



# Deriving Sampling Frequency Charts : example for Dissolved Organic Matter in Brittany, France

François Birgand<sup>1</sup> - Erin Bennett<sup>1</sup> - Gérard Gruau<sup>2</sup>

NC WRRI conference – Raleigh, NC March 31, 2010

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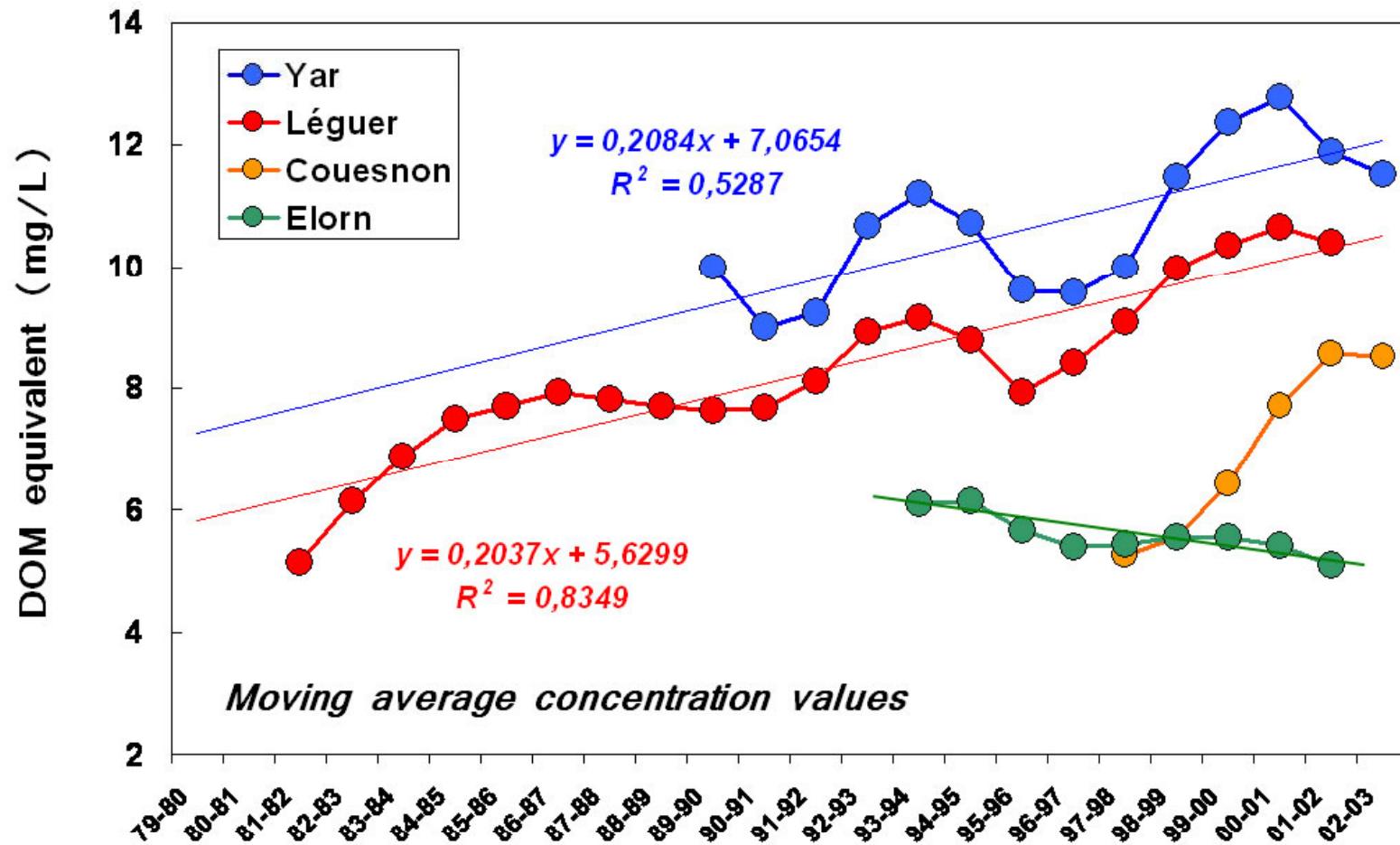
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# How often should one sample ? For what uncertainty in the results?



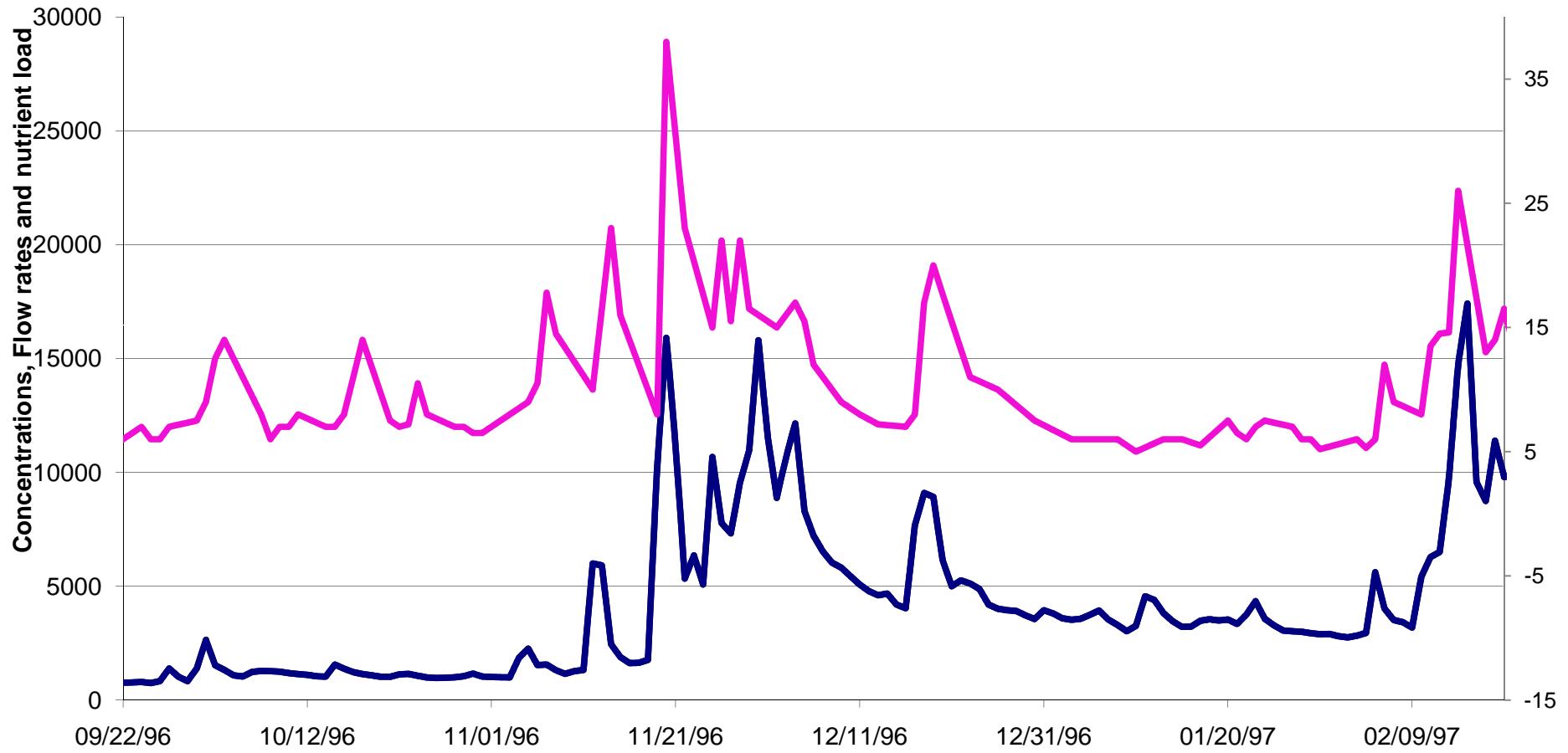
# The DOM problem



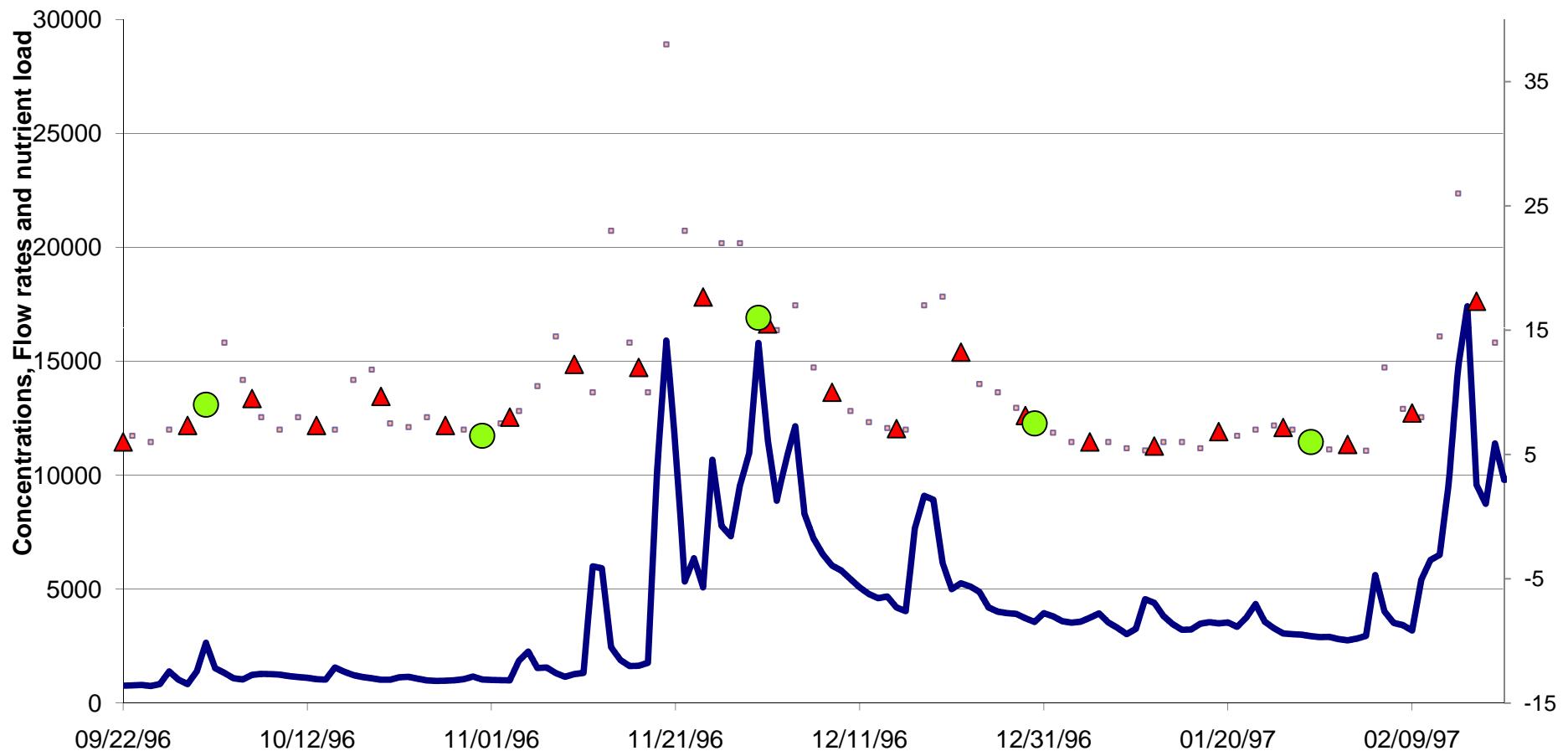
# Sources of uncertainties while measuring nutrient loads and water quality indicators

- Uncertainties on flow rates and cumulated flow
  - Uncertainties due to the sampling location in the water column
  - Uncertainties due to sample degradation between sampling and analysis
  - Uncertainties of laboratory analyses
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- Uncertainties associated with infrequent sampling

# In a perfect world, continuous data...



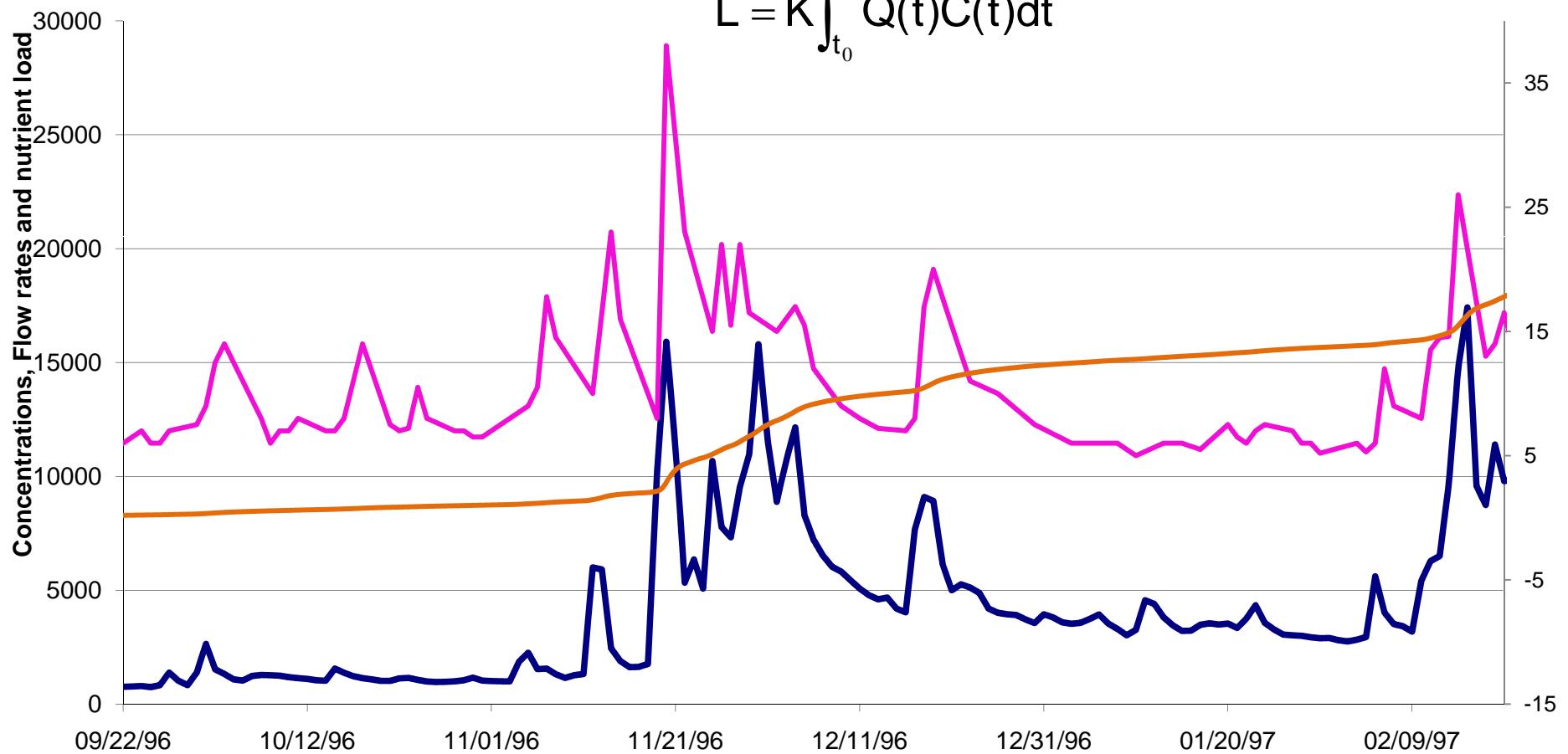
# Discrete sampling...



# Calculating nutrient annual loads

Definition :  $L = K \int_{t_0}^T L(t)dt$

$$L = K \int_{t_0}^T Q(t)C(t)dt$$



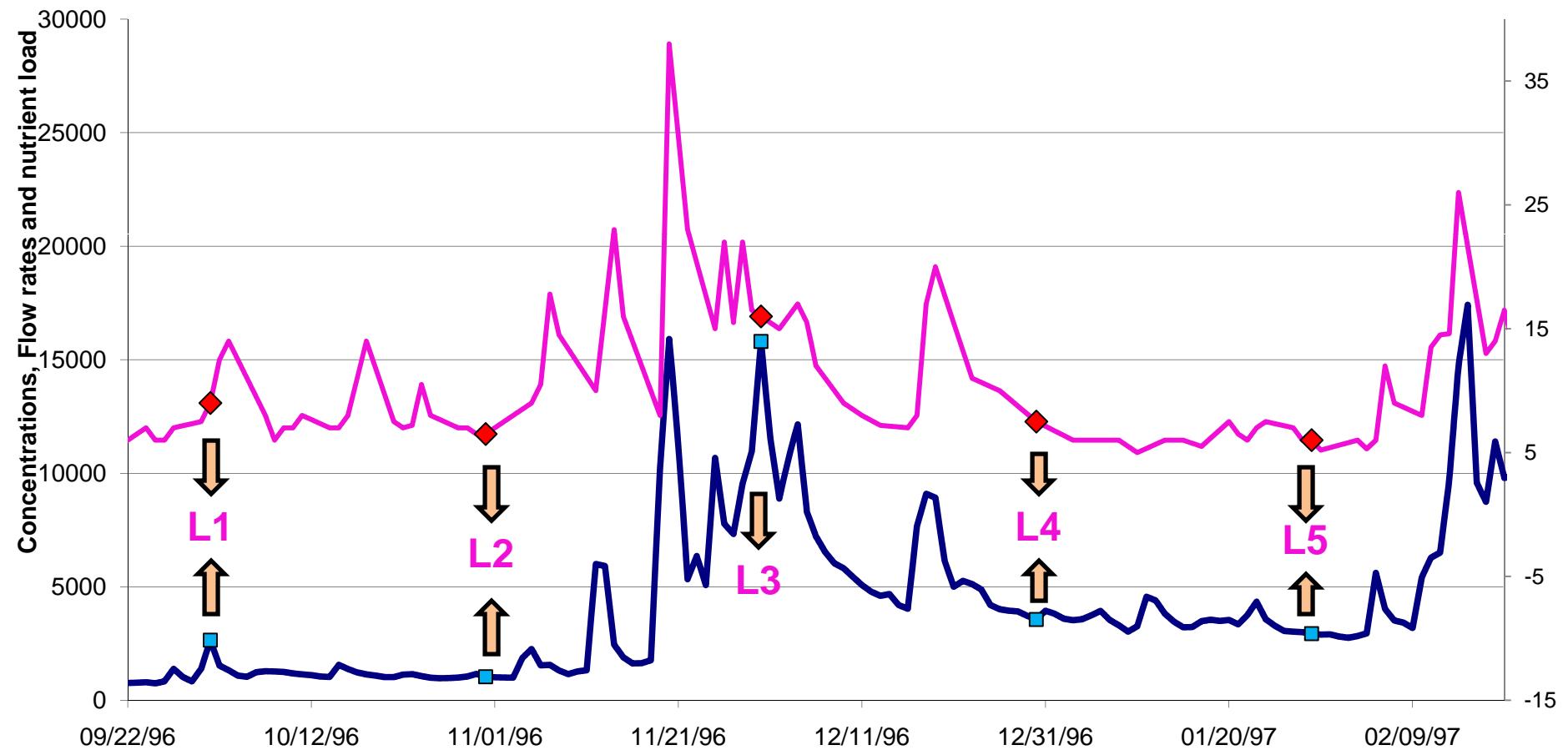
# Objectives

- Investigate and document the level of uncertainties induced by infrequent sampling
- Provide tools to guide watershed managers:  
Sampling frequency charts

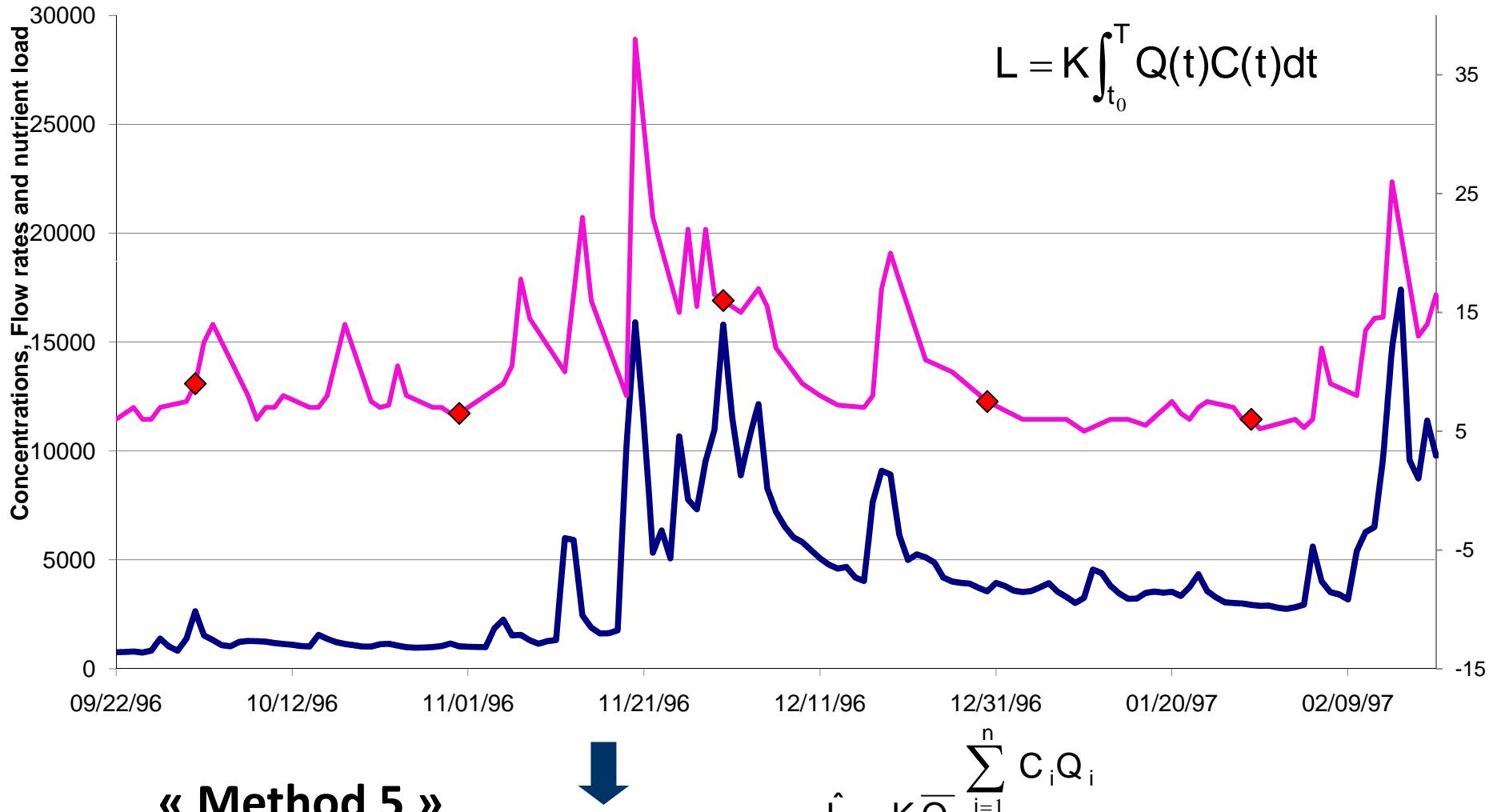
# Method

- 4 reference watersheds (60 to 400 km<sup>2</sup>)
  - DOM
- Numerical simulations of sampling strategies from reference watersheds
- 16 flux calculation algorithms and sampling strategies tested
  - “Averaging” methods
  - Linear interpolation method
  - Regression methods
  - Composite sampling

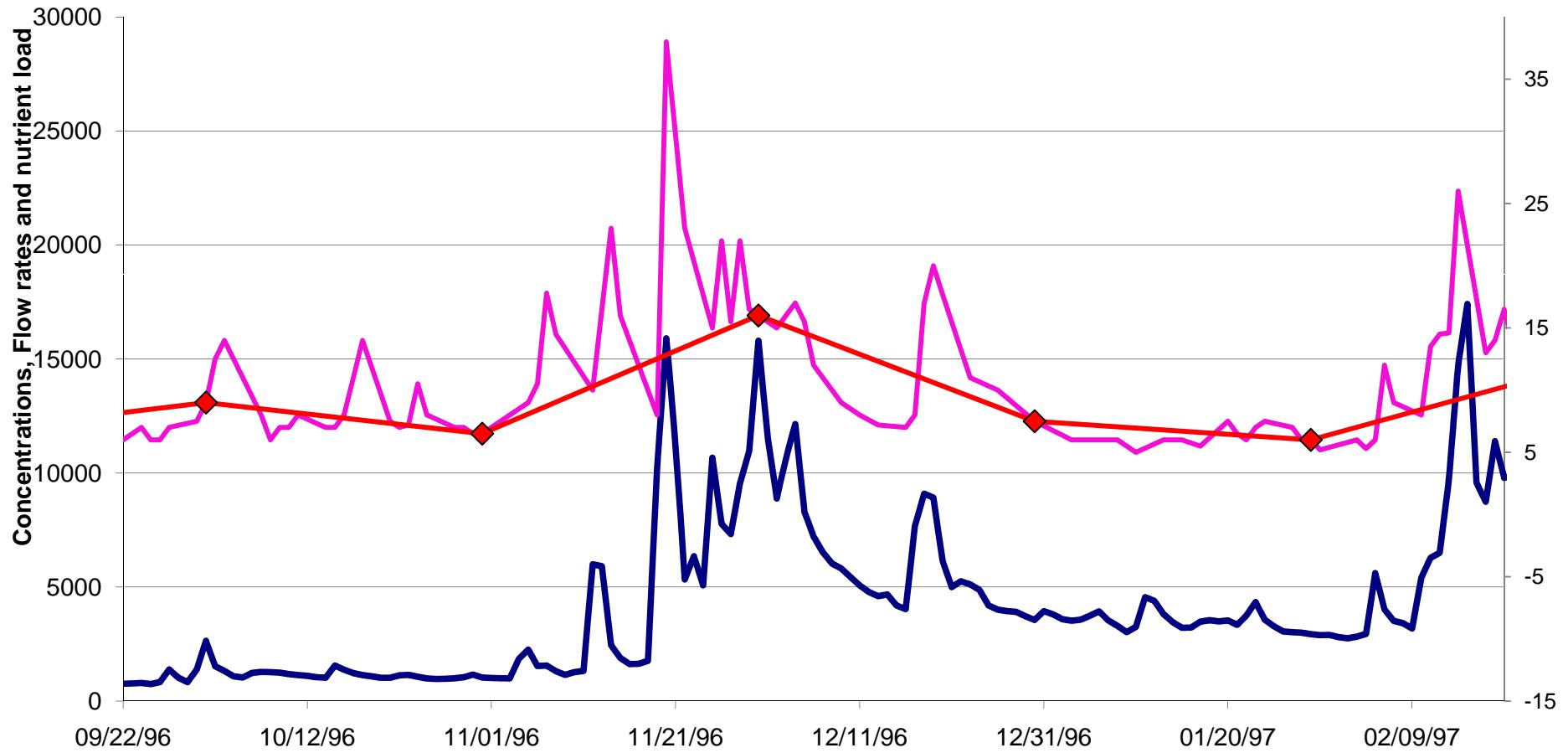
# Fluxes: « Averaging » methods



# Fluxes: « Averaging » methods



# Linear interpolation



Linear interpolation

$$\hat{L} = K \sum_{k=1}^n C_k^{\text{int}} Q_k$$

# 16 strategies and methods tested

$$1 \quad \hat{L} = K \left( \sum_{i=1}^n \frac{C_i}{n} \right) \left( \sum_{i=1}^n \frac{Q_i}{n} \right)$$

[Preston et al., 1989]

$$2 \quad \hat{L} = K \sum_{i=1}^n \frac{C_i Q_i}{n}$$

[Preston et al., 1989]

$$9 \quad \hat{L} = K \sum_{i \in n} C_i Q_i \left( 1 + \frac{\sum_{j \in N \setminus n} Q_j^2}{\sum_{i \in n} Q_i^2} \right)$$

[Cooper, 2005]

$$3 \quad \hat{L} = K \sum_{i=1}^n C_i \overline{Q}_{i,i-1}$$

[Meybeck et al., 1994]

$$4 \quad \hat{L} = K \bar{Q} \sum_{i=1}^n \frac{C_i}{n}$$

[Shih et al., 1992]

$$5 \quad \hat{L} = K \bar{Q} \frac{\sum_{i=1}^n C_i Q_i}{\sum_{i=1}^n Q_i}$$

[Littlewood, 1992]

$$8 \quad \hat{L} = K \bar{Q} \frac{\bar{l}}{\bar{q}} \frac{1 + \frac{1}{N} \frac{S_{lq}}{\bar{l}\bar{q}}}{1 + \frac{1}{N} \frac{S_{q^2}}{\bar{q}^2}} \text{ with } \bar{l} = \sum_{i=1}^n C_i Q_i \quad \bar{q} = \sum_{i=1}^n Q_i$$

$$S_{lq} = \frac{1}{n-1} \sum_{i=1}^n ((Q_i - \bar{q})(C_i Q_i - \bar{l})) \text{ and}$$

$$S_{q^2} = \frac{1}{n-1} \sum_{i=1}^n (Q_i - \bar{q})^2$$

[Cohn, 1995]

# 16 strategies and methods tested

$$\hat{L} = K \sum_{k=1}^n C_k^{\text{int}} Q_k$$

[Moatar and Meybeck, 2004]

$$\hat{L} = K \sum_{k=1}^n C_k^{\text{ext}} Q_k \quad \ln(C_i) = a \ln(Q_i) + b$$

[Cohn et al., 1989]

[Ferguson, 1986]

$$\hat{L} = K \sum_{k=1}^n C_k^{\text{ext}} Q_k \times \exp\left(\frac{s^2}{2}\right) \quad \text{with} \quad s^2 = \frac{\sum_{i=1}^n (\ln(C_i) - (a \times \ln(Q_i) + b))^2}{n-2}$$

[Duan, 1983]

$$\hat{L} = K \sum_{k=1}^n C_k^{\text{ext}} Q_k \times \frac{\sum_{i=1}^n \exp(\ln(C_i) - (a \times \ln(Q_i) + b))}{n},$$

$$\hat{L} = K \sum_{k=1}^n C_k^{\text{ext}} Q_k \times g_m\left(\frac{m+1}{2m} \times (1-V) \times s^2\right)$$

[Cohn et al., 1989]

$$\hat{L} = K \sum_{b \in B} L_b \quad [\text{Schleppi et al., 2006}]$$

$$L_b = \left( \frac{1}{180} \sum_{i=1}^{180} C_i \right) \times \sum_{i=1}^{180} Q_i$$

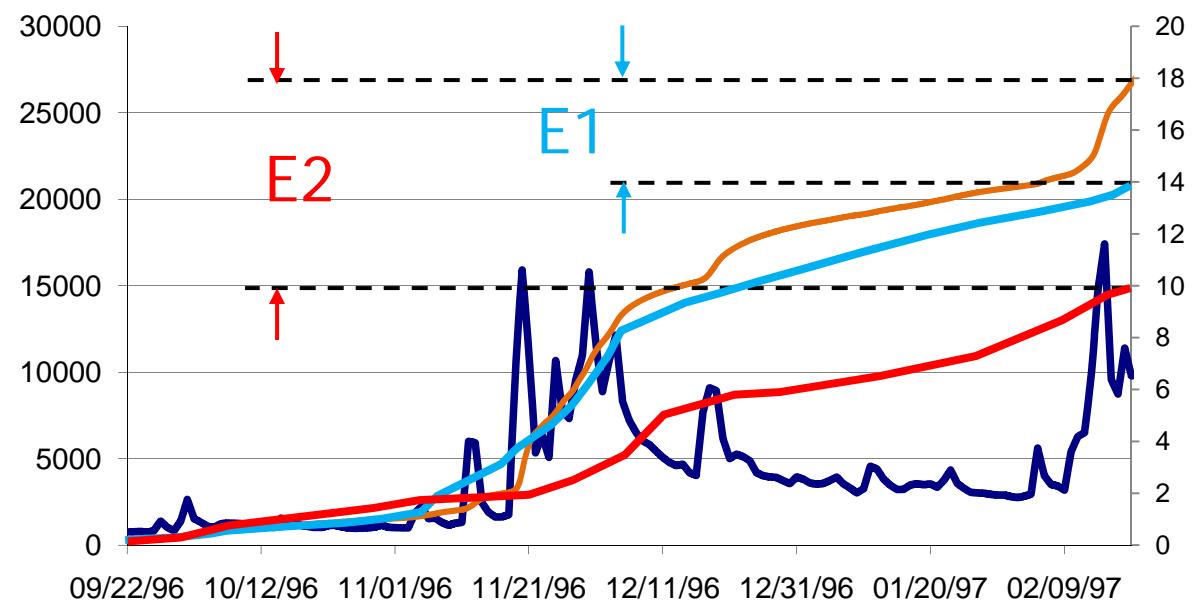
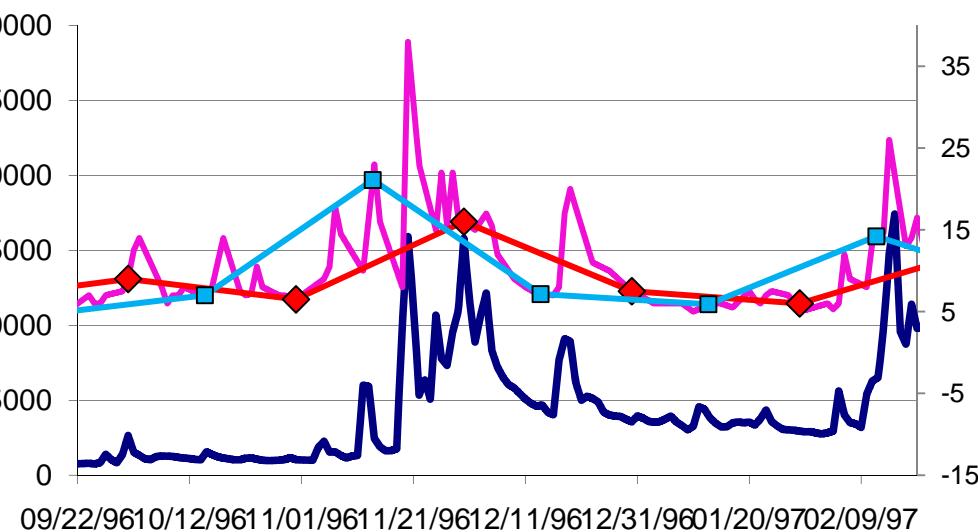
$$L_{\text{int}} = K' \times \sum_{k \in K} C_k^{\text{int}} Q_k$$

$$\hat{L} = \sum_{b \in B} L_b + \sum_{\text{int}=1}^P L_{\text{int}}$$

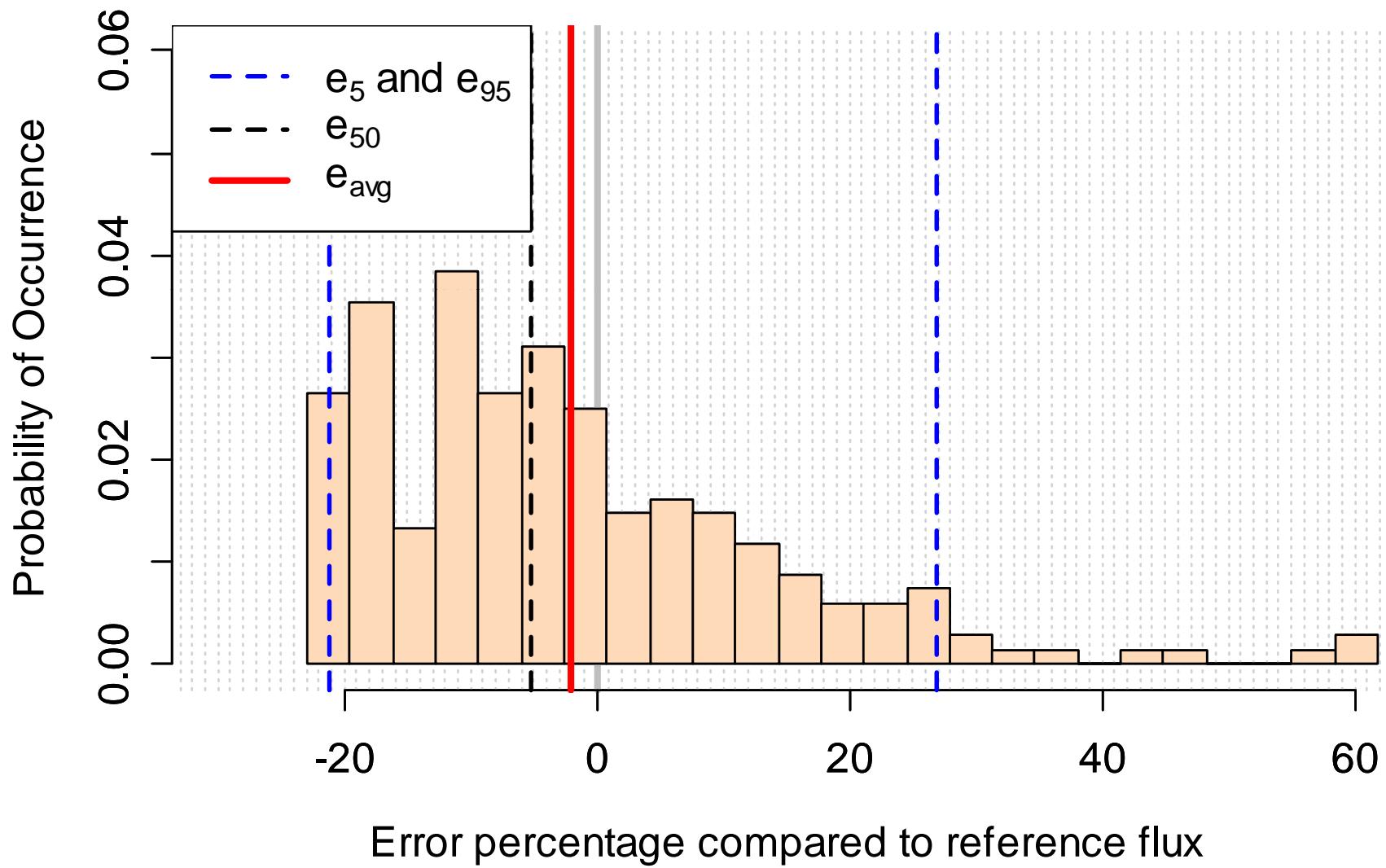
[Schleppi et al., 2006]

$$L_b = K \times \left( \frac{1}{n} \sum_{i=1}^n C_i \right) \times \sum_{i=1}^n Q_i$$

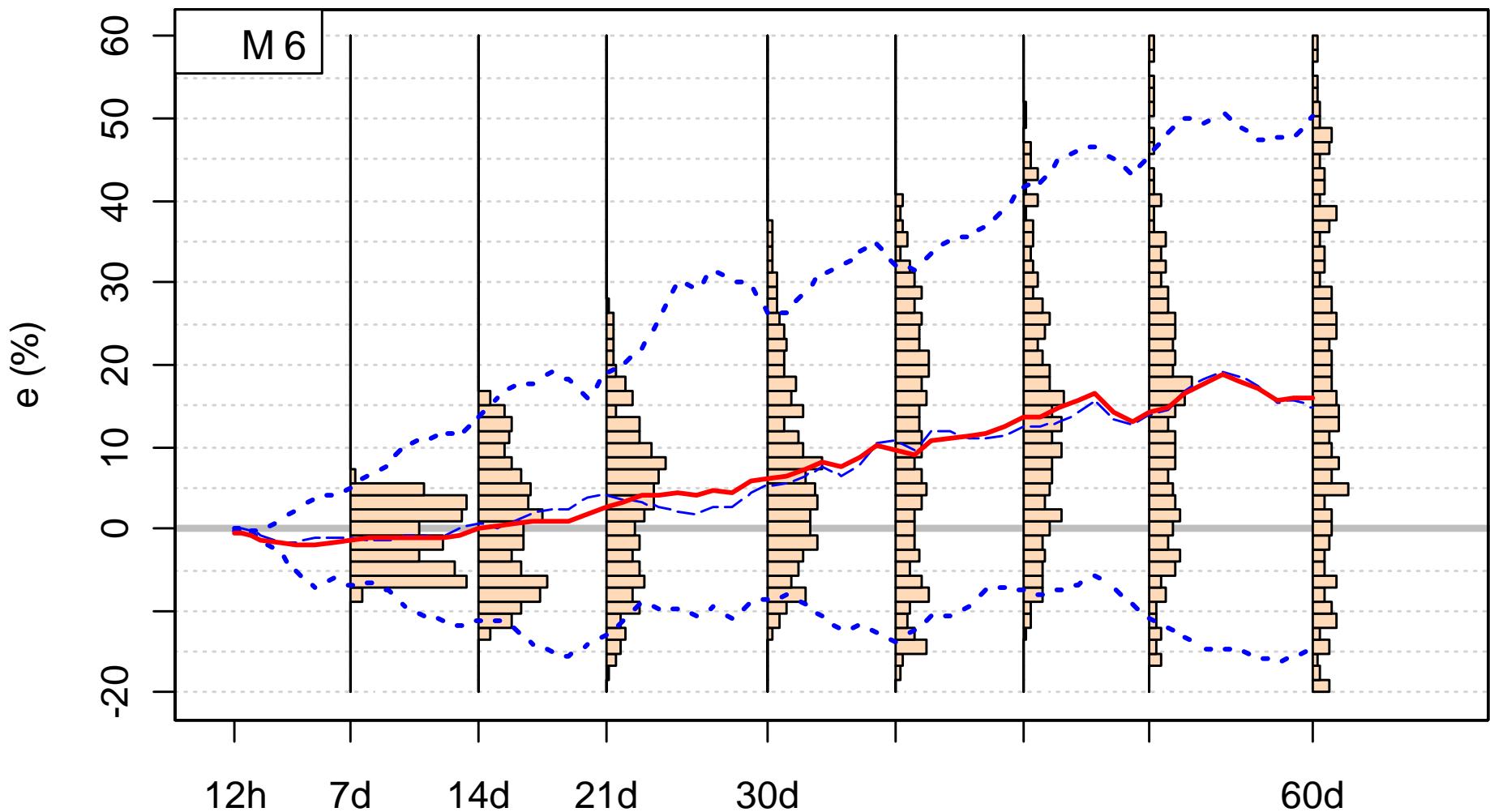
# An infinite number of possible errors



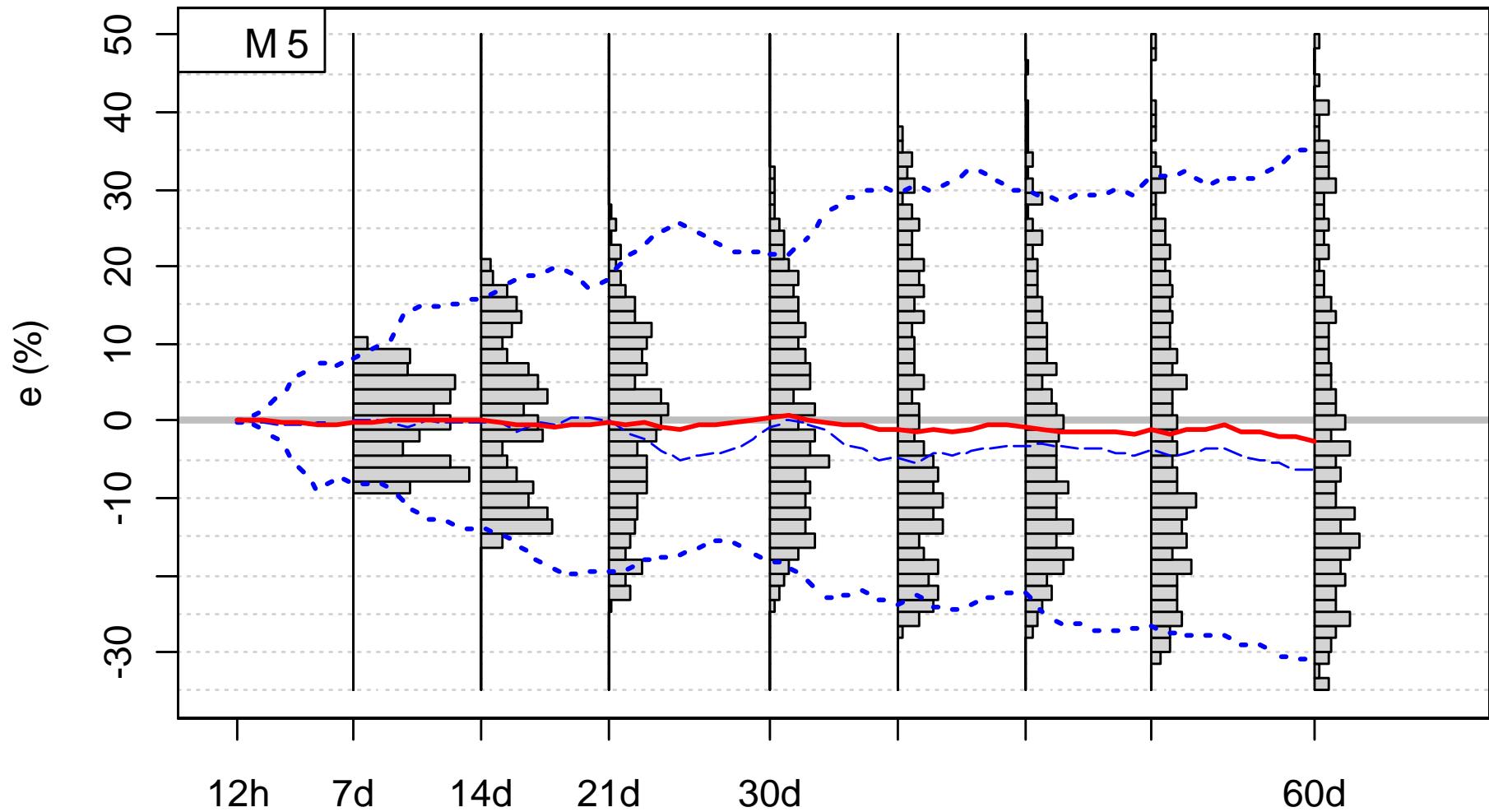
# Error Distributions



# Errors as a function of sampling frequency



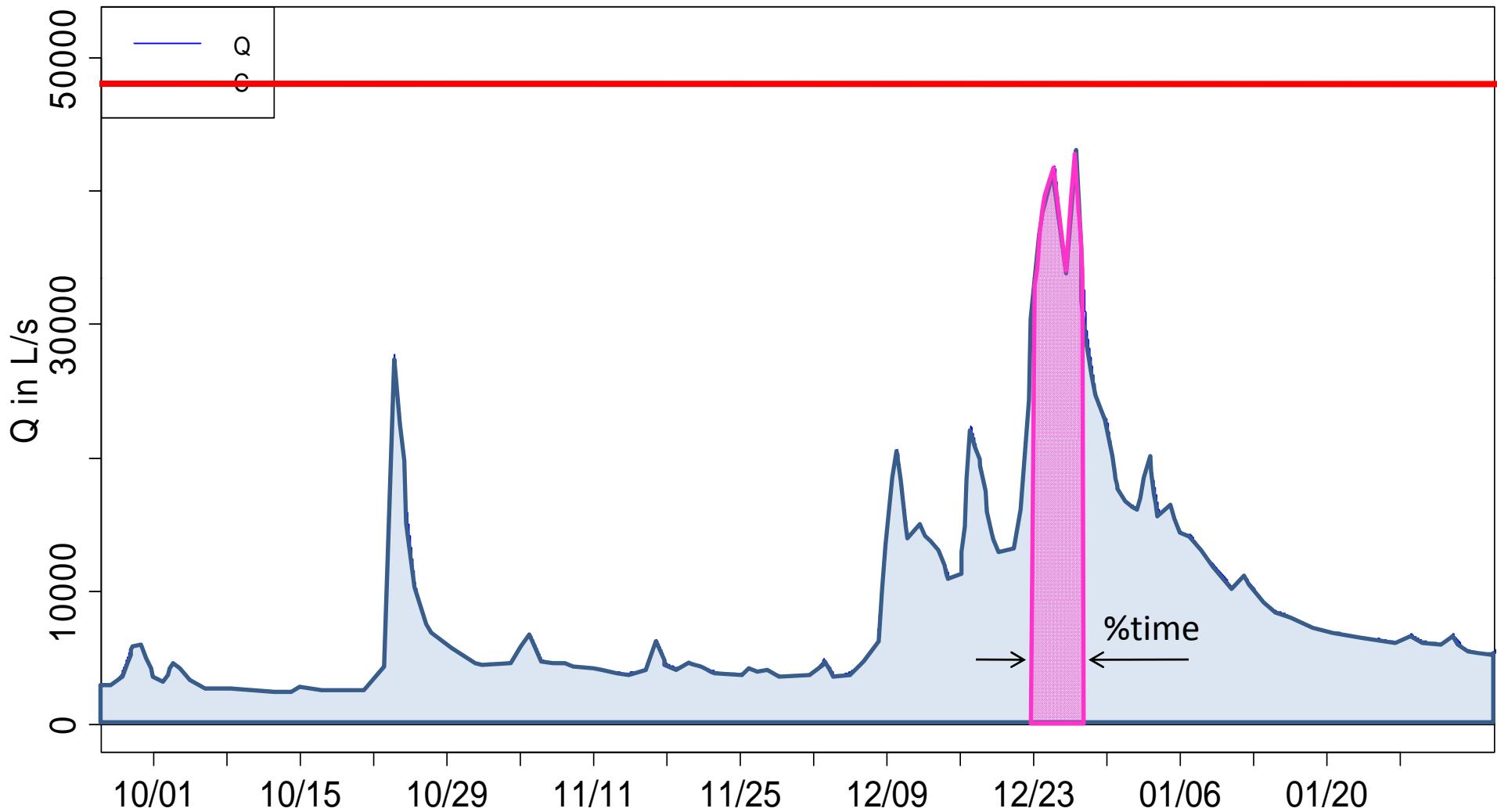
# Flow weighted average: best method



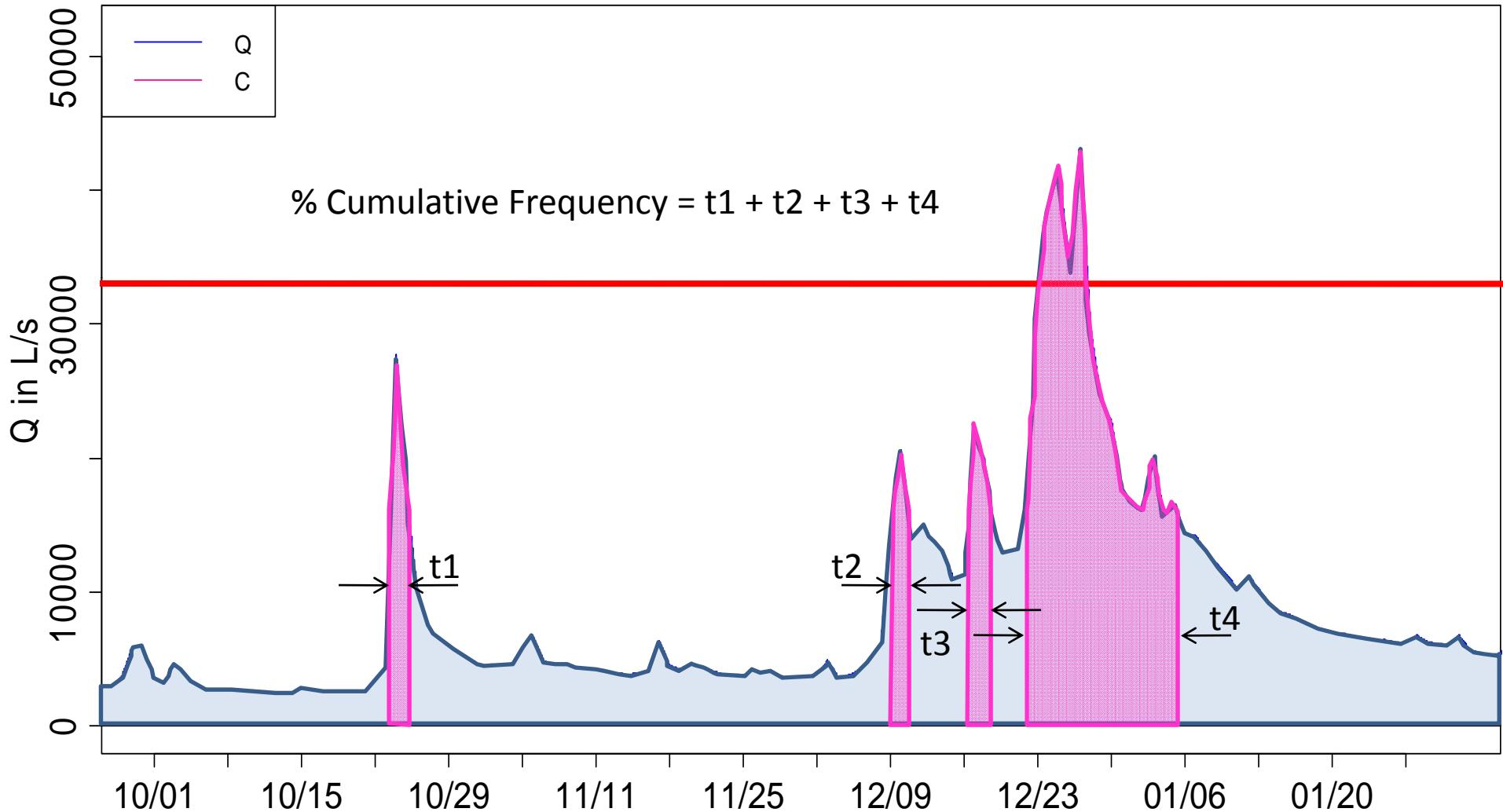
**COULD ONE PREDICT THE MAGNITUDE  
OF ERRORS?**

**CASE STUDY: DISSOLVED ORGANIC  
MATTER IN BRITTANY, FRANCE**

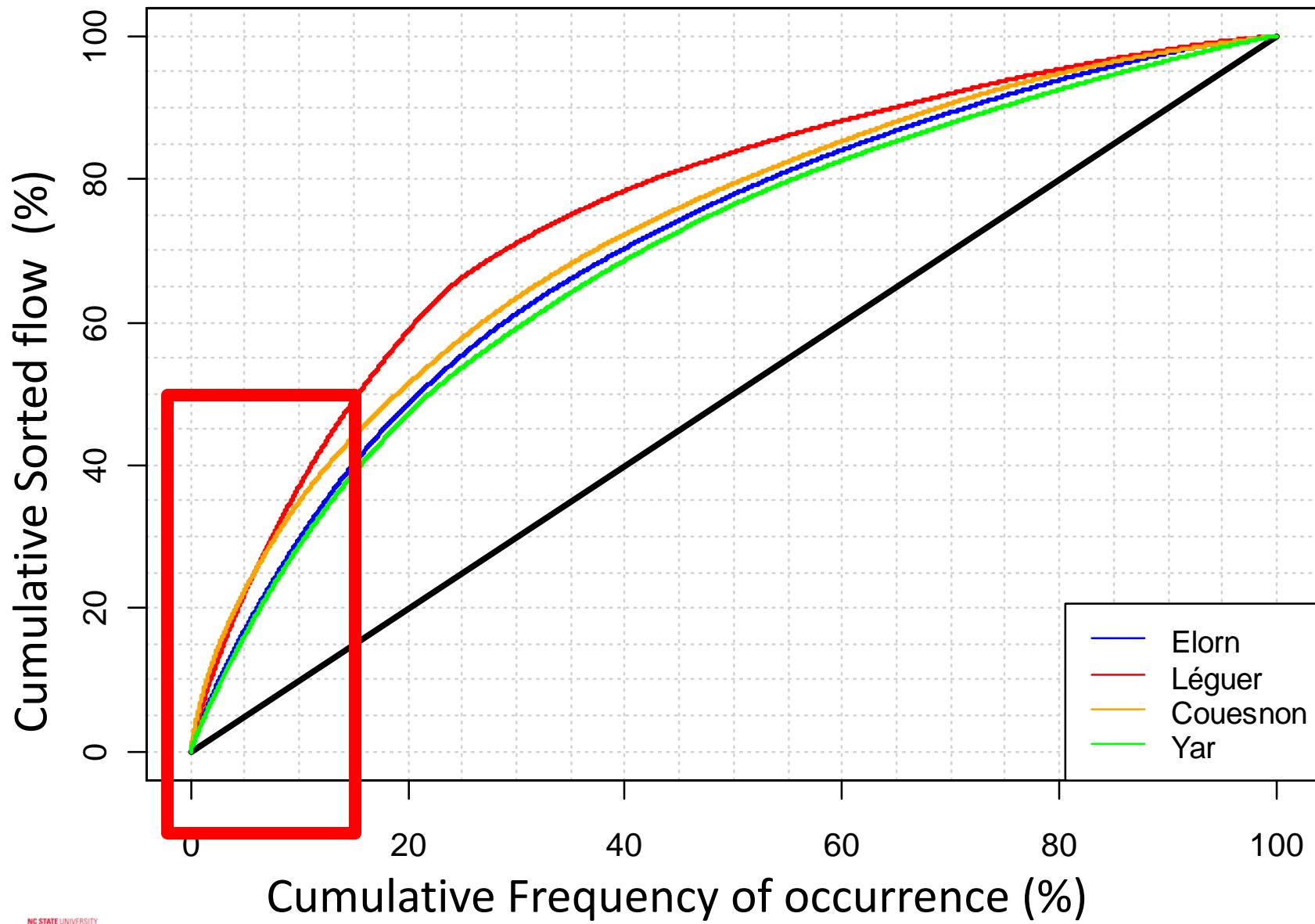
# Deriving watershed reactivity indicators



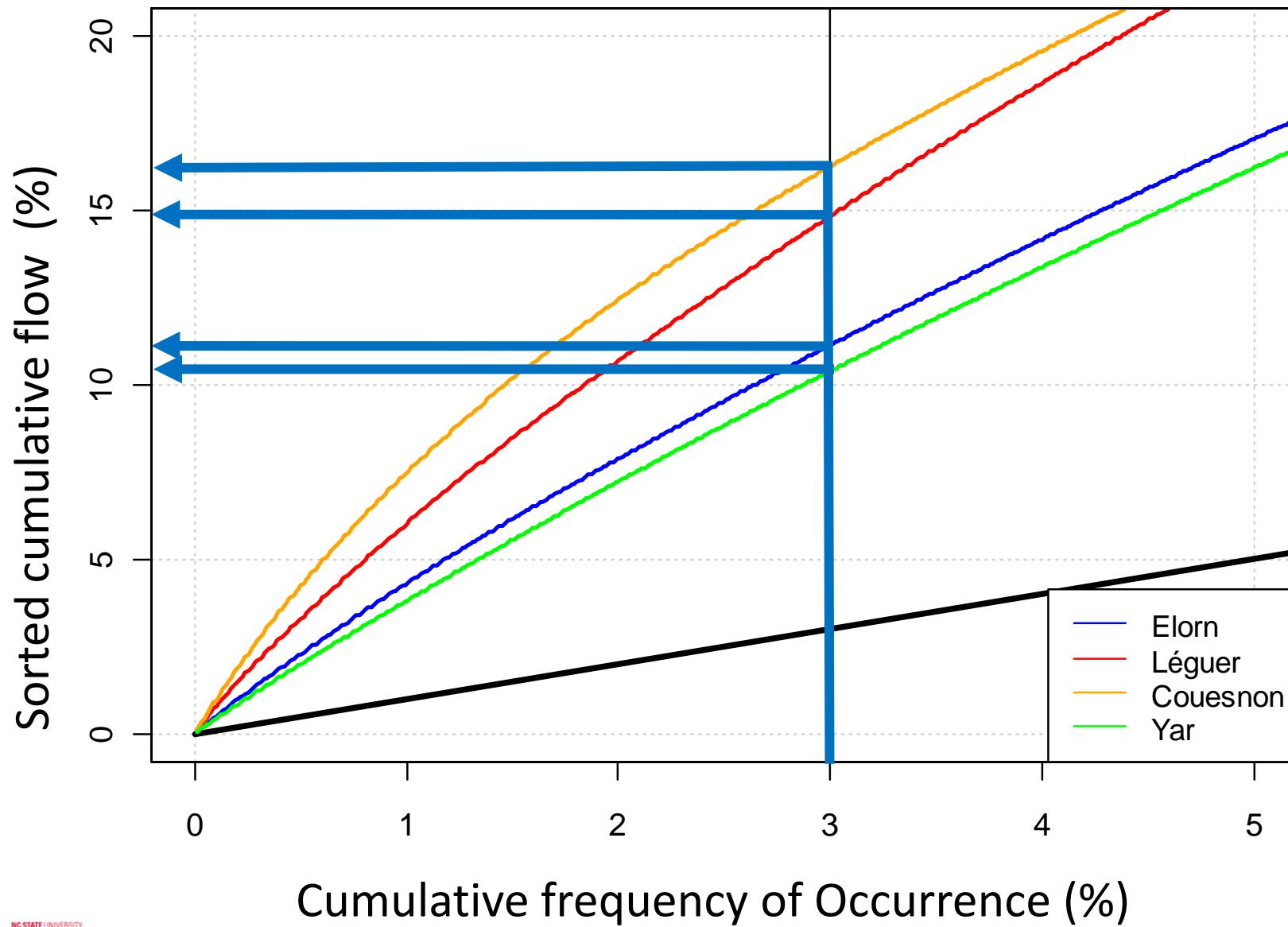
# Deriving watershed reactivity indicators



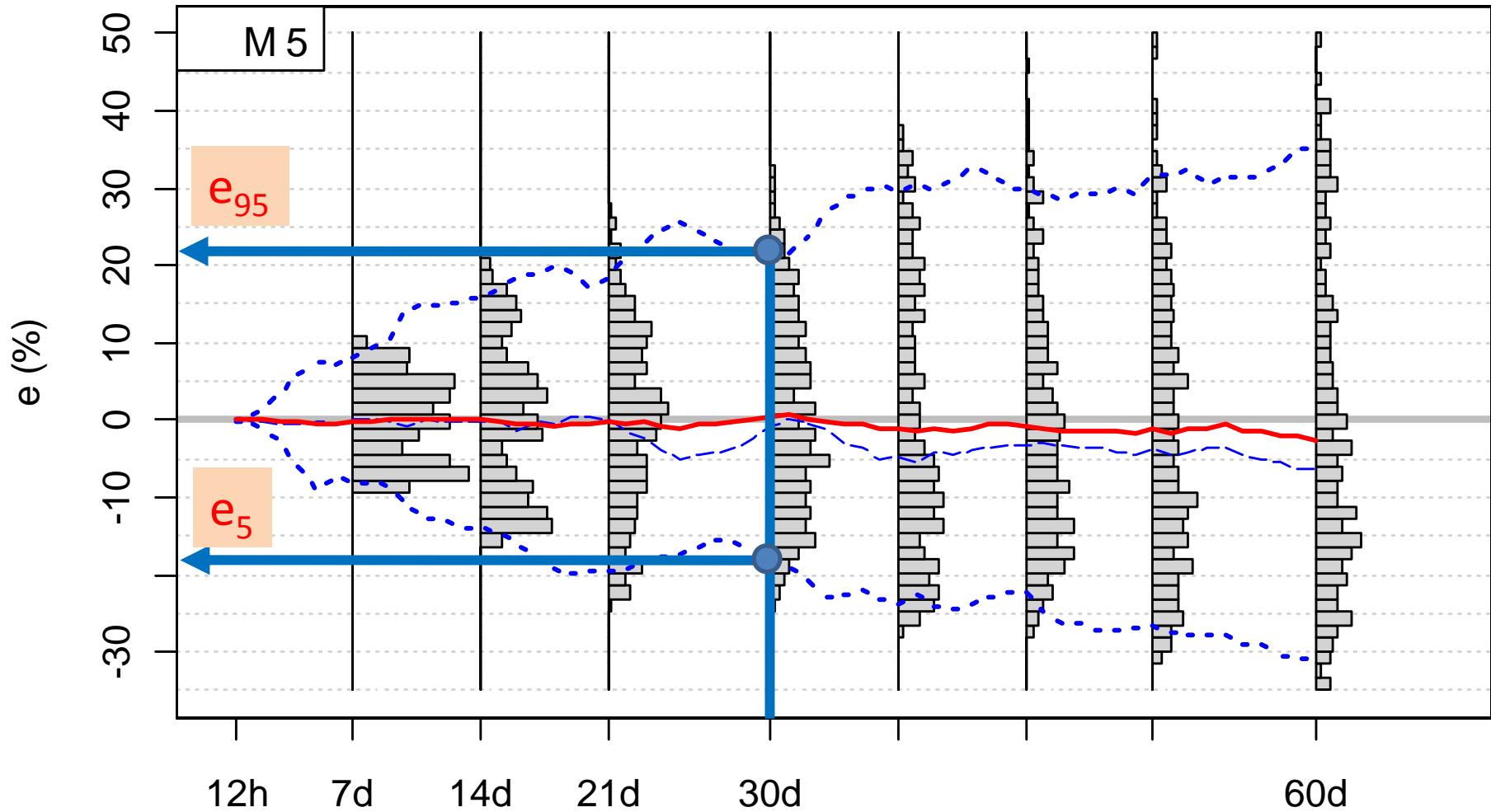
# Sorted cumulative flow frequency



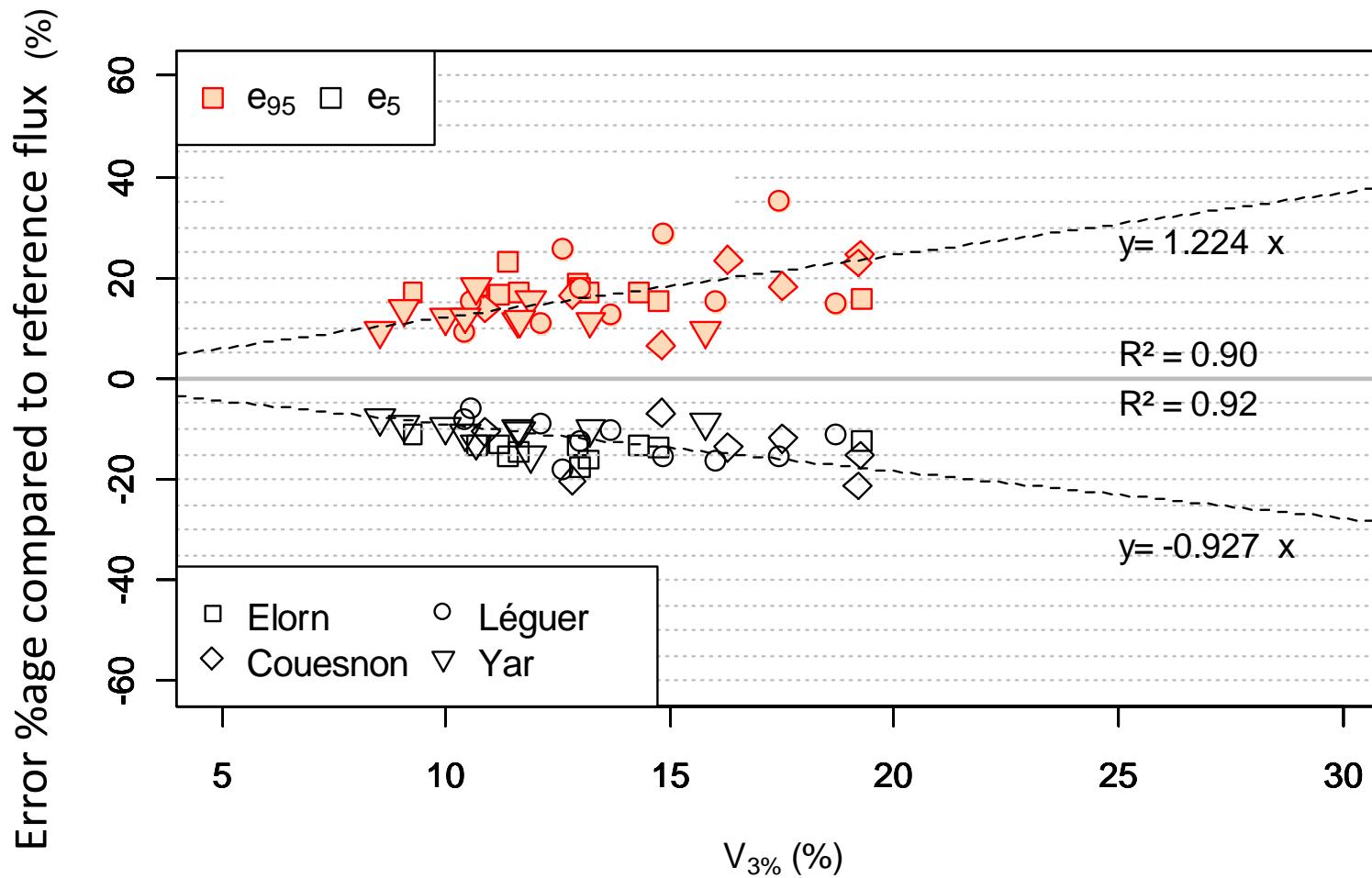
# Indicator $V_{3\%}$



# Errors on the annual flux estimator

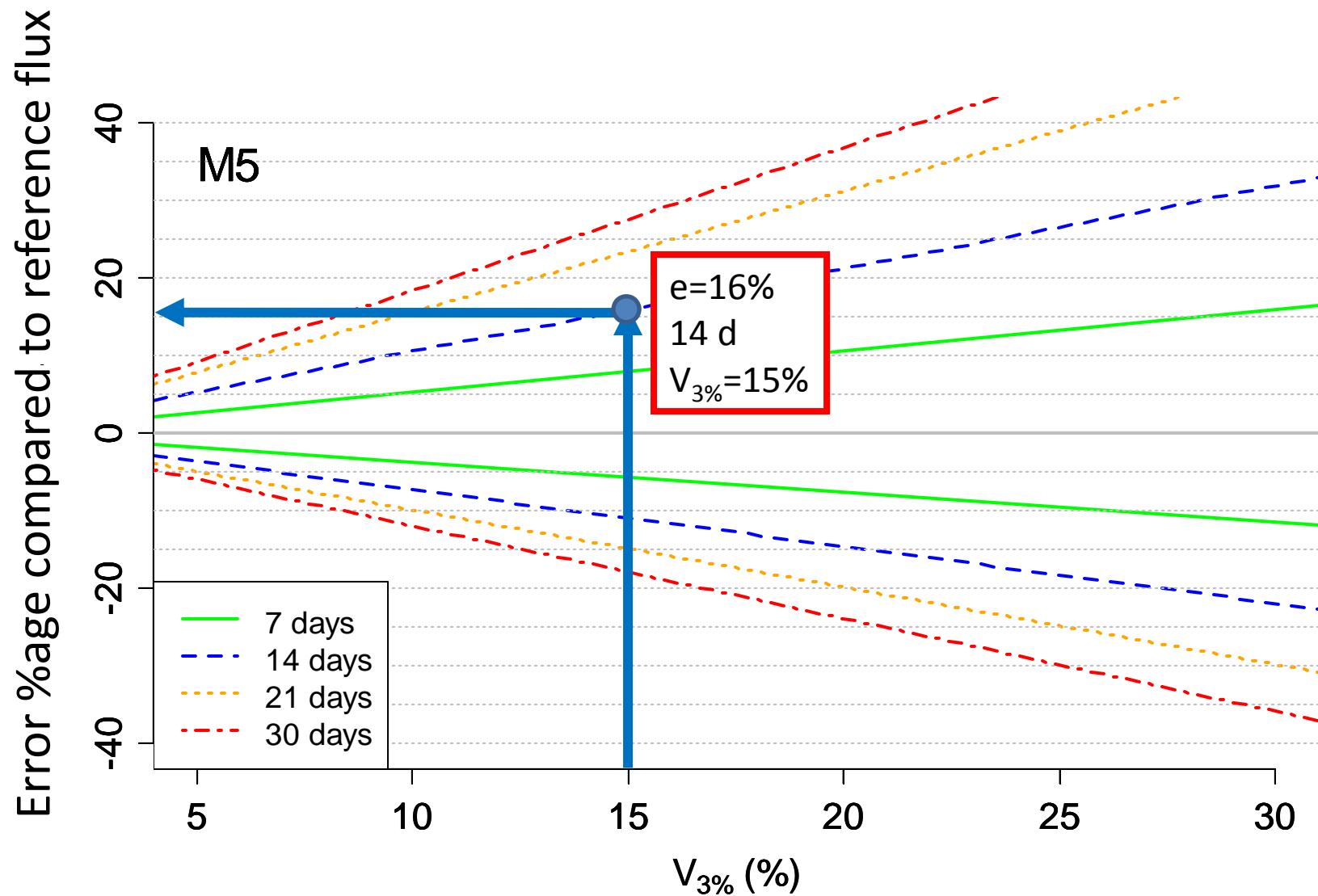


# Link between $V_{3\%}$ and estimator errors

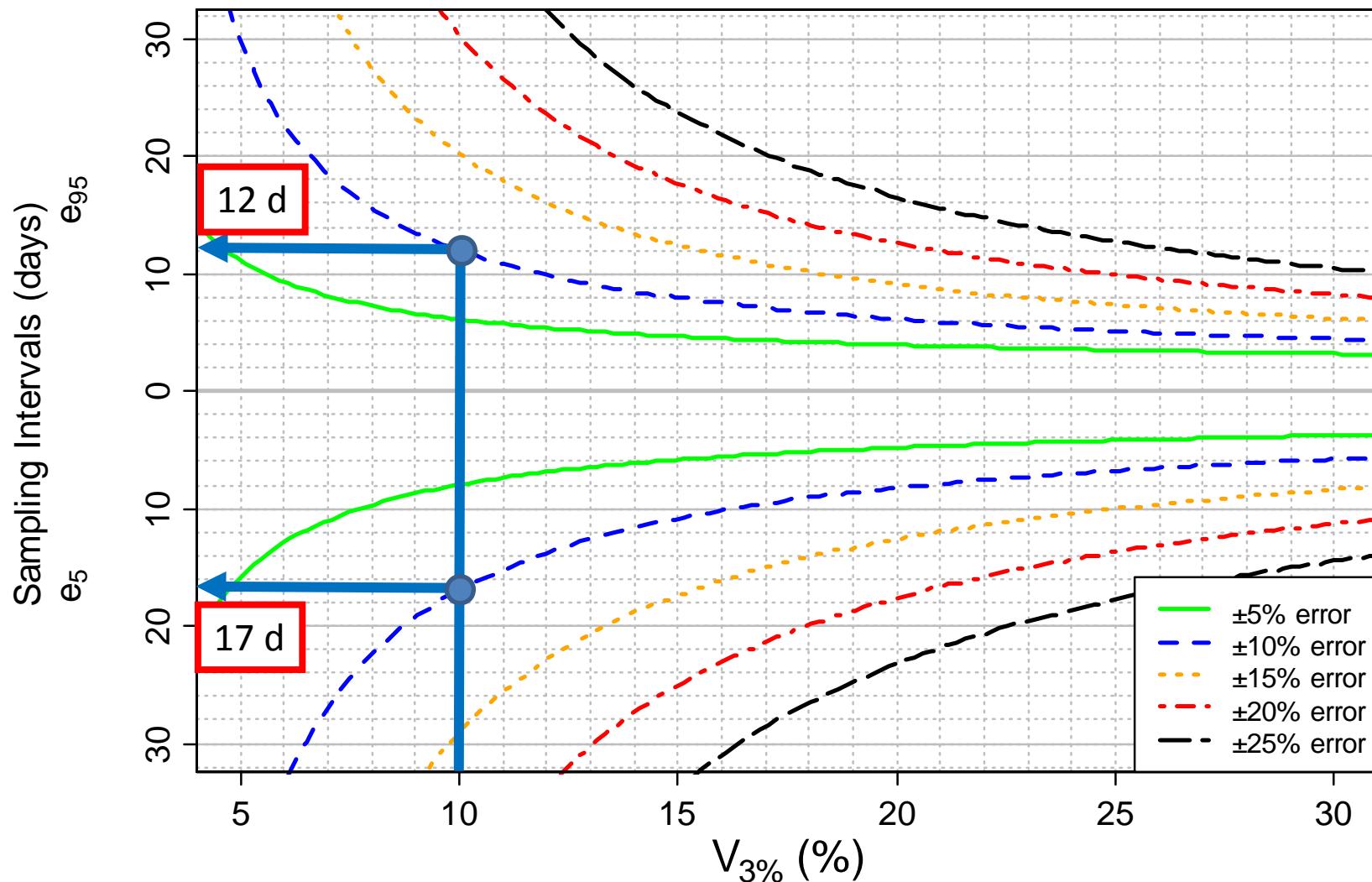


Percentage of the annual volume flowing in 3% of the time  
corresponding to the highest flow

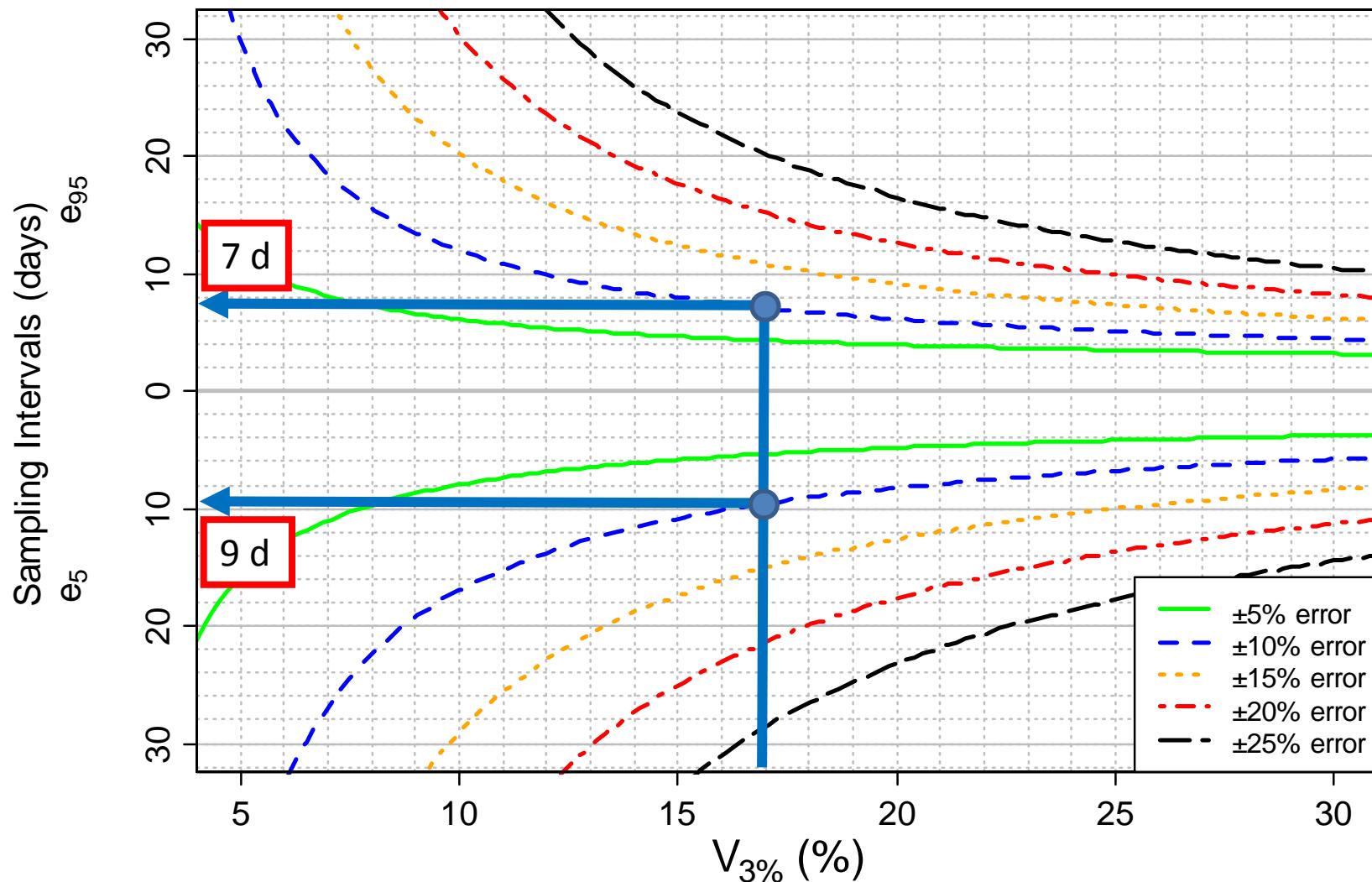
# Unique link between errors and $V_{3\%}$



# Guideline curves for DOM in Brittany, France



# Guideline curves for DOM in Brittany, France



# Conclusions

- Infrequent sampling does imply errors on water quality indicators such as annual fluxes and concentration indicators
- Flow weighted concentration method best for this region
- Uncertainties depend largely on watershed hydrological reactivity

# Conclusion (Con'd)

- Annual flux for bi-monthly sampling: -13% to +17%, slightly biased ( $V_{3\%} = 15\%$ )
- Errors on monthly sampling are rather low compared to other pollutants such as TSS (e.g. 200%) but higher than for nitrate
- Apply the same and other statistical methods to North Carolina data
- Join the study, share your data!!



Thank you for your  
kind attention!

francois\_birgand@ncsu.edu