide masses as input variables.

3 Model development

3.1 Physically based modeling for pesticide trapping and extraction in a VFS

As summarized in the previous section, VFSMOD provides hydrological simulations for all PWC-VFS modeling systems (or similar systems with other versions of USEPA framework), while pesticide simulations in a VFS have been developed independently by different research groups during the last decade. One issue in the current approach for continuous modeling of VFS (Figure 2) is the separated simulations of trapping (from runoff to VFS) and extraction (from VFS to runoff) of pesticides. The two processes actually occur simultaneously during a runoff event (Figure 4). A new modeling approach is proposed here to formulate transport processes of pesticide in a VFS.

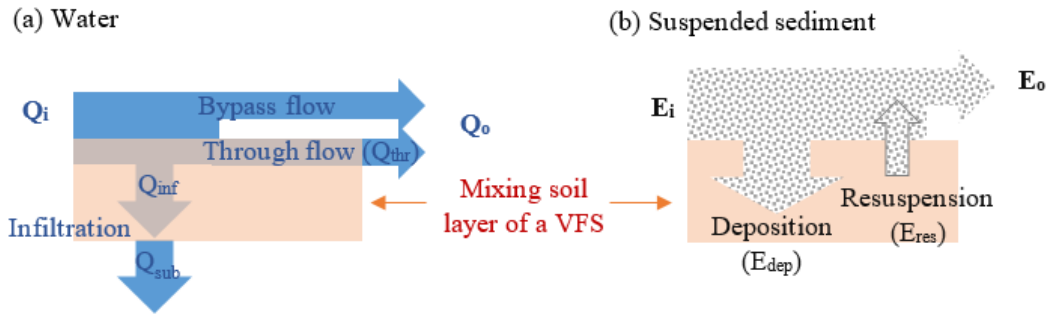

Figure 4. Interactions between the mixing soil layer of a VFS and the incoming (a) water flow and (b) suspended sediment. Qin includes both runoff from the drainage field and precipitation on the VFS

For dissolved pesticide in the mixing layer, the mass balance aggregated during the runoff event is expressed as,

$$\Delta(VC) = Q_{\text{inf}}C_{\text{i}} - Q_{\text{sub}}C - Q_{\text{thr}}C \quad (9)$$

where V (m^3) is the water volume in the mixing layer of a VFS, C and C_i (kg/m^3) are the dissolved pesticide concentrations in the mixing layer and in the incoming flow, respectively, Q_{inf}, Q_{sub}, and Q_{thr} (m^3) are the infiltration from runoff to VFS (predicted by VFSMOD), percolation to subsurface, and lateral flow interacting with the mixing layer, respectively. Pesticide dispersion ($D\frac{\partial^2 C}{\partial z^2}$) is not included since the dispersion coefficient (D) is set to zero in the PWC scenarios (Young, 2016b). The concept of Q_{thr} is taken from PRZM, which considers that only a portion of runoff interacts with the soil mixing layer and extracts dissolved pesticide out of soil matrix (Young, 2016b). The ratio $f_{thr}= Q_{thr}/Q_i$ is named as runoff interacting fraction by following the PRZM terminology. This fraction, also called uptake fraction or pickup fraction in the literature, could be implemented either by partial runoff or by partial concentration, and widely used in runoff and transport models (Leonard et al., 1987; Smith, 1992; Carsel et al., 1998; Ahuja et al., 2000).

The mass balance for sorbed pesticide is,

$$M\Delta S = E_{\text{dep}}S_{\text{i}} - E_{\text{res}}S \quad (10)$$

where M (kg) is the soil mass in the mixing layer, S and S_i (kg/kg[soil]) are the sorbed pesticide concentrations in the mixing layer and in the incoming flow, respectively, E_{dep} (kg[soil]) is the sedimentation of the suspended solids, and E_{res} (kg[soil]) is the resuspension. Equations (9) and (10) are combined for overall mass balance of pesticide in the mixing layer, and organized as,

$$\Delta VC + M\Delta S = (Q_{\text{inf}} + Q_{\text{thr}})C_{\text{i}} - (Q_{\text{sub}} + Q_{\text{thr}})C + E_{\text{dep}}S_{\text{i}} - E_{\text{res}}S \quad (11)$$

Or,

$$VC + MS - P_0 = (Q_{\text{inf}} + Q_{\text{thr}})C_{\text{i}} - (Q_{\text{sub}} + Q_{\text{thr}})C + E_{\text{dep}}S_{\text{i}} - E_{\text{res}}S \quad (12)$$

where $P_0= (V_0C_0+MS_0)$ @ t=0 is the pesticide mass in the mixing layer immediately before a runoff event. The above equation is re-arranged as,

$$(V + Q_{\text{sub}} + Q_{\text{thr}})C + (M + E_{\text{res}})S = (Q_{\text{inf}} + Q_{\text{thr}})C_{\text{i}} + E_{\text{dep}}S_{\text{i}} + P_0 \quad (13)$$

It is assumed that the infiltrated water has tried to saturate the mixing layer before loss to subsurface (Muñoz-Carpena et al., 2015). So, at the end of the runoff event,

$$V = Q_{\text{inf}} - Q_{\text{sub}} + V_0 \quad (14)$$

VFSMOD predicts the total effective sedimentation, $\Delta E=(E_{dep}-E_{res})/E_i$, but not its individual components. The mass balance for suspended sediment gives,

$$E_{\text{dep}} = E_{\text{i}}\Delta E + E_{\text{res}} \quad (15)$$

Combining (14) and (15) into (13),

$$(V_0 + Q_{\text{inf}} + Q_{\text{thr}})C + (M + E_{\text{res}})S = (Q_{\text{inf}} + Q_{\text{thr}})C_{\text{i}} + (E_{\text{i}}\Delta E + E_{\text{res}})S_{\text{i}} + P_0 \quad (16)$$

The concentrations are solved as,

$$\begin{cases} C = \dfrac{(Q_i\Delta Q + Q_{thr})C_i + (E_i\Delta E + E_{res})S_i + P_0}{V_0 + Q_i\Delta Q + Q_{thr} + (M + E_{res})K_d} \\ S = K_d C \end{cases} \quad (17)$$

Previous modeling studies predicted dissolved concentrations of pesticide above the corresponding water solubility (C_{sol}), especially for hydrophobic compounds. In the ERAs for pyrethroids (USEPA, 2016a), for example, predicted dissolved concentrations exceeded the limit of solubility for bifenthrin, deltamethrin, fenpropathrin in various use patterns. If $C > C_{sol}$ from Eq. (17), the concentration of dissolved pesticide is set as C_{sol}, and that of sorbed pesticide is recalculated from Eq. (16),

$$\begin{cases} C = C_{SOL} \\ S = \dfrac{(Q_i\Delta Q + Q_{thr})C_i + (E_i\Delta E + E_{res})S_i + P_0 - (V_0 + Q_i\Delta Q + Q_{thr})C}{M + E_{res}} \end{cases} \quad (18)$$

Effluent pesticide masses (P_{od} for dissolved phase and P_{op} for sorbed phase, kg) can be calculated as,

$$\begin{cases} P_{\text{od}} = (Q_o - Q_{\text{thr}})C_i + Q_{\text{thr}}C \\ P_{\text{op}} = E_o S_i + E_{\text{res}}(S - S_i) \end{cases} \quad (19)$$

where Q_o and E_o are water and sediment leaving the filter. By definition, $Q_o = (1-\Delta Q)Q_{in}$ and $E_o = (1-\Delta E)E_i$. If there is pesticide in the incoming flow (i.e., $C_i > 0$ and $S_i > 0$), the trapping efficiencies for pesticide in dissolved and sorbed phases can be calculated as,

$$\begin{cases} \Delta P_d = 1 - \dfrac{P_{\text{od}}}{P_{\text{id}}} = \Delta Q + f_{\text{thr}}(1 - \dfrac{C}{C_i}) \\ \Delta P_{\text{p}} = 1 - \dfrac{P_{\text{op}}}{P_{\text{ip}}} = \Delta E + f_{\text{res}}(1 - \dfrac{S}{S_i}) \end{cases} \quad (20)$$

where $f_{thr} = Q_{thr}/Q_i$, or the interacting fraction for runoff extraction of pesticide from the mixing layer, with a range of 0 to $(1-\Delta Q)$. For agricultural fields, the default modeling settings in PWC version 1.52 use $f_{thr} = 0.266$ (Young, 2016a). By calibration with extended field measurements, a more recent study by the PRZM developers suggested an even smaller fraction of 0.19 (Young and Fry, 2017). With higher Manning's roughness coefficient and water-plant interaction, a VFS is associated with a higher interacting fraction than agricultural fields. Therefore, a f_{thr} of 0.4 (more accurately min(0.4, $1-\Delta Q$)) is tested in this study as an initial value. Generally, higher f_{thr} results in higher pesticide removal efficiency, and the effects of f_{thr} on model predictions are also evaluated.

Similarly, $f_{res}= E_{res}/E_i$, denoting the ratio between suspended sediment and the incoming sediment, with a range of 0 to (1-ΔE). Results of previous field and modeling studies suggested that VFS is very efficient for sediment removal (i.e., large value of ΔE). Therefore, f_{res} would be a small value, e.g., up to 0.01 for "almond" scenario or up to 0.20 for "lettuce" scenario (Luo, 2019). This study will run the VFS model with both the minimum (f_{res}=0 or no resuspension) and maximum (f_{res}=1-ΔE) value, and investigate the effect of f_{res} on the prediction of ΔP.

By comparing the equations in (6) and (20), the new modeling approach with physically-based modeling for water-soil exchange of pesticide provides a more general description and prediction of pesticide removal efficiency in a VFS. The previous simplified mechanistic method, $\Delta P_d= \Delta Q$ and $\Delta P_p= \Delta E$, only reflects a subset of the general conditions with special cases such as $f_{thr}= 0$, $f_{res}= 0$, $C_i= C$, and/or $S_i= S$. The new approach also explicitly models pesticide mass gain from a filter, indicated by negative trapping efficiencies of pesticide (ΔP_d and/or ΔP_p) even with positive ΔQ and ΔE values. In this case, the previously contaminated VFS acts as a source by transporting pesticide residues back to the overlying flow.

Finally, the total pesticide reduction is calculated as,

$$\Delta P = 1 - \frac{P_{\mathrm{od}}+P_{\mathrm{op}}}{P_{\mathrm{id}}+P_{\mathrm{ip}}} \tag{21}$$

Note that ΔP is calculated for reporting purpose only, but not used in the model simulation.

3.2 Simulation design for continuous modeling

Equations (18)-(21) establish pesticide transport modeling in a VFS during a runoff event. At the end of the event, the pesticide mass retained in the VFS mixing layer is updated as,

$$P_{\mathrm{m}} = VC + MS \tag{22}$$

P_m is subject to further adjustment by pesticide fate and transport processes during a dry period. Here, a dry period is defined between two runoff events predicted by PRZM. Note that it is possible that a small amount of precipitation (on both the field and VFS) or irrigation (on the field) is observed during a dry period, but does not generate surface runoff.

The first-order kinetics with the aerobic soil metabolism half-life of the pesticide is used for estimating degradation in the mixing layer. The time period for calculating degradation is extended to include the runoff event before the dry period. Therefore, the degradation losses of pesticide not considered during the runoff event, Eq. (16), can be simulated together with the losses during the dry period. Finally, the updated P_m immediately before the next runoff event, P_m at t=0 or P_0, is used as an input variable in the equations (18) or (19) for simulating pesticide transport during the next runoff.

Soil moisture during a dry period is assumed as the same value in the agricultural field predicted by PRZM (Muñoz-Carpena et al., 2015). Therefore, the effect of precipitation on the VFS soil moisture during a dry period is actually considered. This assumption may overestimate soil moistures in VFS soils, due to some irrigation events (but not generating surface runoff) over the fields. To simplify the hydrological simulation, it's assumed that there is no percolation from the

VFS mixing layer during a dry period. For the retained pesticide mass in the mixing layer, this suggests a conservative estimation by minimizing the loss to subsurface.

3.3 Input data

The PWC-VFS system has similar data requirements as PWC modeling, including modeling scenarios, pesticide physicochemical properties, and pesticide application data. It's assumed that the top soil layer of a VFS has the same properties as that of the treated field. PWC scenarios provides most of the required soil input data, including slope (SLP), bulk density (BD), field capacity (FC) wilting point (WP), and organic carbon content. Additional soil properties required by VFSMOD are saturated hydraulic conductivity (VKS), average suction at wetting front (SAV), and contents of clay (CLAY) and sand (SAND). Indexed by soil texture class, representative values for those parameters were available in the literature (Maidment, 1993; Miller and White, 1998) (Table 2).

Table 2. Representative soil properties by textural classification

Class No.	USDA textural classification	Field capacity (-)	Wilting point (-)	VKS (cm/h)	SAV (cm)	SAND (%)	CLAY (%)
1	Sand	0.091	0.033	23.56	4.95	92	3
2	Loamy sand	0.125	0.055	5.98	6.13	82	6
3	Sandy loam	0.207	0.095	2.18	11.01	58	10
4	Silt loam	0.33	0.133	0.68	16.68	17	13
5	Silt	-	-	-	-	10	5
6	Loam	0.27	0.117	1.32	8.89	43	18
7	Sandy clay loam	0.255	0.148	0.30	21.85	58	27
8	Silty clay loam	0.366	0.208	0.20	27.30	10	34
9	Clay loam	0.318	0.197	0.20	20.88	32	34
10	Sandy clay	0.339	0.239	0.12	23.90	52	42
11	Silty clay	0.387	0.250	0.10	29.22	6	47
12	Clay	0.396	0.272	0.06	31.63	22	58

Notes: representative values for saturated hydraulic conductivity (VKS), average suction at wetting front (SAV) are taken from Maidment (1993), which did not report data for soil class #5 (silt). Soil class # and contents of clay (CLAY) and sand (SAND) are retrieved from CONUS-SOIL database (Miller and White, 1998).

Values of field capacity and wilting point in Table 2 are not used in the VFS modeling, but to help determine the relevant soil class for a PWC scenario (Table 3). For some scenarios, the corresponding soil classes are specified in their metadata files (available with early versions of PRZM). If there is no sufficient information, otherwise, the field capacity (FC) and wilting point (WP) in the scenario are compared to the representative values in Table 2 to determine the soil class. In the "alfalfa" scenario for California ("CAalfalfa_WirrigOP"), for example, the reported FC and WP are 0.42 and 0.36, respectively. Based on the minimum root-mean-square error, the scenario (CA alfalfa) is assigned with soil class #12 (clay). This is also confirmed by the scenario metadata, which mentioned that the benchmark soil was set as Sacramento Clay. With a soil class assigned, the representative values for VKS, SAV, SAND, and CLAY can be obtained from Table 2 and used in VFS modeling.

Table 3. Soil properties of the top soil layer for PWC scenarios in California

Crop	Scenario	SLP (%)	BD (kg/L)	FC (-)	WP (-)	OC (%)	Soil type [1]
Alfalfa	CAalfalfa_WirrigOP	2	1.43	0.42	0.36	1.77	Sacramento Clay
Almond	Caalmond_WirrigSTD	2	1.55	0.22	0.1	0.81	Manteca fine sandy loam
Citrus	CAcitrus_WirrigSTD	5	1.59	0.16	0.06	0.46	Exeter loam
Cole crop	CAColeCropRLF_V2	1	1.5	0.334	0.219	1.74	Marimel Silty Clay Loam
Corn	CAcornOP	4.5	1.55	0.223	0.083	0.58	Madera loam
Cotton	CAcotton_WirrigSTD	2.5	1.45	0.36	0.22	0.29	Twisselman clay
Fruit	CAfruit_WirrigSTD	2	1.7	0.218	0.078	0.58	Exeter loam
Grape	CAgrapes_WirrigSTD	2	1.84	0.21	0.1	0.71	San Joaquin loam
Lettuce	CAlettuceSTD	6	1.575	0.295	0.17	0.725	Clay loam [2]
Row crop	CARowCropRLF_V2	1	1.35	0.283	0.148	1.74	Mocho silt loams
Strawberry	CAStrawberry-noplasticRLF_V2	1.5	1.65	0.12	0.039	0.58	Oceano series
Sugarbeet	CAsugarbeet_WirrigOP	2	1.4	0.359	0.255	3.48	Exeter loam
Tomato	CAtomato_WirrigSTD	0.25	1.3	0.38	0.25	0.95	Stockton Clay
Wheat	CAWheatRLF_V2	4.5	1.55	0.282	0.133	0.44	San Joaquin series (loam)

Note: [1] Soil type is extracted from the scenario metadata provided by USEPA. [2] No metadata for California lettuce scenario. Soil type is determined as clay loam based on the provided soil properties.

PWC runs at a daily time step, while the hydrological simulation in a VFS (VFSMOD) is a runoff event-based model. Therefore, the daily runoff entering a VFS is assumed to be one aggregated event. The same assumption is applied to the runoff generation in many surface water models at daily time step, such as SWAT (USDA, 2016). The aggregated daily runoff is characterized by total runoff volume (predicted by PRZM), duration, and runoff distribution over the duration. For rainfall-induced runoff, its duration is calculated as (rainfall volume)/(rainfall intensity). The rainfall volume for each day is retrieved from weather data associated with crop scenarios (USEPA, 2016c), while the rainfall intensity can be determined from the Precipitation Frequency Data Server by the National Oceanic and Atmospheric Administration (NOAA, 2019). For example, the rainfall intensity for the Sacramento area is 2 mm/hour (for a 24-hour period, 1-year recurrence interval). For irrigation tail water, the duration is calculated by (irrigation volume)/(irrigation rate), where the volume is predicted by PRZM and the rate is predefined in the crop scenarios (USEPA, 2016c). It's noted that the irrigation rate in the PWC scenarios are significantly lower than that suggested in the previous version for most of the crops (USEPA, 2006b). Triangular hydrography (with peak flow rate = 2× average rate, and peak time

= (runoff duration)/2.67) is used for distributing the total runoff over its duration (Muñoz-Carpena, 2013).

4 Case studies

4.1 Modeling settings

The newly developed model is used to simulate pesticide removal efficiency by a 10-ft VFS under PWC scenarios, the label-required or recommended size for agricultural applications of pyrethroids and neonicotinoids. Compared to previous studies (Luo, 2017b, 2019), the improvement in this study is mainly on the modeling approach for pesticide simulations in a VFS. Therefore, the case studies only characterizes the mitigation effects by a VFS, while the relative change of estimated environmental concentrations (EECs) in a receiving water is not presented. Note that, according to the previous results (Luo, 2017b, 2019), the EEC reduction is usually significantly lower than the removal efficiency by a VFS, mainly because the contribution of pesticide masses by spray drift to receiving water would not be mitigated by a VFS.

Four pesticides are selected in this study: bifenthrin, chlorpyrifos, imidacloprid, and permethrin. The pesticides represent a wide range of chemical properties especially the K_{OC} values in the order of 10^2 (imidacloprid), 10^3 (chlorpyrifos), 10^4 (permethrin), and 10^5 (bifenthrin). The modeled pesticides are associated with high use amounts and high detections in surface water of California. Their physiochemical properties (Table 4) have been summarized in previous studies based on those used in ERAs by USEPA for bifenthrin (USEPA, 2010, 2016a), chlorpyrifos (USEPA, 2017), imidacloprid (USEPA, 2016b), and permethrin (USEPA, 2011, 2016a).

Table 4. Physiochemical properties of the selected pesticides

Property	Bifenthrin	Chlorpyrifos	Imidacloprid	Permethrin
Molecular weight (g/mol)	422.9	350.57	255.7	391.3
Vapor pressure (torr)	1.8e-7	2.44e-5	1.5E-9	1.48e-8
Water solubility (mg/L)	1.4e-5	1.39	610	5.5e-3
Aqueous photolysis HL (day)	49	52.65	0.2	94
Soil HL (day)	169.2	86.2	254	211
Hydrolysis HL (day)	Stable	72.1	Stable	Stable
Water metabolism HL (day)	466.2	91.2	236	56.7
Sediment metabolism HL (day)	650.2	202.7	81	193
K_{OC} (L/kg)	236,750	6,040	266	76,800

Note: HL = half-life

Pesticide application data (including application timing, rate, method, interval, efficiency, and drift fraction) in the ERAs have been extracted in a model-ready format in the previous study (Xie et al., 2018) (See supplemental Table S2 of that paper). Application data are organized by pesticide and scenario. Modeling for the selected pesticides involved 14 PWC crop scenarios in California: “alfalfa”, “almond”, “citrus”, “cole crop”, “corn”, “cotton”, “fruit”, “grape”, “lettuce”, “row crop”, “strawberry”, “sugarbeet”, “tomato”, and “wheat”. The modeled scenarios also cover all high-risk use patterns for upland production agriculture in SWPP’s Pesticide

Registration Evaluation Model (PREM) (Luo, 2017a). More information on the scenarios such as associated soil properties and landscape descriptions are provided in Table 3.

Note that there are 56 potential "pesticide-scenario" sets (= 4 pesticides × 14 scenarios), but only 39 have been actually modeled in the USEPA ERAs and in this study. Some sets are not modeled, such as "bifenthrin-alfalfa" and "chlorpyrifos-cotton", for which the use patterns may not be registered in California (or only registered for seed treatment), or associated with relatively low uses for the corresponding pesticide. Together with the 14 PWC scenarios, the selected pesticides have K_d values in the range of 0.8-8239 L/kg.

4.2 Hydrological simulation results

VFSMOD results of hydrological simulation (ΔQ and ΔE) are shown in Figure 5 for the 14 PWC scenarios evaluated in this study. Both ΔQ and ΔE are presented as the overall reductions, 1-sum(Q_o)/sum(Q_i), by a 10-ft VFS during the 30-year simulation period (1961-1990). For the 14 scenarios, ΔQ ranges from 6.7% (cole crop) to 83.4% (citrus), and its variation is mainly related to the saturated hydraulic conductivity (VKS, Table 3) and incoming flow (Q_i, averaged over all runoff events). A regression relationship is established as (R^2=78%),

$$\Delta Q = 65.2 - 10.71\ln(Q_{in}) + 12.91\ln(\mathrm{VKS}) \quad (23)$$

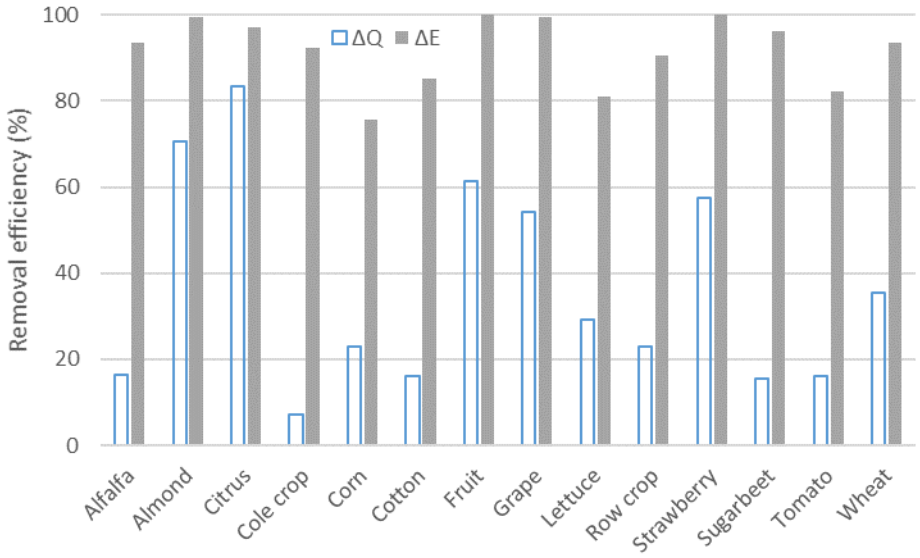

Figure 5. Predict reductions to runoff (ΔQ) and sediment (ΔE) by a 10-ft VFS under the PWC scenarios in California

This equation reflects the long-term (30-year) mitigation effects for runoff reduction by a VFS. It's noteworthy that the equation has the same form and similar coefficient values as those derived in the SWAT model based on 1650 single-event training data (Neitsch et al., 2009) (unit conversion is utilized before comparison since the SWAT equation used Q_i in mm and VKS in mm/hr). The SWAT training data were generated by VFSMOD for a wider range of VFS settings, compared to those modeled in this study, including VFS width (1-20m), soil properties (11 textural classes), and slopes (2-10%).

High efficiency of sediment removal (ΔE) is predicted for all scenarios (74-100%, Figure 5). Results of correlation analysis indicated that ΔE is negatively associated with the concentration of total suspended sediment (TSS, kg/m^3) and positively with runoff reduction (ΔQ). For comparison, a median efficiency of 91% for sediment trapping was summarized from 244 field measurements with a median VFS width of 7.6 m (Reichenberger et al., 2019). For better comparison, 19 data points with 3-m (~10ft) VFS are extracted, showing sediment removals between 71-97%. The field conditions were associated with higher TSS (0.47-10.5 kg/m^3) compared to those predicted with the PWC scenarios (0.0056-5.8 kg/m^3).

4.3 Additional analysis on experimental data for pesticide removal by VFS

The field measurements for pesticide removal by a VFS, either as statistics of individual data or summarized in regression format, are used to evaluate the model predictions. For better serving this purpose, the available experimental data (Reichenberger et al., 2019) are further investigated for their representation of chemical properties and environmental conditions. As mentioned before, the field data are generally measured with water soluble pesticides (Figure 3), with a median K_d of 5.22 L/kg and the 90^{th} percentile of 110 L/kg over the 244 data points. There are only 17 data points, or 7% of the database, associated with K_d> 200 L/kg. Therefore, it's more appropriate to apply the regression equation (3) to pesticides with low or moderate adsorption with K_d< 200 L/kg, but not suitable to hydrophobic compounds such as pyrethroids. For the convenience of description, pesticides are classified according to their adsorption as,

- Low-K_d pesticides with K_d< 200 L/kg, including most of herbicides, neonicotinoids, organochlorines, and organophosphates. The equation (3) calibrated by Reichenberger et al. (2019) will be used to estimate the observed removal efficiency.
- High-K_d pesticides with K_d in the range of (200, 1000). A new regression equation (24) is developed in this study based on the 11 points with Kd> 200 (chlorpyrifos, pendimethalin, and permethrin).
- Extremely high-K_d pesticides with K_d> 1000. No sufficient experimental data are available for these pesticides, and thus no regression equation can be developed. Their removal efficiency by a VFS will be only modeled with mechanistic approach as demonstrated in the next section. More field measurements are needed for validation purpose.

Note that, unlike K_{OC} values, K_d is not specific to a pesticide but also related to the organic carbon content in soil. In this study, for example, chlorpyrifos under most of the PWC scenarios is associated with low K_d. However, the modeling set of chlorpyrifos-sugarbeet (K_d= 210.2) is considered with high value of K_d due to the high organic carbon content in the scenario (3.48% compared to 0.29-1.77% in other scenarios).

Based on the available experimental data (Reichenberger et al., 2019), 17 data points with K_d> 200 L/kg are extracted to build a new regression equation for high-K_d pesticides. The idea of separate regression equations for different adsorption levels has been implemented in previous studies, with a cutoff K_{OC} value of 9930 (Sabbagh et al., 2009) or 9000 (Chen et al., 2016), and significantly different regression equations were derived for the two groups of pesticides with K_{OC} lower or higher than the cutoff value. Compared to K_{OC}, K_d is a better predictor for phase

distribution by considering both the chemical property (K_{OC}) and soil property (organic carbon content).

Compared to pesticides with low K_d values, the reduction (ΔP) of high-Kd pesticides are more related to sediment reduction (ΔE). The correlation coefficients are 0.786 for all pesticides and 0.939 for those with Kd> 200 L/kg. Based on the 17 data points with Kd> 200 L/kg, a new regression model is developed (R^2= 94%),

$$\Delta P = -14.94 + 0.2786\Delta Q + 0.878\Delta E \quad (24)$$

Compared to the relationship calibrated with all pesticides, Eq. (3), the regression equation for high-Kd pesticides (> 200 L/kg) is associated with a higher coefficient on ΔE (0.878 vs. 0.4892), and generally predicts high ΔP compared to Eq. (3). Nash-Sutcliffe coefficient (NSE) suggests higher prediction performance by the new equation (NSE=0.94) vs. the previous one (0.80).

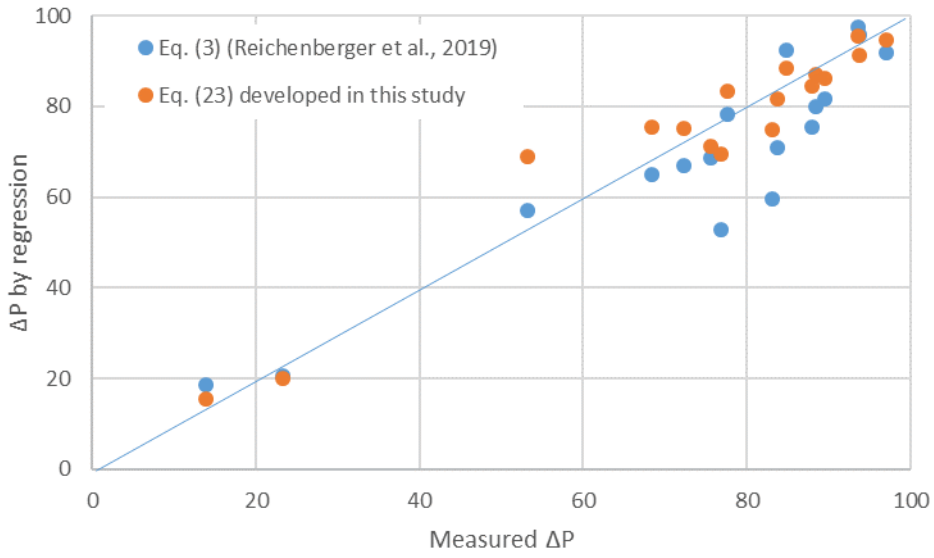

Figure 6. Comparison of the two regression equations for VFS removal efficiency of high-K_d pesticides, based on the 17 data points with K_d> 200 L/kg in the experimental dataset compiled by Reichenberger et al. (2019)

Based on the equations (3) and (24), a dataset of pesticide removal efficiencies (Table 5) can be generated from field measurements to validate the results from mechanistic modeling. Hydrological simulation results are taken from VFSMOD modeling under the 14 selected PWC scenarios (Figure 5). Together with the scenario-specific soil properties (organic carbon content and clay content), the predicted daily hydrologic variables from PRZM (Q_{in} and E_{in}) and VFSMOD (ΔQ and ΔP) are used to estimate the "observed" removal efficiency with Eq. (3) for Kd< 200 and Eq. (24) for K_d in (200, 1000).

Table 5. Pesticide removal efficiency by a VFS estimated by regression equations

Scenario	bif K_d	bif ΔP	chl K_d	chl ΔP	imi K_d	imi ΔP	perm K_d	perm ΔP
Alfalfa	4190.5	NA	106.9	51.4	4.7	44.7	1359.4	NA
Almond	1917.7	NA	48.9	72.8	2.2	68.7	622.1	93.0
Citrus	1089.1	NA	27.8	67.5	1.2	66.9	353.3	87.0
Cole crop	4119.5	NA	105.1	44.6	4.6	43.4	1336.3	NA
Corn	1373.2	NA	35.0	51.3	1.5	57.0	445.4	66.7
Cotton	686.6	65.2	17.5	60.3	0.8	60.2	222.7	72.5
Fruit	1373.2	NA	35.0	69.6	1.5	70.6	445.4	88.9
Grape	1680.9	NA	42.9	71.5	1.9	67.8	545.3	87.4
Lettuce	1716.4	NA	43.8	55.0	1.9	51.1	556.8	70.6
Row crop	4119.5	NA	105.1	50.5	4.6	48.2	1336.3	NA
Strawberry	1373.2	NA	35.0	67.8	1.5	67.1	445.4	89.3
Sugarbeet	8238.9	NA	210.2	49.9	9.3	49.6	2672.6	NA
Tomato	2249.1	NA	57.4	55.1	2.5	49.2	729.6	67.7
Wheat	1041.7	NA	26.6	56.6	1.2	57.3	337.9	80.0

Notes: [1] "bif"= bifenthrin, "chl"= chlorpyrifos, "imi"= imidacloprid, and "perm"= permethrin. [2] "NA" indicates K_d> 1000 for which no sufficient experimental data and regression equations available to estimate its removal efficiency. [3] Shaded cells suggest K_d in the range (200, 1000) and their ΔP values are estimated from Eq. (24), while other values are from Eq. (3) for K_d< 200. [4] This table presents results from hydrological simulations; some sets of pesticide-scenario may not be modeled for pesticide simulations, see more information in Table 6.

4.4 Pesticide removal efficiencies under PWC scenarios

For the pesticides and PWC scenarios selected in the case studies, the predicted removal efficiencies (ΔP) by a 10-ft VFS range from 41.2% to 98.9% (Table 6). Note that ΔP here is the overall mass reduction, calculated as the relative change between the total influent and total effluence masses of pesticide through the VFS during the 30-year simulation period. For a quick comparison, experimental dataset reported event-based efficiencies of pesticide removal in the range of 5.6-100%, with filter sizes of 0.5-20.1m (Reichenberger et al., 2019).

For each PWC scenario, there is a general increasing trend for ΔP from water-soluble to hydrophobic compounds. For example, predicted ΔP values for "cole crop" are 41.2% for imidacloprid, 47.8% for chlorpyrifos, 81.6% for permethrin, and 94.4% for bifenthrin (Table 6). This is related to the high sediment removal efficiency (ΔE) predicted for all scenarios (Figure 5). Most of the incoming particle-bound pesticide masses are trapped with sedimentation in a VFS. As a hydrophobic chemical, therefore, bifenthrin is predicted with high ΔP for all scenarios.

Table 6. Predicted efficiencies of pesticide removal (ΔP, %) by a 10-VFS under 14 PWC scenarios (f_{res}= 0 and f_{thr}= 0.4)

Scenario	Bifenthrin	Chlorpyrifos	Imidacloprid	Permethrin
Alfalfa	NA	50.8	NA	81.1
Almond	98.7	75.7	69.0	90.6
Citrus	97.2	73.3	67.3	91.9
Cole crop	94.4	47.8	41.2	81.6
Corn	81.3	53.8	NA	66.4
Cotton	76.7	NA	50.7	NA
Fruit	NA	75.3	70.9	92.4
Grape	98.9	NA	65.5	93.7
Lettuce	87.5	NA	52.5	73.6
Row crop	93.0	NA	48.7	87.0
Strawberry	90.4	71.5	70.2	81.2
Sugarbeet	NA	78.6	NA	NA
Tomato	80.6	NA	NA	67.2
Wheat	NA	54.6	NA	NA

Notes: To be consistent with USEPA's ERAs (USEPA, 2010, 2011, 2016a, b, 2017), some pesticide-scenario sets are not modeled (indicated by "NA").

For each pesticide-scenario set in this study, the model-predicted removal efficiency (Table 6) is compared to that estimated from the regression equation derived from experimental data (Table 5). Specifically, the modeling sets with K_d between 0 to 200 L/kg, including all scenarios with imidacloprid and most of scenarios with chlorpyfiros (except for the "sugarbeet" scenario, K_d= 210.19), are compared to the results from the regression equation (3). The modeling sets with K_d between 200 to 1000 L/kg (i.e., most of scenarios with permethrin and the "sugarbeet" scenario with chlorpyrifos), are compared with the results from the newly derived equation (24) for high-K_d pesticides. Except for the "cotton" scenario (K_d= 686.6), modeling results for bifenthrin are not considered for validation since there are not relevant experimental data to estimate its removal efficiency in a VFS.

In summary, modeling sets of pesticide and scenario with K_d< 1000 are validated with the corresponding removal efficiency summarized from regression equations over field measurements (Figure 7). The Nash-Sutcliffe coefficient (NSE) between the predictions and the observations (estimated by the regression equations) is 0.89 for all data in Figure 7, or 0.87 for chlorpyrifos, 0.87 for imidacloprid, and 0.81 for permethrin. Higher uncertainty is associated with Eq. (24), to which the results of bifenthrin and permethrin are compared. Only 17 experimental data points are available for building Eq. (24), compared to 244 points for Eq. (3) used in the validation of the model predictions for chlorpyrifos and imidacloprid. The model performance is also affected by the interacting factor (f_{thr}), which will be discussed in Section 4.6.

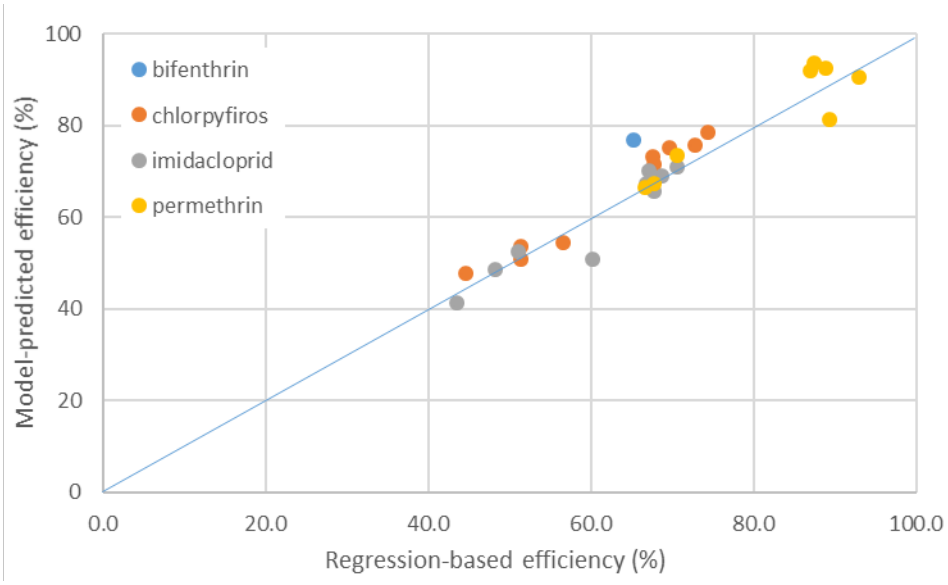

Figure 7. Model validation on the predicted pesticide removal efficiency for pesticide-scenario sets with K_d< 1000 L/kg, based on Table 5 and Table 6.

Bifenthrin and permethrin under some PWC scenarios have higher K_d values (up to 8238.9 L/kg) than those with the experimental data. The model-predicted ΔP values for bifenthrin (77-99%, Table 6) are significantly higher than those from the regression equations (3) (45-83%) or (24) (63-93%) which was developed based on relatively lower K_d values. This is consistent with the conclusion from (24), where the regression relationship is re-calibrated with a subset of the experimental database with K_d> 200, and the new equation generates higher ΔP values and better performance relative to that built from all data. In summary, it's reasonable to expect a higher VFS removal efficiency for bifenthrin (and other hydrophobic pesticides) than that from the existing empirical trapping equations, and more field data are needed to validate the model predictions for bifenthrin.

4.5 Effects of resuspension

In addition to the results with f_{res}= 0 (no resuspension of previously deposited solids, Table 6), model simulations are conducted with f_{res}= 1-ΔE (the maximum resuspension), and their differences of predicted pesticide removal efficiencies are plotted in Figure 8. For most of the modeling sets, the results without resuspension are equal to or smaller than those with the maximum resuspension and thus represent conservative estimation of removal efficiency by a VFS. For chlorpyrifos and imidacloprid, the differences range from 0-1.3%, with median value of 0, indicating that removal efficiency for water-soluble or moderately soluble pesticides are not sensitive to resuspension. This conclusion is also applied to bifenthrin and permethrin under most of the modeled scenarios, except for "corn", "cotton", "lettuce", and "tomato".

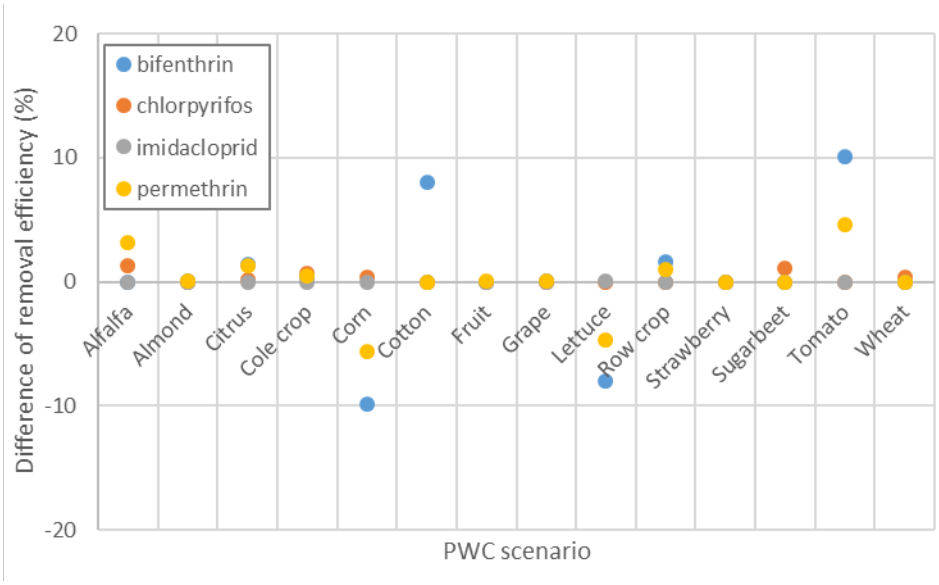

Figure 8. Difference between the predicted pesticide removal efficiencies with f_{res}= 0 (no resuspension) and f_{res}= 1-ΔE (the maximum resuspension). Positive values indicate higher removal efficiency with more resuspension modeled.

Further investigations result in the following findings for the sensitivity of predicted ΔP on resuspension (f_{res}):

1) Soil adsorption (K_d) of the pesticide-scenario set and sediment removal efficiency (ΔE) by the VFS determine the magnitude of the sensitivity.
    a. Resuspension mainly affects the predicted removal efficiency for hydrophobic pesticides (bifenthrin and permethrin in this study), while more water soluble pesticides are generally insensitive to the value of f_{res}.
    b. In addition, the impact of resuspension is predicted with relatively low sediment removals. This explains the fact that the differences on ΔP are predicted for the scenarios of "corn" (ΔE= 75.6%), "cotton" (85.2%), "lettuce" (81.1%), and "tomato" (82.2%), but not for other scenarios with ΔE> 90%.
2) The incoming sediment concentration (TSS) determines the sign (positive or negative) of the sensitivity. The median TSS is 0.8 kg/m^3 over the modeled 14 scenarios. The "corn" and "lettuce" scenarios are associated with much higher TSS of 4.7 and 5.8 kg/m^3, respectively, and the predicted ΔP for bifenthrin is decreasing with f_{res} (i.e., the more the resuspension, the less efficient the pesticide removal. For the "cotton" and "tomato" scenarios with the low TSS of 0.2 and 0.3 kg/m^3, respectively, the predicted ΔP for bifenthrin and permethrin significantly increases with more resuspension (Figure 8).

For model applications, therefore, it's recommended that the model run without resuspension (f_{res}= 0) be first conducted for any pesticide and field conditions. For pyrethroids or other hydrophobic compounds, in addition, if the edge-of-field runoff is associated with high sediment concentrations according to PWC modeling or field measurements, additional model run is needed with the maximum possible resuspension (f_{res}= 1-ΔE). If the 2nd model run predicted a

lower ΔP than the 1st run, the lower value should be reported for the pesticide removal efficiency for regulatory evaluation on VFS mitigation effects.

4.6 Effects of runoff interaction

Table 6 shows the modeling results with 40% runoff interacting with the soil mixing layer in a VFS, or f_{thr}= 0.4. There is a general increasing trend for the predicted pesticide removal efficiency with the interacting fraction. Figure 9 shows an example of the model predictions under the "almond" scenario with fthr changing from 0.0 (no through flow or Q_{thr}= 0) to 1-ΔQ (the maximum interaction or Q_{thr}= Q_{out}, Figure 4). Results are presented as relative values to the predicted ΔP with f_{thr}= 0. Compared to bifenthrin and permethrin, predicted ΔP of chlorpyrifos and imidacloprid are more sensitive to the interacting fraction. Under the "almond" scenario, the maximum runoff interaction would increase the removal efficiency by 1.4 (chlorpyrifos) to 1.5 (imidacloprid) times compared to that predicted without runoff interaction.

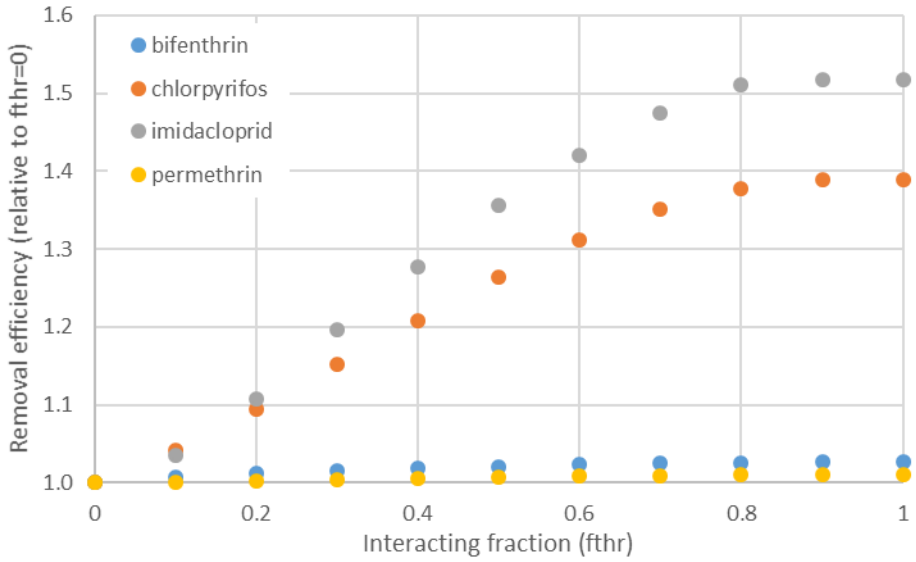

Figure 9. Predicted pesticide removal efficiency with runoff interacting fraction (f_{thr}), shown as relative values to the efficiency predicted with f_{thr}= 0 (no through flow).

Since there is no direct field measurements for the runoff interaction and pesticide extraction, the parameter f_{thr} is determined based on available experimental data on pesticide removal efficiency by a VFS. Similar to the model validation (Figure 7, fthr= 0.4), the modeling results with fthr= 0.3 and 0.5 are compared to the observation dataset prepared in Table 5. Both simulations have lower modeling performance, NSE= 0.774 for f_{thr}= 0.3 and NSE= 0.766 for f_{thr}= 0.5, than the previous one with f_{thr}= 0.4 (NSE= 0.892). A high f_{thr} would result in overestimation of the pesticide removal efficiency, while modeling results with low f_{thr} underestimates it. For the modeling sets used for validation (Figure 7), the average values of predicted ΔP are 64.8% with f_{thr}= 0.3, 68.6% with f_{thr}= 0.4, and 72.3% with f_{thr}= 0.5, compared observed value of 67.2%. Therefore, an interacting fraction of 0.4 is recommended for VFS modeling under the PWC scenarios in California. As expected, this value is higher than the interacting fractions for

agricultural fields calibrated with field measurements as 0.266 (Young, 2016b) or 0.19 (Young and Fry, 2017).

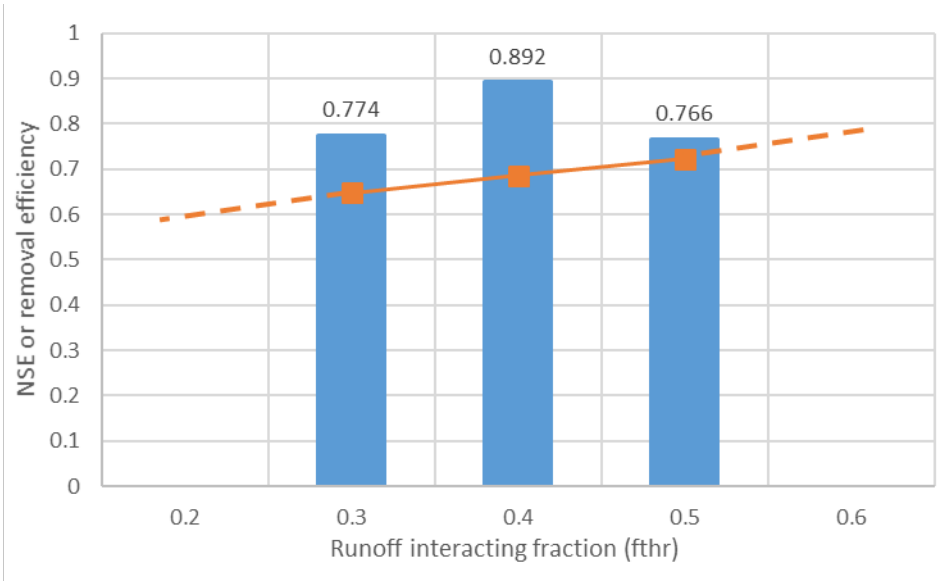

Figure 10. Effects of the interacting fraction (f_{thr}) on the modeling performance (Nash-Sutcliffe efficiency, NSE, as the blue bars) and average values of predicted pesticide removal efficiencies (orange line)

5 Conclusion

The PWC-VFS modeling framework has been improved in this study with a fully mechanistic approach for pesticide simulations in a VFS. Physically-based modeling is used to systematically formulate the simultaneous pesticide transport processes in the runoff-soil interaction. Compared to previous methods for pesticide trapping and extraction in a VFS, the new approach does not prescribe a certain amount of pesticide mass transport between soil and the overlying runoff, and the modeling performance is not affected by regression coefficients varying with available experimental data. The resulting equations for pesticide removal efficiency, Eq. (20), also extend the previous semi-mechanistic method ($\Delta P_d = \Delta Q$ and $\Delta P_p = \Delta E$) to more general field conditions.

The updated PWC-VFS model is demonstrated in case studies with 4 widely-used pesticides (bifenthrin, chlorpyrifos, imidacloprid, and permethrin) under 14 PWC scenarios in California. Model-predicted ΔP is generally not sensitive to the simulation of resuspension of solids and associated pesticides. Therefore, model simulations without resuspension are suggested for conservative estimation of pesticide removal by a VFS, except for hydrophobic pesticides and high sediment loadings. Predicted ΔP values for modeling sets with $K_d < 1000$ (chlorpyrifos, imidacloprid, and some scenarios with permethrin) are compared with experimental data, while there are no sufficient field measurements for the cases with $Kd > 1000$ (bifenthrin in this study).

For PWC scenarios in California, the results of model validation recommend a runoff interaction fraction of 0.4 (i.e., 40% runoff will interact with and extract pesticide from the soil mixing layer), which generates the best modeling performance (NSE= 0.89).

Acknowledgments

The author acknowledges Yina Xie, Xuyang Zhang, Jennifer Teerlink, Kean S. Goh, Nan Singhasemanon, and Edgar Vidrio with California Department of Pesticide Regulation for comments and reviews on the current and previous development of VFS modeling. The author thanks Dirk Young (USEPA), Rafael Muñoz-Carpena (University of Florida), Marty Williams and Amy Ritter (Waterborne Environmental, Inc.), Jane Tang and Oscar Perez-Ovilla (Bayer), Minghua Zhang and Jessica Chen (UC Davis), and Eric Henry (BASF) for valuable discussions in the initialization and development of this study.

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