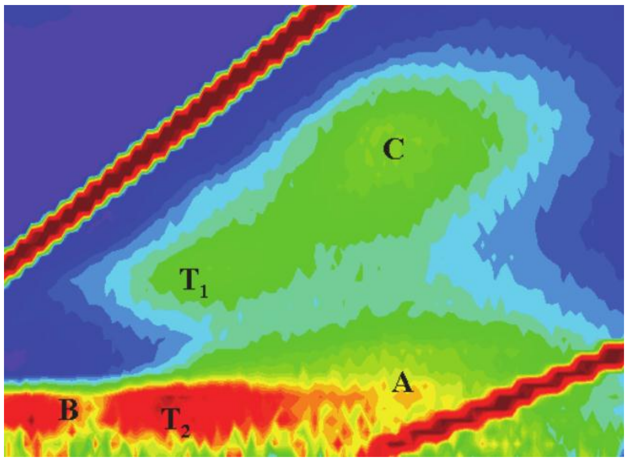
Monitoring dissolved organic matter using submersible tryptophan-like fluorometers



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Knowledge Transfer Partnerships

British Geological Survey
NATURAL ENVIRONMENT RESEARCH COUNCIL

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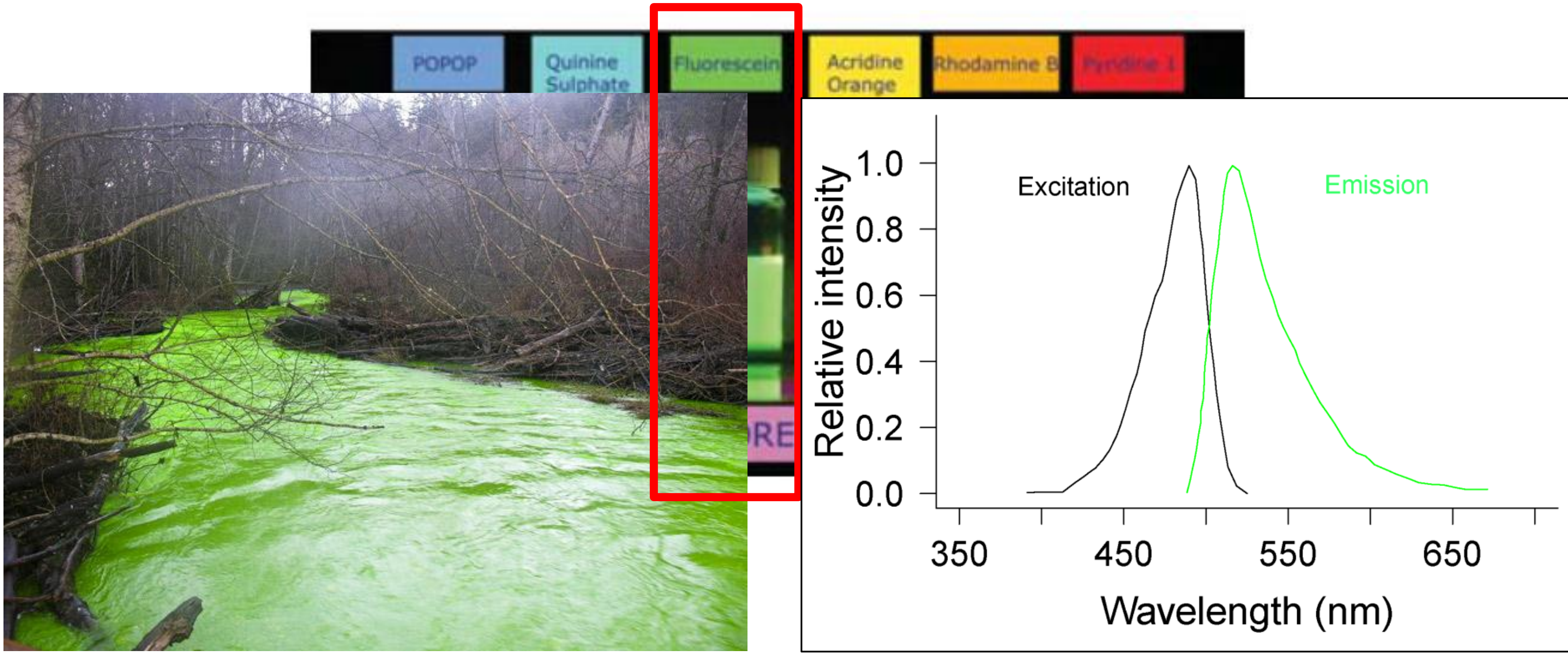
What is fluorescence?

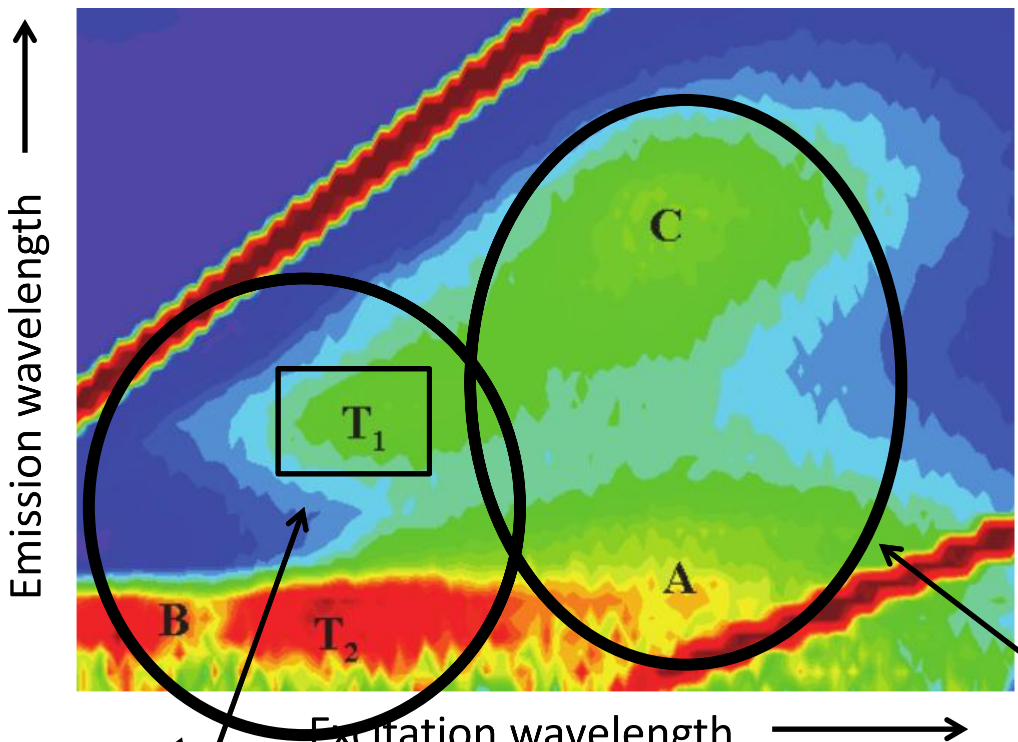
•**Fluorescence**: a form of luminescence which occurs over short time scales at the molecular/atomic level.



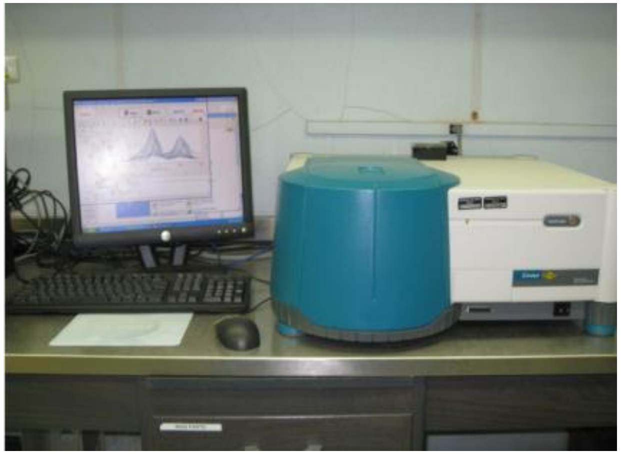
Sjoback et al. (1995) *Spec. Acta A* **51**, 7-21

EEM spectroscopy

Excitation Emission Matrix (EEM)



Bench top scanning fluorometer



Tryptophan - like peak related to microbial activity + correlated with BOD_5

Protein-like compounds (in stream) – indicative of organic enrichment

Humic-like compounds (terrestrial origin)

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

Hudson et al. (2008) ***STOTE*** **391, 149-158**

Fellman et al. (2011) [illegible] 1452

Challenges to in-situ monitoring

- Quenching – e.g. temperature;

  Baker (2005) *Water Research* **39**, 4405

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

  Downing et al. (2012) *Lim. Oce. Methods* **10**, 767

- Inner-filtering - concentration effect;

  Ohno (2002) *Env. Sci. Tech.* **36**, 742

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

  Watras et al. (2011) *Lim. Oce. Methods* **9**, 296

- To date no rigorous tests of submersible tryptophan fluorometers have been conducted.

Study objectives

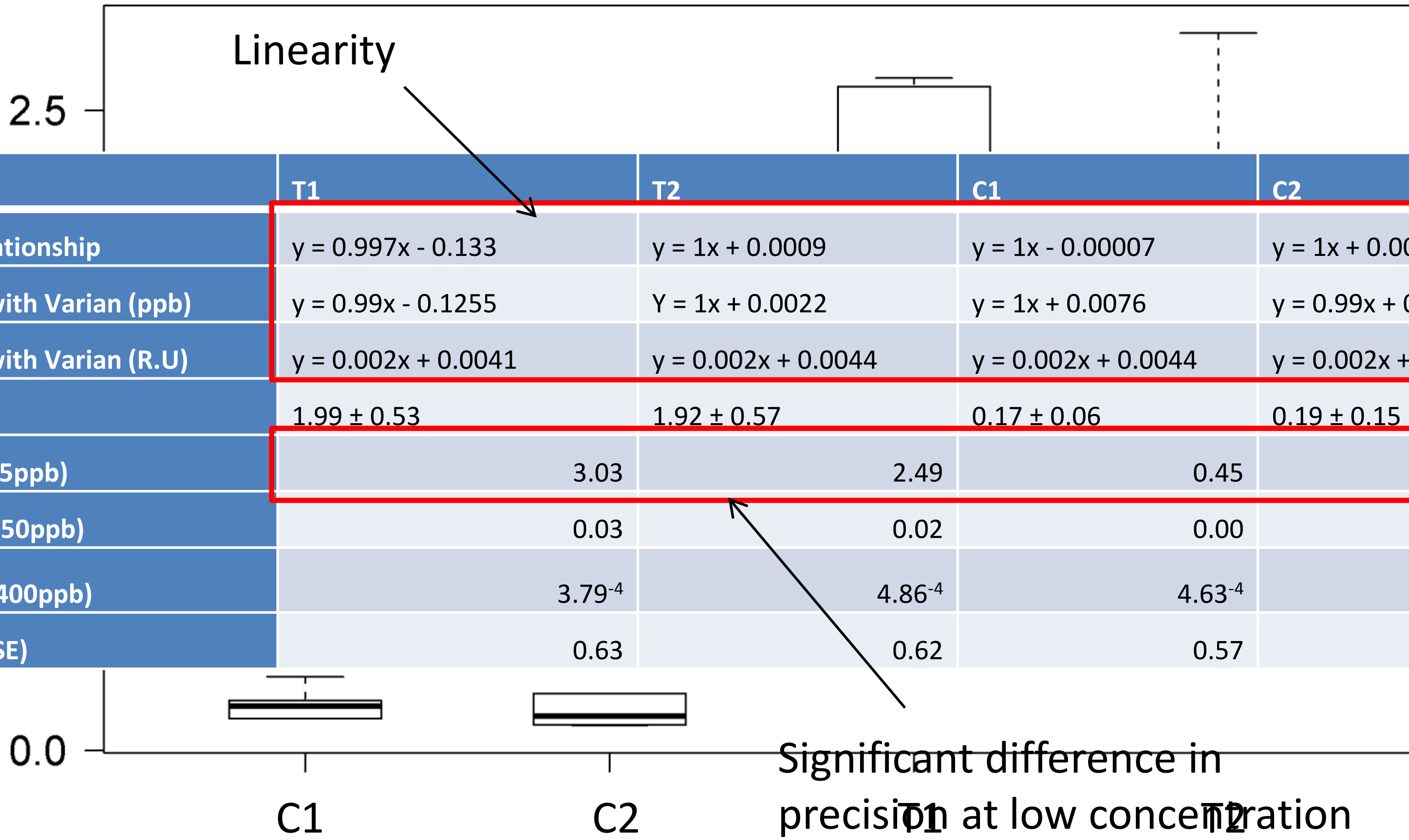
The objectives of this study were to:

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



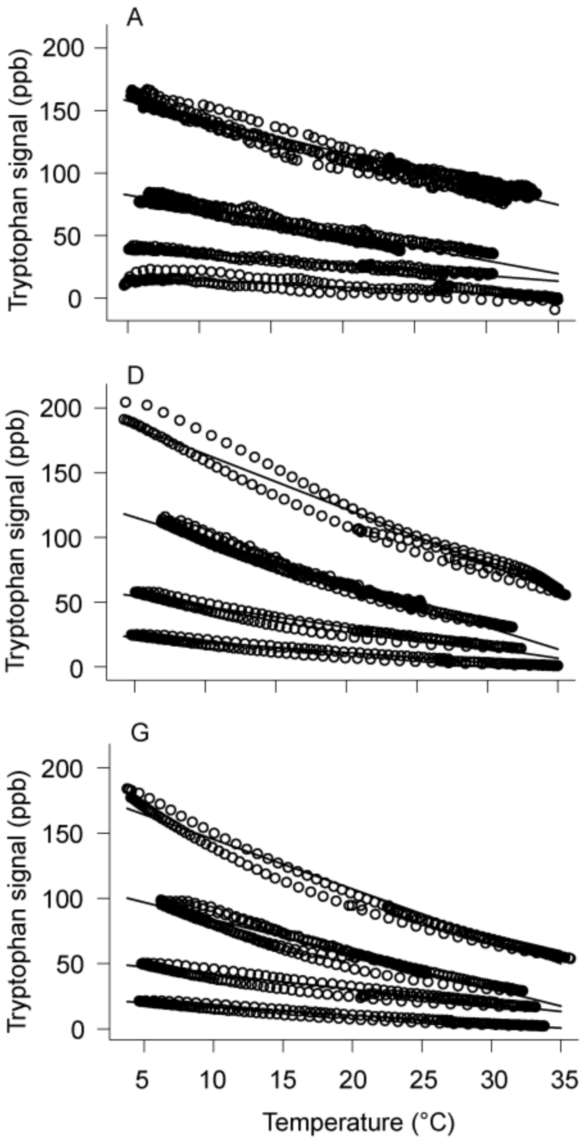
Linearity

	T1	T2	C1	C2
Calibrated relationship	y = 0.997x - 0.133	y = 1x + 0.0009	y = 1x - 0.00007	y = 1x + 0.00006
Relationship with Varian (ppb)	y = 0.99x - 0.1255	Y = 1x + 0.0022	y = 1x + 0.0076	y = 0.99x + 0.0129
Relationship with Varian (R.U)	y = 0.002x + 0.0041	y = 0.002x + 0.0044	y = 0.002x + 0.0044	y = 0.002x + 0.0044
MDL ± SD	1.99 ± 0.53	1.92 ± 0.57	0.17 ± 0.06	0.19 ± 0.15
Precision: CV (5ppb)	3.03	2.49	0.45	0.22
(50ppb)	0.03	0.02	0.00	0.01
(400ppb)	3.79^{-4}	4.86^{-4}	4.63^{-4}	6.27^{-4}
Accuracy (RMSE)	0.63	0.62	0.57	0.58

Significant difference in precision at low concentration

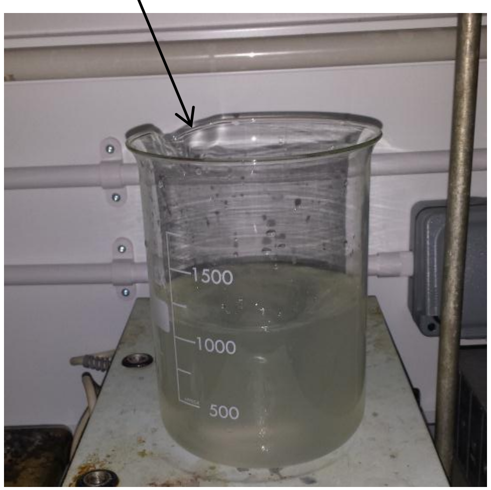
Thermal quenching

Raw data



Turbidity interference

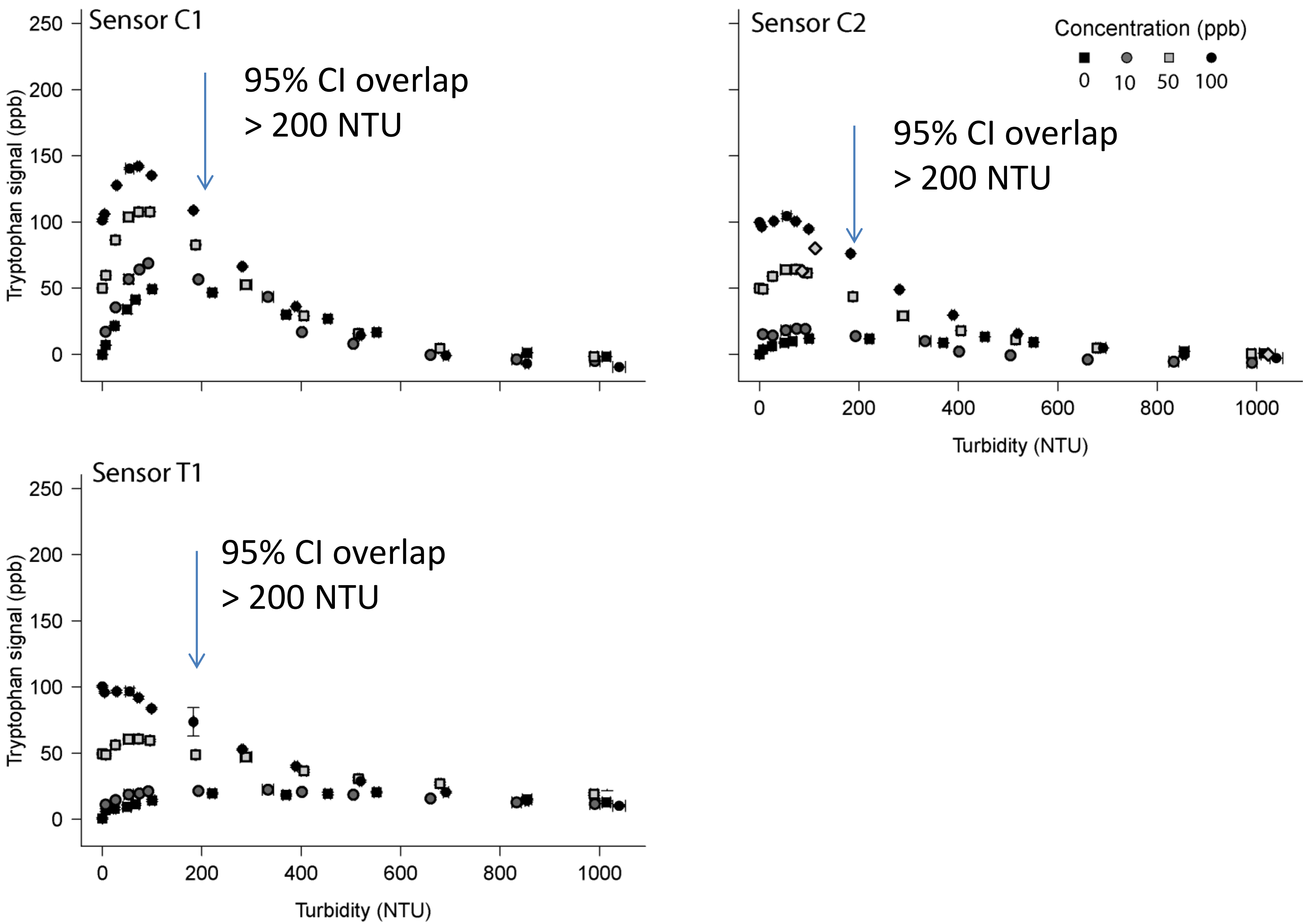
100 NTU



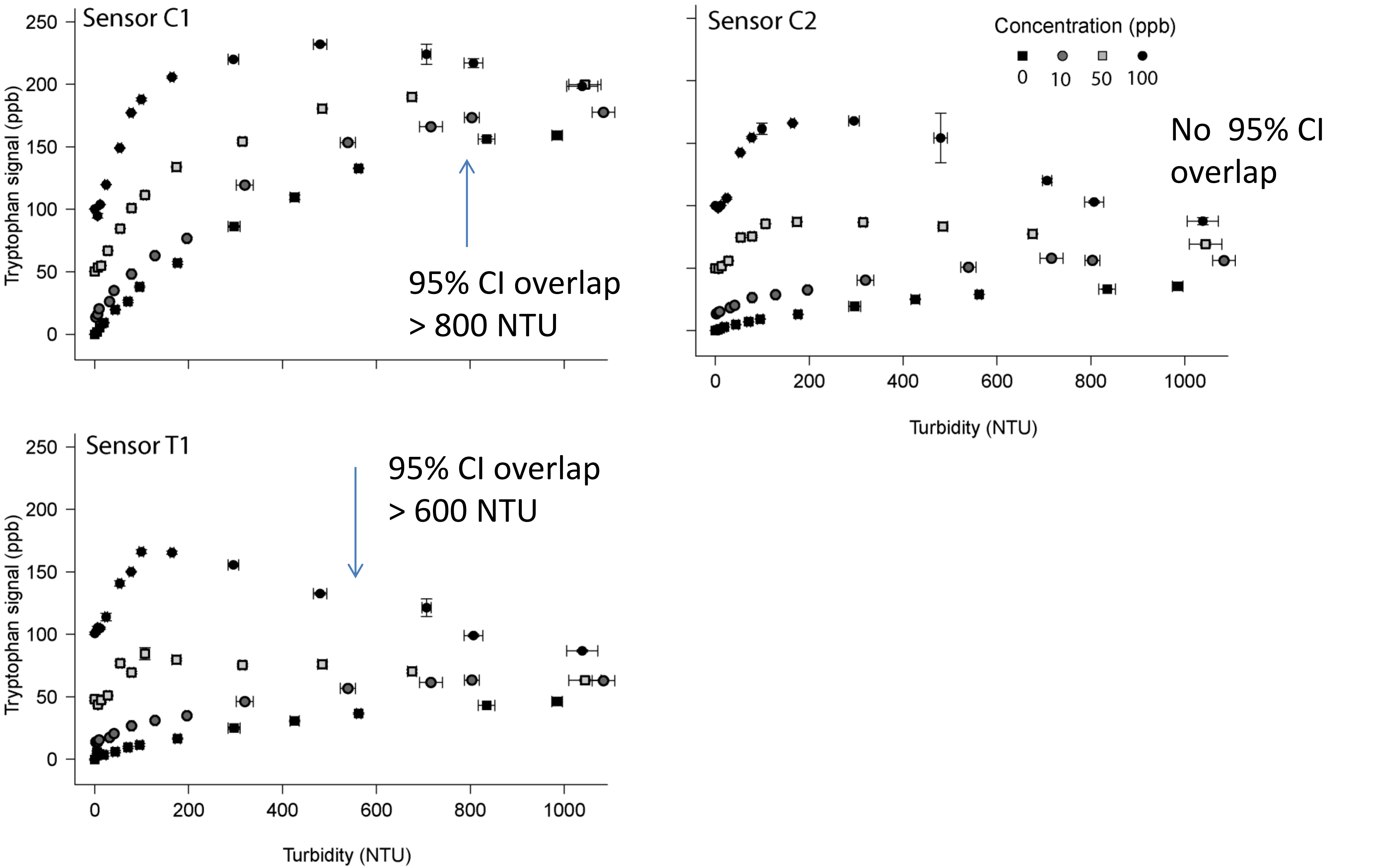
200 NTU

900 NTU

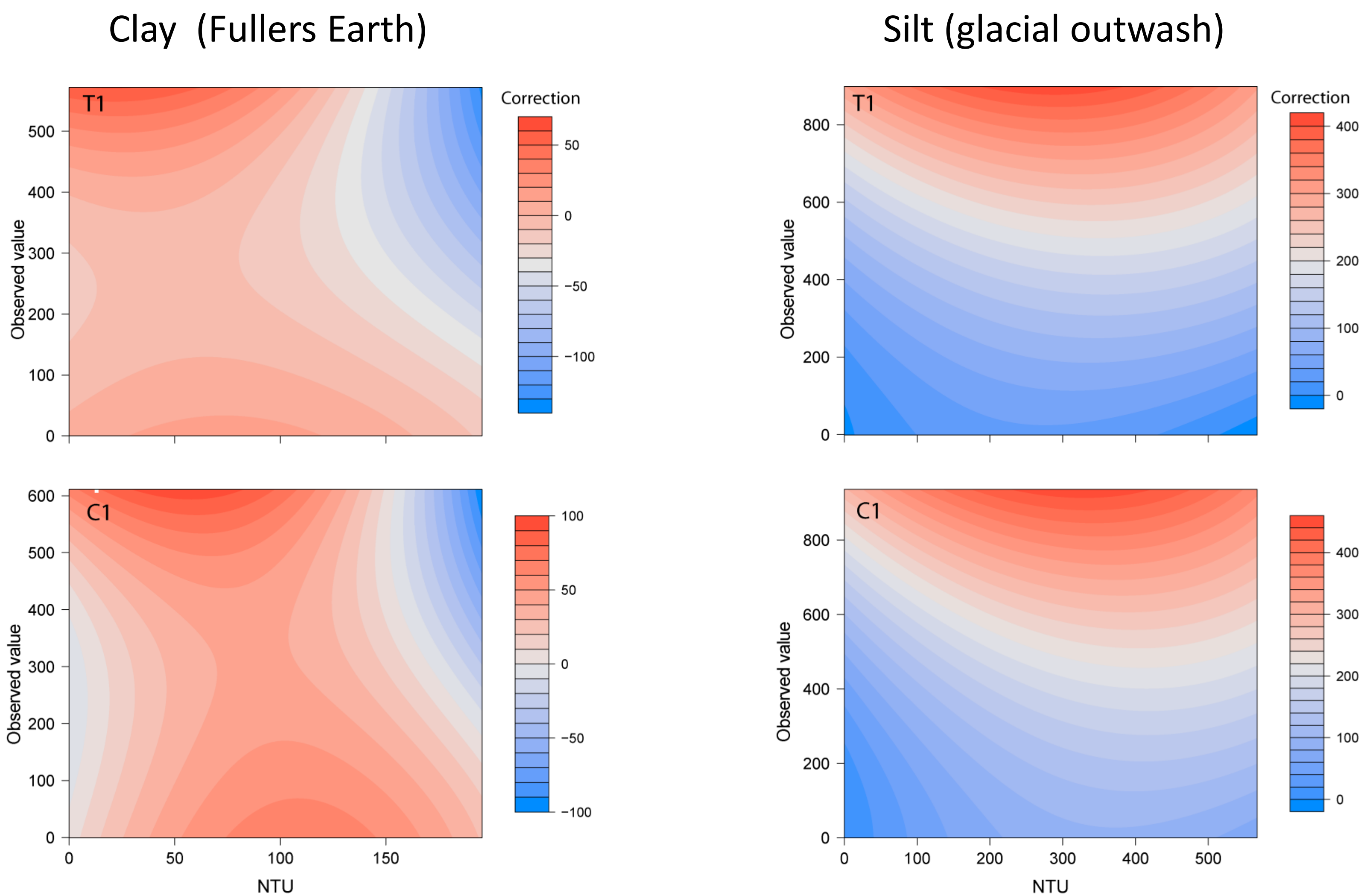
Turbidity interference (clay)



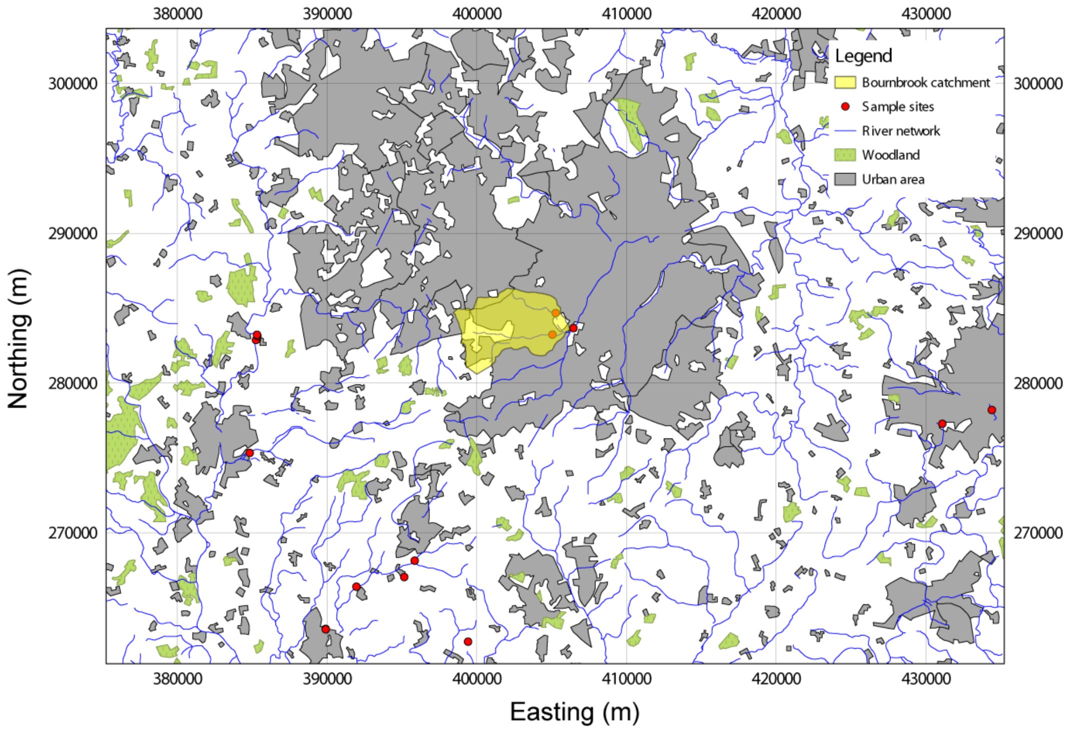
Turbidity interference (silt)



Turbidity correction



Urban field test site



Easting (m)

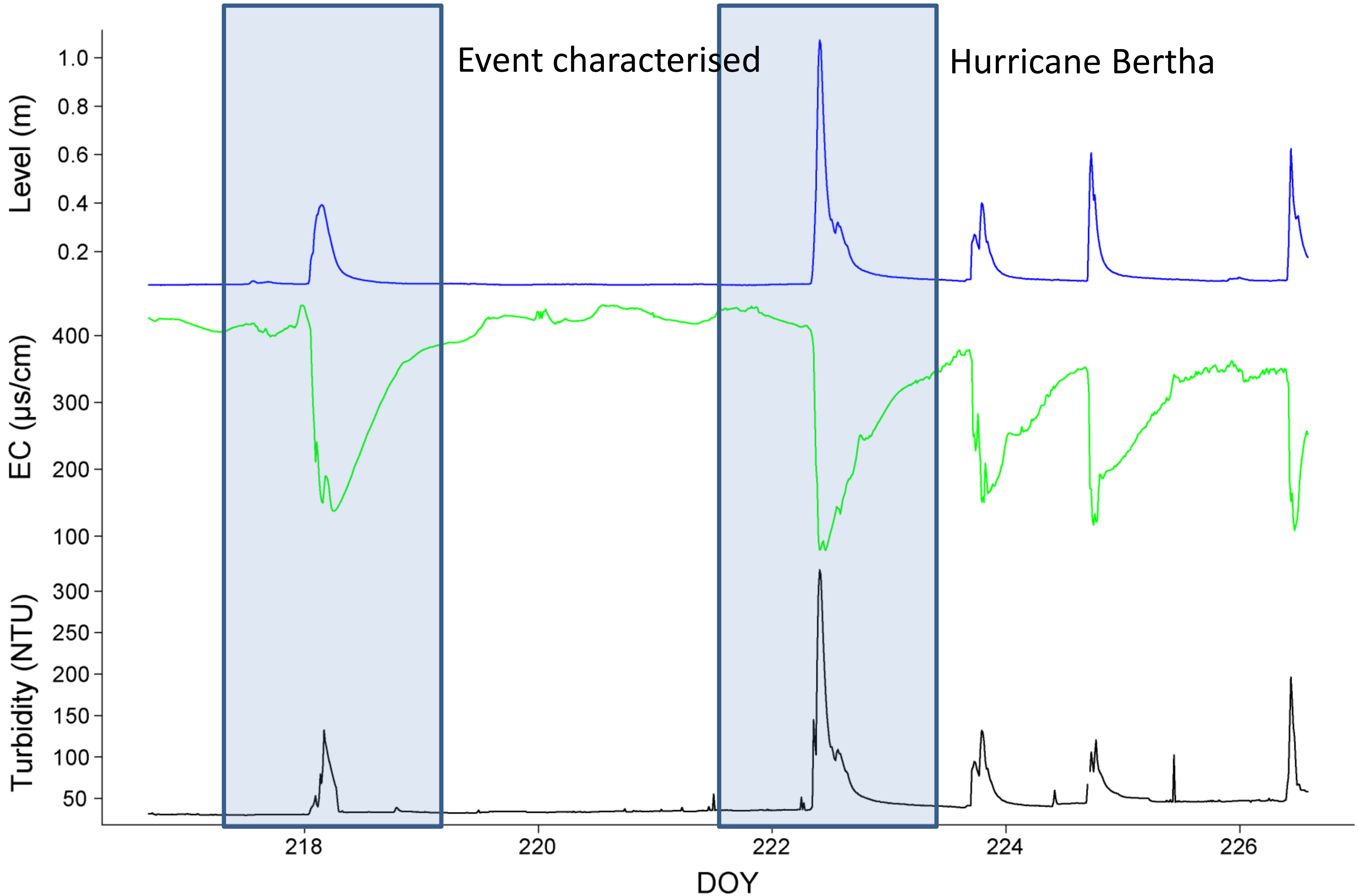
Carstea et al. (2009) *Hydrological Processes* **23**,1937

Urban field test site

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

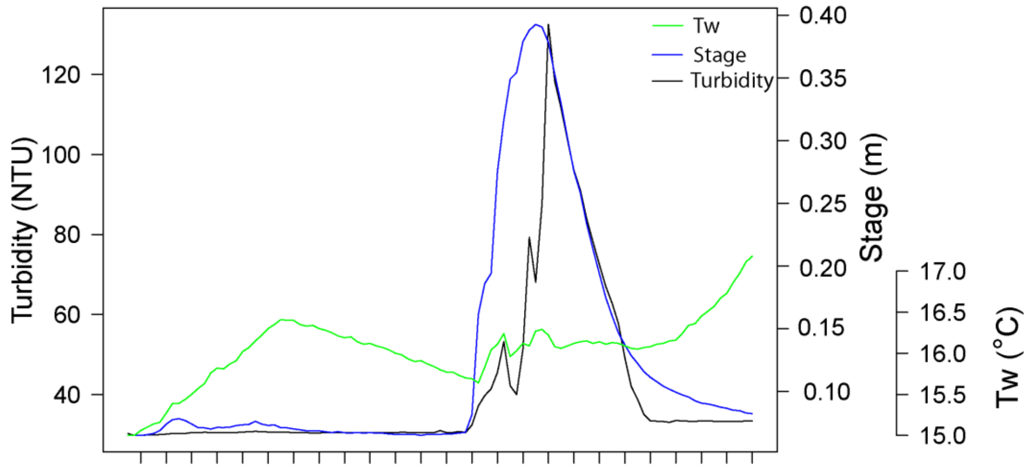
ISCO pump sampler

Field trial

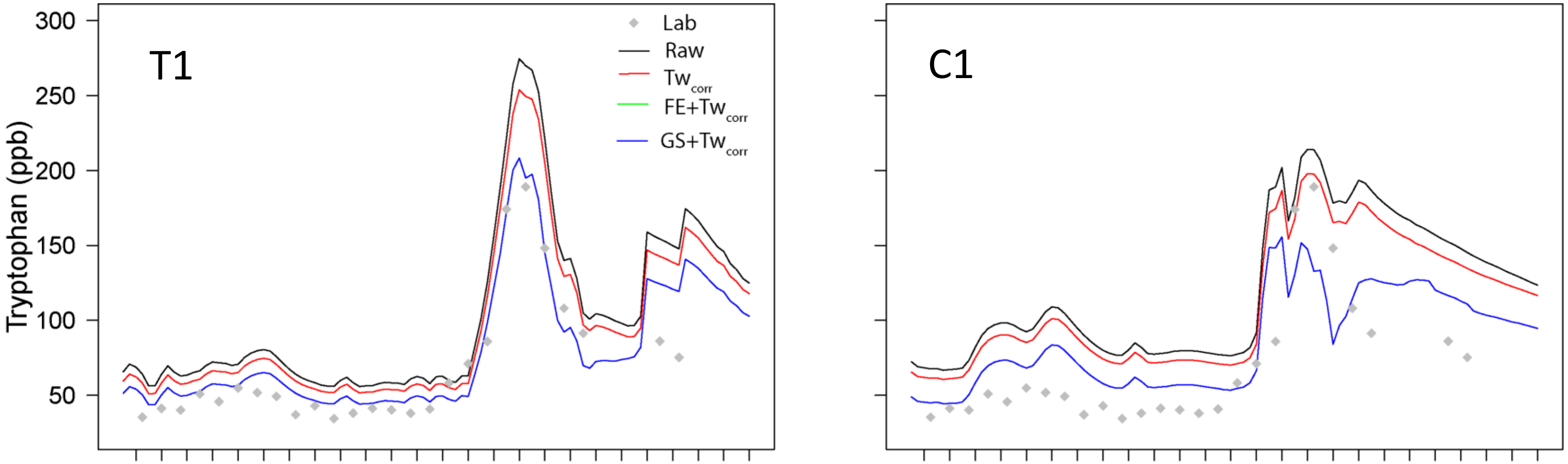


Event characterised
Hurricane Bertha
Level (m)
1.0
0.8
0.6
0.4
0.2
EC (µs/cm)
400
300
200
100
Turbidity (NTU)
300
250
200
150
100
50
218
220
222
224
226
DOY

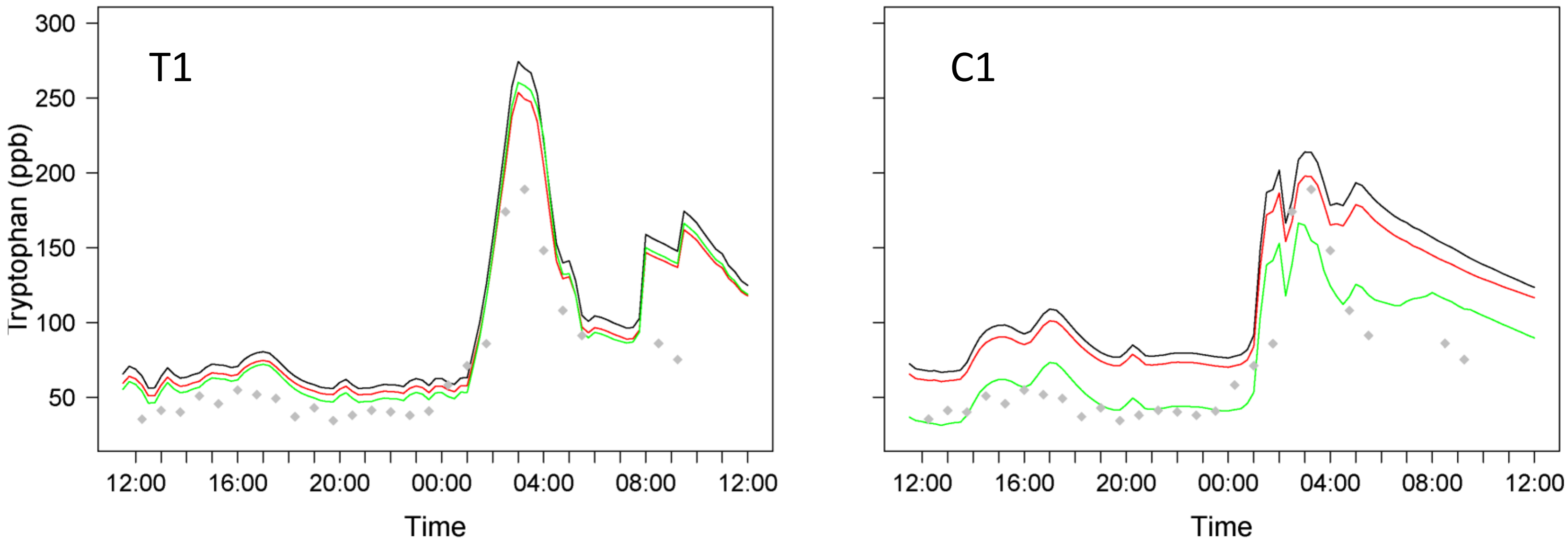
Field trial: raw data



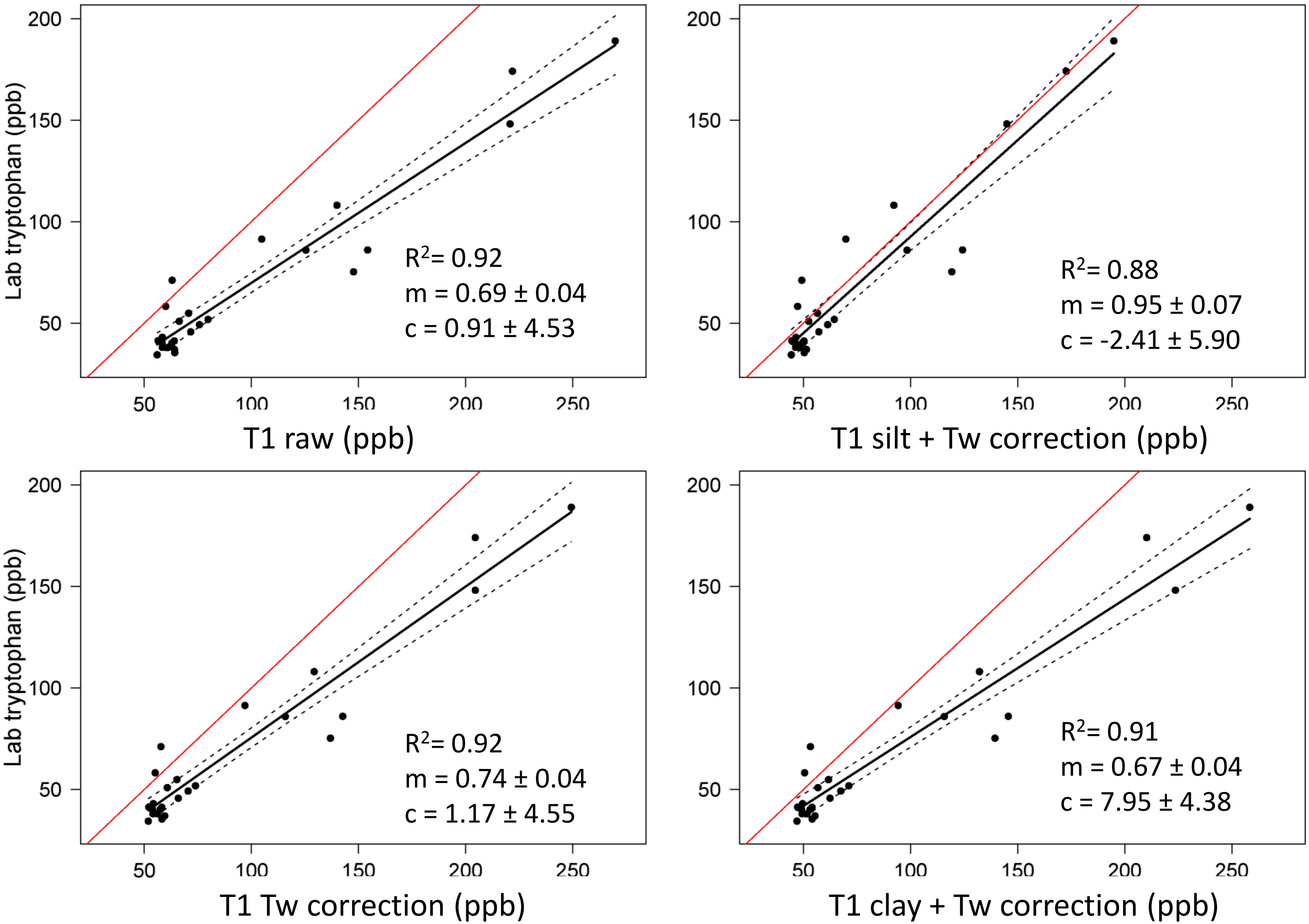
Field trial: corrected data



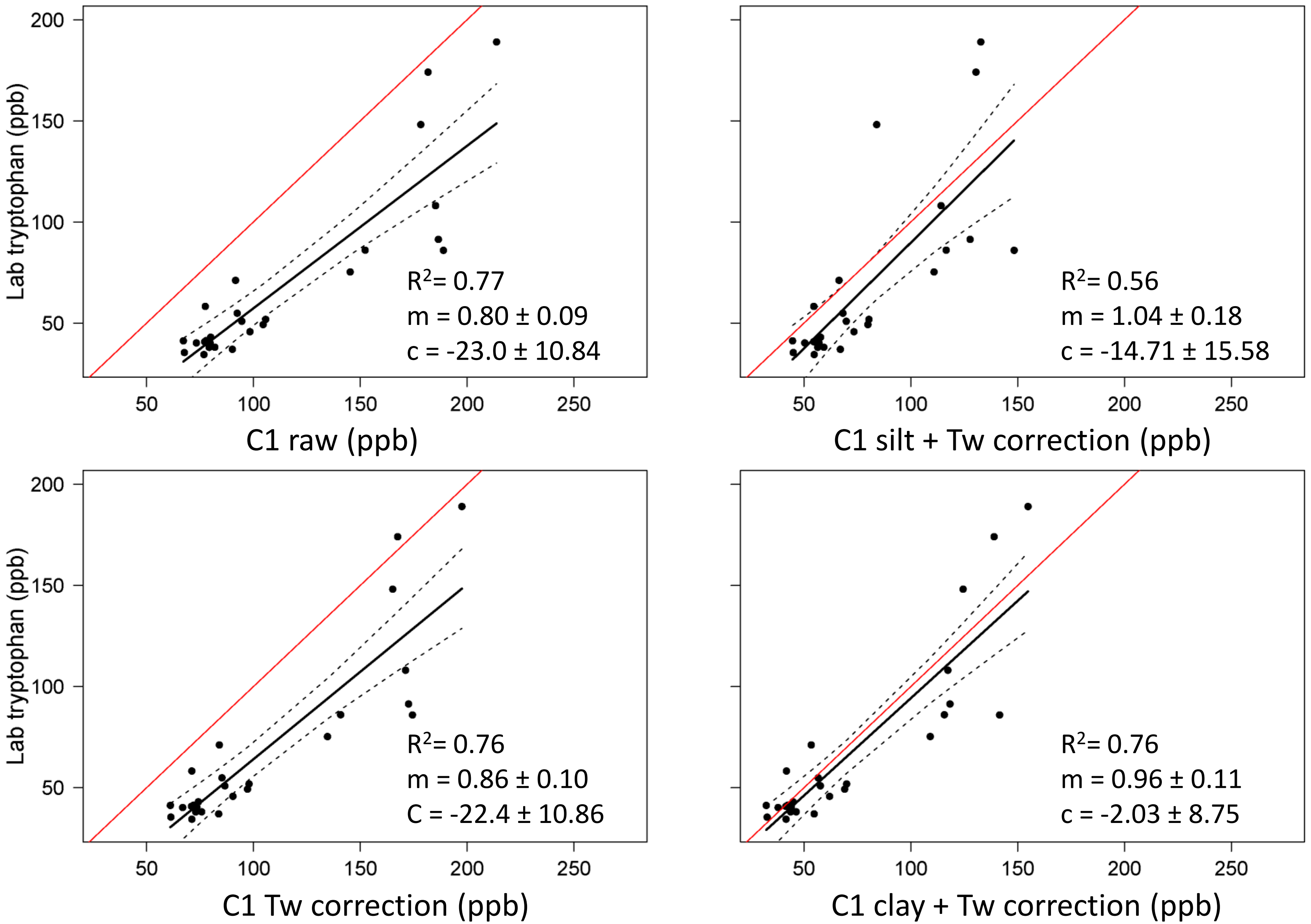
FE = Fullers Earth (clay) *GS = Glacial silt*



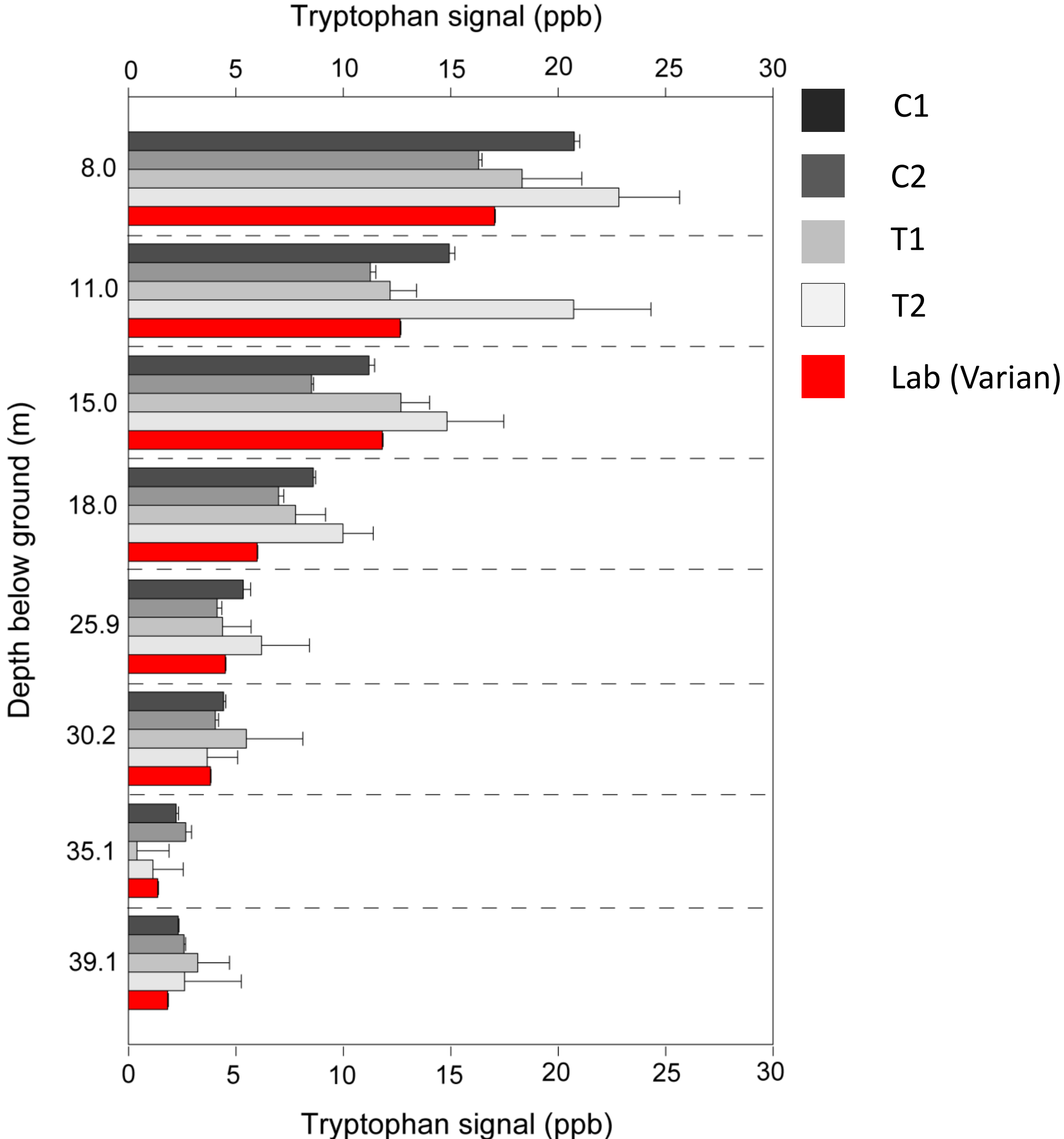
Field trial: corrected data



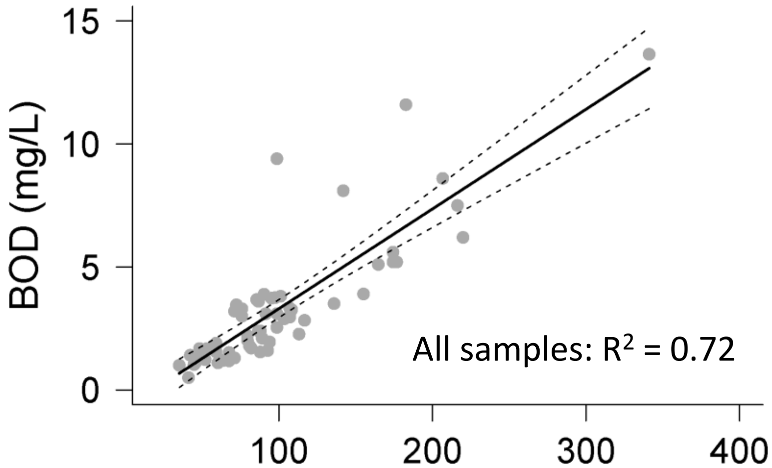
Field trial: corrected data

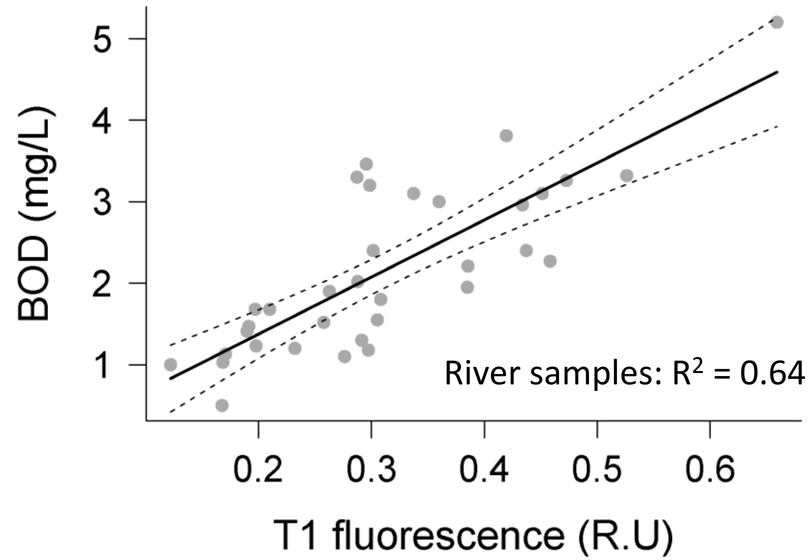


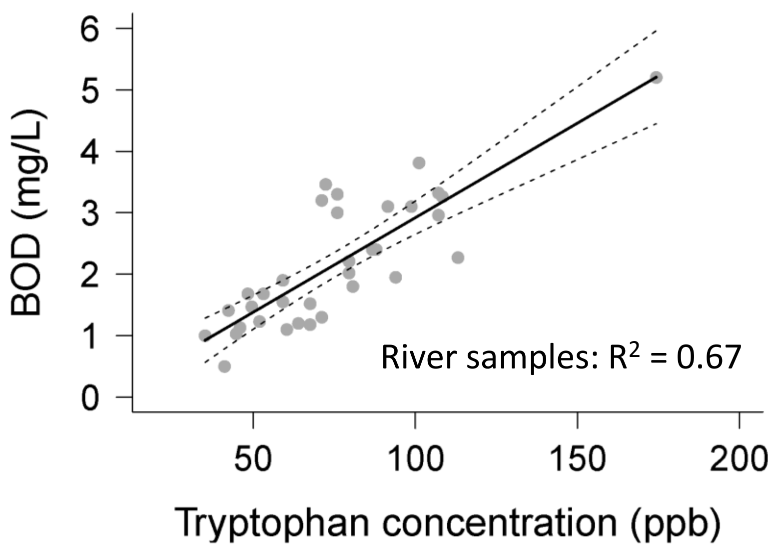
Borehole test

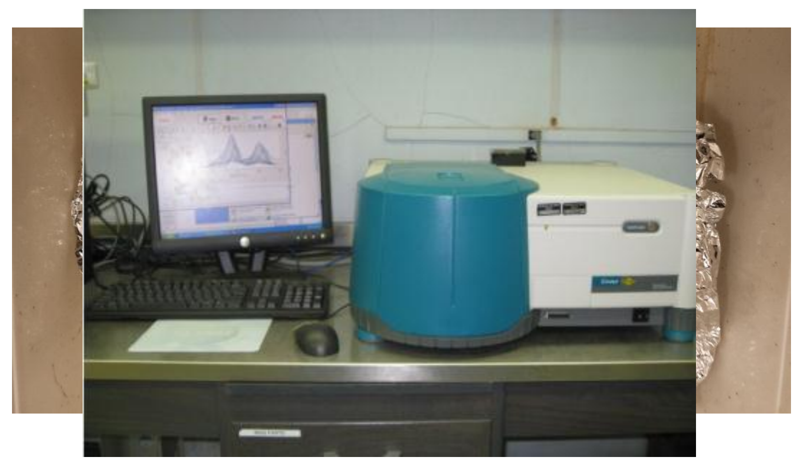


Spatial survey (initial result)









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 **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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