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) = 95th centile of the Multiplicative Factor (MF) distribution.

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

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

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

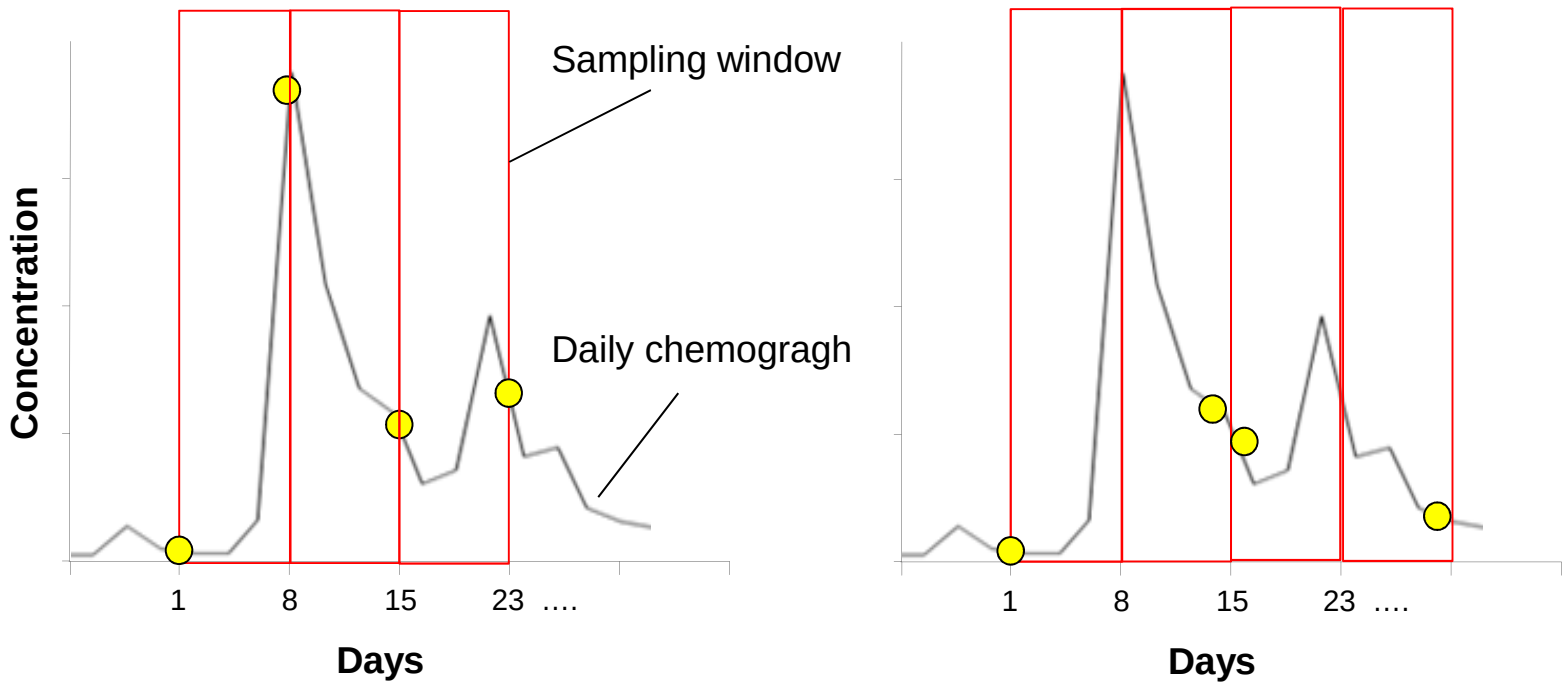
Bias Factor Examples

- 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

1. CDPR (CA); Chlorpyrifos (1996-1997) in Orestimba Crk. Simazine & Molinate (1991-1994) in Sacramento R.
2. NCWQR (OH); Atrazine 62 site-years monitoring (1993-2008) in Maumee, Sandusky, Honey, and Rock.
3. Syngenta 90 site-years atrazine monitoring data (2008-2012) in Mid-West headwater watersheds.

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).

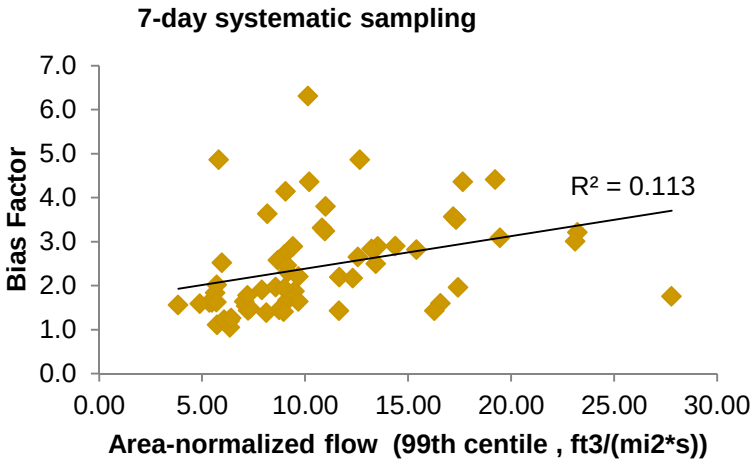
RESULTS: BIAS FACTOR

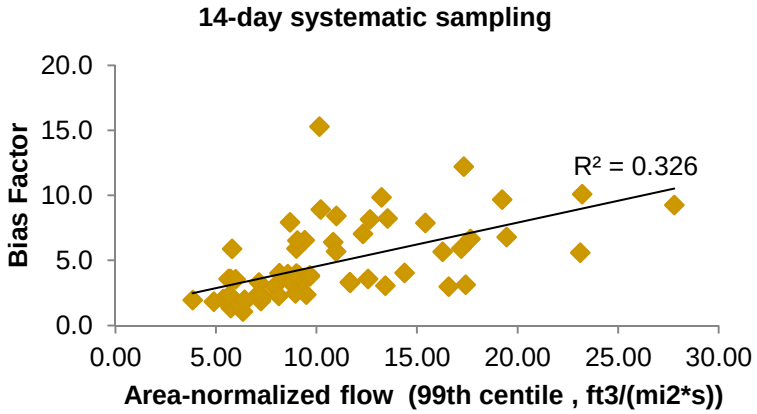
- BF increases as sampling interval increases or as endpoint duration decreases.
- Average BF=2.4 (1.0 to 6.3) for 7-d sampling to estimate true annual peak.
- Highest BF may be driven by peak shape (not necessarily peak magnitude)

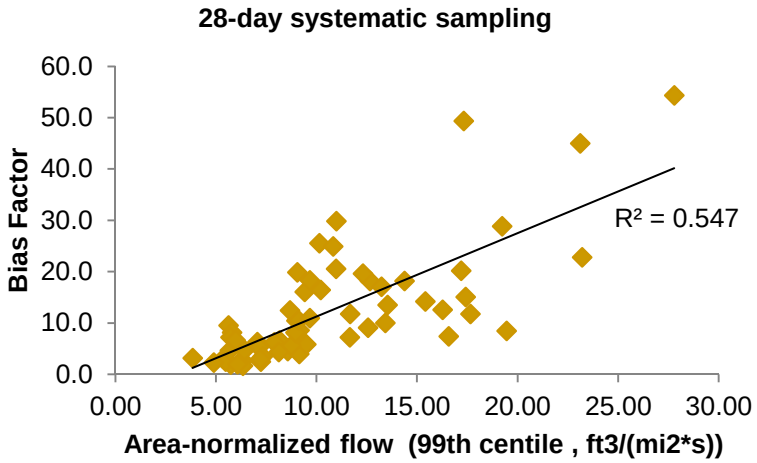
Annual Rolling Average Maxima	Dataset 1: 1996-97 (Chlorpyrifos; 1 site-year)			Dataset 1: 1991-94 (Simazine & Molinate; 6 chemical-years)			Dataset 2: 1993-2008 (Atrazine; 62 site-years)		
	Sampling Interval								
	7-d	14-d	28-d	7-d	14-d	28-d	7-d	14-d	28-d
Max	4.1	8.2	30.3	1.0-2.8	1.0-4.2	1.1-7.5	1.1-6.3	1.1-15.3	1.6-54.3
4-day	2.0	3.7	13.3	1.0-1.9	1.0-2.6	1.1-4.9	1.0-3.5	1.1-9.1	1.6-51.2
7-day	1.8	3.1	11.0	1.0-1.5	1.0-2.6	1.1-3.6	1.0-2.8	1.1-8.4	1.6-45.6
14-day	1.4	2.0	6.9	1.0-1.6	1.0-2.2	1.1-3.7	Not calculated		
30-day	1.3	1.4	4.0	1.0-1.6	1.0-2.0	1.0-3.1	1.1-2.2	1.2-4.6	1.5-18.3
60-day	1.4	1.9	4.2	1.0-1.4	1.0-1.7	1.0-2.4	1.0-2.0	1.2-3.8	1.3-14.2
90-day	1.4	1.9	3.8	1.0-1.3	1.0-1.6	1.0-2.0	1.0-2.1	1.2-3.5	1.3-11.5

BF with Watershed Characteristics

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







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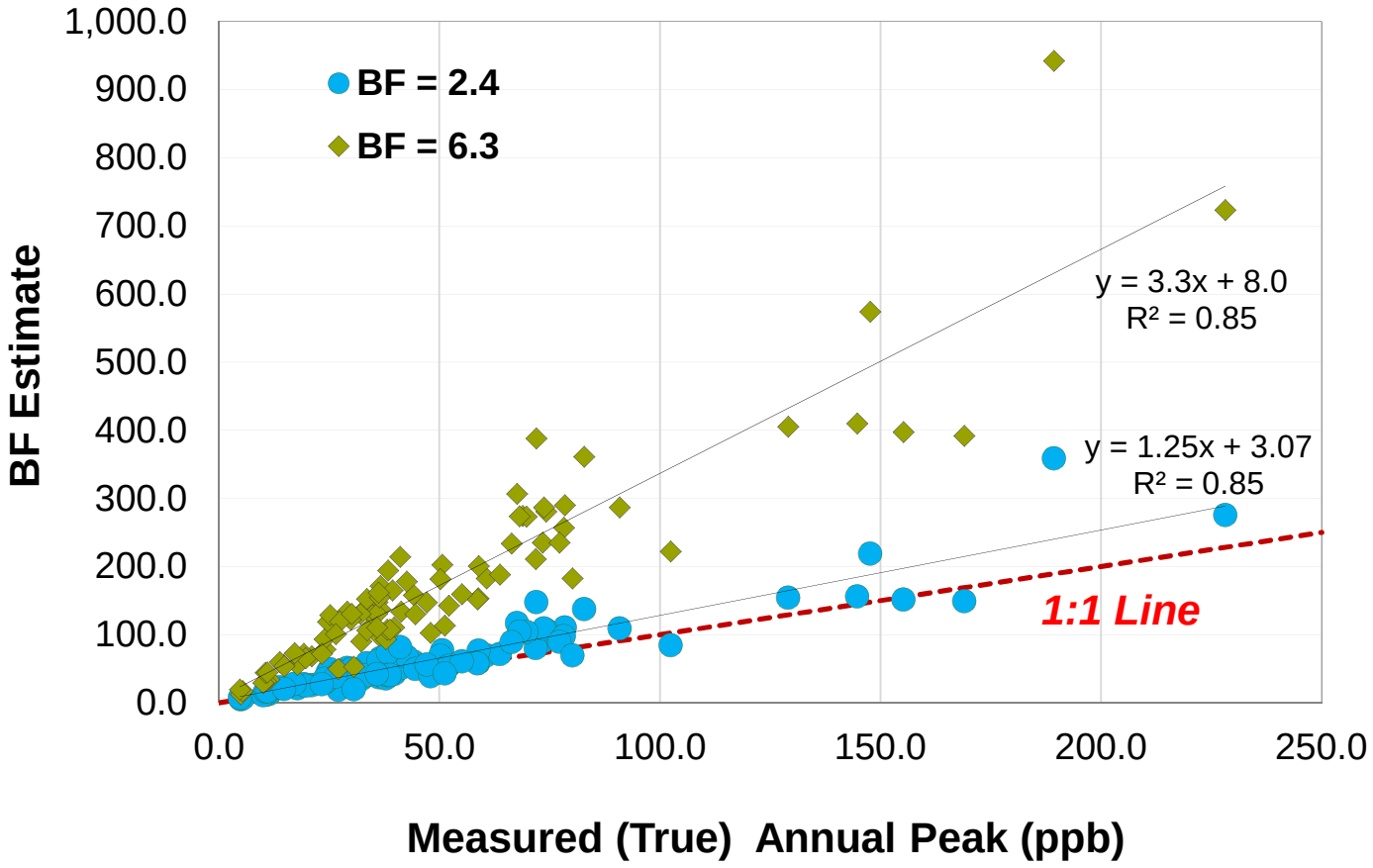
BF Predictions vs. Annual Maximum Concentrations

Dataset 3: 90 watershed-year daily atrazine monitoring dataset (2008-2012).



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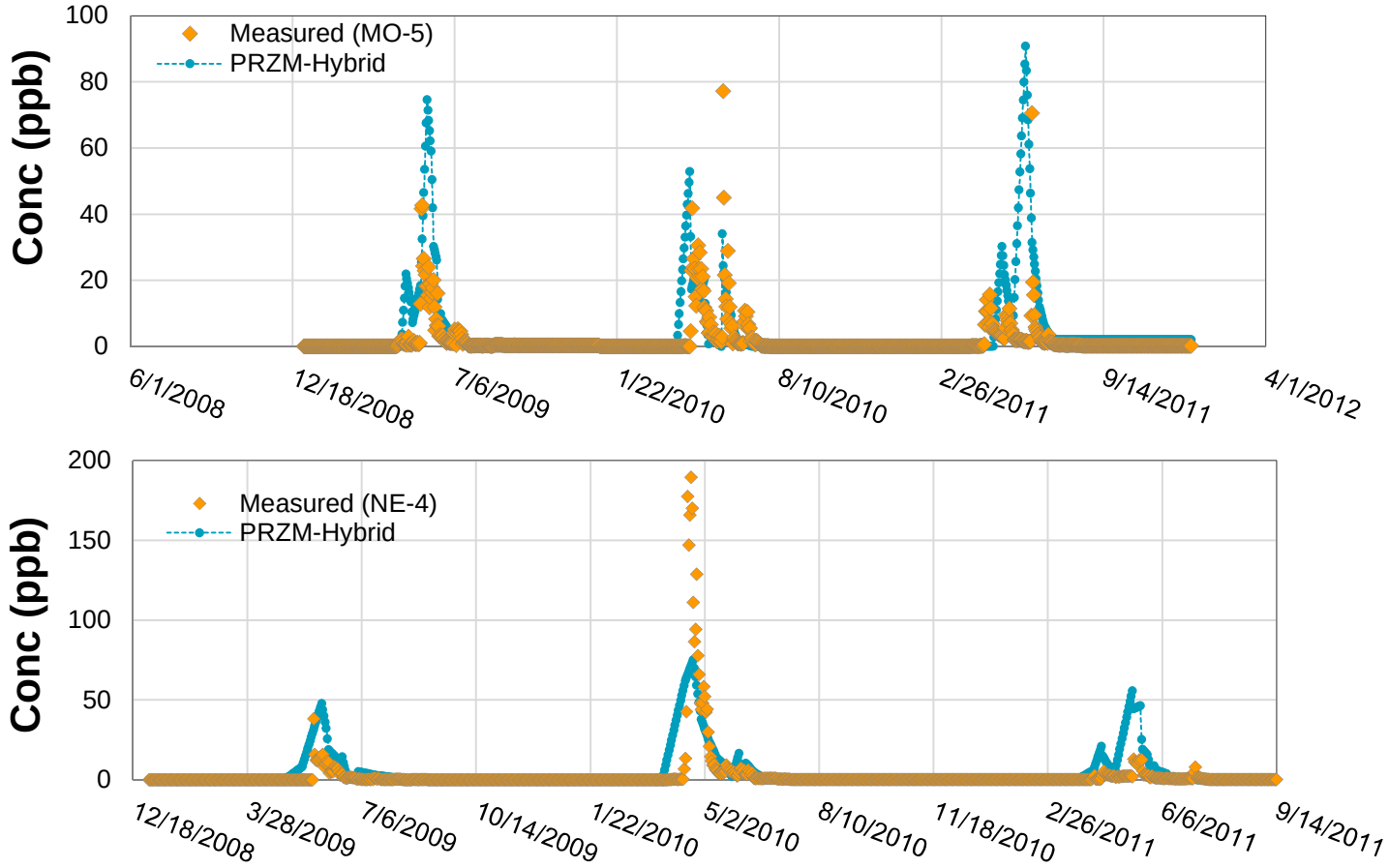
RESULTS: PRZM-HYBRID

Measured and model-predicted atrazine chemograph in two watersheds (2008-11)



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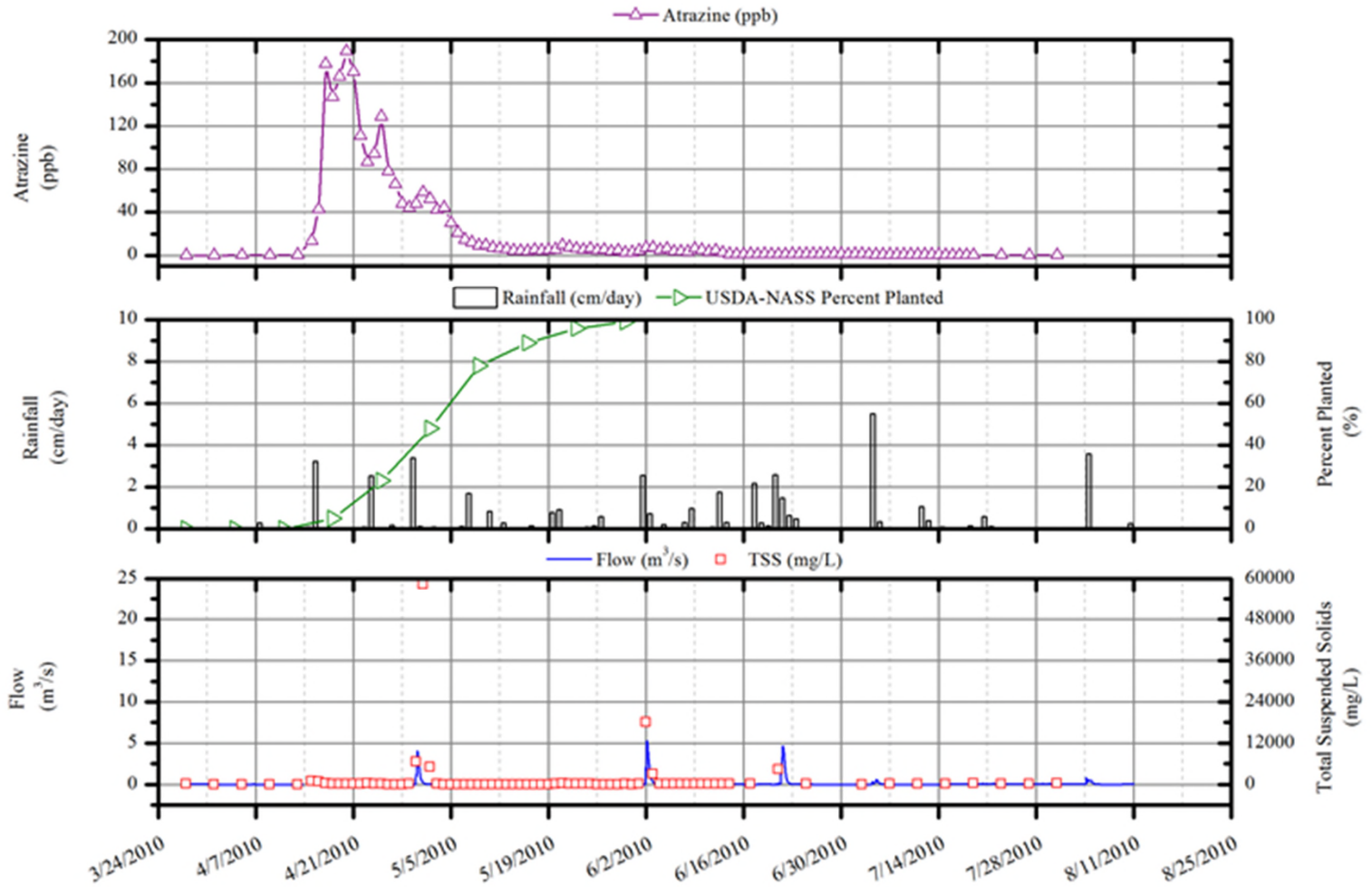
NE-site, 2010
Earlier storm-induced runoff from field to river with little flow – why PRZM-Hybrid under-predicted the 2010 peak



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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!