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# Effect of vegetative filter strip pesticide residue degradation assumptions for environmental exposure assessments

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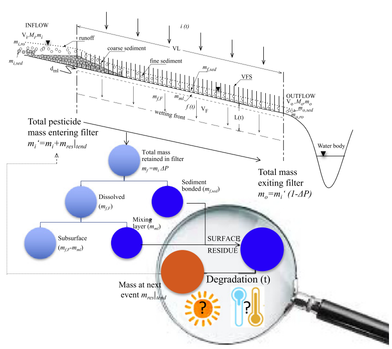
## HIGHLIGHTS

- Updated modeling framework to consider pesticide residues for exposure assessments
- Degradation assumption important in long-term assessment of filter strip residues
- Residue degradation assumption negligible for environmental exposure concentrations
- Various regulatory approaches result in similar higher-tier exposure assessments.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Understanding and simulating the fate and transport of pesticides from a field to adjacent receiving water bodies is critical for estimating long-term environmental exposure concentrations (EECs) in regulatory higher-tier environmental exposure assessments (EEA). The potential of field mitigation practices like vegetative filter strips (VFS) to reduce pesticide pollution is receiving increasing attention. Previous research has proposed a modeling framework that links the US Environmental Protection Agency's (US-EPA) PRZM/EXAMS higher-tier EEA with a process-based VFS model (VFSMOD). This framework was updated to consider degradation and carryover of pesticide residue trapped in the VFS. However, there is disagreement on pesticide degradation assumptions among different regional EEA regulations (i.e. US or European Union), and in particular on how temperature and soil moisture dynamics may affect EECs. This research updated the VFS modeling framework to consider four degradation assumptions and determine if VFS residues and/or EECs differed with each assumption. Two model pesticides (mobile-labile and immobile-persistent) were evaluated for three distinct agroecological scenarios (continental row-crop agriculture, wet maritime agriculture, and dry Mediterranean intensive horticulture) with receiving water bodies and VFS lengths from 0 to 9 m. The degradation assumption was important in long-term assessments to predict VFS pesticide residues (statistically different at $p < 0.01$). However, due to the relatively small contribution of residues on the total pesticide mass moving through the VFS, degradation assumptions had a negligible impact on

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EECs. This indicates that, while important differences exist between EU or US EEAs, the choice of pesticide degradation assumption is not a main source of these differences.



## 1. Introduction

Vegetative filer strips (VFS) are proposed best management or conservation practices to protect receiving water bodies from pesticides, nutrients, bacteria, and antibiotics applied on adjacent agricultural fields (Reichenberger et al., 2007; Sabbagh et al., 2009; Fox et al., 2010, 2011; Muñoz-Carpena et al., 2010; Lin et al., 2011; Fox and Penn, 2013; Lerch et al., 2017). Significant progress has been made regarding the ability to simulate pesticide transport through VFS (Muñoz-Carpena et al., 1999; Muñoz-Carpena and Parsons, 2004) as part of higher-tier environmental risk assessments (Sabbagh et al., 2010, 2013). These VFS simulation tools are based on process-based modeling of flow and sediment transport with a semi-empirical equation for pesticide trapping (Sabbagh et al., 2009). Evaluation of these tools across multiple field datasets suggests good predictive performance (Sabbagh et al., 2009; Poletika et al., 2009; Pan et al., 2017). Questions arose about the environmental risk assessment modeling approaches (Sabbagh et al., 2010, 2013) regarding the influence of pesticide residue stored in the VFS being available during subsequent runoff events. Pesticide trapped in the VFS is subject to degradation between events that govern the available mass able to be transported from the VFS. Muñoz-Carpena et al. (2015) recently proposed a pesticide mass balance approach to estimate pesticide residue and its degradation in the VFS.

Generally, a pesticide first order degradation rate can be expressed as the product of the reference rate ($k_{ref}$) and modifiers for temperature ($k_T$) and soil moisture ($k_\theta$):

$$k = k_{ref} k_T k_\theta \tag{1}$$

Note that $k_{ref}$ is the pesticide degradation rate ($d^{-1}$) at standard temperature and soil moisture conditions ($T_{ref}$ and $\theta_{ref} = \theta_{FC}$ = field capacity) and related to the pesticide half-life ($t_{1/2}$, d) by $k_{ref} = -\ln(0.5) / t_{1/2}$. The original mass balance approach proposed by Muñoz-Carpena et al. (2015) assumed the formulation as utilized by the EU FOCUS (1996) with adjustments for both temperature and moisture content (Nicholls et al., 1982, 1984):

$$k_T = e^{\frac{E_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)} \tag{2}$$

$$k_\theta = \left(\frac{\theta}{\theta_{ref}}\right)^{-\beta} \tag{3}$$

where $T$ = average daily surface soil temperature (K) between events; $T_{ref}$ = 293.15 K; $E_a$ = degradation activation energy (65.4 kJ/mol); $R$ = gas constant; $\theta$ = average daily surface soil moisture content between events [$m^3\ m^{-3}$]; $\theta_{ref} = \theta_{fc}$ = soil field capacity (EU FOCUS, 2006; EFSA, 2008); and $\beta$ is a constant typically assumed as 0.7 (EU FOCUS, 2006).

The mass balance approach proposed by Muñoz-Carpena et al. (2015) only considered the single degradation assumption described above (Table 1). They also only compared acute and chronic aquatic estimated environmental exposure concentrations (EECs) based on the 90th percentile exceedance probability for three US-EPA agroenvironmental scenarios with and without residues and degradation considered. Considering degradation in the VFS was not relatively important if single, large events were controlling the transport process, as is typical for the higher percentiles (90th percentiles) considered in standard exposure assessments. Degradation processes become more important when considering percent reductions in acute or chronic EECs, especially under scenarios with lower pesticide losses such as in the California tomato and Oregon wheat scenarios (Muñoz-Carpena et al., 2015).

Approaches vary for modeling pesticide degradation depending on the regulatory authority. Recent guidance from the North American Free Trade Agreement (NAFTA) Technical Working Group on pesticides (NAFTA, 2015) recommended procedures for determining first-order degradation rate constants from biotransformation/degradation studies. No mention in this guidance document was made regarding adjustments for temperature or soil moisture to degradation constants utilized in modeling field studies. However, an EU Focus Group specifically called for normalization of field-measured dissipation constants for temperature and moisture content (EU FOCUS, 2006). These adjustments are used for both calculating a degradation rate based on a reference temperature from laboratory and field studies and for applying the degradation rate in modeling simulations. The EU Focus Group specifically noted that "…pesticide leaching models can simulate soil temperature and moisture at different depths in soil from standard weather data and their use is recommended if detailed measurements are not available" (EU FOCUS, 2006).

The key idea is that a more complicated degradation assumption of pesticide residue fate in the soil (or in the present case, a VFS) may result in more appropriate EECs. However, how important are various degradation assumptions on resulting EECs? Should a consistent degradation assumption be utilized within an integrated upland and VFS modeling framework when performing EEAs? These questions are important for ensuring adequate environmental protection via the estimation of EECs, understanding the potential impact of considering more complete degradation assumptions to EEC estimation, and identifying to what extent the decision of different EEA regulations concerning pesticide degradation assumption impacts the comparability of EECs. The aim of this study was not to evaluate the absolute importance of degradation assumptions, but its relative importance in the context of all other concurrently operating inputs or processes that control higher-tier EECs. Therefore, specific objectives included: (i) enhancing the VFS pesticide mass balance approach to consider four assumptions of degradation rates with alternative temperature and soil moisture adjustments (including those used by the two major EEA regulators) and (ii) evaluating the impact of considering different degradation assumptions on pesticide residue and across a range of exceedance probabilities EECs for two model pesticides (mobile-labile and immobile-persistent) in three distinct agroecological scenarios.

## 2. Methods and materials

### 2.1. Enhanced mass balance framework and degradation equations

VFSMOD (Muñoz-Carpena et al., 1999, 2015; Muñoz-Carpena and Parsons, 2004) has been coupled for use with US-EPA (Sabbagh et al., 2010) and EU FOCUS (2007) models in long-term higher-tier surface runoff pesticide EEA frameworks where flow, sediment and pesticide runoff at the end of the field is calculated by the model PRZM (Lin et al., 2007; EU FOCUS, 2001, 2010). Then, VFSMOD routes the field outflows through a VFS of desired characteristics to estimate potential load reductions before entering the aquatic environment as predicted by EXAMS (recently replaced with the Variable Volume Water Model, VVWM, but resulting in very similar EECs) (Burns, 1990; Jackson et al., 2005) or TOXSWA (Horst et al., 2003) in the US or EU, respectively. Although with some differences, this conceptual approach (long-term simulation of coupled field-VFS-waterbody) applies to commonly used, higher-tier pesticide EEAs (see Table 2 in DEFRA, 2013).