Generating Water Quality Rating Curves using *in situ* Spectrophotometers

François Birgand, Beth Allen, Chiao-Wen Lin, Randall Etheridge, Cayelan Carey

---

A little story

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

- SUNA V2
- HydroCycle-PO4
- Cyclop-C6

- Field UV-vis spectrophotometers

- Spectro::lyser from S::CAN, Austria
The spectrometric process analyser

The measuring principle – Lambert Beer

Radiation $I_0$
Emitted by Light Source

Concentration

Radiation $I$
Passing the Sample

Optical Pathlength OPL [mm]

Absorption Spectra

Absorbance Coefficient (m$^{-1}$) vs. Wavelength (nm)

- High NO3-N
- Low NO3-N
Absorption Spectra

30 sensor-years
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

**NO₃⁻N**

<table>
<thead>
<tr>
<th>Station</th>
<th>Regression Equation</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>UP</td>
<td>Y = 1.15 X</td>
<td>0.68</td>
</tr>
<tr>
<td>MD</td>
<td>Y = 0.95 X</td>
<td>0.81</td>
</tr>
<tr>
<td>DN</td>
<td>Y = 0.87 X</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Y = Lab measured values
X = Predicted values

**DOC**

<table>
<thead>
<tr>
<th>Station</th>
<th>Regression Equation</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>UP</td>
<td>Y = 0.69 X</td>
<td>0.11</td>
</tr>
<tr>
<td>MD</td>
<td>Y = 0.98 X</td>
<td>0.58</td>
</tr>
<tr>
<td>DN</td>
<td>Y = 0.82 X</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Y = Lab measured values
X = Predicted values
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
One-on-one regressions

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

\[
\text{MES} = 0.009x \times \text{Turb}^2 + 0.6021 \times \text{Turb} + 5.3539
\]

\[
\text{MES} = 0.003x \times \text{Turb}^2 + 0.5743 \times \text{Turb} + 9.5971
\]
Multi-dimensional space

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

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
### Results without local calibration

#### NO₃-N

<table>
<thead>
<tr>
<th>Station</th>
<th>Regression Equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UP</td>
<td>$Y = 1.15X$</td>
<td>0.68</td>
</tr>
<tr>
<td>MD</td>
<td>$Y = 0.95X$</td>
<td>0.81</td>
</tr>
<tr>
<td>DN</td>
<td>$Y = 0.87X$</td>
<td>0.48</td>
</tr>
</tbody>
</table>

$Y = \text{Lab measured values}$  
$X = \text{Predicted values}$

![Graph showing Manufacturer Predicted NO₃-N at UP](image)

### Results after PLS calibration

#### NO₃-N

<table>
<thead>
<tr>
<th>Station</th>
<th>Regression Equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UP</td>
<td>$Y = 1.00X$</td>
<td>0.98</td>
</tr>
<tr>
<td>MD</td>
<td>$Y = 1.01X$</td>
<td>0.98</td>
</tr>
<tr>
<td>DN</td>
<td>$Y = 1.00X$</td>
<td>0.98</td>
</tr>
</tbody>
</table>

$Y = \text{Lab measured values}$  
$X = \text{Predicted values}$

![Graph showing PLSR Predicted NO₃-N at UP](image)
PLSR calibration vs. Instrument calibration

Results without local calibration

- DOC

<table>
<thead>
<tr>
<th>Station</th>
<th>Regression Equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UP</td>
<td>$Y = 0.69 X$</td>
<td>0.11</td>
</tr>
<tr>
<td>MD</td>
<td>$Y = 0.98 X$</td>
<td>0.58</td>
</tr>
<tr>
<td>DN</td>
<td>$Y = 0.82 X$</td>
<td>0.49</td>
</tr>
</tbody>
</table>

$Y = \text{Lab measured values}$

$X = \text{Predicted values}$
Results after PLS calibration

**DOC**

<table>
<thead>
<tr>
<th>Station</th>
<th>Regression Equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UP</td>
<td>$Y = 1.01X$</td>
<td>0.97</td>
</tr>
<tr>
<td>MD</td>
<td>$Y = 0.99X$</td>
<td>0.92</td>
</tr>
<tr>
<td>DN</td>
<td>$Y = 1.00X$</td>
<td>0.94</td>
</tr>
</tbody>
</table>

$Y = $ Lab measured values  
$X = $ Predicted values

Results for TKN in a tidal marsh

(Graphs from Fileval, Ritter and Muñoz-Carpent, 2013, JH)
Results for TP in our marsh

{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
$R^2 = 0.94$
Results for PO4

\[ p = 0.41 \]

(Graphs from Fiteval, Ritter and Muñoz-Carpensa, 2013, JH)
<table>
<thead>
<tr>
<th></th>
<th>NO$_3$-N</th>
<th>NH$_4$-N</th>
<th>TDN</th>
<th>TKN</th>
<th>DOC</th>
<th>TP</th>
<th>PO$_4$-P</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>UP</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in spring and summer</td>
<td>0.93</td>
<td>0.17</td>
<td>0.68</td>
<td>0.67</td>
<td>0.91</td>
<td>0.95</td>
<td>0.94</td>
</tr>
<tr>
<td>NSE (%) unsatif.</td>
<td>(0%)</td>
<td>(100%)**</td>
<td>(0%)</td>
<td>(0%)</td>
<td>(0%)</td>
<td>(0%)</td>
<td>(7.4%)**</td>
</tr>
<tr>
<td>in fall and winter</td>
<td>0.94</td>
<td>0.97</td>
<td>0.89</td>
<td>0.87</td>
<td>0.85</td>
<td>0.97</td>
<td>0.88</td>
</tr>
<tr>
<td>NSE (%) unsatif.</td>
<td>(0%)</td>
<td>(15%)**</td>
<td>(0%)</td>
<td>(0.1%)</td>
<td>(0%)</td>
<td>(0%)</td>
<td>(33%)**</td>
</tr>
<tr>
<td><strong>MD</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in spring and summer</td>
<td>0.98</td>
<td>0.80</td>
<td>0.92</td>
<td>0.87</td>
<td>0.92</td>
<td>0.88</td>
<td>0.92</td>
</tr>
<tr>
<td>NSE (%) unsatif.</td>
<td>(0%)</td>
<td>(2%)</td>
<td>(0%)</td>
<td>(0%)</td>
<td>(0%)</td>
<td>(0.1%)</td>
<td>(9.4%)</td>
</tr>
<tr>
<td>in fall and winter</td>
<td>0.95</td>
<td>0.75</td>
<td>0.94</td>
<td>0.71</td>
<td>0.93</td>
<td>0.81</td>
<td>0.74</td>
</tr>
<tr>
<td>NSE (%) unsatif.</td>
<td>(0%)</td>
<td>(35%)**</td>
<td>(0%)</td>
<td>(22%)**</td>
<td>(0%)</td>
<td>(8.8%)</td>
<td>(29%)**</td>
</tr>
<tr>
<td><strong>DN</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in spring and summer</td>
<td>0.93</td>
<td>0.10</td>
<td>0.85</td>
<td>0.80</td>
<td>0.91</td>
<td>0.95</td>
<td>0.94</td>
</tr>
<tr>
<td>NSE (%) unsatif.</td>
<td>(0%)</td>
<td>(100%)**</td>
<td>(0%)</td>
<td>(5.2%)</td>
<td>(0%)</td>
<td>(0%)</td>
<td>(0%)</td>
</tr>
<tr>
<td>in fall and winter</td>
<td>0.93</td>
<td>0.71</td>
<td>0.85</td>
<td>0.84</td>
<td>0.92</td>
<td>0.97</td>
<td>0.95</td>
</tr>
<tr>
<td>NSE (%) unsatif.</td>
<td>(0%)</td>
<td>(39%)**</td>
<td>(0.1%)</td>
<td>(2.7%)</td>
<td>(0%)</td>
<td>(0%)</td>
<td>(1%)</td>
</tr>
</tbody>
</table>

More esoteric WQRC...
Sulfate in Kervidy, Brittany

P value = 0.40

Silica in Kervidy, Brittany

Evaluation of NSE: From ACCEPTABLE to VERY GOOD

Presence of outliers (C-test): NO
Model bias: NO
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:
  o Regression must be robust
  o Have as wide a concentration range as possible
  o Have calibration samples stratified
    o Along concentration range
    o Along time to correct for fouling
  o 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
  o Only mean to capture stochastic events intrinsically linked with hydrological processes
  o Capture the effects of biogeochemical processes on water quality
  o 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
  o A lot more work
  o A lot more money
• Cannot be added as ‘one of the sensors’
  o No place for ‘I can do it all’
  o Collaboration is key

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
Thank you for your attention!

Questions?

Add on:
explore both space and time resolution
Temporal resolution

Affordable Spatial resolution

Necessary new space-time Area to explore

Current Methods

Temporal resolution

NC STATE F. Birgand

NC STATE
Bioreactor rejuvenation experiment

Mutiple models

Predictions

Eq1: \([NO3T−1]_{IR} = 1.277 \times 10^{1.161 \times T}\)

Eq2: \([NO3T−1]_{IR} = 45.7 \times 10^{0.006 \times T} \times [DOC]^{3.5} + [DOC]\)

Eq3: \([NO3T−1]_{IR} = 70.2 \times 10^{0.0077 \times T} \times [DOC]^{4.3} + [DOC] \times e^{−0.043 \times HRT}\)

Eq4: \([NO3T−1]_{IR} = 85.5 \times 10^{0.0079 \times T} \times [DOC]^{4.4} + [DOC] \times e^{−0.043 \times HRT} \times [NO3T−1]^{3.9} + [NO3T−1]\)

[DOC]: leaching rate

Measurem