Refining Pyrethroid Aquatic Exposure Assessments by Incorporating Measured Landscape and Environmental Variability using Probabilistic Approaches. I – Overview – Concepts for Refining Lower Tier Exposure Estimates.

Paul Hendley[1], Amy Ritter[2], Chris Holmes[2] and Dean Desmarteau[2].

[1] Phasera Ltd., Bracknell, UK. [2]Waterborne Environmental Inc., Leesburg, VA.

PYRETHROID WORKING GROUP

Abstract

Regulatory aquatic exposure modeling at lower tiers typically uses standard scenarios based on assumptions designed to ensure model output is extremely conservative. To improve the accuracy of lower tier exposure assessments, these assumptions need to be examined to prioritize opportunities for refinement. Selected refinements should be quantifiable as numerical distributions of real-world variability which can be incorporated into exposure assessment frameworks via probabilistic modeling. National and regional distributions of landscape-related runoff/erosion and drift load transport from treated areas into receiving waters are an important and quantifiable source of variability in lower tier aquatic assessments. Additionally, for uses incorporating multiple aerial applications each season, the real-world co-occurrence of wind speed/direction across sequential seasonal applications has significant and quantifiable variability. The combined effect of these two real-world distributions on probabilistic distributions of potential aquatic pyrethroid exposure is a very significant reduction relative to lower tier predictions. However, other unchanged scenario assumptions ensure the predictions remain conservative.

Background

In the 1990's Steven Johnson at USEPA listed some important questions for risk assessors including:

► What are the effects of concern? ► Why are they of concern? ► What is the magnitude and probability of these effects?

Estimation of the potential aquatic impact of a pesticide use pattern requires understanding potential magnitude and probability of exposures that might cause effects. The USEPA FIFRA (Federal Insecticide Rodenticide and Fungicide Act) process uses a tiered approach to cost effectively evaluate potential aquatic risk. The tiered scheme starts with an extremely conservative single-point estimate of exposure for comparison with worst case effects data. Where this indicates the potential for risk, more sophisticated lower-tier model scenarios are used to estimate crop-specific exposures. This lower tier modeling is used to identify taxa that may need a more refined analysis by more sophisticated exposure assessment.

Currently USEPA is examining nine synthetic pyrethroids as part of the Registration Review process. The lower tier exposure modeling indicates generally that fish and mollusk taxa are expected to be unaffected by any pyrethroid uses. However, other invertebrates – especially arthropods – are indicated as being potentially at risk using extremely conservative approaches and a refined exposure and effects assessment is needed. This poster describes Pyrethroid Working Group (PWG) thinking on designing refinements appropriate for the pyrethroid class of insecticides; however, many of these refinements are also relevant for other classes of pesticide.

Standard Lower Tier Aquatic Exposure Approach

Lower tier exposure estimates use these key inputs:

- Crop specific pesticide label and required mitigations.
- Chemical behavior from laboratory studies.
- Environmental runoff /erosion at single location (e.g. Soil, slope, tillage).
- Corresponding 30-year history of precipitation/temperature.
- Standard levels of drift entry for every application based on droplet size.

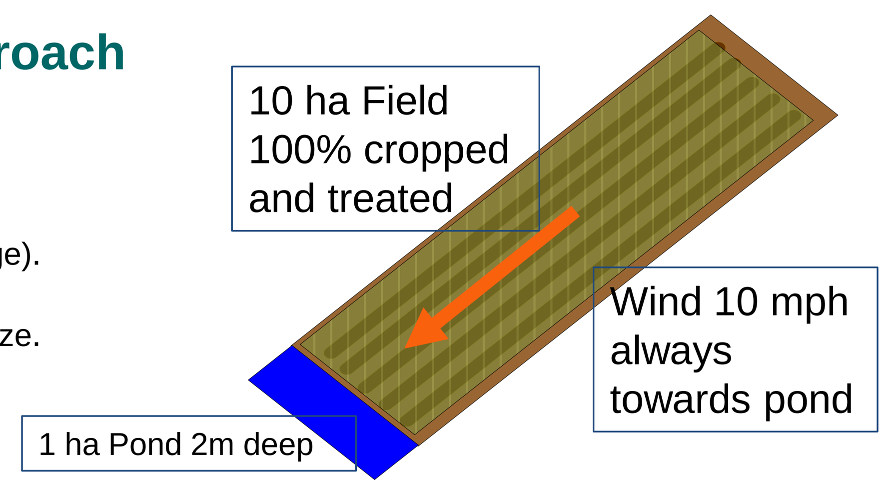


Fig 1: standard lower tier scenario

The lower tier models use a standard field pond scenario (see Fig 1) and compute daily concentrations in a receiving water body based on:

- Inputs of chemical on certain days:
  - Dissolved/adsorbed loads in modeled rain-driven runoff/erosion from treated fields.
  - Aerial drift loads on application days (spray buffer if labelled, max rates, minimum intervals).
- Daily time step repartition of chemical between sediment and water phase.
- Separate daily time step estimates of chemical degradation in sediment and water phase.

Models are run using local daily weather for 30 yrs with chemical applied to the same crop each year

- Water column, pore water and sediment concentrations estimated daily
- Post processing computes annual maxima for each of 30 years for instantaneous and 24hr, 21day and many other time weighted average metrics
- 90th centile year annual maximum of desired metrics used for risk assessment

Topics Identified by PWG for Possible Higher Tier Refinement

PWG investigated the following aspects of the lower tier exposure assessment approach from the perspective of higher tier refinements specifically targeted at pyrethroids.

- Assumptions regarding chemical inputs given the comprehensive data available for pyrethroids
- The relevance of current modeling default assumptions and algorithms given the exceptional hydrophobicity of pyrethroids
- The mass balance of water and sediment in receiving waters (e.g. inflow/outflow and burial)
- Relevance of the standard scenario for each crop
- Sources of potential uncertainty impacting
  - The concentrations expected in a potentially exposed water body
  - The probability of water bodies being exposed

Chemical Degradation Inputs for Pyrethroid Exposure Modeling

Due to the extensive data available for individual pyrethroids and for the class, PWG has used mean half-life data from high quality recent literature comparative water sediment studies and regulatory soil degradation programs. For some pyrethroids soil photolysis can be significant.

Characteristic Pyrethroid Behavior in Water Bodies has Significant Implications

Because pyrethroids have a remarkable and unique set of properties – especially their extreme hydrophobicity – a very detailed conceptual model of their behavior in aquatic systems has been developed – see Figure 2. Key implications include:

- Due to the importance of pyrethroid adsorption behavior, Equilibrium Partitioning theory (EqP) dominates pyrethroid risk assessment; therefore careful measurements of the K_{OC} that relates to the freely available (i.e. bioavailable) residues (K_{OCSPME}) have been made using standard sediments for nine pyrethroids. Pyrethroids degrade much faster than most hydrophobic chemicals due to their ester bond. This explains why they do not bioaccumulate to any significant extent in ecosystems. Pyrethroid degradates are not biologically active.
- Pyrethroid hydrophobicities mean that their transport to water bodies is largely as chemical adsorbed to sediment and that their behavior in water bodies is driven by adsorption/desorption to particulates
  - Efficiency of sediment transport & all sources of adsorption in water bodes become significant. Vegetative filter strips very effective for pyrethroids
  - Receiving water models must properly account for sediment/water deposition, resuspension, burial, and exchange behaviors
- Substantial data (mesocosms & other studies) indicate that pyrethroids degrade chemically very rapidly in natural waters as well as adsorbing strongly to all organic materials producing very fast dissipation rates which are much faster than those measured in laboratory studies.
- The speed and extreme extent of adsorption of pyrethroids mean that default assumptions about instantaneous and rapid mixing of residues in receiving waters are much less realistic than they are for more water soluble molecules
- Large body of pyrethroid monitoring data exist (especially CA) -studies indicate that sediment residues within water bodies highly spatially variable
- Literature indicates that there are many other pyrethroid-specific behaviors that impact potential aquatic EECs

Resulting Basic Model Refinements – Pyrethroid Tier II+AR

- Soil photolysis applied when soil is unshaded and best available mean laboratory soil and water/sediment degradation data used
- K_{OCSPME} coefficients are used for modeling water column and pore water EECs.
- AGRO-2014 is used in place of EXAMS as receiving water model – better sediment handling and calibrated with pyrethroid field data
- 10-ft Vegetative Filter Strip (VFS) is required on all pyrethroid labels and the VFSMOD model has been included to modify water/ sediment/chemical transport from treated field to receiving waters.
- Pyrethroid labels specify droplet size and no-spray buffers (ground/air) – these are incorporated via AgDrift and RegDisp models.
- For many crops, early season applications target soil pests and are therefore applied by ground. Agronomic Realism (AR) used to specify ground/aerial methods for each labeled application but maximum numbers of applications and maximum rate retained.

PWG Novel Probabilistic Model Refinements

PWG made a detailed analysis of lower tier model scenario default assumptions and potential sources of uncertainty – see Fig 3. As a result, PWG prepared detailed lists of sources of potential uncertainty & prepared significant crop-specific Spatial Landscape Databases.

NHD+ catchment analysis for crop-of-interest (CoI) - 2008-2012 cropping

- Proximity of crops to NHD+ stream reaches
- Percent cropped area (PCA) analyses
- Relative vulnerability to pyrethroid and sediment runoff and erosion
- High statistical confidence due to size of catchment populations

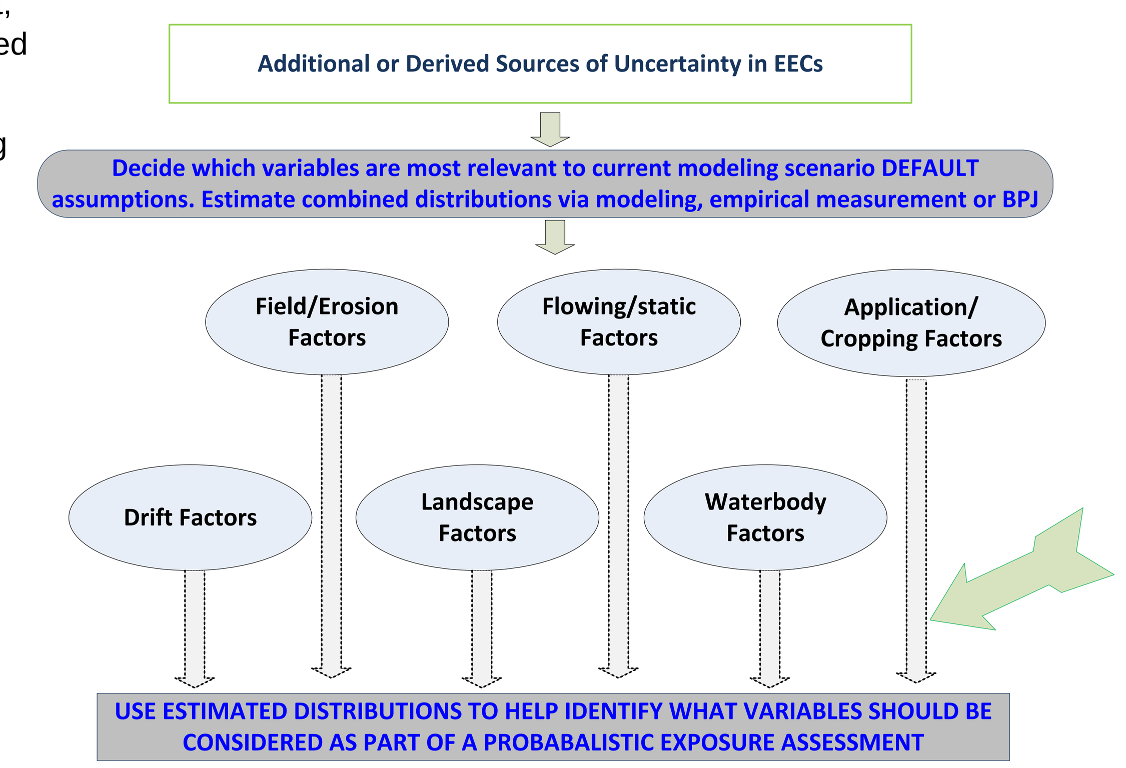
In addition, Pyrethroid specific use data has been abstracted from AgroTrak® and CA PUR Data

- Pyrethroid use data & market share estimates
  - Use data for all crops, individual crops & for all pyrethroids & each individual AI
- Percent Treated Area
- Percent applied by ground or air (not PUR)

Also evaluated potential impacts of other sources of uncertainty

- The magnitude/duration of potential residues in exposed ponds
- The likelihood of finding water bodies that might be exposed
- Potential impact of uncertainties that cannot easily be quantified by current models

Figure 3: Potential sources of uncertainty considered



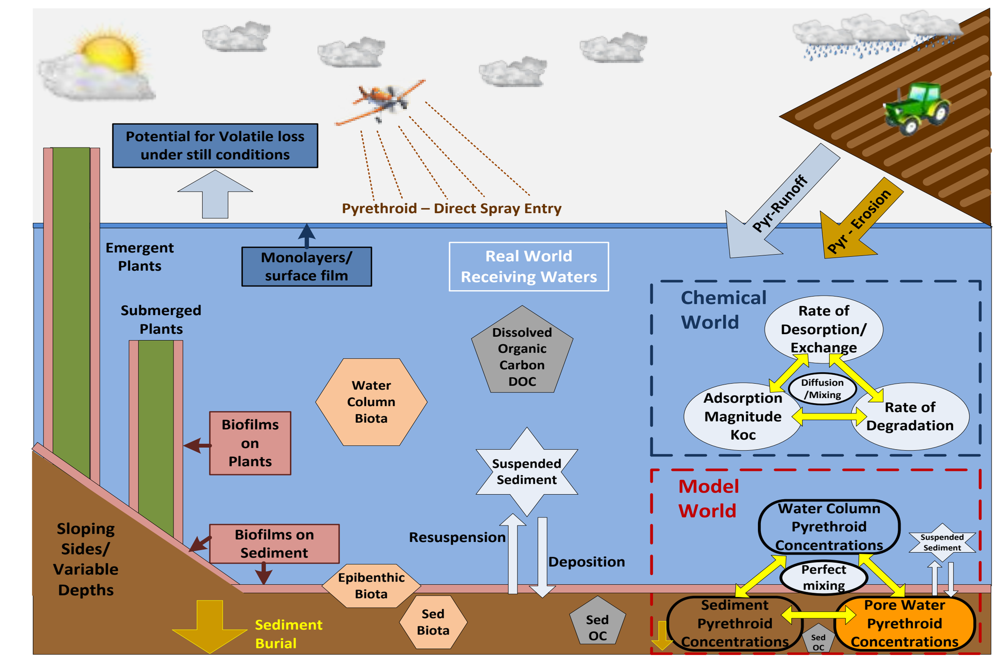


Figure 2: Detailed conceptual model of pyrethroid behavior in receiving waters.

Landscape Probabilistic Data Significantly Impact EEC Distributions

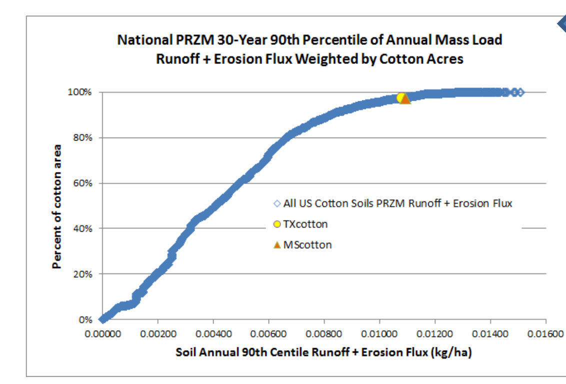


Fig 4: Crop-specific runoff/erosion (R/E) potentials of catchments rank standard EPA scenarios

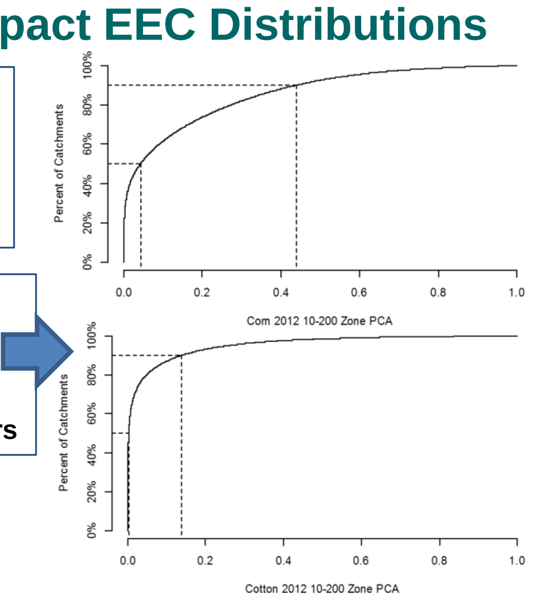
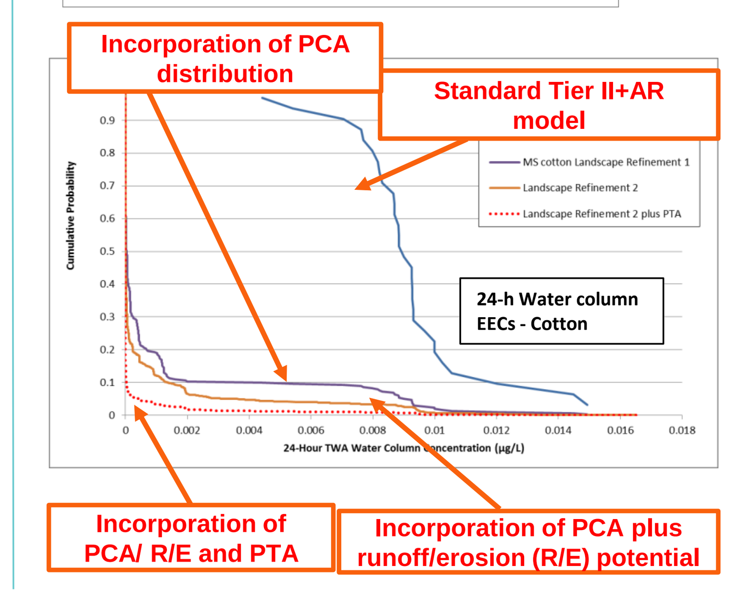


Fig 5: Crop-specific PCA distributions describe vulnerability potential of catchments for delivering chemical to receiving waters



- By addressing default assumption that all watersheds are 100% cropped, a more realistic distribution of likelihood of potential exposure by pyrethroids is developed
  - Still includes maximum rates and Nos. applications
- Spatial databases can be queried to provide national or regional ("hot-spot") landscape distributions
- The additional effect of the percent of the crop treated (PTA) with ANY pyrethroid is also a key uncertainty ignored in the standard lower tier scenario

Additional Factors Influence EEC Distributions in Exposed Ponds

Several factors tend to reduce standard EECs for EXPOSED water bodies e.g.:

- Field water body degradation rates – Fig. 6
- Field measured wind speed, %RH & temperature for estimating drift load from multi-application events

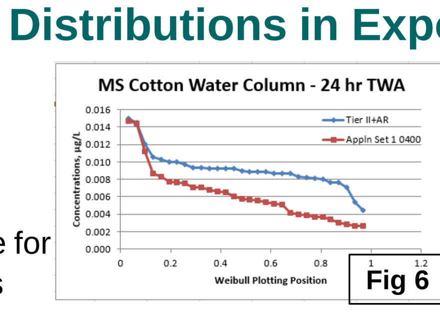


Fig 6

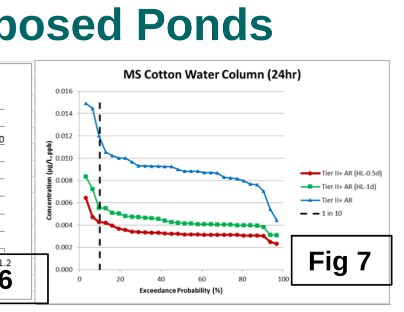


Fig 7

Conclusions

PWG has analyzed factors that influence the standard lower tier modeling and has identified several key quantifiable and non-quantifiable landscape, receiving water and chemical-related uncertainties for detailed evaluation. The resulting probabilistic assessments indicates that there are considerable conservatisms in the current standard regulatory modeling. Accompanying posters provide more details.

Acknowledgement and References

The Pyrethroid Working Group (PWG) is a US task force whose members include eight primary pyrethroid registrants (AMVAC Chemical Corporation, BASF Corporation, Bayer CropScience LP, Cheminova A/S, DuPont Crop Protection, FMC Corporation, Syngenta Crop Protection, LLC, Valent U.S.A. Corporation).