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Generating Water Quality Rating Curves using *in situ* Spectrophotometers

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1

A little story

" … …Troy … … … . Marc … … … hard; … … … … … … … … forehead. … … … … unconscious … … floor, … … … … … face … … Marc … … … all … … … … bad … … … feared."

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A little story

"Marc … … … … catch. … … … ball… ; … missed … … … landed … … …. Troy … … … unconscious … … … … … smile … … … … reassured … … … was … … … not … … … … … feared."

A little story

"Marc and Troy were playing catch. Marc threw the ball hard; Troy missed it and it landed on his forehead. Troy was laying seemingly unconscious on the floor, but the smile on his face quickly reassured Marc that everything was all right and not as bad as he had feared."

New *in situ* sensors available

Spectrophotometers

Field miniature labs

Fluorometers

HydroCycle-PO4

Cyclop-C6

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- Field UV-vis spectrophotometers

- Spectro::lyser from S::CAN, Austria

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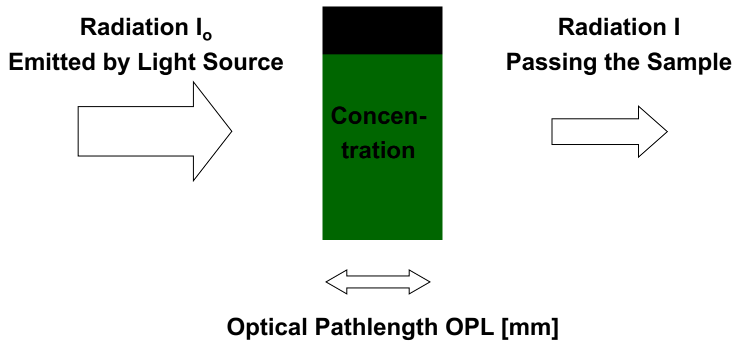
The spectrometric process analyser

The measuring principle – Lambert Beer



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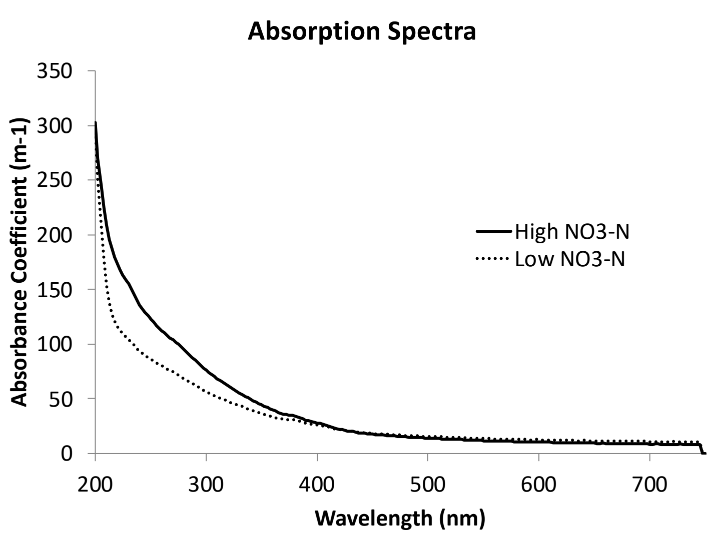

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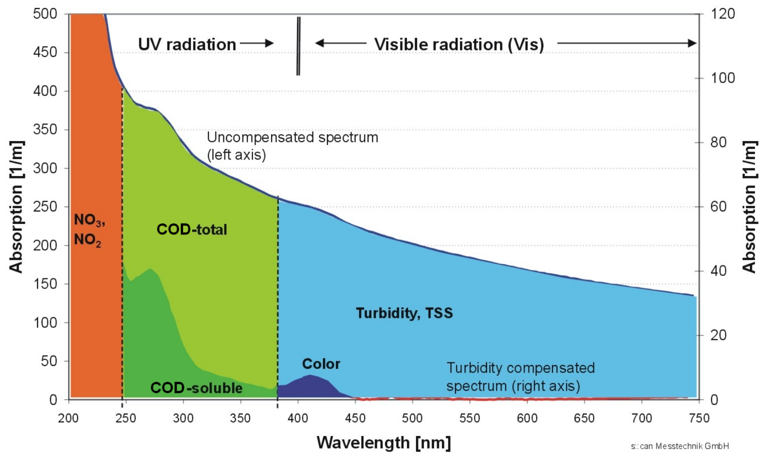
Absorption Spectra



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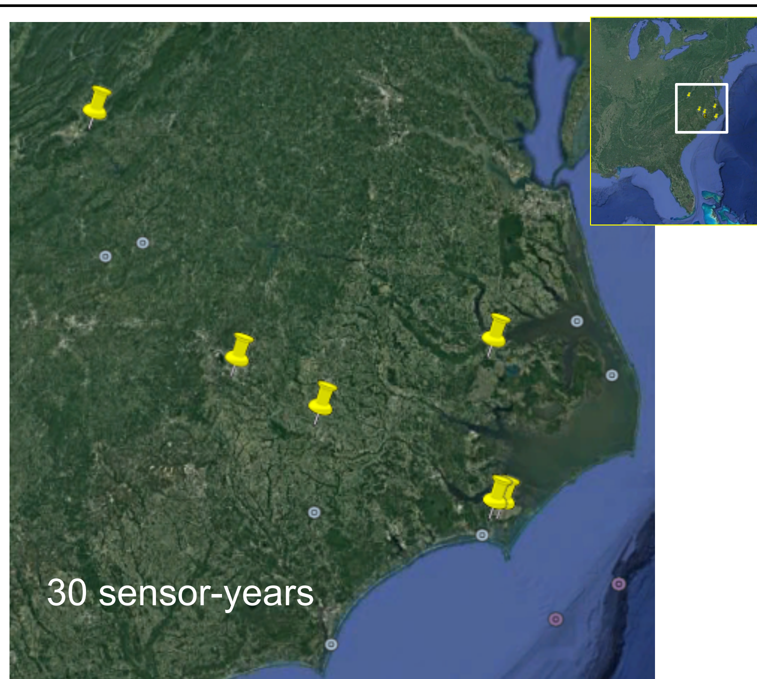

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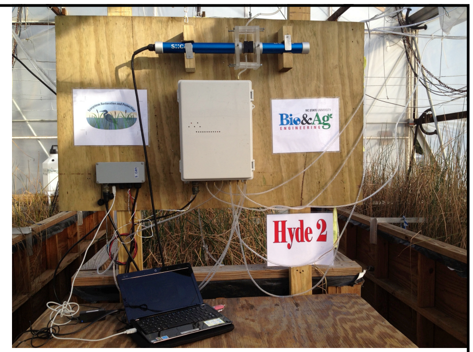
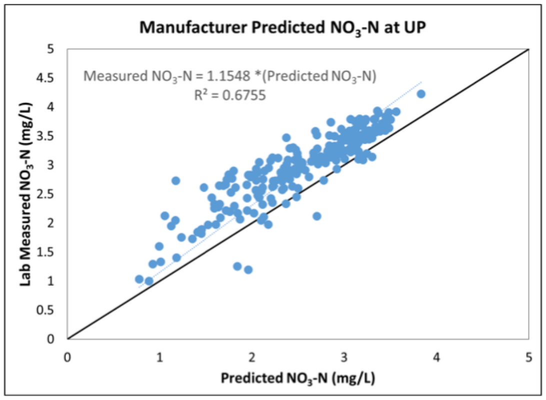


What parameter can we measure?

- Most manufacturers advertise for Nitrate
- Some add DOC and Turbidity

- Other parameters may be linked to turbidity (e.g. TP, PON) or to DOC (e.g. DON)
- Possibly covariability between light absorbance and other parameters?

Results without local calibration



- NO_3-N

Station	Regression Equation	R^2
UP	Y = 1.15 X	0.68
MD	Y = 0.95 X	0.81
DN	Y = 0.87 X	0.48

Y = Lab measured values
X = Predicted values

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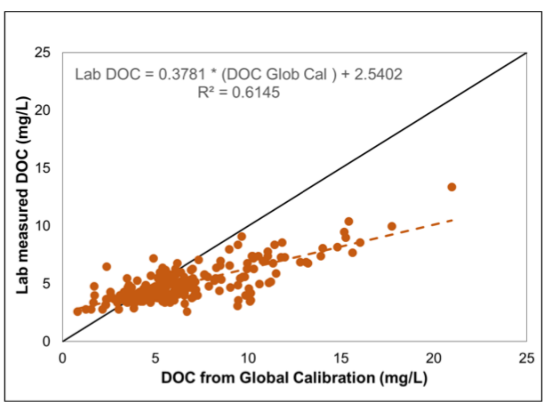
Results without local calibration



- DOC

Station	Regression Equation	R^2
UP	Y = 0.69 X	0.11
MD	Y = 0.98 X	0.58
DN	Y = 0.82 X	0.49

Y = Lab measured values
X = Predicted values

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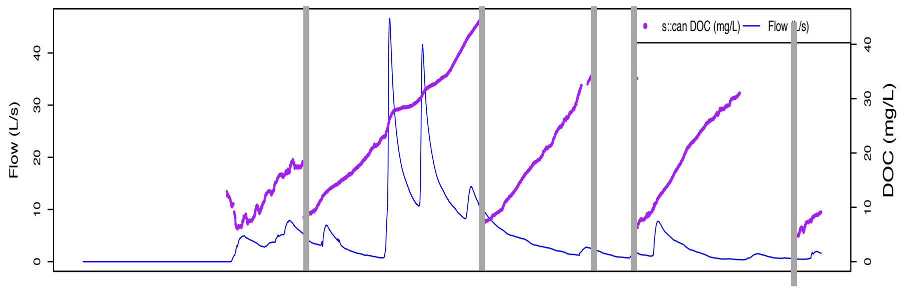

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Need for a unified calibration method

- A method that would:
  - Provide better calibration results
  - That would correct for fouling
  - That would possibly allow calibration of other parameters

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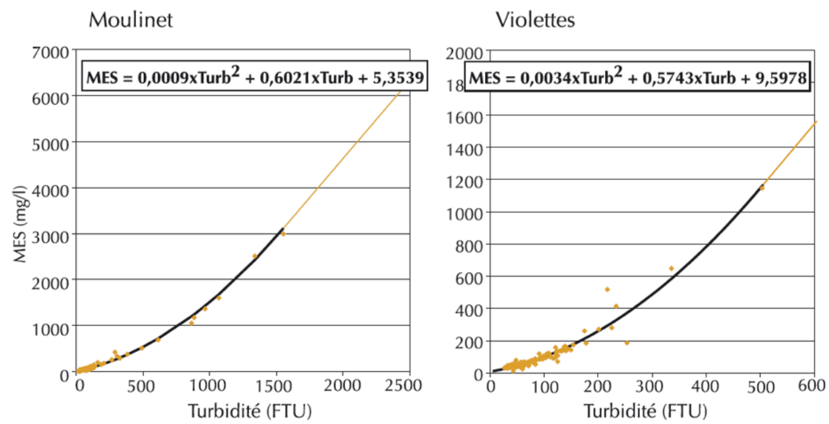
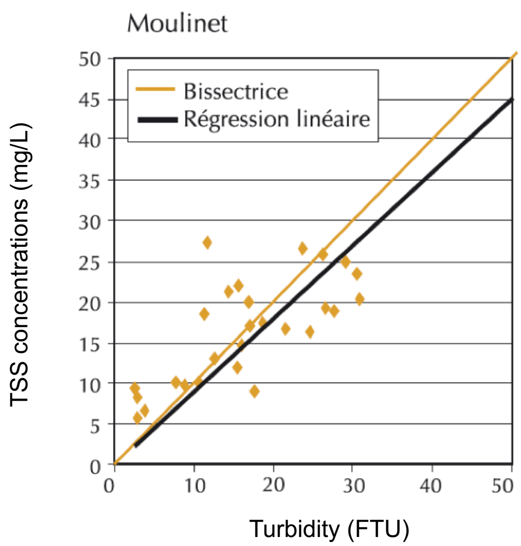
One-on-one regressions

- We like to find linear relationships between one measured and one predicted parameter



One-on-one regressions



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Multi-dimensional space

- Spectrophotometer:
  - Each measurement = 210 absorbance values
- Opens the possibility to create higher level correlations between concentrations and absorbance spectra

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PLSR, unified method?

- *Partial Least Squares Regression* correlates spectral data with chemical concentrations
- Reduces dimensions of system
- Allows selection of the number of dimensions to use in modeling the relationship between uv/vis spectral fingerprint and concentrations

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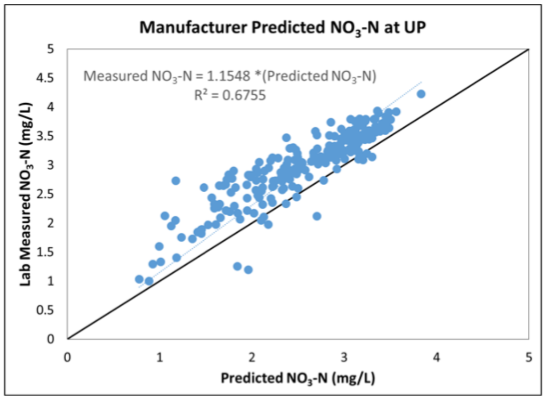
Results without local calibration



- NO_3-N

Station	Regression Equation	R^2
UP	Y = 1.15 X	0.68
MD	Y = 0.95 X	0.81
DN	Y = 0.87 X	0.48

Y = Lab measured values
X = Predicted values

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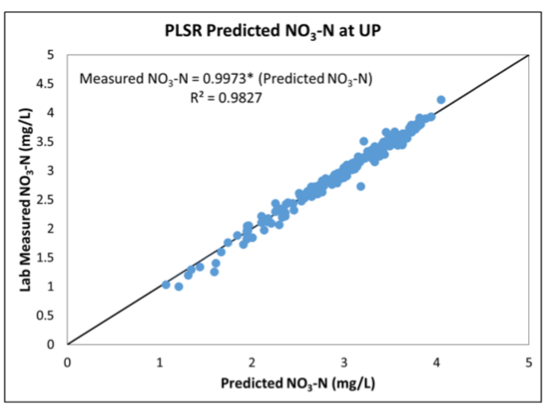
Results after PLS calibration



- NO_3-N

Station	Regression Equation	R^2
UP	Y = 1.00 X	0.98
MD	Y = 1.01 X	0.98
DN	Y = 1.00 X	0.98

Y = Lab measured values
X = Predicted values

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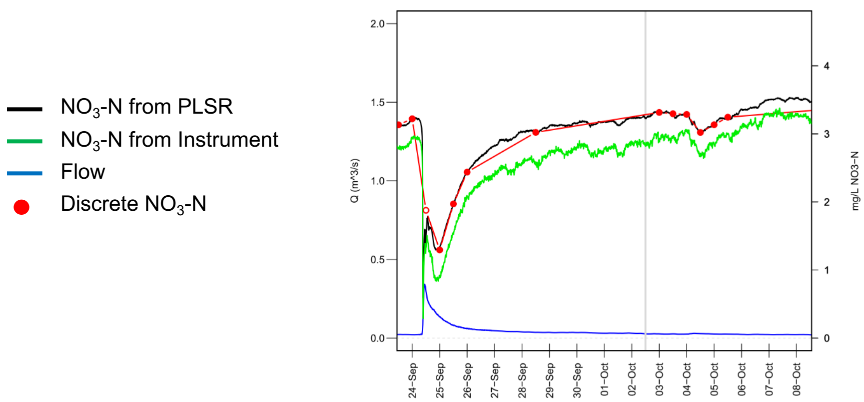
PLSR calibration vs. Instrument calibration



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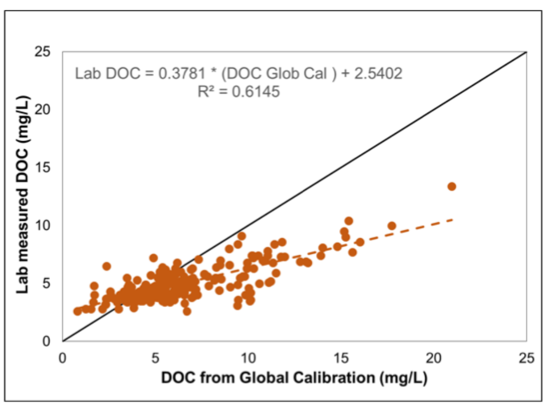
Results without local calibration



- **DOC**

Station	Regression Equation	R^2
UP	Y = 0.69 X	0.11
MD	Y = 0.98 X	0.58
DN	Y = 0.82 X	0.49

Y = Lab measured values
X = Predicted values

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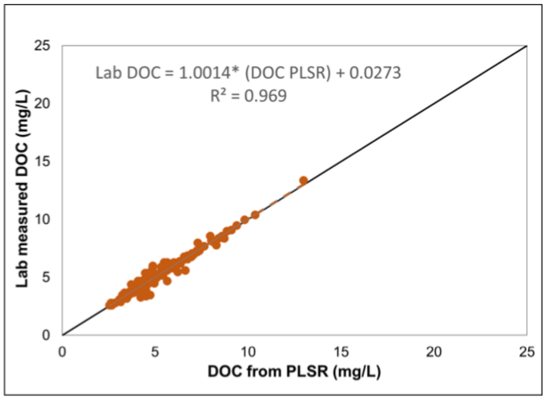
Results after PLS calibration



- **DOC**

Station	Regression Equation	R^2
UP	Y = 1.01 X	0.97
MD	Y = 0.99 X	0.92
DN	Y = 1.00 X	0.94

Y = Lab measured values
X = Predicted values

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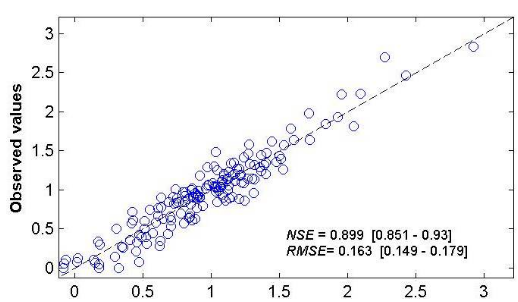
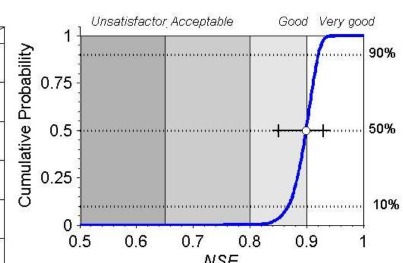
Results for TKN in a tidal marsh





p = 0

(Graphs from Fiteval, Ritter and Muñoz-Carpena, 2013, JH)

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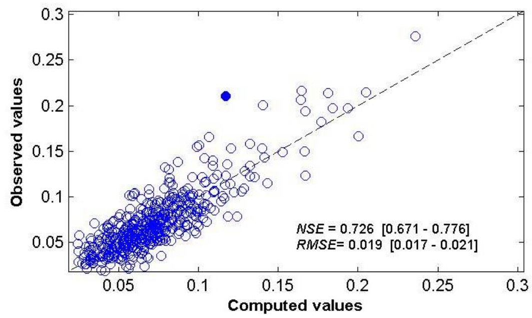
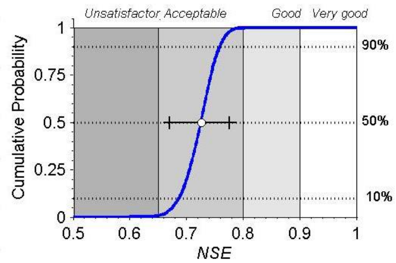
Results for TP in our marsh





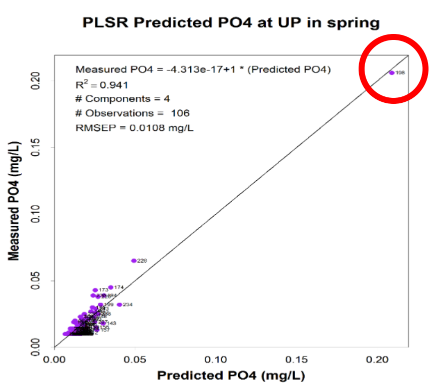
p = 0.006

(Graphs from Fiteval, Ritter and Muñoz-Carpena, 2013, JH)

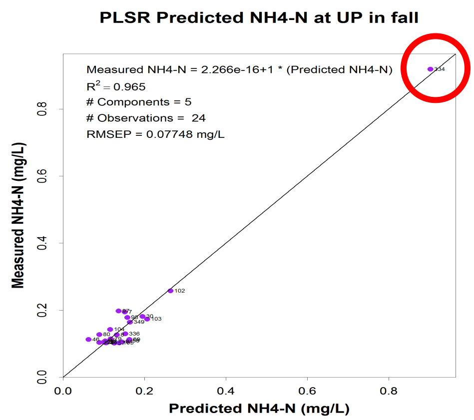
WQ Rating curves

- Hypotheses:
  - Covariability of concentrations and 'color matrix' of water
  - Relationship stable enough to be characterized
  - PLSR: a great first approach to characterize this relationship or 'rating curve'
- Plsr: no predictive power, however

WQRC created and tested so far



PO_4-P
R^2= 0.94



NH_4-N
R^2= 0.97

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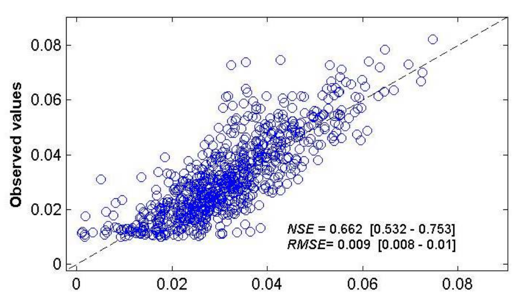
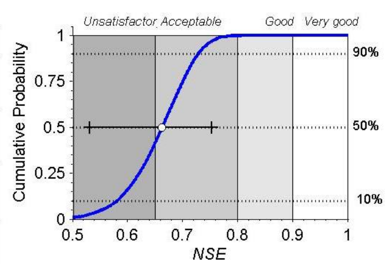
Results for PO4





p = 0.41

(Graphs from Fiteval, Ritter and Muñoz-Carpena, 2013, JH)

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	NO_3-N	NH_4-N	TDN	TKN	DOC	TP	PO_4-P
UP in spring and summer							
NSE (% unsatif.)	0.93 (0%)	0.17 (100%)**	0.88 (0%)	0.87 (0%)	0.91 (0%)	0.95 (0%)	0.94 (7.4%)
UP in fall and winter							
NSE (% unsatif.)	0.94 (0%)	0.97 (15%)**	0.89 (0%)	0.87 (0.1%)	0.85 (0%)	0.97 (0%)	0.88 (33%)**
MD in spring and summer							
NSE (% unsatif.)	0.98 (0%)	0.80 (2%)	0.92 (0%)	0.87 (0%)	0.92 (0%)	0.88 (0.1%)	0.92 (9.4%)
MD in fall and winter							
NSE (% unsatif.)	0.95 (0%)	0.75 (35%)**	0.94 (0%)	0.71 (22%)**	0.93 (0%)	0.81 (8.8%)	0.74 (29%)**
DN in spring and summer							
NSE (% unsatif.)	0.93 (0%)	0.10 (100%)**	0.85 (0%)	0.80 (5.2%)	0.91 (0%)	0.95 (0%)	0.94 (0%)
DN in fall and winter							
NSE (% unsatif.)	0.93 (0%)	0.71 (39%)**	0.85 (0.1%)	0.84 (2.7%)	0.92 (0%)	0.97 (0%)	0.95 (1%)

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More esoteric WQRC…

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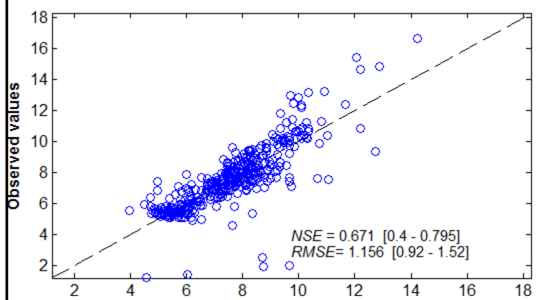
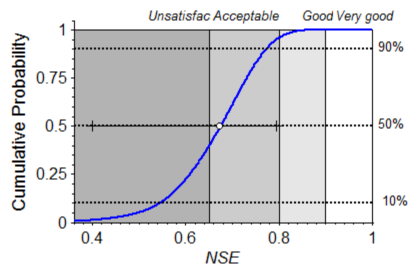
Sulfate in Kervidy, Brittany





P value = 0.40

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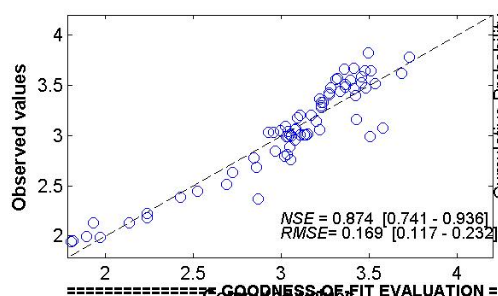
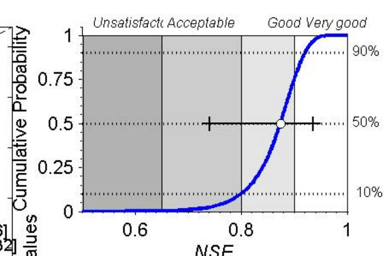
Silica in Kervidy, Brittany





=============== GOODNESS-OF-FIT EVALUATION ============

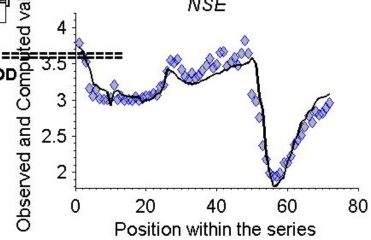
Evaluation of *NSE*: **From ACCEPTABLE to VERY GOOD**

Probability of fit being:

- *Very good* (*NSE* = 0.900 - 1.000): 25.9%
- *Good* (*NSE* = 0.800 - 0.899): 64.3%
- *Acceptable* (*NSE* = 0.650 - 0.799): 9.6%
- ***Unsatisfactory* (*NSE* < 0.650): 0.2%**

Presence of outliers (Q-test): NO

Model bias: NO



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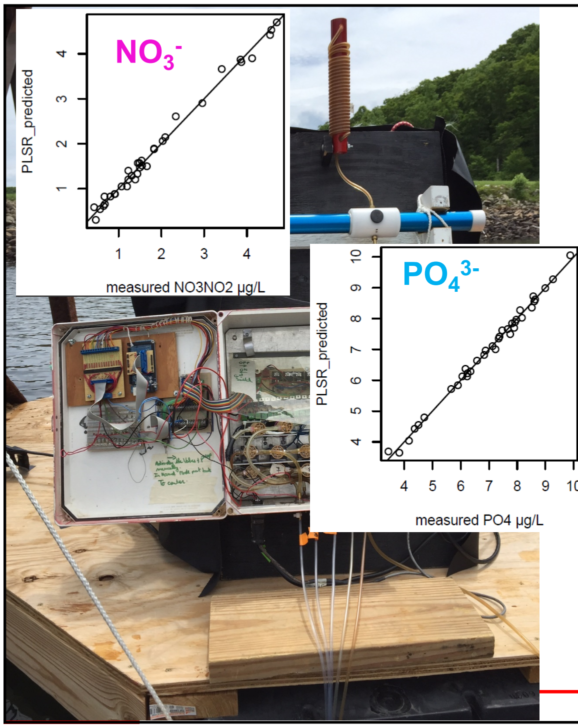
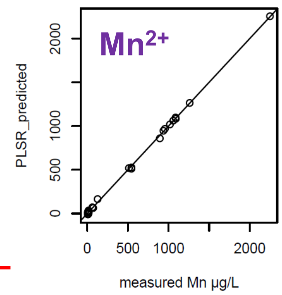


Lake values



Are WQRC for real?

- Hypothesis
  - In many cases, there is a co-variability of 'color matrix of water' and concentrations
- Parameters unrelated to matrix of water have little chance to be well predicted with this method
  - Parameters linked to point sources
- Lakes might be an ideal environment for WQRC

Proper ways to make WQRC?

- Main rules:
  - Regression must be robust
  - Have as wide a concentration range as possible
  - Have calibration samples stratified
    - Along concentration range
    - Along time to correct for fouling
  - The more calibration points the better
- In the process of making a WQ_PLSR package in R!

Additional thoughts

- Sensors give access to a lot of new things
  - Only mean to capture stochastic events intrinsically linked with hydrological processes
  - Capture the effects of biogeochemical processes on water quality
  - Key to improve/revise our models

Additional thoughts

- These instruments need to be very closely maintained to obtained useful data
- A lot more information that comes with
  - A lot more work
  - A lot more money
- Cannot be added as 'one of the sensors'
  - No place for 'I can do it all'
  - Collaboration is key

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Acknowledgments

- R. Etheridge, M. Horstman, B. Smith
- K. Aveni-Deforge, E. Allen, C-W Lin, N. Dobbs, B. Maxwell, T. Gilmore
- C. Carey, M. Burchell, J. Osborne, R. Muñoz-Carpena
- NC DOT
- US DOE
- USDA-NIFA

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Add on:
explore both space and time resolution

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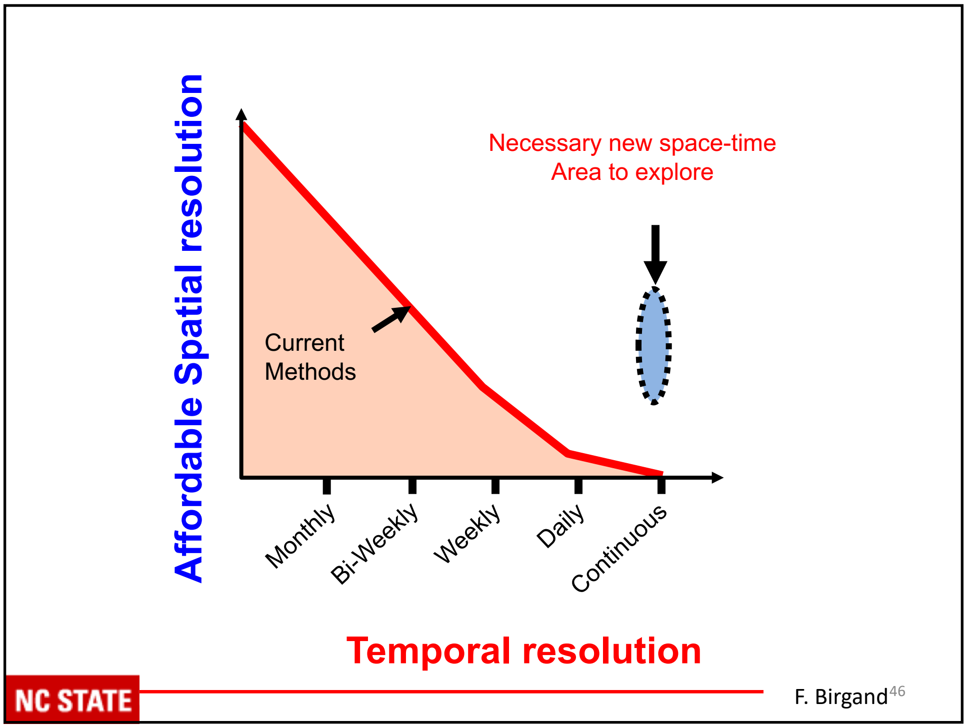
Affordable Spatial resolution
Necessary new space-time
Area to explore
Current
Methods
Monthly
Bi-Weekly
Weekly
Daily
Continuous
Temporal resolution
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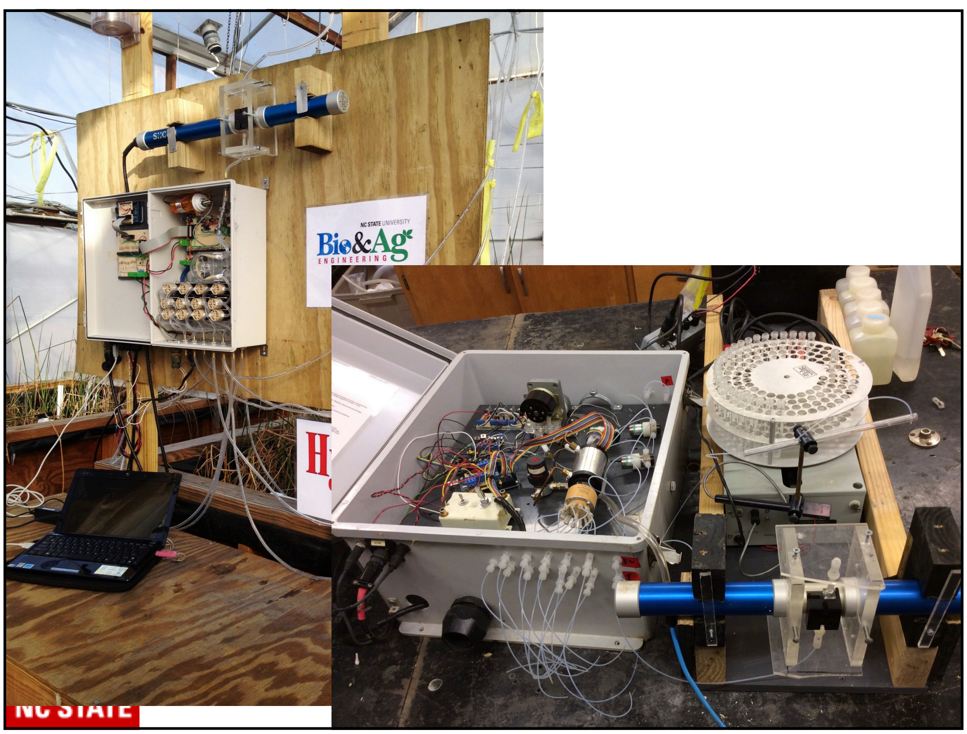
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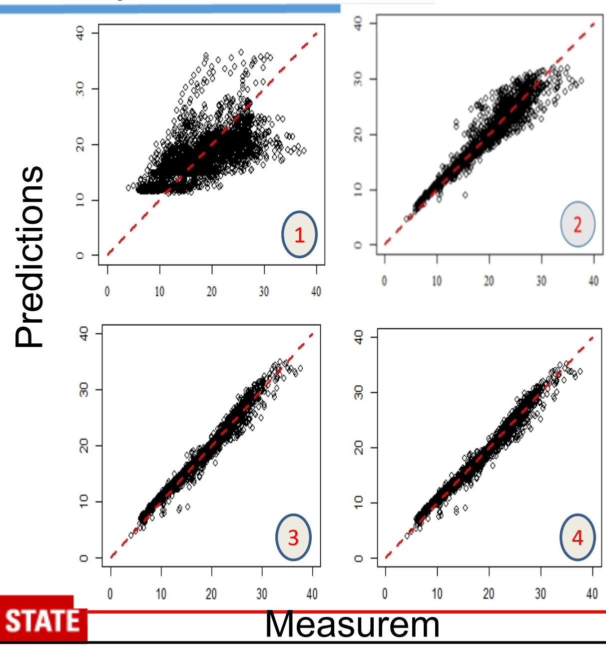
Bioreactor rejuvenation experiment

Mutiple models

[DOC]: leaching rate



Eq1: $[NO_3^{-1}]_R = 1.277 * e^{1.161*T}$

Eq2: $[NO_3^{-1}]_R = 45.7 * e^{0.006*T} * [DOC]/3.5+[DOC]$

Eq3: $[NO_3^{-1}]_R = 70.2 * e^{0.0077*T} * [DOC]/4.3+[DOC] * e^{-0.043*HRT}$

Eq4: $[NO_3^{-1}]_R = 85.5 * e^{0.0079*T} * [DOC]/4.4+[DOC] * e^{-0.043*HRT} * [NO_3^{-1}]/3.9+[NO_3^{-1}]$