



Does mechanistic modeling of filter strip pesticide mass balance and degradation processes affect environmental exposure assessments?



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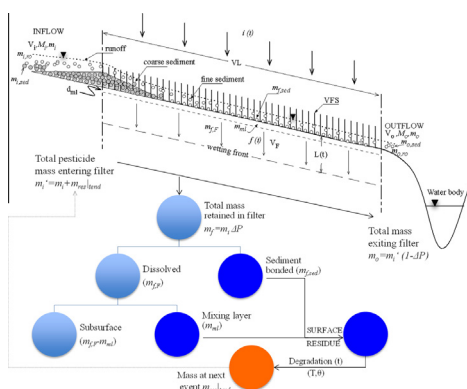
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HIGHLIGHTS

- Updated modeling framework incorporates mass balance and degradation.
- Degradation not important if single, large runoff events control transport.
- Degradation important for scenarios with higher sediment transport and stable pesticides.
- Mechanistic component elucidates pesticide dynamics for long-term assessment.

GRAPHICAL ABSTRACT



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ABSTRACT

Vegetative filter strips (VFS) are a widely adopted practice for limiting pesticide transport from adjacent fields to receiving waterbodies. The efficacy of VFS depends on site-specific input factors. To elucidate the complex and non-linear relationships among these factors requires a process-based modeling framework. Previous research proposed linking existing higher-tier environmental exposure models with a well-tested VFS model (VFSSMOD). However, the framework assumed pesticide mass stored in the VFS was not available for transport in subsequent storm events. A new pesticide mass balance component was developed to estimate surface pesticide residue trapped in the VFS and its degradation between consecutive runoff events. The influence and necessity of the updated framework on acute and chronic estimated environmental concentrations (EECs) and percent reductions in EECs were investigated across three, 30-year U.S. EPA scenarios: Illinois corn, California tomato, and Oregon wheat. The updated framework with degradation predicted higher EECs than the existing framework without degradation for scenarios with greater sediment transport, longer VFS lengths, and highly sorbing and persistent pesticides. Global sensitivity analysis (GSA) assessed the relative importance of mass balance and degradation processes in the context of other input factors like VFS length (VL), organic-carbon sorption coefficient (K_{oc}), and soil and water half-lives. Considering VFS pesticide residue and degradation was not

Abbreviations: EEC, estimated environmental concentration; EPA, Environmental Protection Agency; GSA, global sensitivity analysis; K_{oc} , organic-carbon sorption coefficient; t_s , pesticide half-life in the soil; t_{wa} , aerobic/anaerobic aquatic metabolism half-life; VFS, vegetative filter strip; VL, length of the vegetative filter strip along the direction of flow.

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important if single, large runoff events controlled transport, as is typical for higher percentiles considered in exposure assessments. Degradation processes become more important when considering percent reductions in acute or chronic EECs, especially under scenarios with lower pesticide losses.

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1. Introduction

Vegetative filter strips (VFS) reduce sediment and pesticide movement to receiving water bodies through infiltration and reduction of runoff flow volumes, by contact between the sediment and pesticide with vegetation and soil in the VFS, and by increasing hydraulic roughness to reduce the flow velocity and allow sediment-bound pesticide to settle out of the runoff (Reichenberger et al., 2007; Muñoz-Carpena et al., 2010; Sabbagh et al., 2009; Fox et al., 2010). Recent research has documented the importance of considering site-specific temporal variability in regard to predicting pesticide trapping efficiency of VFS (Muñoz-Carpena et al., 2010; Sabbagh et al., 2009; Fox and Sabbagh, 2009; Poletika et al., 2009; Fox et al., 2010).

Sabbagh et al. (2009) suggested a generalized regression-based approach for predicting VFS pesticide trapping that depends on the infiltration and sediment trapping efficiency. Using studies reported in the peer-reviewed literature, they proposed an empirical trapping efficiency model for pesticides dependent on the infiltration, sedimentation, pesticide and soil properties. Filter strip length (VL) in the direction of flow was not explicitly a statistically significant parameter in the empirical model although the VL indirectly influenced other significant parameters. They also proposed a procedure linking a mechanistic-based VFS model for predicting infiltration and sediment reduction relative to specific storm event conditions. The mechanistic model utilized was VFSSMOD (Muñoz-Carpena et al., 1999; Muñoz-Carpena and Parsons, 2004), a numerical storm-based design model. During the rainfall-runoff event, VFSSMOD calculates the dynamic hydrological and sediment transport processes occurring in the VFS. For this it uses initial conditions (soil, water, vegetation) and boundary conditions (rainfall, inflow runoff from the field) and calculates outflow hydrographs and sedigraphs for the storm, as well as the water and mass balances at the end of the storm (see [Supporting Information, Fig. S-1](#)). This combined mechanistic-empirical approach significantly improved predictions of pesticide trapping over empirical equations based simply on physical characteristics of the VFS.

The mechanistic-empirical approach was further evaluated by Poletika et al. (2009). They reported a combined field/modeling study investigating the effect of runoff volume and flow concentration on removal of chlorpyrifos and atrazine by VFS. The field experiments demonstrated that increased flow volume at the ranges investigated in their study had a minor impact on removal efficiency while flow concentration reduced removal performance regardless of the drainage area ratio. The integrated mechanistic-empirical approach for pesticide removal was capable of predicting runoff volume, sediment, and chemical reductions by the filter strip under both uniform and concentrated flow conditions. The modeling further supported the conclusion that flow uniformity was the primary driver in these experiments for pesticide trapping efficiency.

Muñoz-Carpena et al. (2010) and Fox et al. (2010) investigated the importance of various input factors on predicted sediment and pesticide reductions. The most important parameters for predicting pesticide trapping using the linked model were those representing infiltration and sediment reduction. Pesticide-specific

input factors were of secondary importance. Simple linear or non-linear regressions based on VFS physical characteristics (e.g., slope, length, and roughness) were deemed insufficient without considering the VFS hydrological and sedimentological conditions and the interaction between input factors (Muñoz-Carpena et al., 2010). Also, concentrated flow significantly raised interactions among the system components, enhancing the relative importance of processes that were latent under shallow flow conditions (Fox et al., 2010). The complex VFS behavior highlighted in their two studies further warrants the need for process-based modeling to be able to predict the performance of VFS under a wide range of specific hydrological conditions.

VFSSMOD has been coupled for use with U.S. EPA models in a long-term, higher-tier pesticide environmental assessment framework (Sabbagh et al., 2010, 2013), where flow, sediment and pesticide runoff at the end of the field is calculated by the model PRZM (Lin et al., 2007). Then, VFSSMOD routes it from the field through a VFS of desired characteristics to estimate potential load reductions before entering the aquatic environment as predicted by EXAMS (Burns, 1990; Jackson et al., 2005; Sabbagh et al., 2010, 2013). Although with some differences, this conceptual framework (long-term simulation of coupled field-VFS-waterbody) applies to all commonly used higher tier pesticide environmental exposure assessments (e.g., EU-FOCUS with TOXSWA for surface water modeling).

More recently, Sabbagh et al. (2013) applied the integrated exposure framework (PRZM/VFSSMOD/EXAMS) for three, 30-year U.S. EPA scenarios: Illinois corn, California tomato, and Oregon wheat. The potential ranges in acute and chronic estimated environmental concentrations (EECs) varied as a function of EPA scenario and application timing. Percent reductions in acute EECs were typically less than percent reductions in chronic EECs because acute exposure was driven primarily by large individual rainfall and runoff events. They also concluded that generic specification of VFS design characteristics equivalent across scenarios should be avoided. A limitation of this framework was the lack of mass balance and degradation of pesticide within the VFS. More specifically, the existing version of VFSSMOD within the framework assumed that after an event, if the pesticide was trapped by the VFS, then pesticide mass could not be transported out of the VFS in a later event (Sabbagh et al., 2013). The focus of the existing framework was specifically on immobilization of the pesticide by the VFS assuming that the most significant loading threat is due to surface transport to the aquatic body during the runoff event.

Therefore, the objectives of this research were two-fold: (i) develop and apply a VFSSMOD pesticide mass balance component (and its integration within the long term, higher-tier exposure assessment) to estimate surface pesticide residue in the buffer at the end of a runoff event and its degradation towards the next runoff event; and (ii) compare results of the upper 90th percentile of the acute (peak) and chronic (60-d) aquatic EECs and percent reductions in EECs by the VFS with and without the addition of mass balance and degradation processes and across various scenarios. Also, whereas previous studies investigated percent reductions in acute and chronic EECs, unique to this study was the comparison between absolute acute and chronic EECs and percent reduction

due to the VFS because of the general difference between pesticide losses between scenarios.

2. Methods and materials

2.1. Updated modeling framework: filter pesticide mass balance and degradation component

Herein, a simplified VFSSMOD pesticide mass balance and degradation component is proposed to estimate surface pesticide residue for VFS efficiency calculations. The new VFSSMOD component is based on simplified calculations of pesticide mass balance and degradation on the surface of the VFS, performed after the simulation of pesticide trapping and transport through the filter. Table 1 summarizes the main assumptions contained in the proposed new module. The pesticide residue is determined from the water, sediment and pesticide mass balance components calculated by VFSSMOD at the end of each runoff event. The residual pesticide in solid phase is estimated as pesticide bonded to the sediment trapped in the filter during the event. Some of the pesticide is trapped and can infiltrate and is not available for runoff in the next event, and some, which resides in the mixing layer, is available for runoff in the subsequent event but degrades in the meantime (Fig. 1).

Total residual surface pesticide after the event, i.e. attached to sediment trapped on the filter and on the mixing layer, is handled as a conservative worst-case scenario from a water quality perspective in the receiving water body where all mass is available for degradation and transport (and trapping) towards the next event. The total residual surface pesticide mass retained in the filter at the end of the event is degraded with daily time increments based on the soil decay rate. Depending on the degradation routine selected, the temperature and soil water content (provided by PRZM) until the next runoff event in the series may also contribute to degradation.

2.1.1. Pesticide partitioning and residue

In the EU and U.S., higher-tier assessments rely on the model PRZM for estimation of runoff water (Sabbagh et al., 2010, 2013), sediment and pesticide mass leaving the agricultural field (or similar source area). This provides total incoming mass (water,

sediment and pesticide) into the filter. If linear sorption equilibrium between solid and dissolved pesticide phases is assumed, the pesticide can be partitioned using the distribution coefficient value K_d [$L^3 M^{-1}$] for the particular pesticide:

$$K_d = \frac{S}{C} = \frac{m_p/M_s}{m_d/V_w} \quad (1)$$

where S [$M M^{-1}$] is pesticide adsorbed to the sediment/soil, C [$M L^{-3}$] is the dissolved pesticide concentration, m_p and m_d [M] are mass of pesticide in solid (sorbed to sediment particles) and liquid phases, M_s [M] is the mass of sediment in runoff, and V_w [L^3] is the volume of the liquid phase (runoff). Notice also that K_d is related to the organic carbon sorption coefficient K_{oc} [$L^3 M^{-1}$], which is more commonly available for pesticides, and the soil percentage organic carbon (f_{oc} , %):

$$K_d = \frac{K_{oc}f_{oc}}{100} \quad (2)$$

For each event, dissolved pesticide and the component sorbed to eroded soil/sediment trapped in the filter is calculated using the linear equilibrium assumptions (K_d) based on PRZM inputs (incoming pesticide mass, m_i , sediment mass M_i , and runoff inflow, V_i), VFSSMOD outputs (sediment trapped and out, M_i and M_o , runoff outflow, V_o), and soil mixing layer characteristics (depth d_{ml} [L], saturated water content θ_s [–] and bulk density ρ_b [$M L^{-3}$]) (Fig. 1). Note that d_{ml} is a conceptual parameter that attempts to simulate the active layer of the soil that will exchange pesticide with the runoff and control the extraction and availability of a pesticide from the top soil. Ahuja (1986, 1990) noted that non-uniform exchange could occur from soil depths up to 2 cm. Early versions of PRZM originally specified d_{ml} as 1 cm and the later versions of PRZM (version 3) contained in the current pesticide assessment framework use 2 cm supported by inverse calibration against observed field data (Suarez, 2005). For consistency with the PRZM field component and to generate conservative estimates of pesticides in runoff from the VFS, $d_{ml} = 2$ cm was used in the new VFS component. Future research should investigate the influence of various conceptualizations of extraction models and depths on EECs. The residual pesticide in the surface of the VFS after the event is calculated as the mass of the pesticide deposited with the sediment during the event (solid phase), plus the amount contained in the mixing layer based on a linear equilibrium during the event (Fig. 1).

A central assumption of the calculations proposed is that for the short-duration of a typical runoff event (minutes to hours) the solid phase (sediment) pesticide concentration will not change during the event so that the incoming (S_i), filter-trapped (S_f) and outgoing (S_o) solid phase concentrations are equivalent:

$$S_i \approx S_f \approx S_o \quad (3)$$

This assumption is reasonable for compounds with degradation half-lives greater than 1 d, which applies to most of the compounds used in the field. For these conditions, the partition of the incoming pesticide mass (m_i) can be estimated assuming perfect mixing of total mass of sediment, pesticide, and inflow and linear adsorption equilibrium between the liquid or dissolved (m_{di}) and solid or particulate (m_{pi}) phases:

$$m_i = m_{pi} + m_{di} \quad (4)$$

$$m_{di} = m_i - m_{pi}$$

$$K_d = \frac{S_i}{C_i} = \frac{m_{pi}/M_i}{m_{di}/V_i} \quad (5)$$

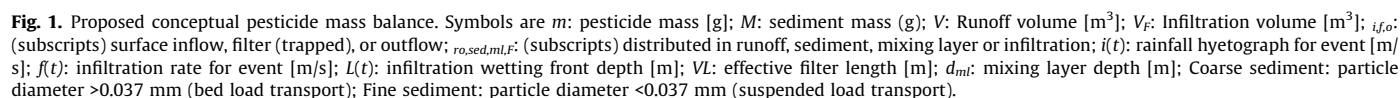
$$m_{pi} = \frac{m_i M_i K_d}{V_i + M_i K_d}$$

$$S_i = \frac{m_{pi}}{M_i} = \frac{m_i K_d}{V_i + M_i K_d}$$

Table 1

Main assumptions and operational constraints of the proposed pesticide degradation module.

Component	Assumptions/Limitations
Pesticide mass balance	<ul style="list-style-type: none"> Linear adsorption equilibrium Saturation of sediment-adsorbed pesticide concentration ($S_i \approx S_f \approx S_o$), i.e. it does not change during short time event Mixing zone with fixed depth, porewater concentration at the end of event equivalent to that of infiltrating water.
Pesticide degradation	<ul style="list-style-type: none"> Soil mixing layer daily temperature considered equal to air temperature Soil mixing layer daily moisture approximated as the average moisture for the root zone Liquid and solid phase pesticide in mixing layer is lumped together with trapped sediment-bonded mass to calculate degradation Activation energy for degradation and the moisture exponent values are valid for field conditions
Incoming pesticide (next event)	<ul style="list-style-type: none"> All residual mass in mixing layer after degradation is added to new field incoming mass for next event in time series



where V_F and V_o are the volumes of water retained in the filter and exiting as runoff, respectively, calculated in VFSSMOD, and V_R is the rainfall volume for the event. Thus, the pesticide trapped in the mixing layer (m_{ml}) is estimated as the sum of the pore water ($m_{ml,a}$) and solid phase ($m_{ml,s}$) masses:

$$m_{ml} = m_{mld} + m_{mlp} \approx (\theta_s C_F + \rho_b S) V_{ml} \\ = (\theta_s + K_d \rho_b) C_F d_{ml} \cdot b \cdot VL \quad (10)$$

Note that the mixing layer bulk density (ρ_b [M L⁻³]) can be estimated for mineral soils based on the VFS top soil saturated water content (θ_s [-], an existing VFSMOD input) by assuming the specific density of the soil $\rho_s = 2.65$ kg L⁻¹ and the following equation:

$$\theta_s \approx 1 - \frac{\rho_b}{\rho_s} \rightarrow \rho_b \approx (1 - \theta_s) \rho_s \quad (11)$$

Finally, the total mass of surface pesticide considered in the degradation calculations between events is the sum of the pesticide adsorbed to the sediment trapped during the event and the pesticide (solid and liquid phases) contained in the mixing layer:

$$m_{res} = m_{f, sed} + m_{ml} \quad (12)$$

2.1.2. Residual pesticide degradation between events

The dissolved pesticide in the mixing layer arising from the infiltration component is considered part of the surface residual mass for pesticide degradation calculations. Thus, the residual pesticide in the filter (m_{res}) is lumped into single mass component (mixing layer and adsorbed sediment trapped on surface) and degraded as a function of time (first order decay), where k (d) is the pesticide degradation rate:

$$\frac{dm_{res}}{dt} = -k m_{res} \\ m_{res}|_{t_1} = m_{res}|_{t_0} e^{-kt} \quad (13)$$

Generally, the degradation rate can be expressed as the product of the reference rate (k_{ref}) and modifiers to incorporate the effects of temperature (k_T) and moisture (k_θ):

$$k = k_{ref} * k_T * k_\theta \quad (14)$$

$$k_T = e^{\frac{E_a}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right)} \quad (15)$$

$$k_\theta = \left(\frac{\theta}{\theta_{ref}} \right)^{-\beta} \quad (16)$$

where T is the average daily surface soil temperature (K) between events; θ is the average daily surface soil moisture between events [m³ m⁻³]; $T_{ref} = 293.15$ K; $\theta_{ref} = \theta_{FC}$ the soil field capacity; $E_a = 65.4$ kJ mol⁻¹ (EU Focus, 2006; EFSA, 2008); and $\beta = 0.7$ (EU FOCUS, 2006). Note that k_{ref} is the pesticide degradation rate (d⁻¹) at standard conditions of T (T_{ref}) and θ (θ_{ref} = field capacity) and related to the pesticide half-life ($t_{1/2}$, d) by $k_{ref} = \ln(2)/t_{1/2}$ for first-order kinetics.

The calculations are carried out on daily time steps between each event. Soil temperature is needed on the top soil mixing layer ($d_{ml} = 2$ cm based on PRZM). Based on the heat transport equation, the air temperature attenuates and delays in time through the soil profile until reaching a constant temperature deeper in the profile. A reasonable approximation for a very thin surface layer on the top of the soil (d_{ml}) is $T \approx T_{air}$. Soil moisture (θ) is estimated based on FAO-56 crop water stress-adjusted method (FAO, 1998) with the program THETAFAO (Muñoz-Carpena, 2013). For the U.S., the output parameter (THET) from the PRZM model is used to estimate daily soil moisture.

Finally, the residual pesticide mass at the beginning of the next event ($m_{res}|_{t_{end}}$) is considered as a conservative worst-case scenario for the receiving water body to be fully mixed with the new incoming pesticide mass into the filter (m_i). For this, it is added to the incoming pesticide mass into the filter for the next event, and the pesticide trapping efficiency calculated for that event (ΔP) is

applied to the sum (m_i') to obtain the outflow total pesticide mass leaving the filter in runoff at the end of the event (m_o):

$$m_i' = m_i + m_{res}|_{t_{end}} \\ m_o = m_i' (1 - \Delta P) \quad (17)$$

2.1.3. Pesticide partitioning of the filter outflow

In order to link the pesticide outflow concentration from the VFS with aquatic models representing the water body adjacent to the field in current regulatory frameworks (EPA-EXAMS, EU-TOXSWA), it is necessary to estimate the partitioning of the total sediment outflow mass from the filter into dissolved and particulate fractions. As before, the partition of the outcoming pesticide mass (m_o) can be estimated assuming perfect mixing of total mass of sediment pesticide and outflow, and linear adsorption equilibrium between the liquid or dissolved (m_{do}) and solid or particulate (m_{po}) phases:

$$m_o = m_{p_o} + m_{d_o} \\ m_{d_o} = m_o - m_{p_o} \quad (18)$$

$$m_{p_o} = \frac{m_o M_o K_d}{V_o + M_o K_d} \quad (19)$$

2.2. Application of the updated framework across higher-tier scenarios

Similar to Sabbagh et al. (2013), three distinct U.S. EPA scenarios were considered: Illinois corn, Oregon wheat, and California tomato. These scenarios were selected to provide a wide range of hydrological and sedimentological conditions (see Supporting Information, Tables S-1 through S-7): Midwestern continental row-crop agriculture (Illinois Corn), wet maritime extensive agriculture (Oregon wheat), and dry Mediterranean irrigated intensive horticulture (California tomato). It should be realized that results presented in this research are limited to the scenarios that the U.S. EPA developed for regulatory aquatic exposure assessments. However, the tools that are used in this research are applicable to other field and VFS conditions.

Soils data as specified by the U.S. EPA scenario were used explicitly in the aquatic exposure assessments. Climate data from meteorological stations specified in the U.S. EPA scenarios were used for conducting 30-yr simulations. The effect of the environment (location, rainfall, soil) was captured in three scenarios analyzed in this research. Field and VFS slopes were assumed uniform as prescribed in the U.S. EPA scenario. Vegetation type in the VFS was assumed to be mixed grass, and default parameters for VFS vegetation characteristics were used. A source of uncertainty when simulating actual VFS performance is the condition of the VFS relative to upkeep and maintenance (regular mowing to maintain design height and vegetation uniformity, resetting by leveling and reseeding every 5-yr). This research assumed a well-maintained VFS with uniform shallow overland flow across the entire VFS width rather than concentrated flow (Muñoz-Carpena et al., 2010; Fox et al., 2010).

Within each U.S. EPA scenario, simulations were performed with a wide range of potential values for the pesticide fate and transport parameters: K_{oc} of 20, 200, and 2000 L kg⁻¹; t_s (pesticide half-life in the soil) = 10, 100, or 1000 d; and t_w (aerobic/anaerobic aquatic metabolism half-life) = 10, 100, or 1000 d. Each scenario had different application dates, rates, and number of applications that corresponded to typical insecticide timing and rates. The IL corn scenario had four applications at 0.11 kg ha⁻¹ starting on 1-July with a 3-day interval. The OR wheat scenario had two 0.043 kg ha⁻¹ applications at a 3-day interval starting 26-September. The CA tomato scenario had five applications at

0.05 kg ha⁻¹ starting on 15-April with a 3-day interval. For all scenarios, ground application was assumed so that no drift was simulated. Drift was not modeled so that all the EECs in the waterbody were based on mass loads from the VFS. Typical VFS lengths of VL = 0, 1, 5, and 9 m were simulated. Simulations were also performed without (IDG = 0 as in the existing modeling framework) and with mass balance and degradation (IDG = 1, new framework). As a result a total of 648 long-term (30-yr) simulations were performed across all scenarios, with 486 of them (having a VFS, VL > 0 m) used for the global sensitivity analysis (described in the next section) and the rest (VL = 0) for testing consistency with previous results (Sabbagh et al., 2010, 2013). Output variables of interest included both the acute (peak) and chronic (60-d) EECs and percentage EEC reductions (%EEC reduction) by the VFS.

2.3. Variability in results and global sensitivity analyses

Variability in predicted absolute EECs and %EEC reduction across the range of input factors previously discussed were investigated first using boxplots. Because they are based on statistics that do not require assumptions about the shape of the underlying output distributions, boxplots robustly provide more information about samples and effects than conventional error bars (Krzywinski and Altman, 2014). In order to quantify the importance of the various parameters in the updated modeling framework, global sensitivity analysis (GSA) was conducted following Muñoz-Carpena et al. (2007, 2010).

The Morris elementary effects screening method (Morris, 1991; Campolongo et al., 2007) with the improved sampling uniformity scheme (Khare et al., 2015) was used to identify input factor importance for model simulations with and without degradation. Important factors are identified by two statistics (μ^* , σ) denoting direct and interaction effects, respectively, plotted on a (μ^* , σ) plane. Larger separation from the origin along the μ^* axis indicates higher importance of the input factor (direct effects), and along the σ axis indicates their interactions (higher order effects). The reader is referred to a number of papers that further discuss the methodology of Morris for GSA (Muñoz-Carpena et al., 2007, 2010; Campolongo et al., 2007; Khare et al., 2015). Researchers have proposed qualitative thresholds above which the input factors' main influence is in the form of direct effects or higher order/interactions (Morris, 1991; Campolongo et al., 2007). For example, Morris (1991) proposed a threshold line based on μ_i (mean of

elementary effects with their individual signs), and Chu-Agor et al. (2011) proposed a 1:1 line for revised μ_i^* (mean of absolute value of elementary effects); both are used in this paper.

GSA was conducted comparing simulations with (IDG = 1, proposed framework) and without (IDG = 0, existing framework) degradation to determine if input factor importance changed when including the degradation process. IDG was thus included as an additional input factor to complete the final GSA sample set {IDG, VL, K_{oc} , t_s , t_w }. Without degradation (IDG = 0), the results were utilized to verify the previous GSA results (Sabbagh et al., 2013). GSA results were investigated for the two outputs of interest: actual EEC and %EEC reduction.

3. Results and discussion

The updated framework with degradation (IDG = 1) typically led to higher EECs as compared to the existing version of VFSSMOD where a buffer is used with no degradation (IDG = 0) between runoff events. This statement was especially true for cases with greater sediment transport into the VFS as in the case of the IL corn scenario and for stable pesticides with larger K_{oc} (Fig. 2). Acute EECs ranged between 0.5 and 23.7 $\mu\text{g L}^{-1}$ in the IL corn scenario, 0.0–2.2 $\mu\text{g L}^{-1}$ in the OR wheat scenario, and 0.0–0.9 $\mu\text{g L}^{-1}$ in the CA tomato scenario (Fig. 3). Note that these values are 90th percentile EECs which the U.S. EPA uses in their risk assessments. The magnitude of the EECs between the scenarios was in line with expectations (U.S. EPA, 2003) considering the land use, weather, and soils used in each scenario (i.e., Midwestern continental row-crop agriculture, wet maritime extensive agriculture versus dry Mediterranean irrigated intensive horticulture). More specifically, the Illinois corn scenario included a soil in a highly erodible land use zone and therefore was expected to have greater sediment transported into and through the VFS.

For absolute EECs, median values without (IDG = 0, existing framework) and with (IDG = 1, proposed framework) degradation were similar, which suggests that including degradation was not of significant importance in any of the scenarios. The effect of VL was apparent for absolute EECs: as VL increased, the median and range of absolute EECs decreased. However, the change in the total variability of the absolute EECs due to VL was smaller than the overall variability observed in the scenarios. Therefore, for acute absolute EECs, variability in other parameters led to the variability

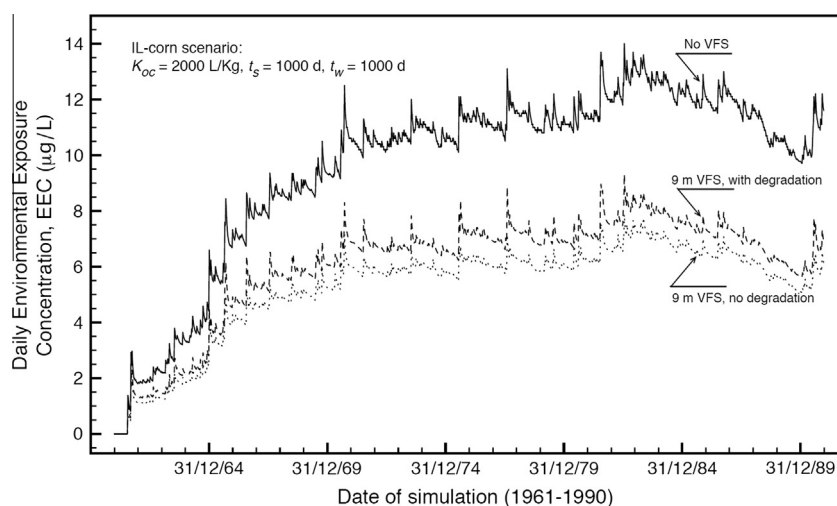


Fig. 2. Daily environmental exposure concentrations (EECs) for the U.S. EPA Illinois corn scenario predicted by EXAMS for a stable pesticide (1000-d aquatic and soil dissipation half-lives) without (No VFS) and with a 9-m long vegetated filter strip (9 m VFS) with the original version of VFSSMOD (no degradation) and the new framework (with degradation).

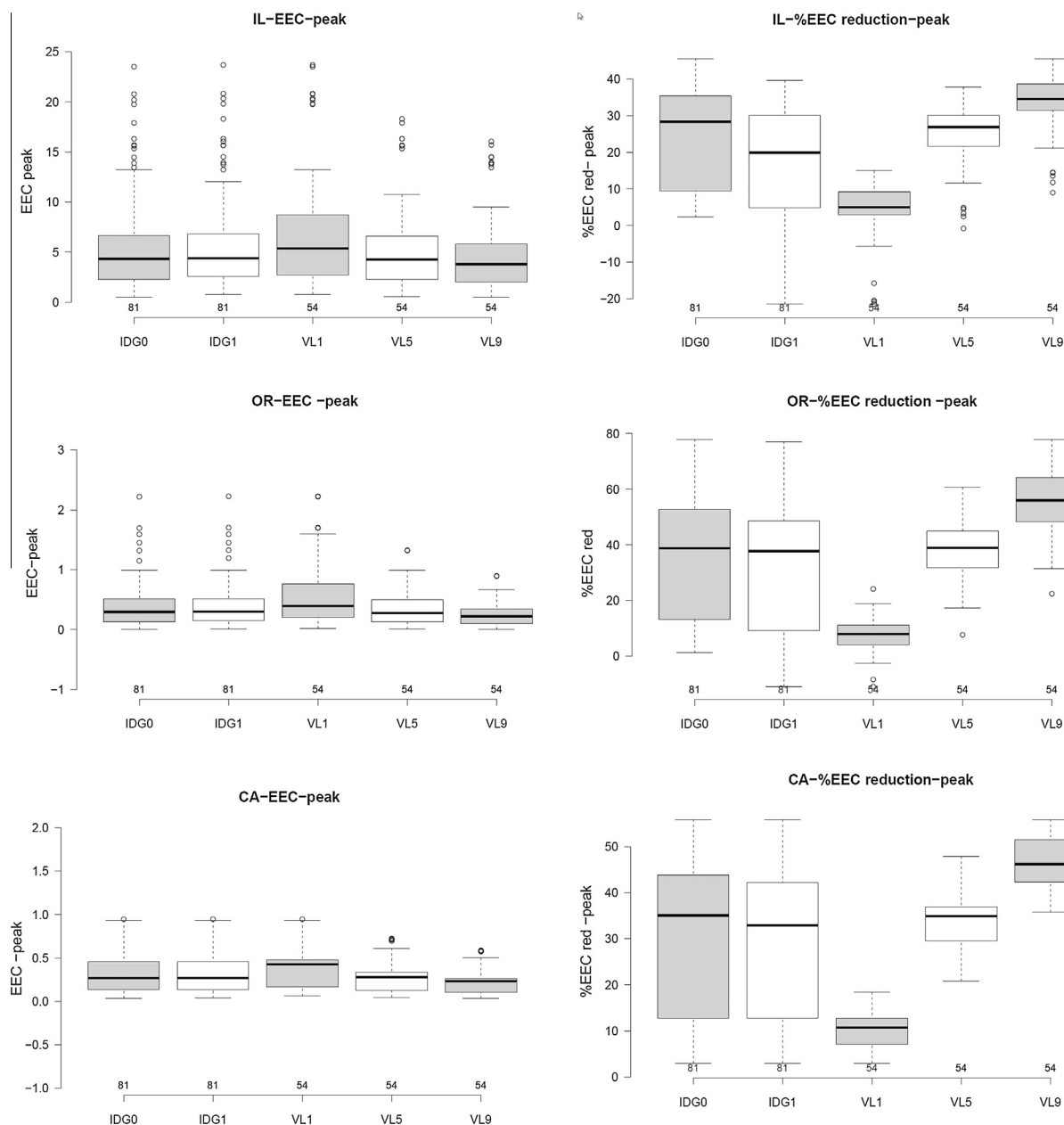


Fig. 3. Box plots of acute (peak) absolute (left, in $\mu\text{g L}^{-1}$) and percent reduction (right, in %) in estimated environmental concentration (EEC) for IL corn, OR wheat, and CA tomato scenarios. Note: IDG0 = without degradation; IDG1 = with degradation; VL1, VL5 and VL9 = 1, 5, and 9-m long VFS, respectively. Numbers below each box and whisker plot is the number of simulations within each category.

in the simulated EECs (Fig. 3). The Morris results confirmed this observation, suggesting t_w , t_s , and K_{oc} were the most important input factors for the IL corn and OR wheat scenarios, and t_w and K_{oc} were most important for the CA tomato scenario (Fig. 4). Including mass balance/degradation (IDG = 1 or 0) was consistently ranked as one of the least important input factors in the Morris analysis.

For percent reductions in acute EECs, differences in the median and range were observed when comparing simulations without and with degradation (Fig. 3). Note that percent reductions in acute EECs could be negative when simulating degradation in the VFS because all percent reductions were calculated with respect to the scenario without a VFS. Negative values occur for small length VFS and for pesticides with a high K_{oc} and long soil half-life, which leads to higher residue concentrations. While the medians are similar with or without degradation, considerable differences were

observed in the range especially at the lower end of the distribution (i.e., smaller percent reductions). Percent reductions in acute EECs ranged between -21.4% and 45.6% in the IL corn scenario, -10.9% and 77.9% in the OR wheat, and 3.0% and 55.8% in the CA tomato scenarios. In all three scenarios including degradation in the VFS resulted in a lower median and range in the percent reductions compared to cases without degradation. Similar to the absolute EECs, a stronger influence on the output variability for percent reductions was observed for VL than other input factors such as degradation. As expected, percent reductions in acute EECs increased as VL increased. The Morris results once again confirmed these observations as VL was consistently the most important input factor for each scenario (Fig. 4). In this case, degradation (IDG = 0 or 1) was not always the least important factor in leading to variability in the percent reductions in the acute EECs. Note that similar median values were observed, especially in the absolute

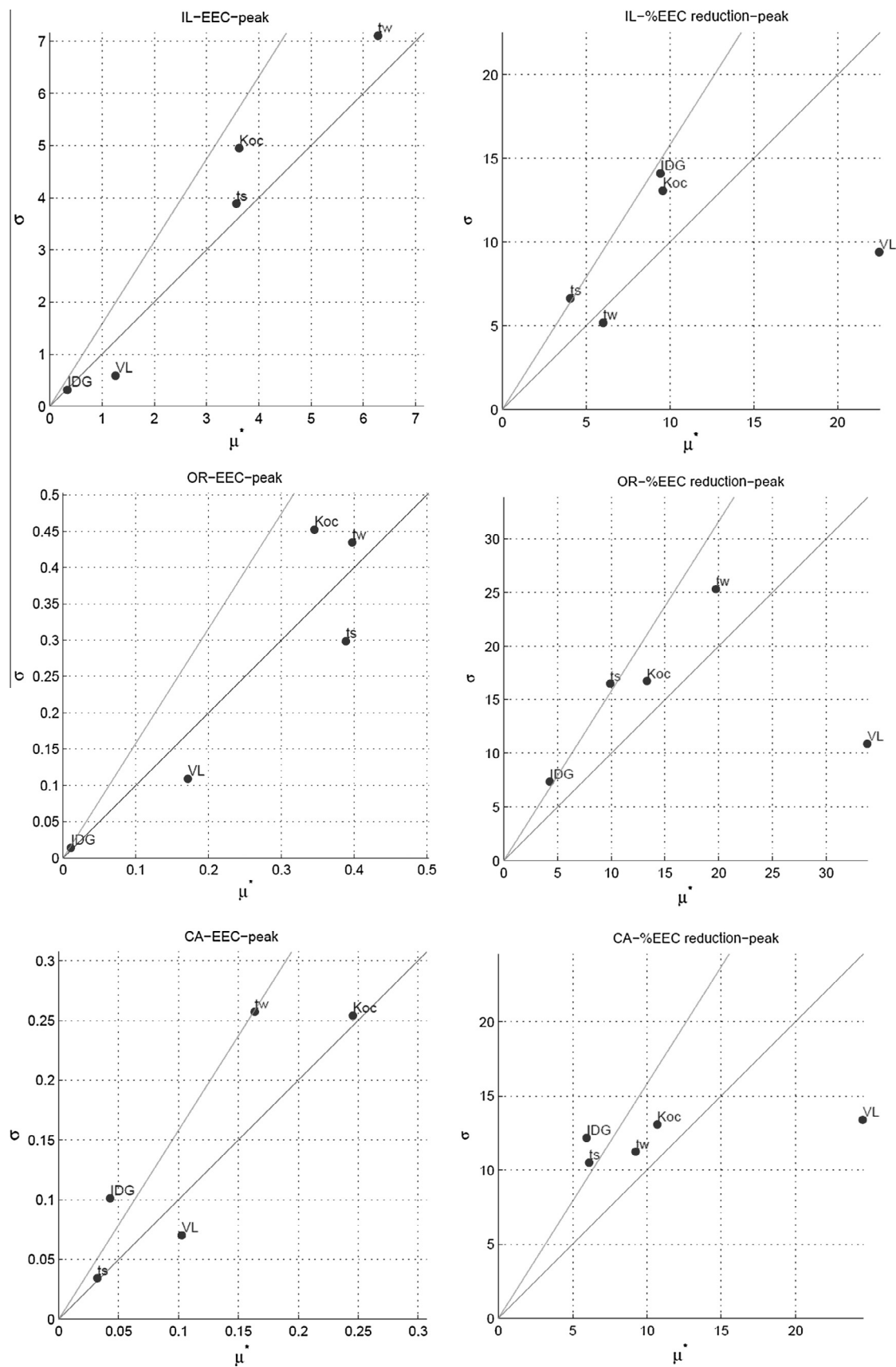


Fig. 4. Global sensitivity analysis on acute (peak) absolute (left) and percent reduction (right) in estimated environmental concentrations (EECs) for IL corn, OR wheat, and CA tomato scenarios. Larger separation from the origin in the Morris (μ^* , σ) plane indicates higher importance of the input factor or their interactions. Lines in graph indicate thresholds above which the effect of the factors is primarily through interactions (see text for explanation).

acute EECs, because these values were controlled by large rainfall/runoff events that were transporting pesticide mass through the VFS. There was no set efficiency of the VFS, but rather the efficiency depended on rainfall intensity and duration, infiltration in the VFS, and sedimentation in the VFS (Fox et al., 2009, 2010; Muñoz-Carpena et al., 2010). Such dependency on transport processes rather than physical characteristics of the VFS supports the need to use a process-based, mechanistic simulation framework such as the one proposed in this research.

For chronic (60-d) absolute EECs, the modeling simulations suggested similar ranges to the acute EECs, but in general smaller median values (Fig. 5). The range in the chronic absolute EECs were $0.1\text{--}23.2\ \mu\text{g L}^{-1}$ for the IL corn scenario, $0.0\text{--}2.2\ \mu\text{g L}^{-1}$ for the OR wheat scenario, and $0.0\text{--}0.9\ \mu\text{g L}^{-1}$ for the CA tomato scenario. Corresponding percent reductions for the chronic EECs ranged between -14.1% and 45.0% in the IL corn scenario, -5.7% and 79.4% in the OR wheat, and 5.9% and 61.6% in the CA tomato

scenarios. The range for the IL corn scenario was slightly lower than the acute EECs as the chronic analysis allows more time for degradation to occur within the receiving water. Similar results were observed relative to input factor importance between the acute and chronic simulations (Fig. 6). For absolute EECs, VL and degradation (IDG = 0 or 1) were typically lower ranked parameters in terms of importance. The VL becomes the most important factor when considering percent reductions in chronic EECs.

Consideration of degradation in the VFS (IDG = 1) was not as important if single, large runoff events control the transport process. Large runoff events transport most of the pesticide mass through the VFS without allowing for deposition within the VFS and the buildup of pesticide residues. Subsequent events will then not transport enough pesticide mass stored in the VFS to influence the estimated EEC. Therefore, the original modeling framework proposed by Sabbagh et al. (2010, 2013) that assumed insignificant residue in the VFS prior to an event was generally adequate when

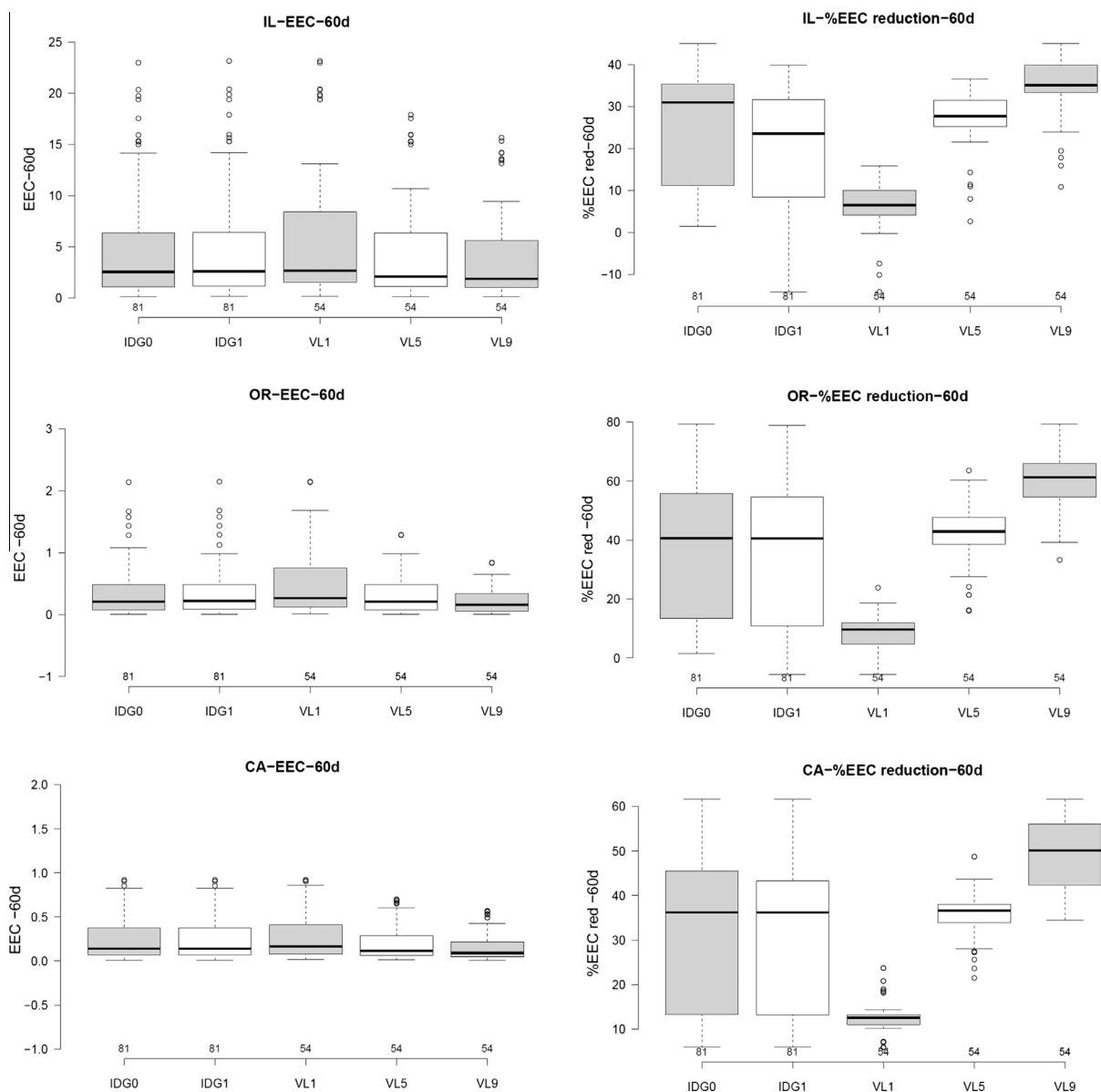


Fig. 5. Box plots of chronic (60-d) (left, in $\mu\text{g L}^{-1}$) and percent reduction (right, in %) in estimated environmental concentrations (EEC) for IL corn, OR wheat, and CA tomato scenarios. Note: IDG0 = without degradation; IDG1 = with degradation; VL1, VL5 and VL9 = 1, 5, and 9-m long VFS, respectively. Numbers below each box and whisker plot is the number of simulations within each category.

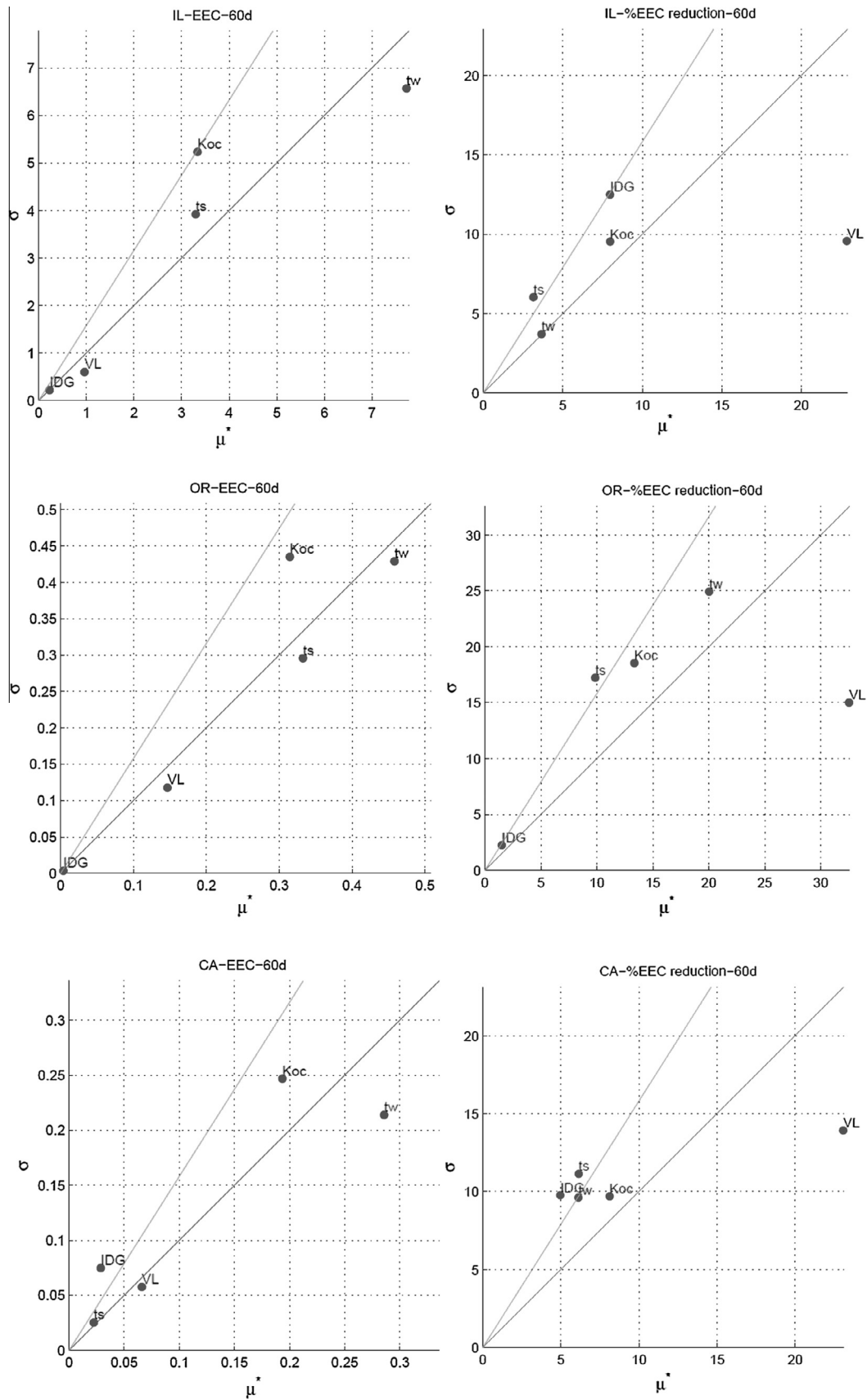


Fig. 6. Global sensitivity analysis on chronic (60-d) absolute (left) and percent reduction (right) in estimated environmental concentrations (EECs) for IL corn, OR wheat, and CA tomato scenarios. Larger separation from the origin in the Morris (μ^* , σ) plane indicates higher importance of the input factor or their interactions. Lines in graph indicate thresholds above which the effect of the factors is primarily through interactions (see text for explanation).

considering the median or upper percentiles of absolute acute or chronic EECs that typically represent the large runoff events of the long-term series. Degradation processes become more important when considering percent reductions in acute or chronic EECs especially at the lower range of the probability distributions.

4. Conclusions

The updated modeling framework proposed for pesticide environmental exposure assessment in this research elucidates filter strip pesticide dynamics for long-term assessment. The framework incorporated a mass balance and degradation process in the filter strip, significantly expanding upon the previous framework. Based on the three U.S. EPA scenarios considered in this research, considering degradation was not important if single, large runoff events controlled pesticide transport through the vegetative filter strip. Including the mass balance and degradation was important when considering percent reduction in exposure concentrations.

Note that PRZM/EXAMS is not the only pesticide exposure assessment framework used by the U.S. EPA and other regulatory agencies, but they are based on the similarly coupled “field-waterbody” long-term simulation concept. For example, the U.S. EPA’s new alternative framework called the Surface Water Concentration Calculator (SWCC) is based on PRZM/Variable Volume Waterbody Model (VWWM) (U.S. EPA, 2014), and EU-FOCUS uses a different waterbody model (TOXSWA). Here we aimed at specifically assessing the influence of storage and degradation of pesticide within the VFS. Therefore, frameworks investigated in previous research (Sabbagh et al., 2010, 2013) were used to isolate the effects of mass balance and degradation processes on the exposure assessment.

One of the steps in the model validation is to ensure that a model is predicting the correct responses relative to conceptual theory. Future research is needed to conduct further model evaluation with field testing. Although a wealth of field data exists for testing an event-based model similar to the existing framework being used in VFSSMOD (e.g., Lacas et al., 2005; Reichenberger et al., 2007; Poletika et al., 2009; Sabbagh et al., 2009), additional data sets are needed for testing the proposed framework. Field work should consider degradation by monitoring a series of runoff and pesticide loading events where pesticide concentrations are monitored over time both within and exiting the VFS. Multiple samples at different spatial and vertical locations in the VFS are needed, especially to estimate the mass that is being deposited in the mixing layer.

Future research should also investigate the incorporation of VFSSMOD into other exposure modeling frameworks with various waterbody models and across other scenarios. For example, the three scenarios investigated in this research were clay and clay loam soils, which are more prone to runoff. If a sandy soil were selected, the VFS would most likely be more effective in sediment trapping and infiltration. It should again be emphasized that these results assumed flow uniformity through the VFS; however, flow concentration may occur due to structural variability within the VFS. Poletika et al. (2009) and Fox et al. (2010) specifically addressed the impact of flow uniformity/concentration as a primary driver on pesticide trapping efficiency showing that the integrated VFSSMOD and empirical trapping efficiency equation predicted these conditions well, but this influence may be necessary for future VFS design. With that said, the addition of the new VFS mass balance and pesticide degradation component proposed in this research allows for a mechanistic analysis on the internal dynamics of the pesticide trapping process for all transport events, beyond the limited information contained in the upper percentiles of the EEC assessment process.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2015.07.010>.

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