Monitoring dissolved organic matter using submersible tryptophan-like fluorometers

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**Fluorescence**: a form of luminescence which occurs over short time scales at the molecular/atomic level.

EEM spectroscopy

Excitation Emission Matrix (EEM)

Bench top scanning fluorometer

Humic-like compounds (terrestrial origin)

Tryptophan-like peak related to microbial activity + correlated with BOD$_5$

However… Not suitable for remote field sites or if high resolution records are required.

Fellman et al. (2012) Lim. & Oce. 55, 2452
Challenges to in-situ monitoring

- Quenching – e.g. temperature;

- Matrix interference – e.g. suspended particles in water column;

- Inner-filtering - concentration effect;

- Measurement repeatability - between/within sites and between sensors;

- To date no rigorous tests of submersible tryptophan fluorometers have been conducted.
The objectives of this study were to:

1. Test the performance of two commercially available tryptophan fluorometers in the lab;

2. Develop empirical correction factors to account for fluorescence quenching and matrix interference;

3. Undertake a field trial to assess sensor performance and test correction factors.
## Minimum Detection Limit (MDL) and precision

### Table

<table>
<thead>
<tr>
<th></th>
<th>T1</th>
<th>T2</th>
<th>C1</th>
<th>C2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calibrated relation</strong></td>
<td>( y = 0.997x - 0.133 )</td>
<td>( y = 1x + 0.0009 )</td>
<td>( y = 1x - 0.00007 )</td>
<td>( y = 1x + 0.00006 )</td>
</tr>
<tr>
<td><strong>Relationship with Varian (ppb)</strong></td>
<td>( y = 0.99x - 0.1255 )</td>
<td>( Y = 1x + 0.0022 )</td>
<td>( y = 1x + 0.0076 )</td>
<td>( y = 0.99x + 0.0129 )</td>
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<tr>
<td><strong>Relationship with Varian (R.U)</strong></td>
<td>( y = 0.002x + 0.0041 )</td>
<td>( y = 0.002x + 0.0044 )</td>
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<tr>
<td><strong>MDL ± SD</strong></td>
<td>( 1.99 ± 0.53 )</td>
<td>( 1.92 ± 0.57 )</td>
<td>( 0.17 ± 0.06 )</td>
<td>( 0.19 ± 0.15 )</td>
</tr>
<tr>
<td><strong>Precision: CV (5ppb)</strong></td>
<td>3.03</td>
<td>2.49</td>
<td>0.45</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>(50ppb)</td>
<td>0.03</td>
<td>0.02</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>(400ppb)</td>
<td>3.79(^4)</td>
<td>4.86(^4)</td>
<td>4.63(^4)</td>
</tr>
<tr>
<td><strong>Accuracy (RMSE)</strong></td>
<td>0.63</td>
<td>0.62</td>
<td>0.57</td>
<td>0.58</td>
</tr>
</tbody>
</table>

### Significant difference in precision at low concentration
Thermal quenching

Raw data
Turbidity interference

100 NTU

900 NTU

200 NTU
Turbidity interference (clay)

Sensor C1
95% CI overlap
> 200 NTU

Sensor C2
95% CI overlap
> 200 NTU

Sensor T1
95% CI overlap
> 200 NTU
Turbidity interference (silt)

Sensor C1

Tryptophan signal (ppb)

Sensor C2

Concentration (ppb)

Sensor T1

Tryptophan signal (ppb)

95% CI overlap

> 800 NTU

No 95% CI overlap

> 600 NTU
Turbidity correction

Clay (Fullers Earth)

Silt (glacial outwash)
Urban field test site

Urban field test site

Chelsea fluorometer and Manta 2
- Stage
- Turbidity
- EC
- Tw
- Tryptophan

ISCO pump sampler
Field trial

Event characterised

Hurricane Bertha
Field trial: raw data
Field trial: corrected data

FE = Fullers Earth (clay)  GS = Glacial silt
Field trial: corrected data

**R(\textsuperscript{2}) = 0.92**

\(m = 0.69 \pm 0.04\)

\(c = 0.91 \pm 4.53\)

**R(\textsuperscript{2}) = 0.88**

\(m = 0.95 \pm 0.07\)

\(c = -2.41 \pm 5.90\)

**R(\textsuperscript{2}) = 0.91**

\(m = 0.67 \pm 0.04\)

\(c = 7.95 \pm 4.38\)
Field trial: corrected data

\[ R^2 = 0.77 \]
\[ m = 0.80 \pm 0.09 \]
\[ c = -23.0 \pm 10.84 \]

\[ R^2 = 0.76 \]
\[ m = 0.86 \pm 0.10 \]
\[ c = -22.4 \pm 10.86 \]

\[ R^2 = 0.76 \]
\[ m = 0.96 \pm 0.11 \]
\[ C = -2.03 \pm 8.75 \]
Borehole test

Tryptophan signal (ppb)

Depth below ground (m)

- 8.0
- 11.0
- 15.0
- 18.0
- 25.9
- 30.2
- 35.1
- 39.1

- C1
- C2
- T1
- T2
- Lab (Varian)
Spatial survey (initial result)

- All sites: $R^2 = 0.60$
- River sites: $R^2 = 0.91$

Habitat type:
- Canal
- Pond
- River
- Effluent

- River samples: $R^2 = 0.67$
- All samples: $R^2 = 0.72$
- River samples: $R^2 = 0.64$
Conclusions

- Quenching of $T_1$ fluorescence was identified in the lab and varied between sensors (Turner & Chelsea)

- Temperature compensation appears relatively simple but evidence of \textit{hysteresis} requires further investigation

- Sediment particle size influenced sensor response to turbidity increases (implies site specific calibrations may be necessary)

- Field tests highlight the potential to develop and apply correction factors to improve in-situ data output during both baseflow and event conditions

- Further work will improve correction factors for BOD$_5$ - $T_1$ fluorescence relationships
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