Pesticide Surface Water Monitoring: Bias Factors to Estimate Peak Concentrations and PRZM-Hybrid to Complete Measured Chemographs

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INTRODUCTION

- Abundant pesticide aquatic monitoring data with variable sampling frequency and fewer daily samples.

- Challenges to estimate potential exposure maxima (peak, rolling average concentrations) based on non-daily data.

- Objective: Present two new approaches to improve estimates of potential maximum concentrations.

  - Empirical **Bias Factor (BF)**: Multipliers derived from available daily/near daily datasets to estimate the potential “missed peaks” in non-daily samples.

  - Deterministic **PRZM-Hybrid** model: New algorithm to determine likely chemical application timing for daily chemograph construction.
BIAS FACTOR APPROACH

Bias Factor (BF) = 95\textsuperscript{th} centile of the Multiplicative Factor (MF) distribution.

\[
MF = \frac{\text{True value}}{\text{Sub-sample value}}
\]

Endpoint of interest (e.g., peak or max rolling averages) from daily or near daily data

Endpoint of interest (peak or max rolling averages) from sampling of non-daily intervals
Bias Factor Examples

- If BF ≈ 1, same as true value.
- The closer BF is to 1, the more accurate in predicted maxima.
- If BF = 2, true value may be potentially missed by a factor of 2 if daily samples were taken.
Two Ways of Sub-Sampling

Systematic: fixed sampling interval

Stratified: random in each sampling window

- Bias factors by systematic sampling is generally smaller than stratified random sampling
PRZM-HYBRID APPROACH

• Deterministic field scale model PRZM
• New algorithm to determine field “workability” for chemical application timing (crop GDD, label use time window, soil moisture, and rainfall).
• Actual pesticide use rate within watershed estimated by CRD survey data.
• Predictions of concentrations in edge-of-field runoff water (weighted by soil-area and percent crop in watershed).
DATA SETS


2. NCWQR (OH); Atrazine 62 site-years monitoring (1993-2008) in Maumee, Sandusky, Honey, and Rock.


First two data sets for BF determination, and third data set for independent validation.
Bias factor calculation

● True value
   1. Daily measured dataset.
   2. Endpoint: Annual rolling average maxima: Peak, 4-d, 7-d, 14-d, 30-d, 60-d, 90-d ……

● Sub-sample value
   1. Systematic sub-sampling intervals: 7-d, 14-d, & 28-d
   2. Linear interpolation for each sub-sampling interval creates daily time series.
   3. Calculate endpoint (same as above).
RESULTS: BIAS FACTOR

- BF increases as sampling interval increases or as endpoint duration decreases.
- Average BF = 2.4 (1.0 to 6.3) for 7-d sampling to estimate true annual peak.
- Highest BF may be driven by peak shape (not necessarily peak magnitude)

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BF with Watershed Characteristics

(BF for annual peaks; Dataset 2: NCWQR atrazine monitoring, 1993-2008).

7-day systematic sampling

R² = 0.113

14-day systematic sampling

R² = 0.326

28-day systematic sampling

R² = 0.547
BF Predictions vs. Annual Maximum Concentrations

RESULTS: PRZM-HYBRID

Measured and model-predicted atrazine chemograph in two watersheds (2008-11)
NE-site, 2010
Earlier storm-induced runoff from field to river with little flow – why PRZM-Hybrid under-predicted the 2010 peak
CONCLUSIONS

- BF=f(duration of endpoint, sampling interval/frequency).
  - For all (69 site-yr.-chemical) data, avg. BF=2.4 (range=1.0-6.3) for 7-d sampling interval for true annual maximum (BF larger for 14-d & 28-d sampling intervals).
  - Highest BF may be driven by peak shape (not necessarily peak magnitude)
- BF=f(WS characteristics - hydrology, area-normalized flow).
  - BF larger for more responsive/smaller WS.
- PRZM-Hybrid provides reasonable chemograph estimates.
  - Peak concentration=f(storm-induced runoff and timing)
RECOMMENDATIONS

● Use BF based on watershed characteristics (large vs. small; flowing vs. static), develop statistical confidence using multi-site and multi-year data sets.

● Use BF to
  - Improve monitoring study design (e.g., optimize sampling frequency based on different watershed characteristics)
  - Guide deterministic modeling (screening for higher tier model refinement)

● Use combined monitoring and modeling to refine exposure estimates.
End of Presentation.

Thank you!