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Predicting pesticide removal efficacy of vegetated filter strips: A meta-regression analysis

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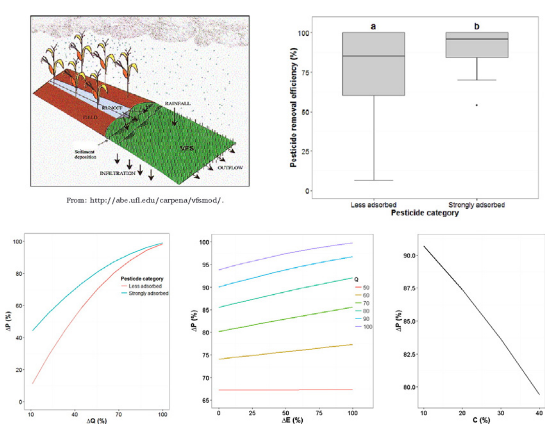
HIGHLIGHTS

- A meta-regression model for predicting VFS pesticide removal efficacy was built.
- The model was developed and tested by a set of statistical metrics.
- Pesticide adsorption property was significant in explaining VFS efficacy.
- Interactions among hydrological and pesticide adsorption processes were significant.

GRAPHICAL ABSTRACT



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ABSTRACT

Vegetated Filter Strips (VFS's) are widely used for alleviating agricultural pesticide loadings to surface water bodies. However, effective tools are lacking to quantify the performance of VFS's in reducing off-site pesticide transport. In this study, we applied meta-regression to develop a model for predicting VFS pesticide retention efficiency based on hydrologic responses of VFS's, incoming pollutant characteristics and the interaction within and between these two factor groups ($R^2 = 0.83$). In cross-validation analysis, our model ($Q^2 = 0.81$) outperformed the existing pesticide retention module of VFSMOD ($Q^2 = 0.72$) by explicitly accounting for interaction effect and the categorical effect of pesticide adsorption properties. Based on the 181 data points studied, infiltration had a leading, positive influence on pesticide retention, followed by sedimentation and interaction between the two. Interaction between infiltration and pesticide adsorption properties was also prominent, as the influence of infiltration was significantly lower for strongly adsorbed pesticides. In addition, the clay content of incoming sediment was negatively associated with pesticide retention. Our model is not only valuable in predicting VFS performance, but also provides a quantitative characterization of the interacting VFS processes, thereby facilitating a deeper understanding of the underlying mechanisms.

1. Introduction

The use of pesticides to manage pest infestation has been a common agricultural practice worldwide for decades. From 2005 to 2009, over

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6.5 billion kg of pesticides were applied annually on global agricultural lands (FAO, 2015). Off-site movement of pesticides into surface water bodies was observed, and in many cases, pesticides were detected at concentrations exceeding water-quality criteria, thus posing severe threats to aquatic organisms and human health (Reichenberger et al., 2007; Zhang and Goodhue, 2010). In California's Central Valley, for instance, pesticides residues are routinely detected in surface water at concentrations exceeding US EPA Aquatic Life Benchmarks (Starner and Zhang, 2011). Surface runoff is one of the primary pathways by which pesticides are transported. Edge-of-field losses of pesticides carried by surface runoff can be more than 10% of the amount of pesticides applied when severe rainfall occurs soon after pesticide application (Schulz, 2004). In order to ensure surface water quality, growers and regulators need to develop effective mitigation plans to reduce off-site transport of pesticides from croplands.

Vegetated filter strips (VFS's) are a best management practice for alleviating agricultural pesticide loadings to surface water bodies (FOCUS, 2007; USDA-NRCS, 2013; USDA-NRCS, 2015; USEPA, 2002). They are strip(s) of vegetation typically placed at the lower edge of a field to intercept surface runoff. As runoff passes through a VFS system, the erect vegetation stems pose an abrupt increase in hydraulic resistance to surface flows. Consequently, the runoff flow velocity is reduced which promotes infiltration and decreases the sediment transport capacity of flow. Sediment deposition occurs when the reduced transport capacity is less than the inflow sediment loads (Barfield et al., 1979). Pesticides transported in the dissolved phase are removed from surface runoff through infiltration into the soil matrix while sediment-bound pesticides settle out of the flowing water through sedimentation. Sorption to the soil surface, vegetation leaves, stems and residues are also important mechanisms for pesticide retention. Pesticides trapped within a VFS are subject to subsequent degradation, which is enhanced by higher microbial activities occurring in the presence of perennial vegetation (Krutz et al., 2005).

VFS's have been implemented across the world for decades, demonstrating their effectiveness in water quality improvement (Arora et al., 2010; Krutz et al., 2005; Norris, 1993). However, considerable variation in VFS pesticide removal efficacy was observed in experimental studies. In herbicide runoff studies, pesticide removal efficiency of VFS's of two drainage to buffer area ratio treatments of 15:1 and 30:1 ranged from 8 to 100% under natural rainfall (Arora et al., 1996) and from 47 to 83% in simulated runoff (Arora et al., 2003). For different filter lengths (the dimension parallel to runoff flow), inflow rates and herbicide concentration, herbicide reduction varied between 46 and 92% (Klöppel et al., 1997). VFS's built with varying vegetation species and lengths removed herbicides and insecticides by 32 to 96% (Schmitt et al., 1999). As VFS length increased, VFS atrazine removal efficiency increased from 44 to 100% (Patty et al., 1997) and from 31 to 80% (Mickelson et al., 2003), whereas short VFS's with lengths of 0.5 to 4 m (Tingle et al., 1998) and 3 m (Otto et al., 2012) were effective in removing herbicides by at least 80%. Trapping percentages of herbicides were above 90% for VFS's located in a karst watershed with high infiltration capacity (Barfield et al., 1998), and ranged from 40 to 85% for VFS's constructed on cracking vertisol soils (Popov et al., 2006). Flow concentration reduced VFS's removal efficacy of chlorpyrifos and atrazine from 85% to 21%, and from 62% to 12%, respectively (Poletika et al., 2009).

Such large variation in VFS performance is mainly attributed to the multiplicity of processes and factors involved in VFS pesticide removal (Lacas et al., 2005). The major processes that contribute to VFS pesticide removal have been identified as infiltration, deposition, sorption and degradation (Krutz et al., 2005; Zhang et al., 2010). The key factors that influence these processes can be divided into two categories: (1) properties of a VFS system, such as filter length, slope, soil texture, structure and antecedent moisture, and vegetation height, density and species; and (2) properties of pollutant inflow, such as rate and amount of rainfall and surface runoff, sediment particle size distribution, and the solubility, hydrophobicity and degradation rate of the pesticides.

Empirical equations have been developed to estimate VFS efficacy based on filter properties such as length and slope (Neitsch et al., 2005; Zhang et al., 2010). However, these equations can only include a limited number of factors and therefore often fail to adequately characterize VFS performance. This limitation has been partially addressed through an effort to incorporate VFS hydrological responses as explanatory variables in calculating the VFS pesticide retention efficiency (%), ΔP (Sabbagh et al., 2009):

$$\Delta P = 24.79 + 0.54(\Delta Q) + 0.52(\Delta E) - 2.42\ \ln\left(F_{ph} + 1\right) - 0.89(C)$$

where ΔQ, ΔE, F_{ph} and C represent runoff volume reduction (%), sediment mass reduction (%), pesticide phase distribution factor (fraction of dissolved over sediment-bound pesticide mass in inflow) and clay content of incoming sediment (%), respectively. Recently, this equation has been integrated into the Vegetated Filter Strips Modeling System (VFSMOD), a 1-D, field-scale model that routes the incoming runoff through a VFS and predicts its pollutant trapping efficiency (Muñoz-Carpena et al., 1999; Muñoz-Carpena and Parsons, 2014). The hydrologic responses of a VFS system (ΔQ and ΔE) are simulated by the hydrology and sediment filtration modules of VFSMOD and then fed into the pesticide retention equation for calculating the final ΔP.

The pesticide module of VFSMOD has shown its potential in predicting VFS pesticide removal efficacy (Poletika et al., 2009; Sabbagh et al., 2009; Winchell et al., 2011). However, it has been found that for strongly adsorbed pesticides, only F_{ph} and ΔE remained significant whereas for weakly to moderately adsorbed pesticides, ΔQ was the only significant predictor (Sabbagh et al., 2009). Nevertheless, the model development team proposed the single empirical equation as robust for all pesticides. One modification which may improve predictive accuracy is to replace the continuous variable (F_{ph}) with a categorical variable to specify the impact of pesticide adsorption properties, as observed in the literature (Arora et al., 2010; Krutz et al., 2005; Reichenberger et al., 2007). The original model also excludes interaction between explanatory variables, which has been widely recognized as critical in determining VFS performance. Arora et al. (2010) concluded from their literature review that the relationships between ΔQ and ΔE with ΔP were largely dependent on pesticide adsorption properties. For strongly adsorbed pesticides, ΔP has a relatively strong association with ΔE while for moderately to weakly adsorbed pesticides, ΔP is mainly dependent on ΔQ (Krutz et al., 2005). Infiltration also interacts with adsorption/sedimentation processes. Popov et al. (2006) observed that adsorption/sedimentation played a more important role in trapping herbicides at low flow depth. Therefore, by reducing flow depth, higher ΔQ is likely to lead to stronger associations between ΔE and ΔP.

Meta-analysis is a powerful statistical method of research synthesis for creating generalizations from the results of many separate experiments (Koricheva et al., 2013). The goal of this study is to develop a model to predict VFS pesticide removal efficacy using a meta-regression approach. Specifically, the objectives include: (1) extracting and aggregating data from the literature for model development and validation; (2) testing the significance of pesticide adsorption properties in explaining variation in VFS pesticide retention; and (3) exploring interaction among hydrologic processes occurring in VFS and incoming pollutant characteristics. A set of statistical metrics (adjusted R^2, Mallow's C_p, $AICc$, BIC, F statistic of general linear test and Q^2 of cross validation) were applied to ensure the robustness of the proposed regression model. This study is the first modeling effort which explicitly and quantitatively accounts for the impacts of (1) pesticide adsorption categories, and (2) interactions among VFS hydrologic processes and incoming pollutant properties on VFS pesticide removal efficacy. The developed model not only serves as a valuable tool for predicting VFS performance, but also contributes to a deeper understanding of the complex, interacting VFS processes and factors responsible for pesticide retention.

2. Materials and methods

2.1. Variable selection

In this study, five factors were initially determined as essential for model development. These include ΔQ (runoff volume reduction, %), ΔE (sediment mass reduction, %), C (clay content of incoming sediment, %), *Cat* (pesticide category), L (VFS length, m) and the response variable ΔP (pesticide mass reduction, %). Other VFS construction parameters, such as slope and soil texture, were not included in this analysis since (1) they are partially incorporated in VFS hydrologic responses (ΔQ and ΔE), and (2) we tried to limit the number of variables used for VFS performance prediction. Reduction was calculated as the difference between the inflow and outflow quantities divided by the inflow quantity. Pesticides were divided into two categories (Sabbagh et al., 2009): strongly adsorbed ($K_{oc}>9000$ ml/g) and weakly to moderately adsorbed pesticides ($K_{oc}\leq 9000$ ml/g). The general framework of the model serves as a critical basis for developing literature selection criteria.

2.2. Literature review and data extraction

Eight studies published through 2007 were taken from a previous review of this topic (Sabbagh et al., 2009). A systematic literature review was conducted to find more recent studies using the following scientific databases and web search engine: Melvyl, Scopus, Web of Science and Google scholar. Abstract-based relevance screening was first applied using the following key words: vegetated filter strip or vegetated buffer, pesticide, and runoff. The selected studies were further screened to exclude studies that contained insufficient information on the variables of interest (i.e. ΔQ, ΔE, C, *Cat*, L, ΔP). Finally, a total of 16 studies that satisfied our screening criteria were included in this meta-analysis, 8 studies from Sabbagh et al. (2009) and the other 8 studies selected in our review (Table 1). These studies were carefully examined to record the quantities or levels of ΔQ, ΔE, C, *Cat*, L and ΔP and other general information such as author, year, location, pesticide chemical, soil type and vegetation species. A total of 181 data points were collected for the subsequent analyses. The study areas of the compiled data set encompassed the middle and eastern USA, western and central Europe, and Australia.

2.3. Data set characteristics

Table 2 summarizes the continuous variables included in the full model. Great variation was observed in VFS removal efficiency of water (ΔQ), sediment (ΔE) and pesticides (ΔP), which ranged from 0 to 100%. The clay content of the incoming sediment (which approximates the clay content of soil in the upslope source area) varied between 6 and 45%, encompassing the common range for agricultural soil. The maximum length of VFS (L) recorded was 20.1 m, which was less than the 30-m optimal length reported by Zhang et al. (2010). Based on our study data, however, ΔP was substantially negatively skewed and 100% pesticide reduction was frequently observed (Table 2). In other words, although less than 30 m, the VFS's included in our data set were able to achieve considerable pesticide reduction in many cases, making the applicability domain of our model large enough for practical use.

2.4. Statistical analysis

Data extracted from the selected studies were analyzed using a set of statistical procedures. Distributions and relationships among variables were visually inspected using scatterplot matrix. Box-and-whisker plot was created to examine the distribution of ΔP by pesticide category. As ΔP is not normally distributed, the non-parametric Mann–Whitney U test was applied to compare the differences in the mean ranks between strongly and weakly to moderately adsorbed pesticides at significance level of 0.01.

Meta-regression is essentially multiple regression but applied to investigate the effects of explanatory variables across different studies (Borenstein and Wiley, 2009). This approach is frequently used in meta-analysis. In this study, meta-regression was conducted to examine the relationships between VFS pesticide removal efficacy and the explanatory variables. Initially we planned to apply a mixed effect model that incorporates random effects to account for heterogeneity across studies (Chow, 2013). However, most studies did not have replications or did not report within-study variation, making it impossible to accurately estimate between-study variation. Therefore, a fixed effect model was employed in this study. As the distribution of ΔP was negatively skewed, reflection and square root transform was applied

Table 1
Summary of the experimental studies used for development and evaluation of the VFS pesticide retention model.

Study	Location	VFS length (m)	Pesticide chemical	Soil type	Vegetation species	Sample size
Arora et al. (2003)	IA, USA	20.1	Atrazine, metolachlor, chlorpyrifos	Loam	Brome grass, blue grass	6
Arora et al. (1996)	IA, USA	20.1	Atrazine, metolachlor, cyanazine	Silty clay loam	Smooth brome grass	6
Barfield et al. (1998)	KY, USA	4.6, 9.1, 13.7	Atrazine	Silt loam	Bluegrass and fescue sod	12
Boyd et al. (2003)	IA, USA	20.1	Atrazine, acetochlor, chlorpyrifos	Silty clay loam	Brome	6
Klöppel et al. (1997)	Germany	10, 20, 15	Terbuthylazine, isoproturon, dichlorprop-p	Silt loam	Grass	21
Mersie et al. (1999)	VA, USA	2	Atrazine, metolachlor	Sandy loam	Switchgrass	2
Mickelson et al. (2003)	IA, USA	4.6, 9.1	Atrazine	Sandy loam	Brome, Kentucky bluegrass	4
Misra et al (1996)	IA, USA	12.2	Atrazine, metolachlor, cyanazine	Loam	–	12
Patty et al. (1997)	France	6, 12, 18	Lindane, atrazine, isoproturon, diflufenican	Silt loam	Rye grass	18
Pätzold et al (2007)	Germany	6, 12	Metolachlor, terbuthylazine, pendimethalin	Silt loam	Pasture	42
Poletika et al. (2009)	IA, USA	4.6	Atrazine, chlorpyrifos	Silty clay loam	Brome	8
Popov et al. (2006)	Australia	4	Atrazine, metolachlor	Clay	Wallaby grass	12
Rankins et al (2001)	MS, USA	0.3	Fluometuron, norflurazon	Silty clay	Big bluestem, eastern gamagrass, switchgrass, tall fescue	8
Schmitt et al. (1999)	NE, USA	7.5, 15	Atrazine, alachlor, permethrin	Silty clay loam	25-yr-old mixed grass, 2-yr old switchgrass and tall fescue	12
Seybold et al. (2001)	VA, USA	3	Atrazine, metolachlor	Clay loam	Switchgrass	2
Tingle et al. (1998)	MS, USA	0.5, 1, 2, 3, 4	Metolachlor, metribuzin	Silty clay	Tall fescue	10

Table 2
Statistical summary of the continuous variables included in the full model (ΔQ, runoff volume reduction; ΔE, sediment mass reduction; C, clay content of incoming sediment; L, VFS length; ΔP, pesticide mass reduction).

	ΔQ (%)	ΔE (%)	C (%)	L (m)	ΔP (%)
Minimal	0.0	0.0	6	0.3	6.7
First quartile	51.2	66.4	20	4.6	68.0
Median	75.0	91.3	25	10.0	89.0
Mean	71.0	71.9	27	9.8	79.4
Third quartile	93.2	99.6	30	12.2	100
Maximum	100	100	45	20.1	100

(Tabachnick and Fidell, 2007):

$$\Delta P_t = \sqrt{\max(\Delta P) + 1 - \Delta P}.$$

The essence of model development is to strike a balance between the precision of the fit and the number of parameters/variables used to obtain the fit. Although adding variables is likely to improve fitting to the training data set, it could also lead to overfitting which occurs when a model describes random error instead of the mean response. Therefore, model adequacy indicators (adjusted R^2, Mallow's C_p, *AICc*, *BIC* and general linear test) were applied for selecting the most parsimonious set of model variables (Table 3). Both adjusted R^2 and Mallow's C_p are techniques for model selection in regression analysis. Adjusted R^2 is calculated by adjusting R^2 for the loss of degrees of freedom (Theil, 1961). It is generally considered as a quick and easy method for model comparison. Mallow's C_p is an estimate of the standardized mean squared error (*MSE*) of the ordinary least squares estimator $\boldsymbol{b} = (\boldsymbol{X}'\boldsymbol{X})^{-1}(\boldsymbol{X}'\boldsymbol{Y})$ (Mallows, 1973). The optimal subset of predictors is selected with considerations of sample size, effect sizes of predictors, and the degree of collinearity. Both the Akaike's Information Criteria (*AIC*) and the Bayesian Information Criteria (*BIC*) are penalized-likelihood criteria for model selection. As an information-theoretic metric, *AIC* selects the model that minimizes the expected, relative Kullback–Leibler information loss, and is useful in selecting the best model among all competing models (Burnham and Anderson, 2002; Burnham and Anderson, 2004). Its corrected version, *AICc*, is introduced to adjust for small sample size (Burnham and Anderson, 2004). *BIC* is calculated by maximizing the posterior probabilities of alternative models, given the observations (Irizarry, 2001). *BIC* places heavier penalty on models with many variables, resulting in smaller models than Mallow's C_p and *AIC* (James et al., 2014). General linear test using *F* statistic is another frequently used approach for model selection. It can be applied to test whether at least one of the extra variables included in the full model is useful for prediction (Jennings, 2015). The full model included all of the variables and first-order interactions:

$$\text{Full model}: \Delta P_t = f(\Delta Q, \Delta E, C, Cat, L).$$

Exhaustive search algorithm was applied to extract all possible regressions reduced from the full model. These reduced models were then assessed using model adequacy indicators.

After the identification of the best model, statistical diagnostic tests were applied to determine whether all the necessary model assumptions were valid before performing inference. A Q–Q plot of residuals, a histogram of residuals and plots of residuals vs. fitted values and explanatory variables were used to examine the normality and constant variance assumptions. Partial regression plots (also known as "added variable plots") were applied to check the assumption of linearity. In addition, Cook's distances were compared to the *F*-distribution to identify influential observations that might distort the outcome and accuracy of a regression. The variance inflation factor (*VIF*) was employed to assess the degree of multicollinearity between explanatory variables. For model validation, we could not split the data set into independent training and validation data sets as there were only 33 data points for strongly adsorbed pesticides. Therefore, six-fold cross validation was performed by first randomly dividing the sample into six groups and calculating the average statistic from regressing five groups to estimate the remaining one group (James et al., 2014). The statistic used to represent model predictive ability was the predictive squared correlation coefficient Q^2 (Consonni et al., 2009; Consonni et al., 2010):

$$Q^2 = 1 - \sum_{i=1}^{n_{VAL}} \left(\frac{\left(\hat{y}_i - y_i\right)^2 / n_{VAL}}{\sum_{i=1}^{n_{TR}} \left(y_i - \overline{y_{TR}}\right)^2 / n_{TR}} \right.$$

where $\hat{y}_i$, y_i and n_{VAL} in the numerator are the *i*th prediction, observation and sample size of the validation data set, and y_i, $\overline{y_{TR}}$ and n_{TR} in the denominator are the *i*th observation, mean observation and sample size of the training data set. Q^2 can be considered as analogous to R^2 with values near one being desirable. Cross validation was performed 50 times using the data set complied in this study and the average values of Q^2 were recorded for both the developed model and the current VFSMOD pesticide module.

The effect display concept was applied for interpreting and displaying the main effects and interactions among predictors (Fox, 2003). This method is most useful when a complex model structure is under consideration (i.e. polynomial term and/or interaction term in presence). The general procedure is to combine high-order terms with their lower-order relatives (in our case, main effects marginal to an interaction) and allow the predictors appearing in the high-order terms to vary over all possible values, with other predictors fixed at mean values. All the statistical analyses and data visualization were performed in *R*, a free and versatile software environment for scientific computation (R Development Core Team, 2015).

Table 3
Summary of indicators and criteria used for model selection.

Model adequacy indicator	Criterion
$R_a{}^2 = 1 - \frac{MSE}{\frac{SSTotal}{n-1}}$	Proximity to unity
$C_p = \frac{SSE_p}{MSE_F} + 2p - n$	Low C_p that is close to p; Large difference in C_p between the two best models for a given number of variables
$AIC = n \cdot\ , \ln\left(\frac{SSE_p}{n}\right) + 2p$ $AICc = AIC + 2 \cdot p \cdot \frac{p+1}{n-p-1}$	Lowest value
$BIC = n \cdot\ , \ln\left(\frac{SSE_p}{n}\right) + p \cdot\ , \ln(n)$	Lowest value
$F = \frac{\frac{\Delta SSE}{\Delta dfe}}{MSE_F} = \frac{\frac{SSE_R - SSE_F}{dfe_R - dfe_F}}{MSE_F}$	H_0: reduced model; H_a: full model; $\alpha = 0.05$

Note: *SSE*, *dfe*, *MSE*, *SSTotal* and *n* are the sum of squared errors, degree of freedom for error, mean squared error, total sum of squares and sample size of the regression equation, and subscripts *R*, *F* and *p* denote the reduced model, full model and model with *p* regressors.

3. Results

3.1. Distributions and relationships among variables

The distributions and relationships among ΔQ, ΔE, C, L and ΔP are displayed in Fig. 1. As noted above, ΔQ, ΔE and ΔP were negatively skewed, and the skewness of ΔP was largely alleviated after reflection and square root transform. ΔQ showed a strong, positive, linear impact on ΔP, while the isolated effects of ΔE, C, and L were not prominent. Distributions of VFS pesticide removal efficacy are shown in Fig. 2, grouped by pesticide category. In this study, there were 33 and 148 data points for strongly and weakly to moderately adsorbed pesticides, respectively. Results from Mann–Whitney U test indicated that VFS pesticide removal efficiency was significantly higher for strongly adsorbed pesticides than for weakly to moderately adsorbed pesticides, as documented in previous studies (Arora et al., 2010; Krutz et al., 2005; Reichenberger et al., 2007).

3.2. Model development and evaluation

The relationships between model adequacy and the number of predictors are shown in Fig. 3. Both Mallow's C_p and BIC suggested the model with 6 predictors was optimal, whereas adjusted R^2 and $AICc$ indicated the models with 12 and 9 predictors, respectively, were preferred. However, the model with 6 predictors was chosen at this step as adjusted R^2 and $AICc$ gradually stabilize at the model size of 6. In addition, the model of smaller size was preferred as we hoped to limit the number of predictors in order to reduce the degree of collinearity. After applying the general linear test using the F statistic and further adjustment based on diagnostic tests, the final model was developed (Table 4).

In this study, VFS length was not a significant factor in explaining variation in VFS pesticide removal efficacy. Therefore, it was excluded from the final model. The overall goodness-of-fit was satisfactory, with R^2 of 0.83, P-value less than 0.001 (Table 4) and points aligned with the 1:1 line in the scatterplot of model predictions vs. observations (Fig. 4). The result of the six-fold cross validation is illustrated in Fig. 5. In general, the model fitted through cross validation performed equally well as the model fitted using the whole data set, although there was slightly more discrepancy between model predictions and observations (Fig. 5). Our final model obtained an average Q^2 of 0.81, whereas the current VFSMOD pesticide module only attained a value of 0.72. Similar to R^2, Q^2 calculates the proportion of variation (in the validation data set) that the model (with parameters estimated from the training data set) is able to explain. In most environmental studies, a R^2 (therefore Q^2) value greater than 0.5 is considered desirable (Chinkuyu et al., 2004). Although the predictive powers of both models are within the acceptable range, the major advance in our study is that we demonstrated and quantified the importance of interacting VFS processes in explaining VFS performance, which is presented in the next section.

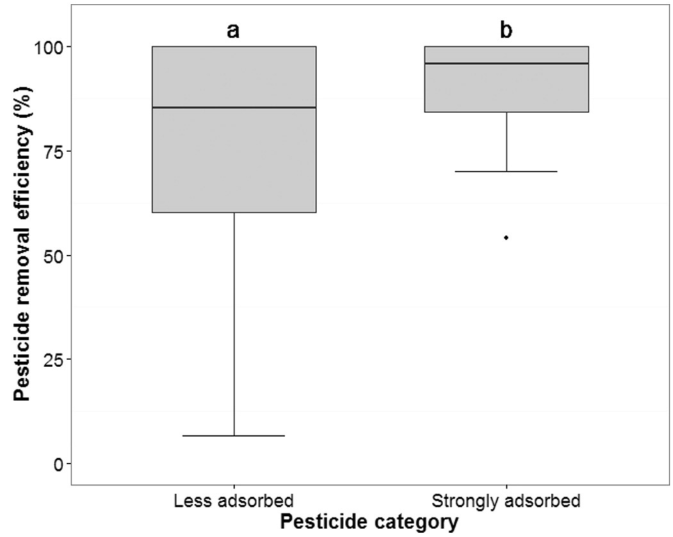

Fig. 2. Pesticide removal effectiveness of VFS by pesticide category. The central rectangle spans the first to the third quartile. The upper/lower whisker extends to the highest/lowest value that is within 1.5 ∗ inter-quartile range. The mean ranks of pesticide groups differ significantly, as denoted by different letters (Mann–Whitney U test on ranks, P = 0.008).

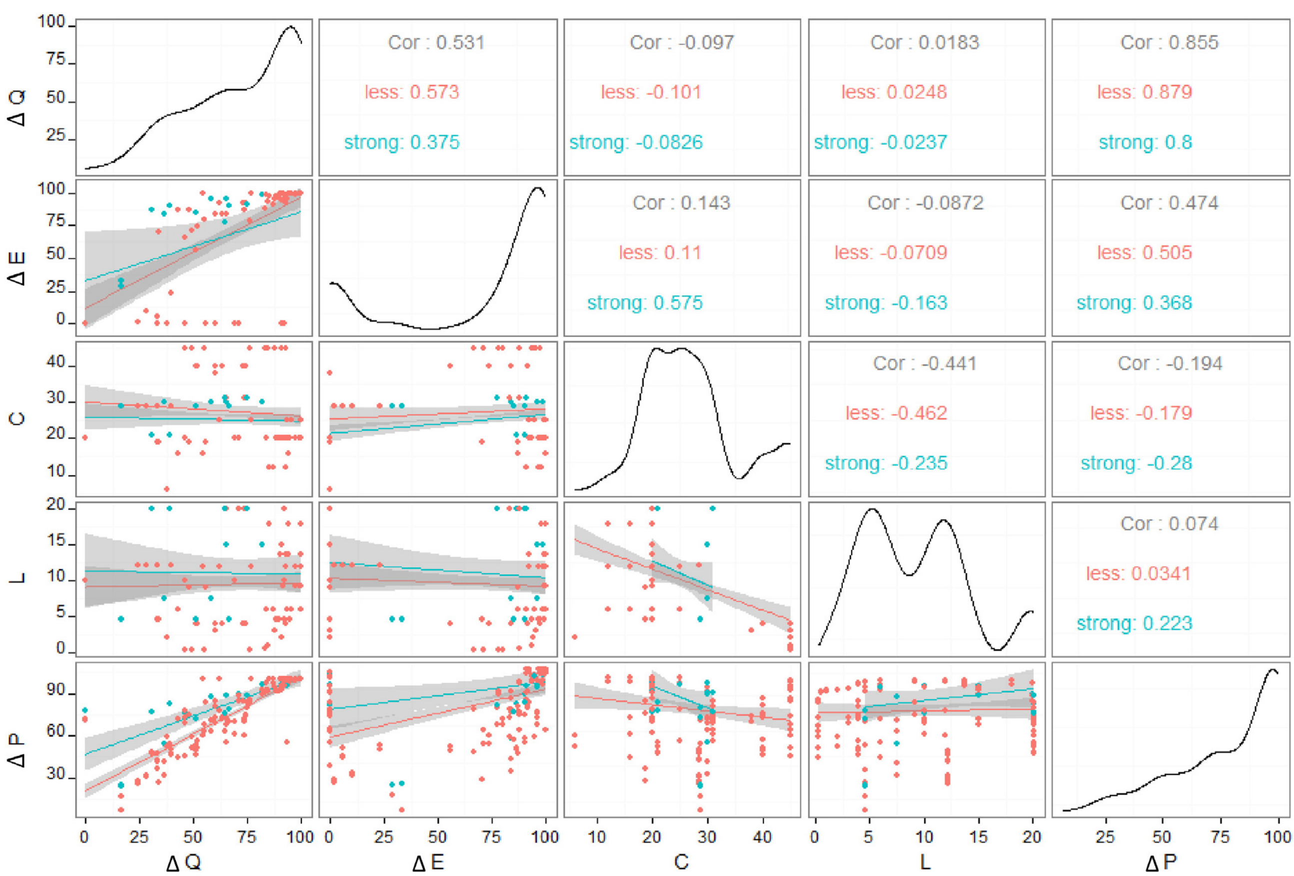

Fig. 1. Distributions and relationships among ΔQ (runoff volume reduction, %), ΔE (sediment mass reduction, %), C (clay content of incoming sediment, %), L (VFS length, m) and ΔP (pesticide mass reduction, %) with Pearson correlation coefficients, color coded by pesticide category (red and blue for weakly to moderately and strongly adsorbed pesticides, respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

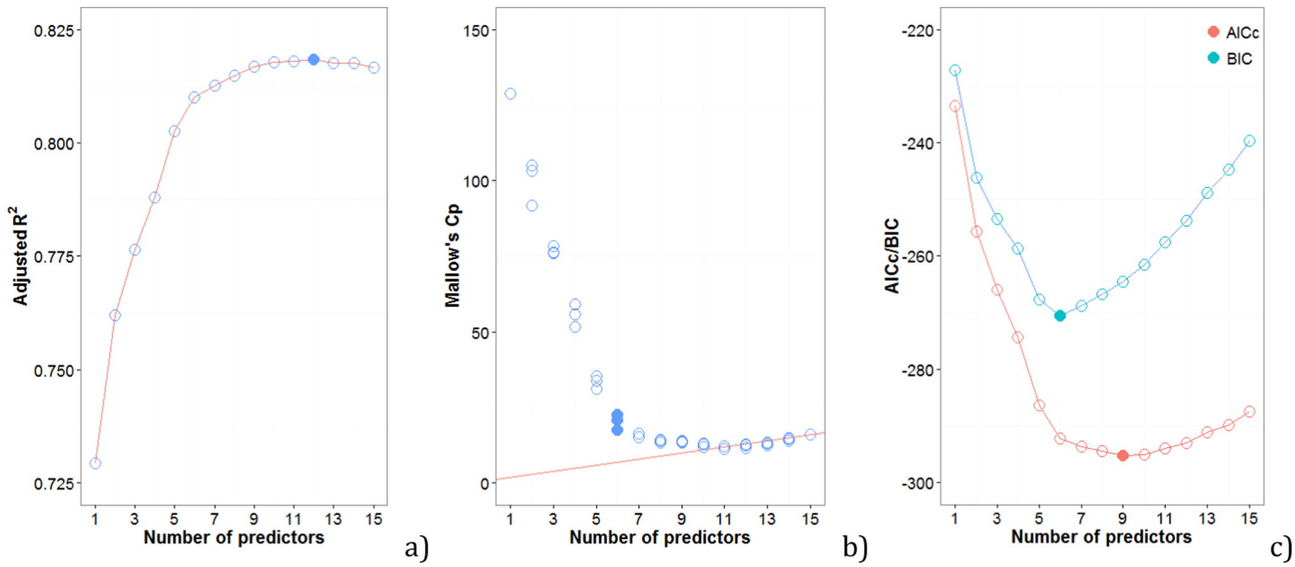

Fig. 3. Relationships between model adequacy and size for a) adjusted R^2, b) Mallow's C_p and c) *AICc* and *BIC* for the best or top three models of each size. The optimal model sizes are marked by solid circles.

3.3. Main effects and interaction

Fig. 6 shows the significant main effects and interaction among predictors in explaining variation in ΔP, plotted at different scales for better visualization of the patterns. ΔQ was strongly, positively correlated with ΔP, and the degree of correlation was stronger for weakly to moderately adsorbed pesticides. The predicted ΔP for strongly adsorbed pesticides was always higher than that for weakly to moderately adsorbed pesticides. The influence of ΔE on ΔP was quite small at low levels of ΔQ (50–60%), but gradually increased as ΔQ increased (70–100%). However, even the maximal impact of ΔE on ΔP was much smaller compared with that of ΔQ. The last graph in the panel shows the negative correlation between C and ΔP, with the strength of the main effect falling between that of ΔQ and ΔE.

4. Discussion

In agreement with previous studies, this study found the categorical influence of pesticide adsorption properties on VFS performance (Arora et al., 2010; Krutz et al., 2005; Reichenberger et al., 2007). By replacing F_{ph} with pesticide category, the model structure is more consistent with the established theory, thereby facilitating the investigation of the interaction between pesticide category and the hydrologic response of a VFS system. In addition to model structure, our model is likely to outperform the current VFSMOD pesticide module in terms of the rigorous statistical procedure that has been carried out. As seen earlier, the distribution of ΔP was substantially negatively skewed (Fig. 1). When we regressed ΔP without transformation, the resulting plots of residuals vs. fitted values and explanatory variables showed a clear sign of heterogeneity of variance. Such heterogeneity was reduced considerably after transforming ΔP. Therefore, the model developed without proper transformation of ΔP is questionable for making inferences. This is the case of the current VFSMOD pesticide module which was developed on the basis of highly negatively skewed ΔP. This factor may partially explain why our model has greater predictive power, as shown in the cross validation test and statistic Q^2 (Fig. 5).

Infiltration of runoff water within VFS's has been identified as one of the major mechanisms responsible for pesticide retention. Infiltration substantially reduced the mass of moderately adsorbed pesticides exiting VFS's (Boyd et al., 2003; Klöppel et al., 1997; Schmitt et al., 1999), especially when runoff almost totally infiltrated within VFS's due to small rainfall amounts (Arora et al., 1996) and/or high infiltration capacity of soils (Barfield et al., 1998; Popov et al., 2006). By reducing

Table 4
Summary of the developed pesticide retention model (ΔQ, runoff volume reduction; ΔE, sediment mass reduction; C, clay content of incoming sediment; Cat, pesticide category; ΔP, pesticide mass reduction).

	Coefficient	Standard error	*P*-value	95% confidence interval	
Equation: $\sqrt{101-\Delta P} \sim \Delta Q + \Delta E + C + Cat + \Delta Q : Cat + \Delta Q : \Delta E$				Lower limit	Upper limit
(Intercept)	8.06	0.45	<0.001	7.17	8.95
ΔQ	−0.07	0.01	<0.001	−0.08	−0.05
ΔE	0.02	0.01	0.012	0.003	0.028
C	0.05	0.01	<0.001	0.03	0.07
Cat	−2.17	0.58	<0.001	−3.32	−1.03
ΔQ:Cat	0.02	0.01	0.009	0.01	0.03
ΔQ:ΔE	−0.0003	0.00008	<0.001	−0.0005	−0.0001
Sample size	181	R squared	0.83	F statistic	P<0.001

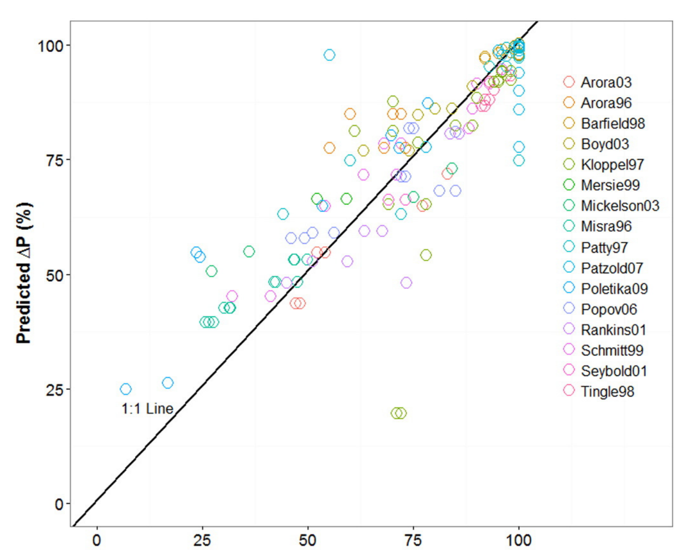

Fig. 4. Multi-linear regression between the predicted and observed pesticide removal efficiency of VFS, by study cases.

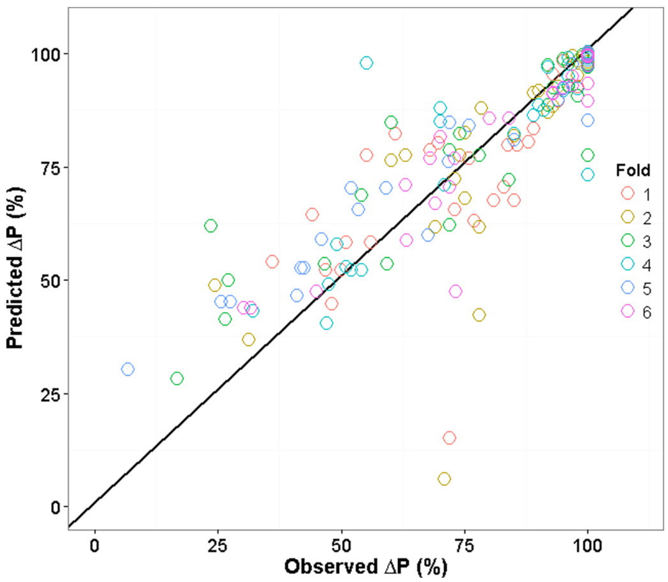

Fig. 5. Six-fold cross validation results for the final model. Only one out of 50 simulation results was selected for illustration. The average Q^2 is 0.81 and 0.72 for our model and the current VFSMOD pesticide module, respectively.

flow depth, infiltration also facilitates sedimentation by decreasing the sediment transport capacity of the remaining runoff flow (Dosskey, 2001), therefore promoting the removal of sediment-bound pesticides. Some studies have found that a large proportion of variation in ΔP could be explained by ΔQ, which is governed by the hydrologic conditions (e.g. soil hydraulic conductivity, initial soil moisture content, degree of flow concentration) of a VFS system (Barfield et al., 1998; Dillaha and Reneau, 1989; Fox et al., 2010; Klöppel et al., 1997; Krutz et al., 2003; Lacas et al., 2005; Muñoz-Carpena et al., 2010; Popov et al., 2006). The model developed here predicted higher ΔP for strongly adsorbed pesticides than for weakly to moderately adsorbed pesticides (Fig. 3a). Such a trend was expected due to different VFS performance in reducing the two carrier phases of pesticides—the water and sediment flow. It is widely acknowledged that the retention of sediment by VFS is greater than that of water. Therefore, the removal efficacy of strongly adsorbed pesticides is likely to be greater than the weakly to moderately adsorbed pesticides, as a larger proportion of pesticides in the former category are transported in the sediment phase (Krutz et al., 2005; Reichenberger et al., 2007).

In an uncertainty analysis study, Muñoz-Carpena et al. (2010) observed that the distribution of ΔP fell between the distributions of ΔQ and ΔE, and would shift to that of ΔQ for weakly to moderately adsorbed pesticides while it would shift to the distribution of ΔE for strongly adsorbed pesticides. In our study, there was no significant interaction between ΔE and pesticide category. However, we did observe interaction between ΔQ and pesticide category. The impact of ΔQ on ΔP was stronger for weakly to moderately adsorbed pesticides (Fig. 3a). As infiltration removes dissolved pesticides from surface runoff directly by diverting part of water flow into the soil matrix (Boyd et al., 2003; Dosskey, 2001; Schmitt et al., 1999; Zhang et al., 2010), the impact of ΔQ is stronger for pesticides that are mainly transported in the dissolved phase. For strongly adsorbed pesticides, the impact of ΔQ on ΔP is not as strong, as smaller proportions of the strongly adsorbed pesticides are transported in the water phase compared with weakly to strongly adsorbed pesticides.

ΔE was positively correlated with ΔP (Fig. 3b). As mentioned earlier, sedimentation is an important process for pesticide retention, especially for strongly adsorbed pesticides which have a higher concentration in sediment than in water flow (Arora et al., 2010). However, the overall impact of sedimentation might be small when compared with infiltration, as the volumetric flow rate is likely to be higher than the volumetric sediment discharge rate by several orders of magnitude. As a result, greater amounts of pesticides are transported in the dissolved phase than the sediment phase of surface runoff (Krutz et al., 2005), reducing the impact of ΔE on ΔP. For a given level of ΔE, ΔP increased with increasing ΔQ (Fig. 3b). This is mainly due to the fact that water and sediment flow are the two major carrier phases for pesticide transport in a VFS system (Arora et al., 2010). Therefore, total pesticide removal efficacy is determined by the reduction in both carrier phases collectively. Interaction between ΔQ and ΔE was also observed in this study, as the influence of ΔE on ΔP gradually increased with ΔQ (Fig. 3b). A possible explanation might be that high infiltration volume decreases runoff flow depth to a greater extent, providing more opportunities for contact between pesticide and sediment. Lower flow depth also facilitates adsorption/sedimentation by decreasing flow velocity and increasing retention time in the VFS (Popov et al., 2006). Consequently, a higher proportion of pesticides would be transported in the solid-phase and settle out of runoff flow with sediment particles.

Several studies have found that particle size distribution of incoming sediment strongly influences VFS sediment trapping performance (Barfield et al., 1979; Dosskey, 2001; Krutz et al., 2005; Lacas et al., 2005; Muñoz-Carpena et al., 2010; Norris, 1993). Sediment from coarse-textured soils could be easily removed within the first few

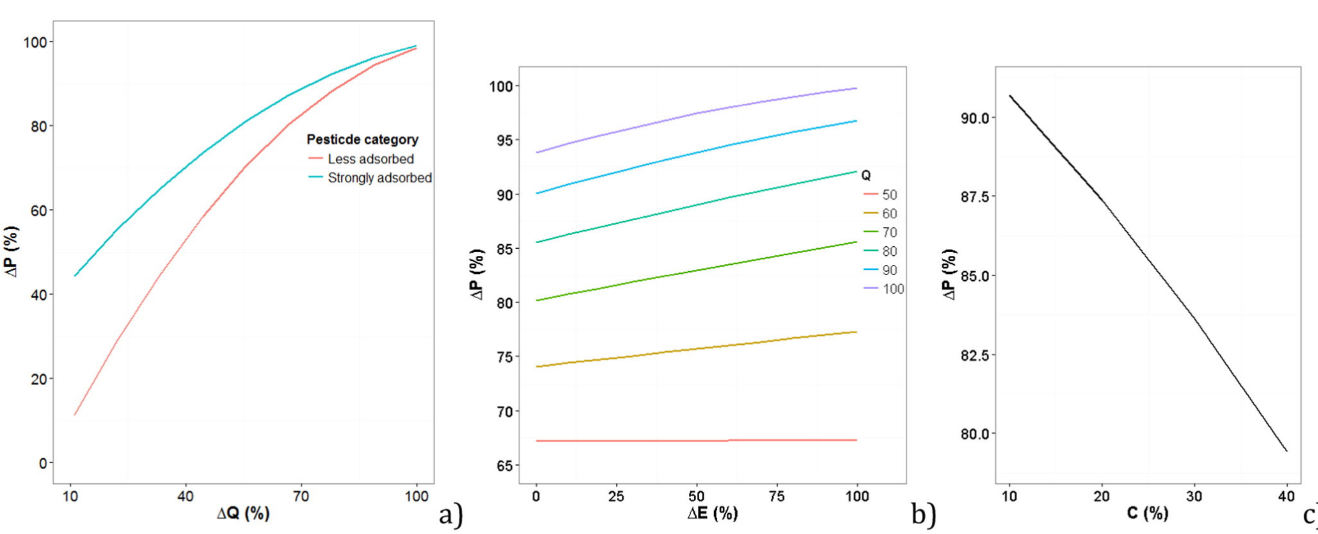

Fig. 6. Relationships between a) ΔP and ΔQ as affected by pesticide category, b) ΔP and ΔE as affected by ΔQ and c) ΔP and C, where ΔP, ΔQ, ΔE and C represent pesticide mass reduction (%), runoff volume reduction (%), sediment mass reduction (%) and clay content of incoming sediment (%), respectively.

meters of the filter, while sediment from finer soils might remain in suspension throughout the filter (Krutz et al., 2005; Lacas et al., 2005). Moreover, pesticide concentration is likely to be higher on finer sediment given its larger specific surface area compared to the coarse sediment (Lacas et al., 2005). Consequently, sediment high in clay content is likely to reduce VFS sediment trapping efficiency, thereby affecting the retention of strongly adsorbed pesticides. This feature was represented in our model, as pesticide removal efficacy was predicted to decrease with increasing clay content of sediment (Fig. 6c). Another explanation for this negative correlation might be that more rapid flow is likely to be generated from source area with poorly-drained soil (high clay content). Such unfavorable hydrologic condition would decrease the overall efficiency of a VFS system in removing pollutants from runoff flow.

VFS length was not a significant predictor in our model (Table 4). This might be attributed to the fact that the relationship between VFS pesticide removal efficacy and its length is essentially non-linear (Fig. 1 and Zhang et al., 2010), but more importantly, that VFS performance is mainly determined by the hydrologic response of a VFS system, which is an implicit function of filter length conditioned by other VFS parameters and pesticide chemical properties (Fox et al., 2010; Muñoz-Carpena et al., 2010; Sabbagh et al., 2009). Longer VFS's were observed to perform better in removing weakly to moderately adsorbed pesticides, as greater length increases the opportunity for infiltration and attachment to sediment particles (Krutz et al., 2005; Zhang et al., 2010). In our model, therefore, the physical dimensions of a VFS together with other parameters are distilled into the hydrologic response of a VFS system, ΔQ and ΔE. These two variables, together with the properties of incoming pollutants (C and Cat), are believed to be sufficient for quantifying the performance of a VFS system in removing pesticide residues from surface runoff.

Although our model does not incorporate VFS length as an explicit variable, it could still be coupled with other hydrologic models for practical use. Physically-based hydrologic models, such as VFSMOD, are able to simulate infiltration and sedimentation processes occurring in VFS's as a function of filter length, soil texture, and other VFS properties. Those hydrologic responses could be fed into our model to predict VFS pesticide removal efficacy. The two modeling systems collectively are capable of predicting VFS performance and identifying optimal VFS design parameters, thereby facilitating the successful implementation of VFS's for surface water protection.

5. Recommendations for future work

More than 80% of the data points used in this study are for weakly to moderately adsorbed pesticides. This is because experiments on pesticide runoff mitigation by VFS's mainly focused herbicides with K_{oc} less than 500 ml/g. Independent data sets for strongly adsorbed pesticides should be developed or identified for further model validation. In addition, more studies on subsurface processes occurring in VFS's are needed. This is particularly critical in areas that are vulnerable to groundwater contamination, i.e., areas with high water tables and heavy-textured soils (Lacas et al., 2005; Reichenberger et al., 2007). Whether VFS's increase or decrease pesticide leaching into groundwater remains controversial, as some observed increased amount of pesticide leachates due to enhanced infiltration in VFS's (Caron et al., 2012; Seybold et al., 2001), while others found leachates under the filter were at very low concentrations as VFS's facilitated pesticide adsorption and degradation (Watanabe and Grismer, 2001).

6. Conclusion

A model was developed for predicting VFS pesticide removal efficiency using a meta-regression approach ($R^2 = 0.83$). Our model is based on hydrologic responses of VFS (infiltration and sedimentation), pollutant characteristics (clay content of incoming sediment and pesticide adsorption category) and the interaction among these factors. Both infiltration and sedimentation had positive impacts on pesticide retention. However, the overall impact of sedimentation was smaller than infiltration, as the volumetric flow rate is likely to be higher than the volumetric sediment discharge rate by several orders of magnitude. Interaction between infiltration and sedimentation was observed, as the influence of sedimentation gradually increased with infiltration. It is possible that higher infiltration volume decreases runoff flow depth to a greater extent, providing more opportunities for contact between pesticide and sediment, thereby facilitating deposition of sediment-bound pesticides. Interaction between infiltration and pesticide adsorption properties was also prominent, as the influence of infiltration was significantly lower for strongly adsorbed pesticides. This is due to the fact that smaller proportions of strongly adsorbed pesticides are transported in the water phase compared with weakly to moderately adsorbed pesticides. Moreover, the clay content of incoming sediment was negatively associated with pesticide retention. This could be attributed to the difficulty in removing fine particles, and thereby the associated pesticides, from runoff flow. Our model outperformed the existing VFSMOD pesticide module not only in predictive power (cross-validation Q^2: $0.81 > 0.72$) but also in terms of model structure and the underlying science foundation. It is believed that our model not only serves as a powerful tool for predicting VFS performance, but also contributes to a deeper understanding of the complex, interacting VFS processes responsible for pesticide removal.

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