Estimation of Annual Maximum Herbicide Concentrations from Sparse Monitoring Data with the Statistical Model SEAWAVE-QEX in a High Agricultural Intensity Catchment in Western Europe

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Pesticide Behaviour in Soils, Water and Air 2022

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Motivation and Introduction

Pesticide surface water monitoring data have rarely been used as the only quantitative measure of exposure

- Infrequent sampling and lack of coverage across the landscape
- Peak concentrations may be missed for greater than daily sampling intervals

Daily sampling may be necessary during active pesticide runoff periods

- The cost of daily monitoring are too high

Can statistical tools be used to derive annual maximum concentrations from sparse sampling?

- SEAWAVE-QEX model

Outline

Introduction and Motivation

Methodology

- SEAWAVE-QEX model
- Study area
- Data summary
- Evaluation methodology

SEAWAVE-QEX results

Conclusions

SEAWAVE-QEX Model

Statistical model developed by USGS

- Estimate daily pesticide concentrations from sparse monitoring data
- Streamflow is main covariate (precipitation or stage data can also be used)

Model input and data requirements

- 3 years of data (daily flow data, at least 12 pesticide samples per year)
- More than 30% of samples need to be greater than the detection limit

Model output

- Several simulations of equally probable daily pesticide concentration values (called traces or conditional simulations)

SEAWAVE-QEX Model

A set of statistical parameters are calculated to solve the following equation:

$$\log(C(t)) = \beta_0 + \beta_1 W(t) + \beta_2 A_{MT}(t) + \beta_3 A_{ST}(t) + \beta_4 (t - t_m) + \sigma[1 + \propto W(t)]^{1/2} Z(t)$$

Seasonal wave

Mid-term and short-term variability

Annual linear trend (t_m is midpoint of multi-year period)

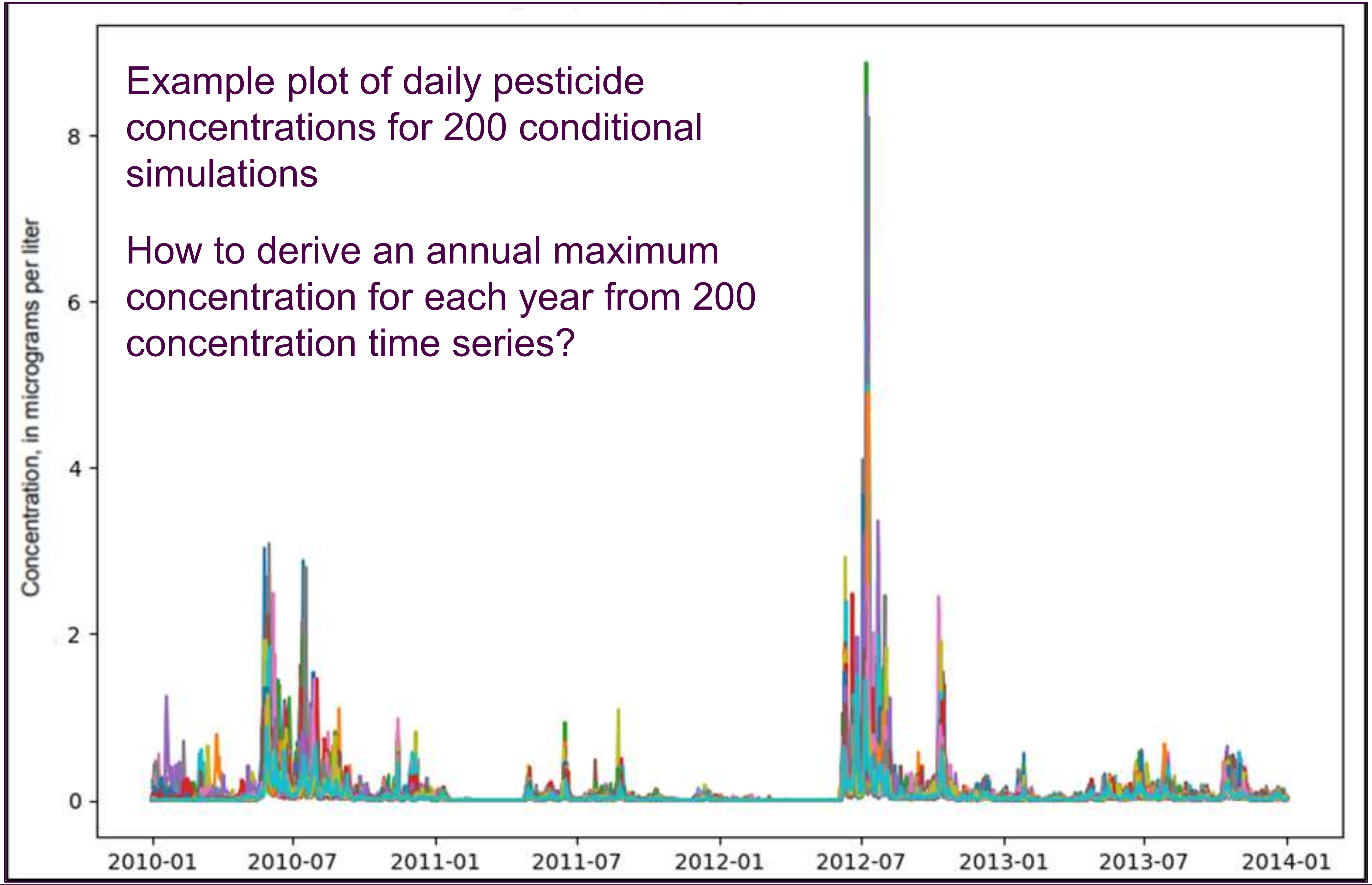
Seasonal heteroscedasticity (non-constant variance)

Normalized residual

Several conditional time series are created with a stochastic component

- Daily concentration value is set to observed concentration, if available, or estimated concentration
- Estimations are calculated as a **random value from population of normalized residuals** times the **seasonal heteroscedasticity** plus **annual linear trend** plus **mid-term** and **short-term variability** plus **seasonal wave** plus a **fitted constant**
- 200 time series per SEAWAVE-QEX were used in this study

Estimation of Annual Maximum Concentrations



Estimation of Annual Maximum Concentrations

Estimate of annual maximum concentrations from a SEAWAVE-QEX run

- Step 1: Calculate the annual maximums for each of the 200 conditional simulations (yields 200 values per year)
  - Step 2 (USGS guidance): Calculate the average of those 200 maxima
  - Step 2 (US EPA guidance): Calculate 99th percentile of those 200 maxima

Model validation: Compare estimated annual maximum concentrations from subsampling scenarios to the observed (true) annual maximum concentration

Study Area: GKb Watershed

Located in the Flanders region of Belgium

- Area: 1030 ha
- Annual precipitation: 600-1000 mm

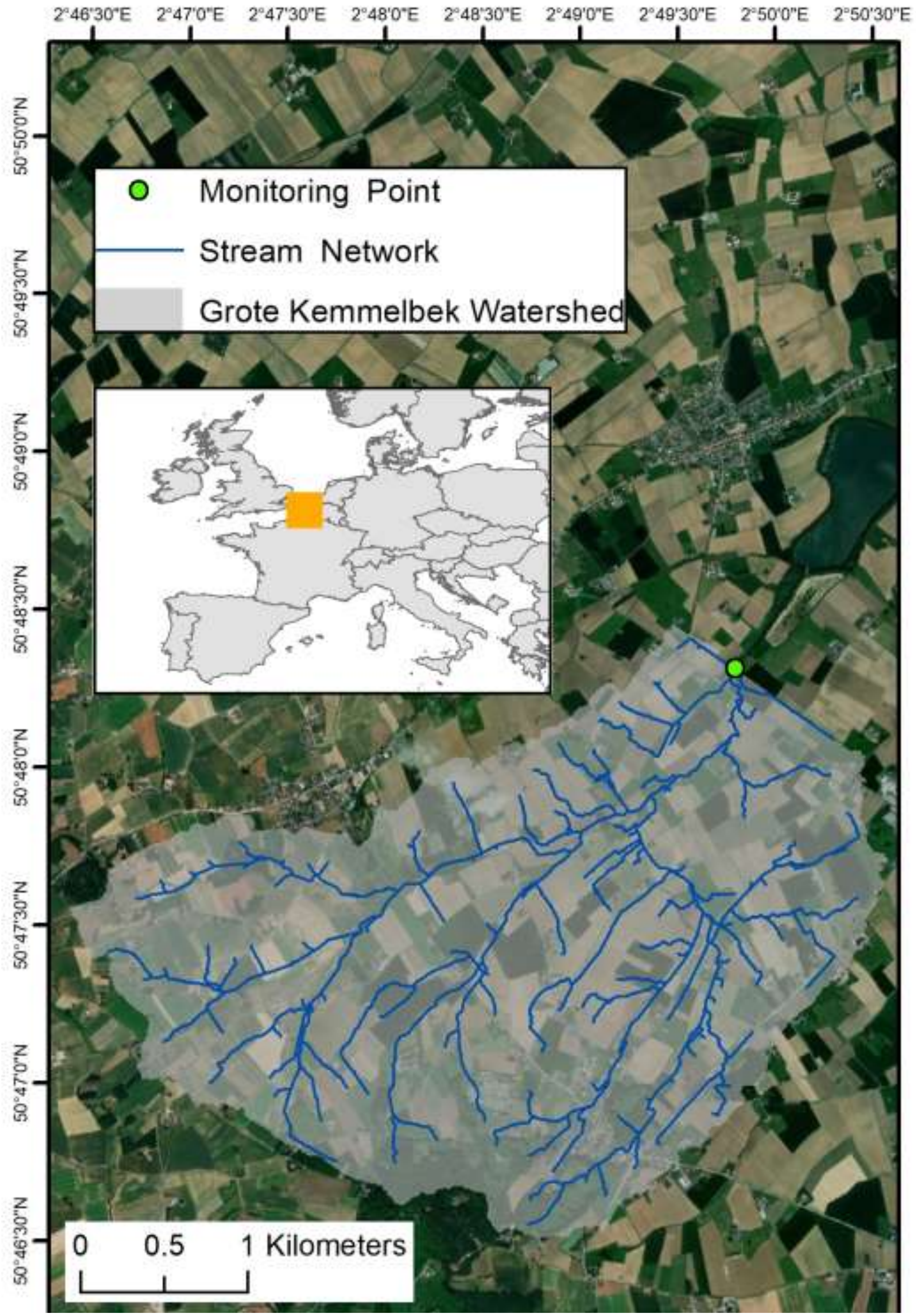
85% watershed under agricultural use

- 36% corn, potatoes and winter wheat

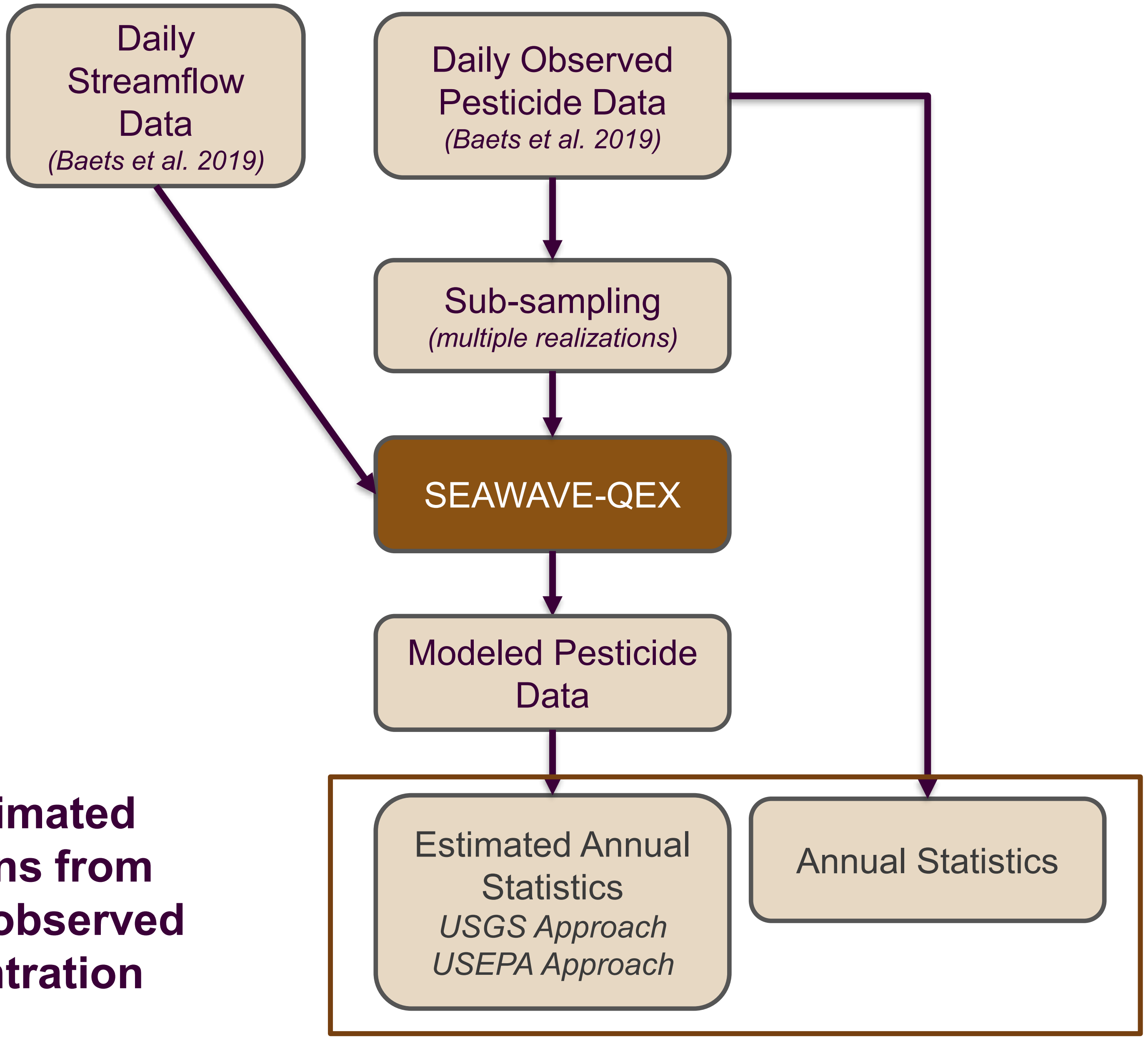
Mostly poor to imperfectly drained soils

- About 50% of the watershed is tile-drained

Daily streamflow and pesticide monitoring data available over a period of 3.5 years



SEAWAVE-QEX Application Process



Model validation: Compare estimated annual maximum concentrations from subsampling scenarios to the observed (true) annual maximum concentration

Data Summary: Pesticide Samples

Four Chemicals were evaluated in this study

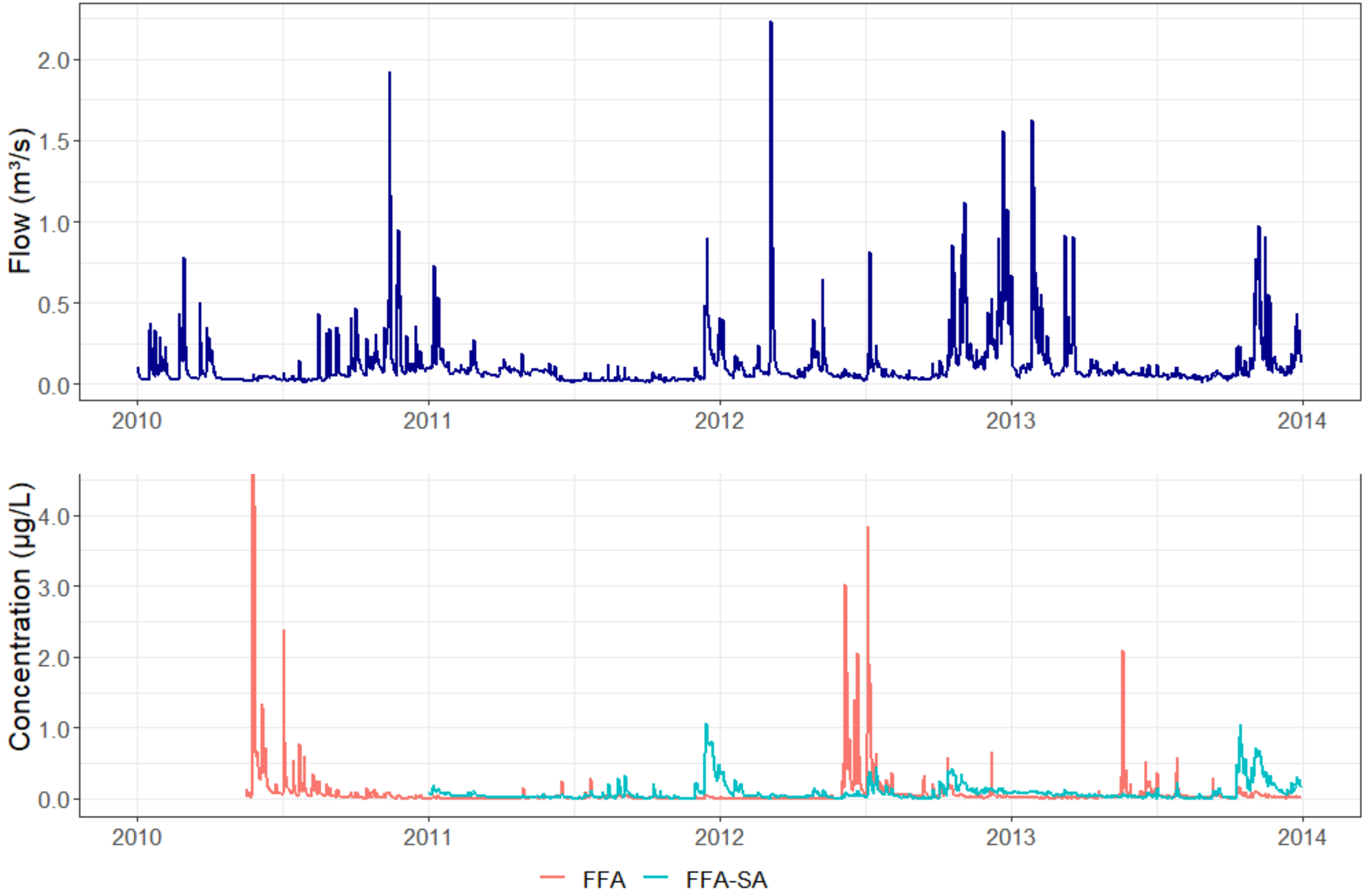
- 3 herbicides: FFA, DFF, IPU
- 1 metabolite: FFA-SA

Almost daily data available:

- For FFA and DFF from May 2010 to Dec 2013.
- For FFA-SA and IPU from Jan 2011 to Dec 2013.

Chemical	LOQ (µg/L)	Koc (mL/g)	DT50 (days)	Number of samples	Percent Samples < LOD	Max Observed Concentration (µg/L)
FFA	0.01	221	12.0	1,268	20%	5.10
FFA-SA	0.01	11	31.6	1,052	2%	1.07
DFF	0.01	3,417	143.2	1,268	32%	0.97
IPU	0.01	122	12.6	1,052	1%	13.55

Data Summary – Streamflow and Concentrations



Subsampling Methodology

One-week, two-week, three-week, and monthly sampling intervals

- One sample every 7, 14, 21 and 30 days

Ordered sampling method

- Strict inter-sample intervals (e.g., sample every Monday)
- Use the next available sample if there is a data gap in the almost daily data
- Mimic monitoring programs

Interval	Number of subsample realizations
7 days	7
14 days	14
21 days	21
30 days	30
Total	72

Scenarios

Chemicals:

- 3 herbicides: FFA, DFF, IPU
- 1 metabolite: FFA-SA

Study Framework Summary

- 72 subsamples for each chemical (based on sub-sampling intervals)
- 1 SEAWAVE-QEX run (yielding 200 daily concentration timeseries) per subsample
- 2 post-processing approaches, each yielding 72 annual maximum concentrations per year for each chemical

Results – FFA Annual Maximum Concentrations

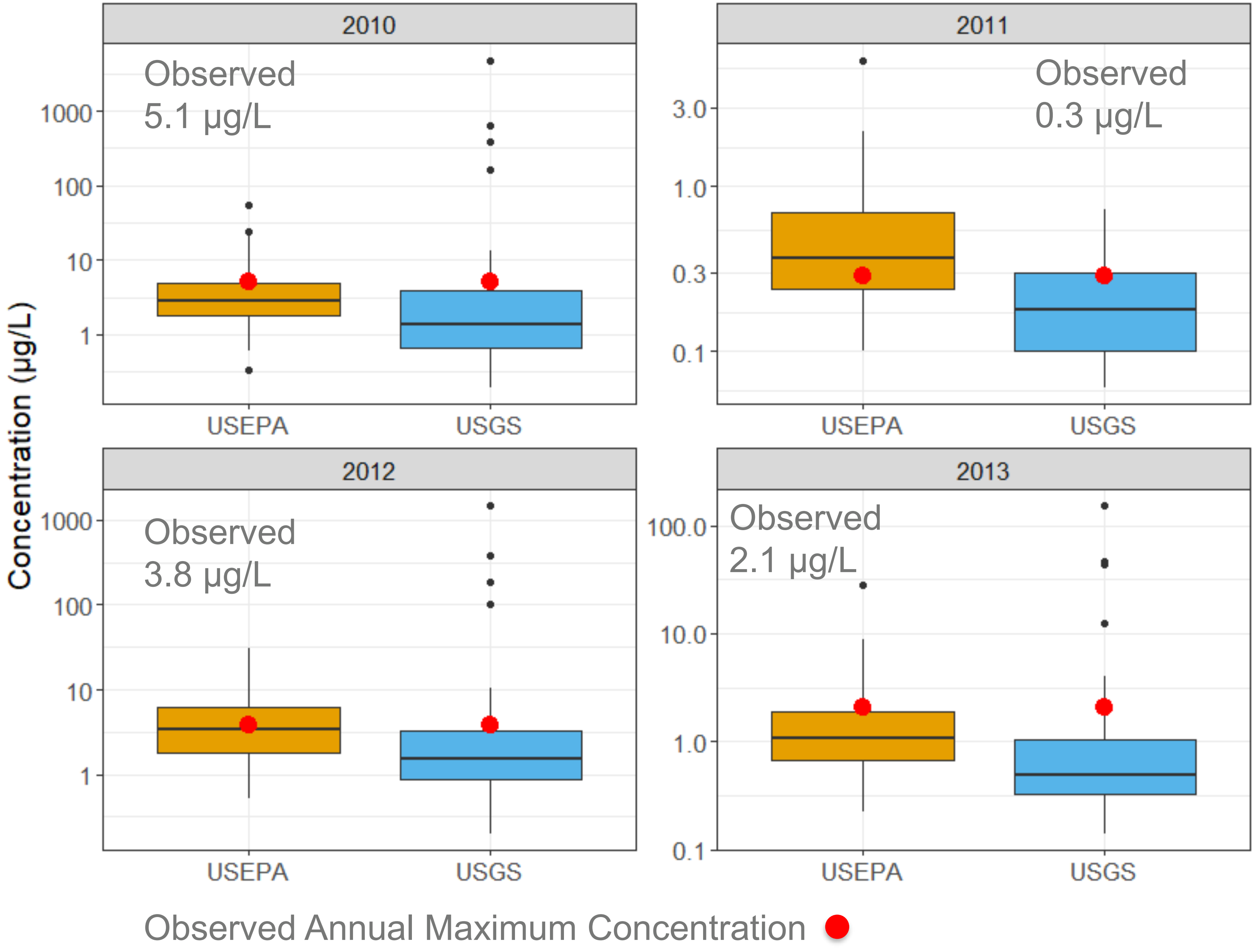
Boxplots show estimated results for the USEPA and USGS approach

- 72 annual maximum concentrations in each boxplot

High variability between the years

- In 2010 and 2012, concentrations are overestimated by several orders of magnitude for some subsamples
- Across all years some subsamples result in an underestimation

High variability between USEPA and USGS approach



Results – FFA-SA Annual Maximum Concentrations

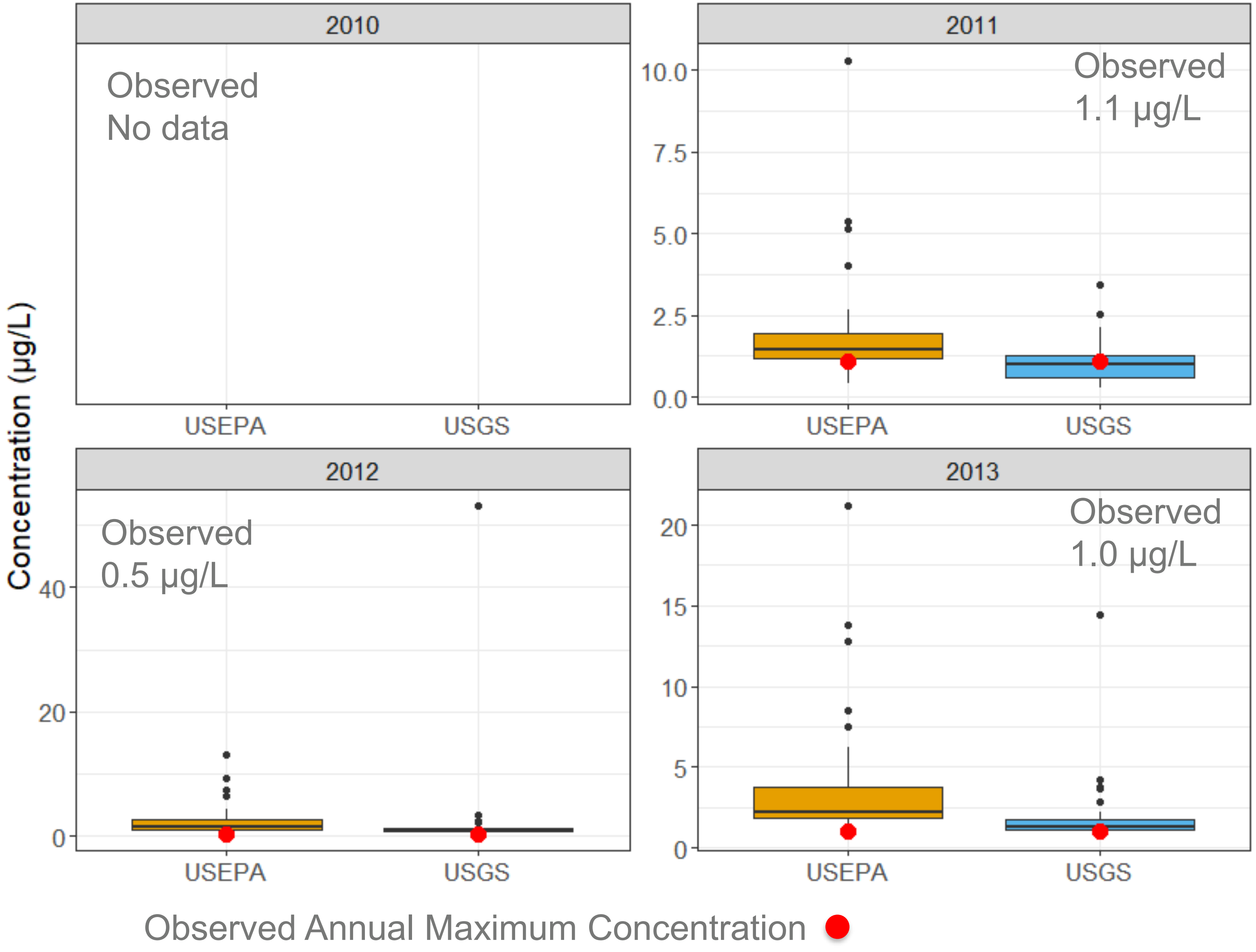
Boxplots show estimated results for the USEPA and USGS approach

- 72 annual maximum concentrations in each boxplot

High variability between the years

- Results are within an order of magnitude of observations
- Some subsamples resulted in unrealistic estimates

High variability between USEPA and USGS approach



Results Summary – Annual Maximum Concentrations

FFA

- High sensitivity to individual observed data points
- Some scenarios yielded results orders of magnitude above observations

FFA-SA

- Estimates within an order of magnitude of the observed (factor 0.24 to 29.0)

DFF

- Inter-annual variations of under- or over-estimations
- Estimates within an order of magnitude of observed results

IPU

- Consistent under-estimation regardless of method or sampling frequency for two out of three years evaluated

Conclusions

Overall, SEAWAVE-QEX did not show an adequate performance

- No clear patterns of under- or over-estimation could be identified
- Overestimation can be several orders of magnitude
- Conclusions and interpretations on subsampling performance are speculative

SEAWAVE-QEX cannot be recommended to replace higher frequency monitoring programs

Future research is needed to understand

- Sensitivity of SEAWAVE-QEX on compound or watershed characteristics (monitoring data with sufficient sampling is challenging)
- Other studies indicated that small watersheds could be problematic

Thank you.

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The study presented here will soon be published in *Integrated Environmental Assessment and Management* (IEAM)