Application of portable *in situ* UV fluorescence sensors in aquatic systems

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Introduction

Natural organic matter (NOM) is a ubiquitous heterogeneous mixture found throughout aquatic ecosystems. Increasingly, fluorescence spectroscopy is being used to monitor aquatic NOM due to its high sensitivity[1]. Benchtop instruments are now available for analysing naturally occurring fluorescent compounds, Fig. 1. There is now a requirement for *in situ* monitoring to: a) avoid issues of associated with sample transportation and storage; b) avoid the cost of labour intensive discrete sampling; and c) provide better temporal measurement resolution.

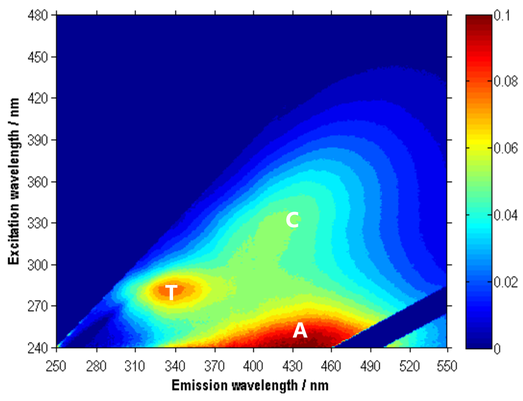

Fig. 1: EEM labelled with common UV fluorescence peaks[2]

Sensor standardisation

CTG's UviLux sensors were developed for *in situ* fluorescence monitoring. They are calibrated to a specific compound, e.g. Tryptophan or PTSA, and historically report output in ppb. However, as can be seen from Fig. 2, the fluorescence of each calibration compound can vary significantly.

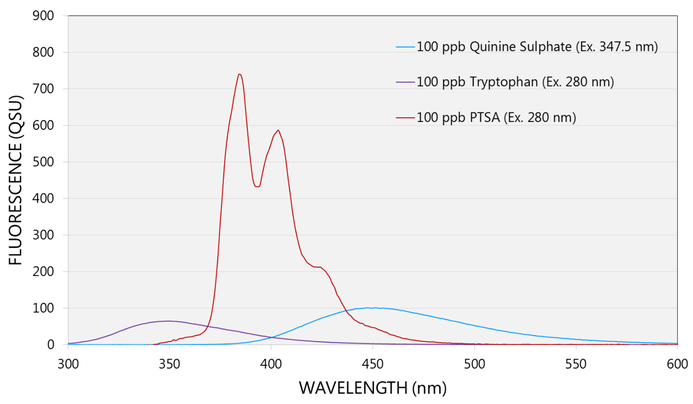

Fig. 2: Comparison of fluorescence output intensity for two different calibration compounds and a fluorescence standard, Quinine Sulphate (Starna® RM-QS00).

To directly compare the output from different types of sensor, the output from each sensor is standardised by cross-correlating the fluorescence of the calibration solutions against a certified reference standard of Quinine Sulphate using a bench-top spectrofluorometer. Fluorescence is reported in Quinine Sulphate Units (QSU), where 1 QSU is equivalent to the fluorescence intensity recorded from 1 ppb Quinine Sulphate at an excitation wavelength of 347.5 nm and an emission wavelength of 450 nm.

Field Data

Fig. 3a shows data from a long term deployment of Tryptophan and CDOM sensors in the effluent stream from a waste water treatment works (WWTW). While there are clear Tryptophan peaks in the data, there is also interference from CDOM fluorescence in the Tryptophan signal, as seen in the correlated diurnal variation in the sensor signals. This increases baseline noise, making it more difficult to discriminate true Tryptophan events.

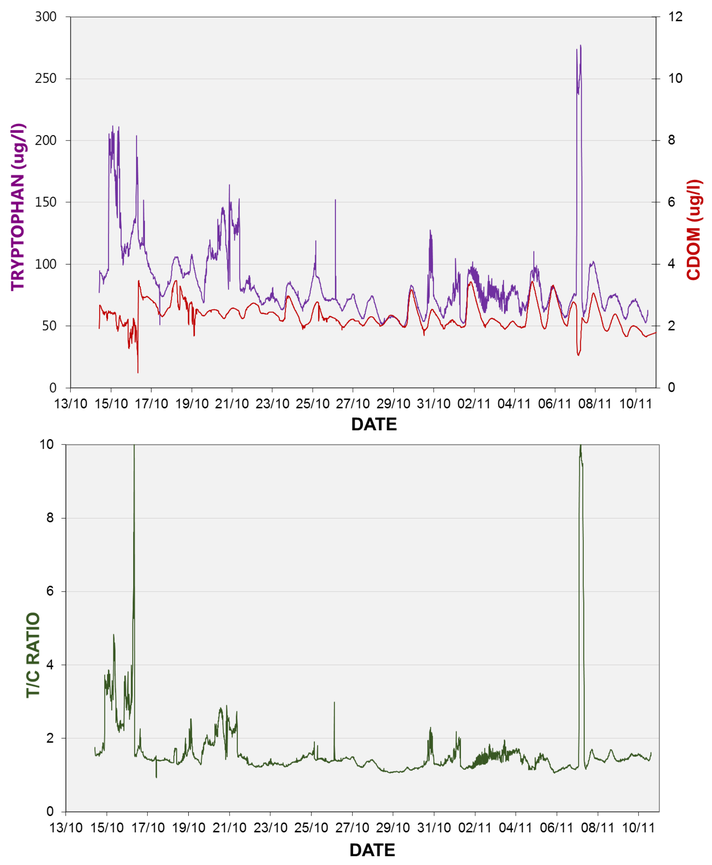

Fig. 3: Data from CDOM and Tryptophan UviLux fluorometers deployed in a WWTW. a) CDOM and Tryptophan signals; b) T/C ratio over the same period.

In Fig. 3b the Tryptophan/CDOM ratio (T/C ratio) has been plotted. The ratio removes the diurnal background variations seen in the original data, thus allowing for a clearer identification of significant Tryptophan peaks and also enabling more sensitive thresholding of the signal for detecting these events.

Because of potential interference arising from broad spectrum CDOM fluorescence, CTG has developed a combined sensor system that reports the individual signals from each sensor along with the T/C ratio for real-time *in situ* monitoring applications, Fig. 4.

Fig. 4: The DualLux combined sensor system.

Fig. 5a presents UviLux data from a river deployment illustrating how another source of interference, in this case turbidity, can adversely attenuate the output from the sensors. However, these effects can again be eliminated by using the T/C ratio, see Fig. 5b.

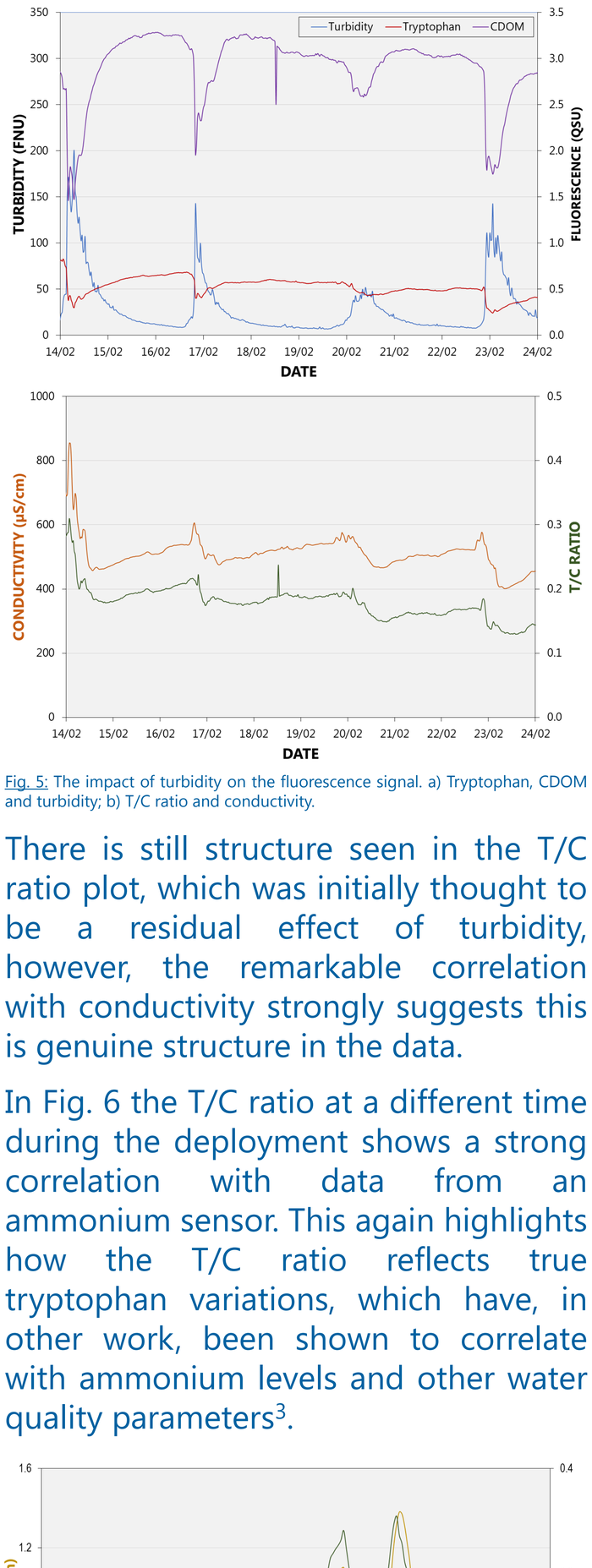

Fig. 5: The impact of turbidity on the fluorescence signal. a) Tryptophan, CDOM and turbidity; b) T/C ratio and conductivity.

There is still structure seen in the T/C ratio plot, which was initially thought to be a residual effect of turbidity, however, the remarkable correlation with conductivity strongly suggests this is genuine structure in the data.

In Fig. 6 the T/C ratio at a different time during the deployment shows a strong correlation with data from an ammonium sensor. This again highlights how the T/C ratio reflects true tryptophan variations, which have, in other work, been shown to correlate with ammonium levels and other water quality parameters[3].

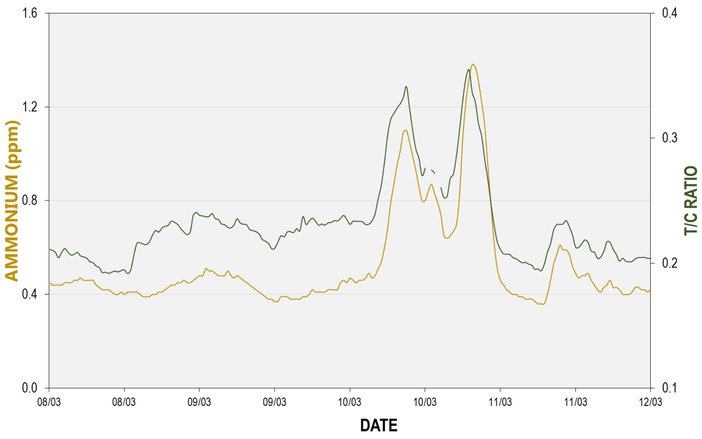

Fig. 6: T/C ratio and ammonium signal.

These results again demonstrate the value of using the T/C ratio to reduce the background interference from non-specific environmental factors.

Conclusions

- Standardising fluorometer calibration is essential for comparing different types of *in situ* sensor and also provides good agreement with benchtop data.
- The Tryptophan/CDOM ratio reduces background interference and highlights key events for warning system applications.
- Single *in situ* fluorometers can be used locally to highlight deviation from a baseline, but the T/C ratio allows for intra-site comparison

Refs: 1. Hudson *et al.* 2007; 2. Coble *et al.* 2014; 3. Baker *et al.* 2004