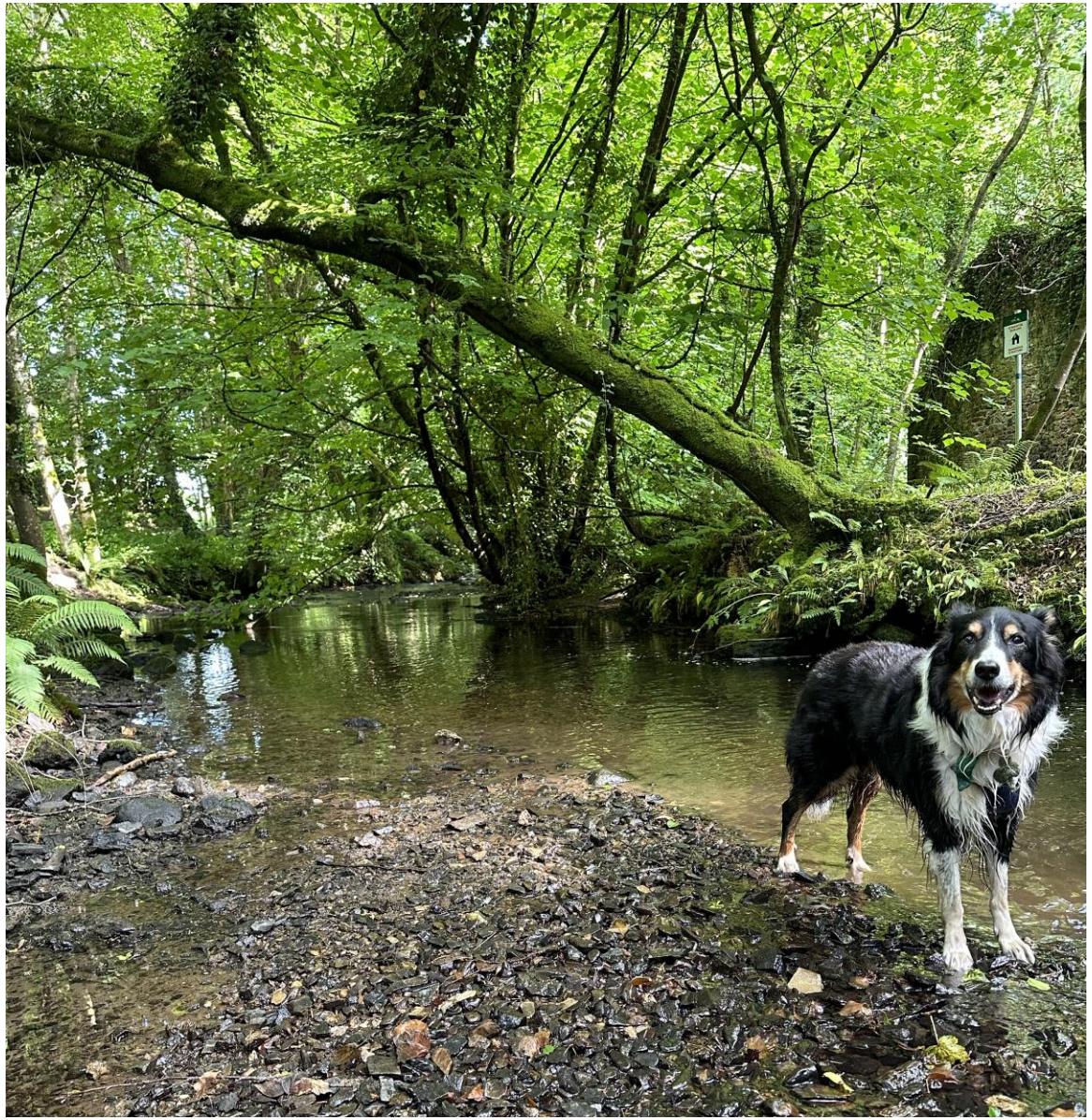
Multiparameter Nutrient Sensor

Joseph O'Mahony

SETU

STREAM



Estuaries

- Defined by the magnitude and seasonality of freshwater inputs.
- Rivers deliver acidified water to estuaries- they also contain a much higher carbon load than seawater.
- Fresh water inputs may induce vertical stratification of estuarine waters.
- Fresh water flows accumulate Nutrients from natural and anthropogenic sources, these are ultimately delivered to the estuary.
- Stratification may lead to significant depth variation in biogeochemical parameters such as pH, DO, salinity and reactive Nitrogen.
- Shallow estuaries are more affected by riverine inputs.
- Changes in wind strength and associated upwelling from the bottom of the estuary may cause significant weather-related events. More significant in deep water.

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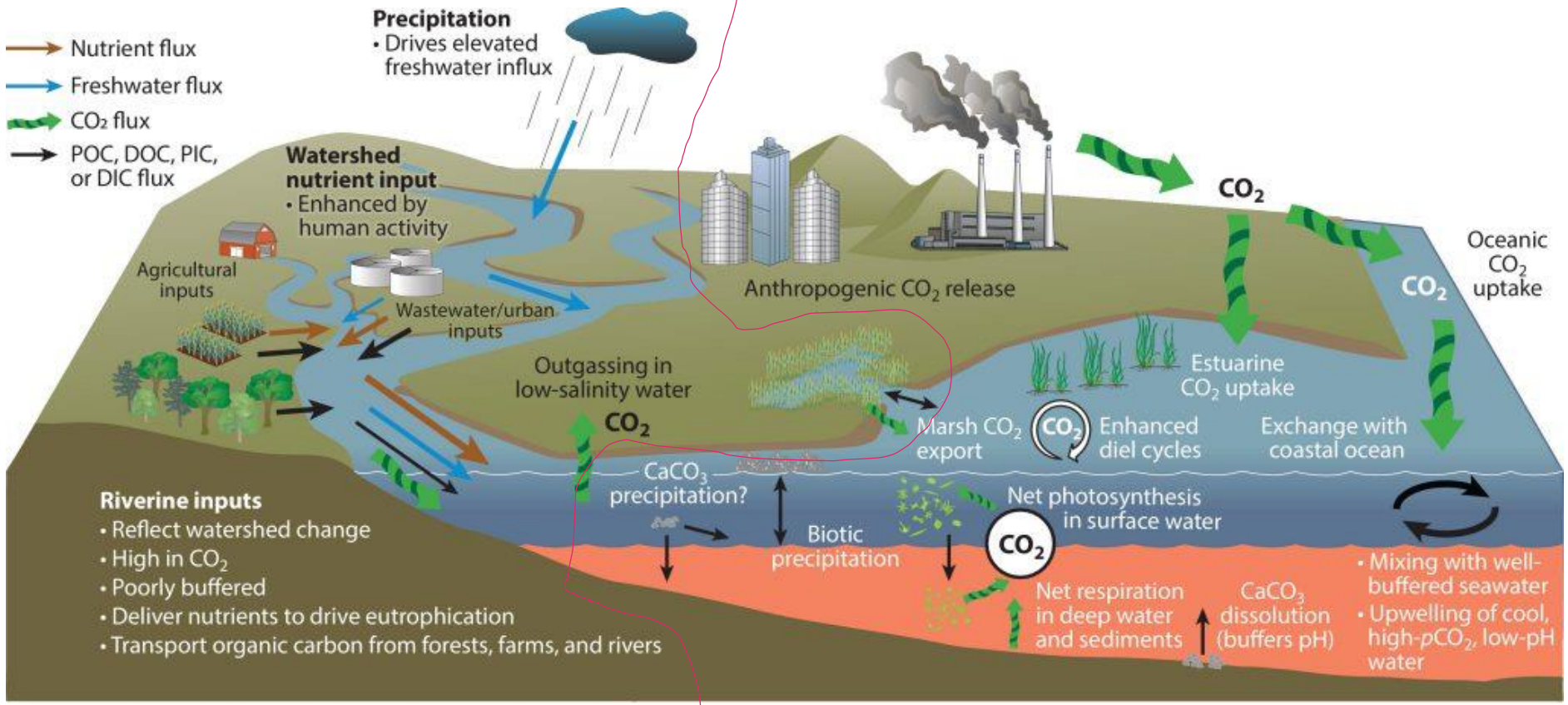
Nutrients



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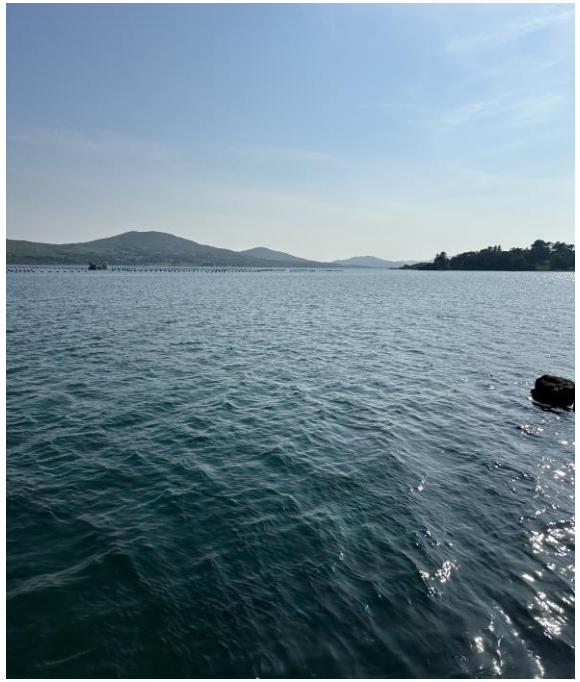
Study Sites



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Equipment

- STREAM Spectral UV sensor
- MEMS Spectrometer with UV – Flash Lamp.
- Pumped system with flow-cell
- Gateway with Windows 10 operating system
- Smart Algorithms for Measurement of Multiple Parameters

- NO3-N
- Carbon
- Dissolved (& Suspended) Solids
- Coloured Dissolved Organic Matter

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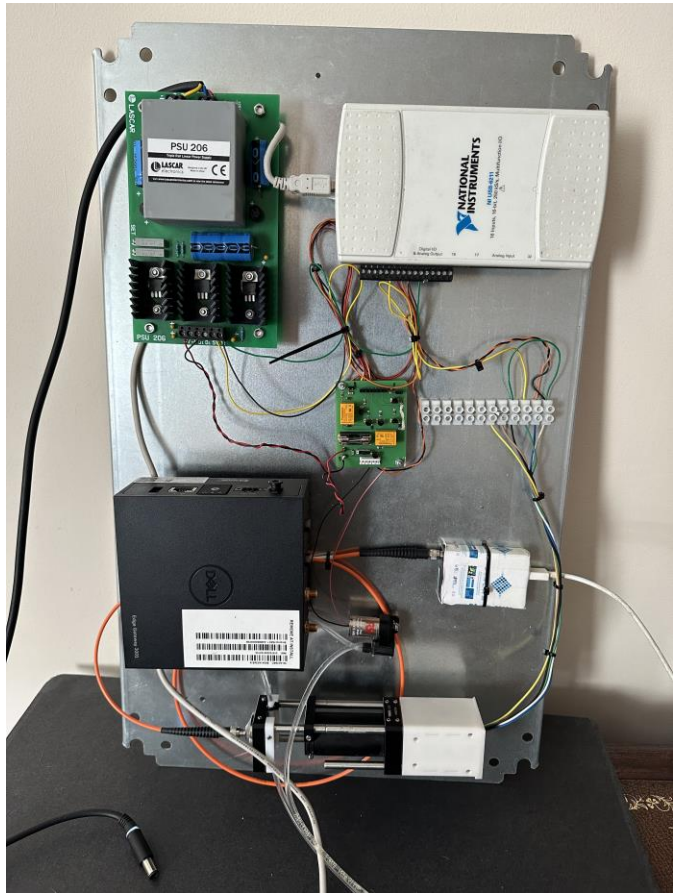
Site Setup



Data Collected – processed and transmitted at 15-minute intervals for 36hrs.

Data collection followed a period of intense rainfall where nutrient flows would be high.

Nutrient flows were too high for commercial sensor.

Cell Pathlength 3.6mm.

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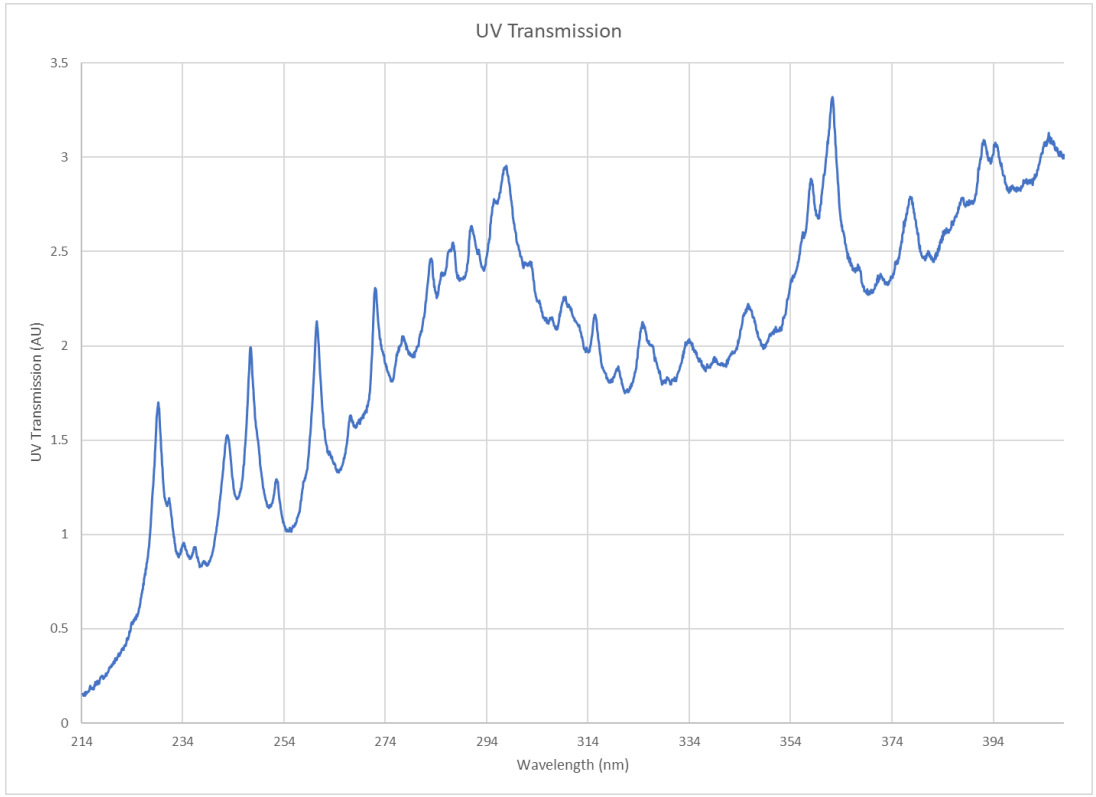
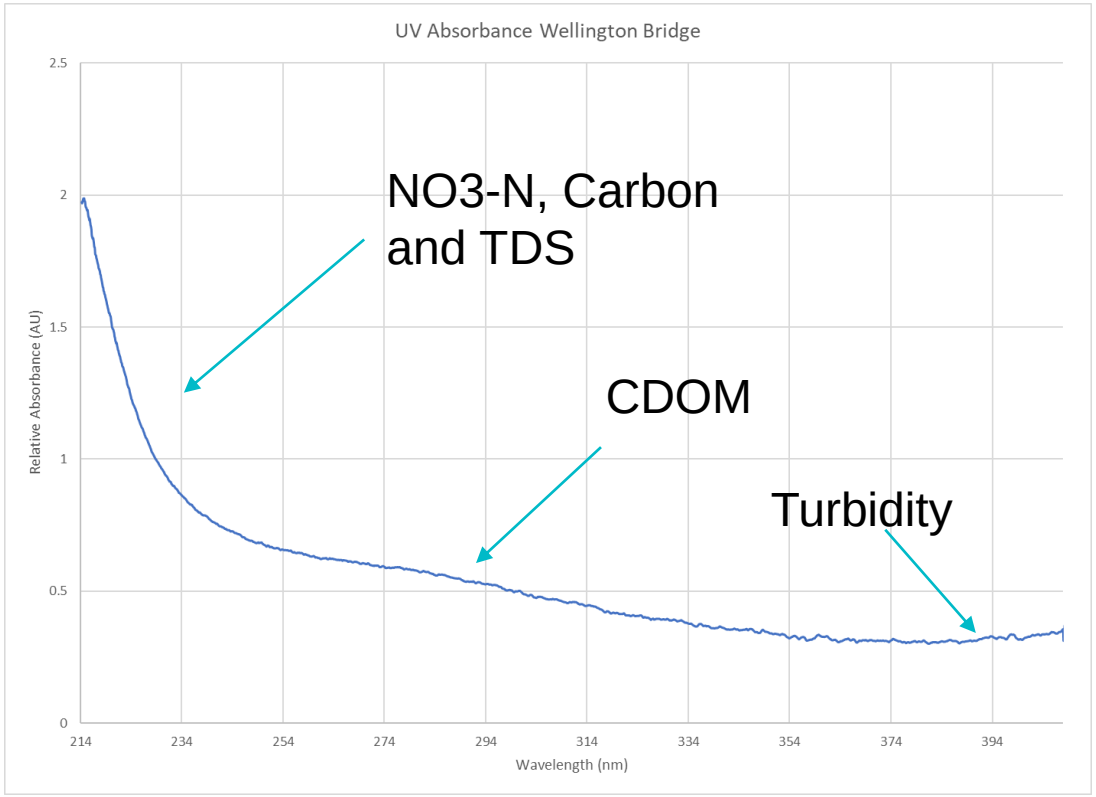
The data curve





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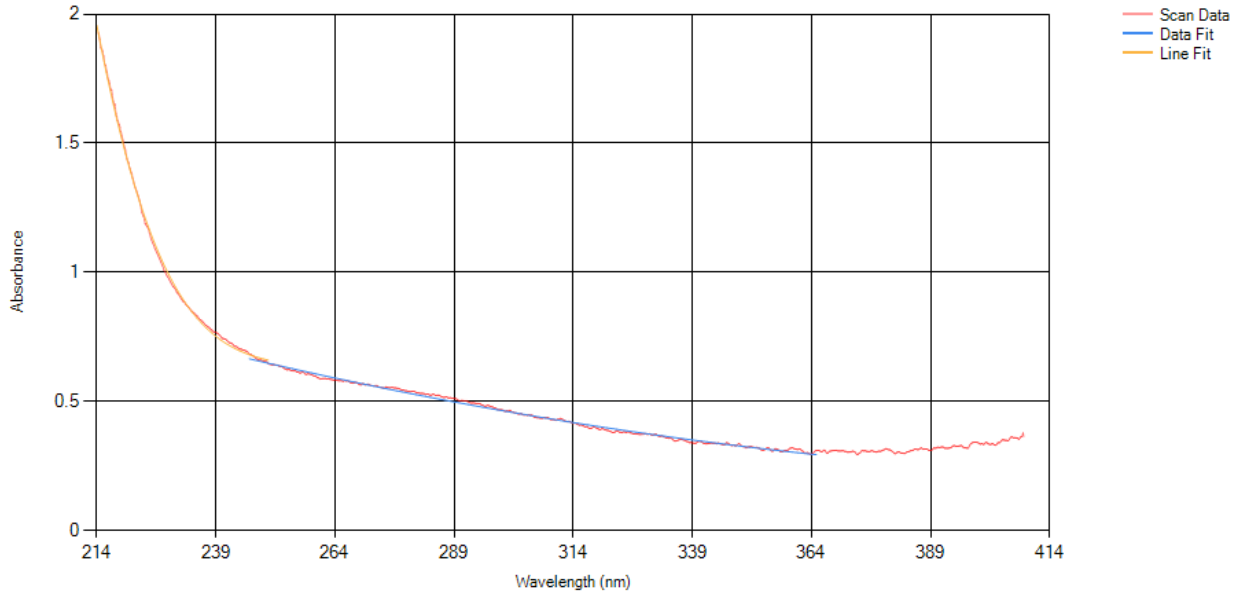
Algorithmic Approach

- Non-Linear Least Squares Fitting to the Left-Hand Side Peak – extracts the NO3-N component.
- Straight-Line and Gaussian fitting to the 240nm to 360nm region – extracts the CDOM component – Humic/Fulvic Acid.
- A more general CDOM can be extracted from the slope of the line in the 240 to 360 nm region.
- Analysis of the Derivative Spectrum can yield more precise information.



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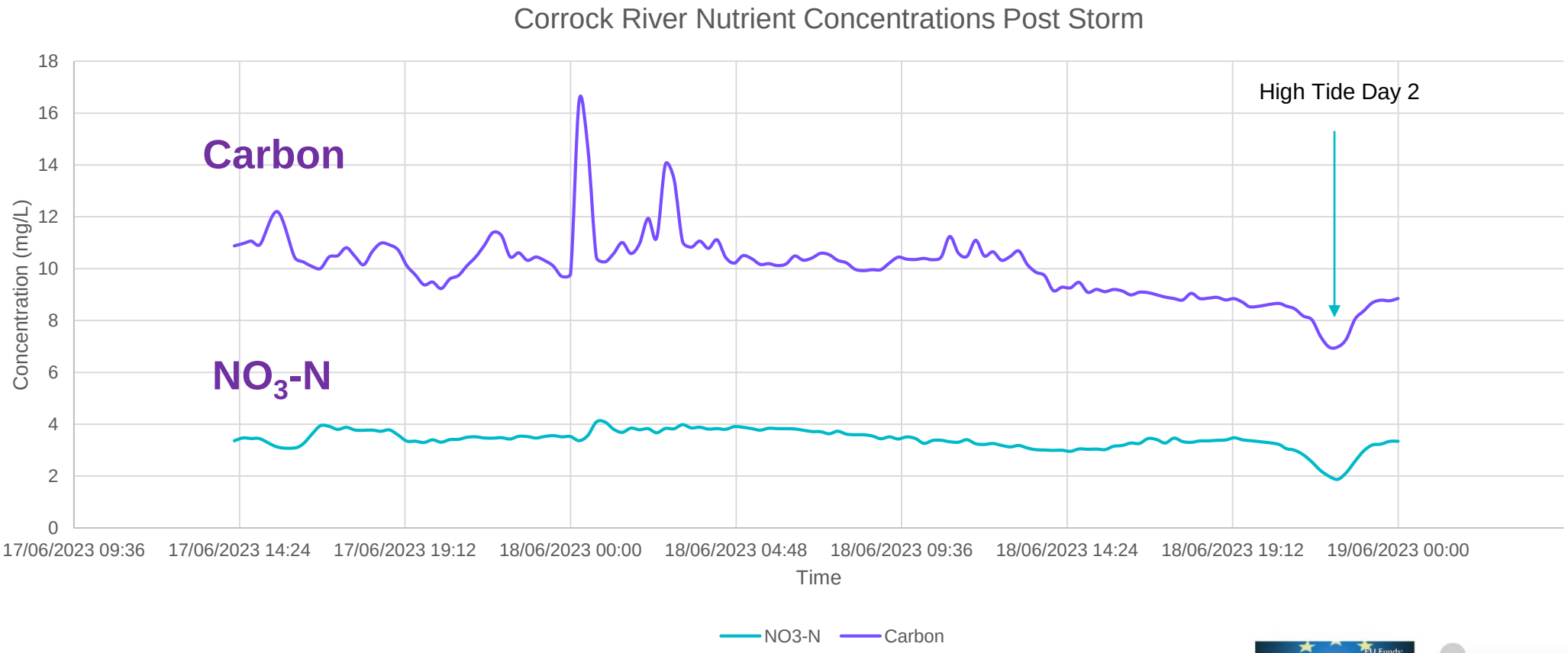
Extracting Nitrogen NO3-N

- A Gaussian fit to the curve in the 214 to 250nm region allows the NO_3-N value to be estimated.
- This estimate will be biased by any DOM present in the sample.
- The sloped line in the spectrum is extrapolated back to 215nm to create a correction factor.
- NO_3-N is calibrated for 215nm
- Carbon is measured at 235nm and calibrated against KHP solution.

Nutrient Concentrations Wellington Bridge



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Extracting - CDOM

- CDOM – Coloured Dissolved Organic Matter
- Normally determined in the visible region of the spectrum.
- Major components contributing to DOM absorb in the UV portion of the spectrum.
- Many systems use fluorescence to determine the amount of DOM that exhibit fluorescence under UV light.

- Absorbance at 250nm or 310nm relate to fulvic acid or humic acid
- Absorbance at 260nm or 380nm relate to UV/Vis Humic Acids
- Absorbance at 265 or 300nm relate to Soil type fulvic acid
- Absorbance at 280nm or 300nm relate to Tyrosine/Tryptophan proteins.

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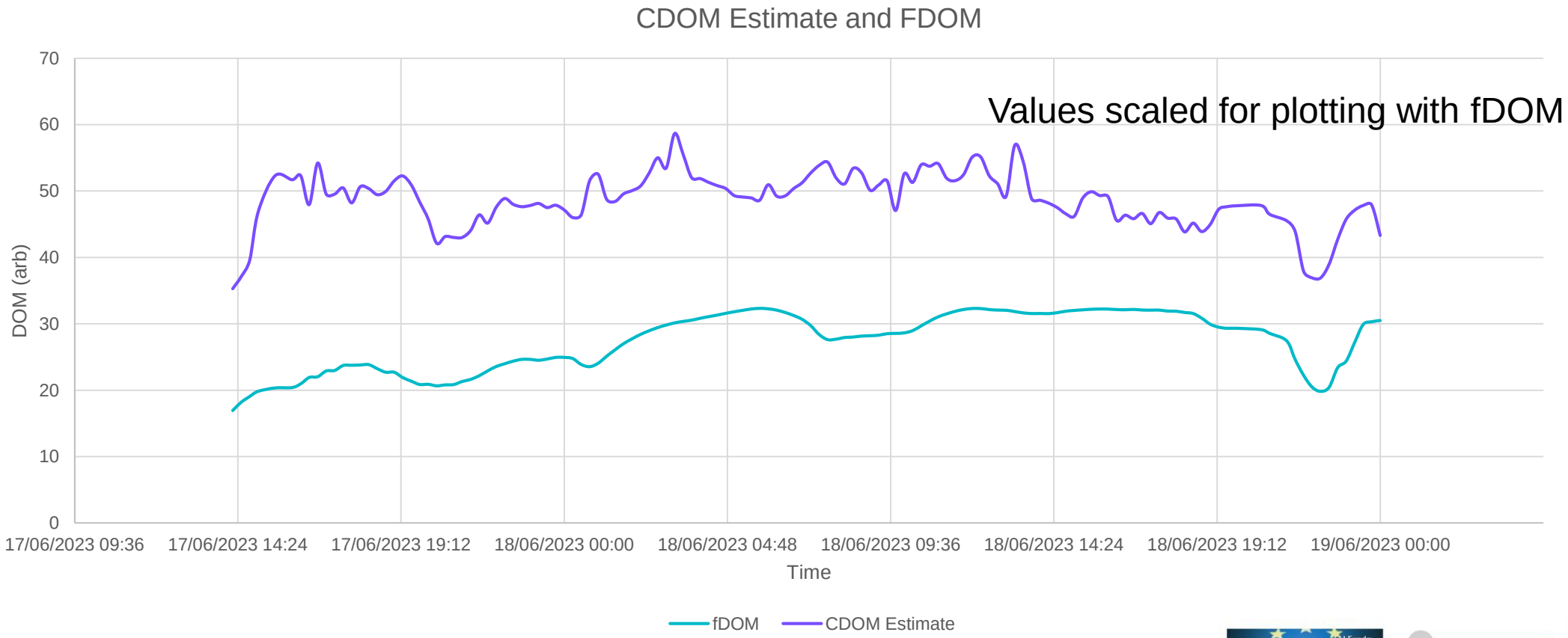
Broadband CDOM Versus FDOM



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Dissolved Solids

- Two types of scattering are prevalent in waters – Rayleigh Scattering and Mie Scattering
- Rayleigh scattering relates to small molecules and provides a greater absorbance at shorter wavelengths. (TDS)
- Mie Scattering relates to larger particles and produces a greater absorbance at longer wavelengths. (Turbidity)
- In the Wellington Bridge data, both can be seen clearly [Slide 7].
- Dissolved solids are effectively a proxy for salinity in fresh water and are normally calculated using conductivity.
- An estuary would be considered to have very high dissolved solids. ~30-40g/L
- Rate at which the short wavelength signal increases depends on the quantity of dissolved solids.

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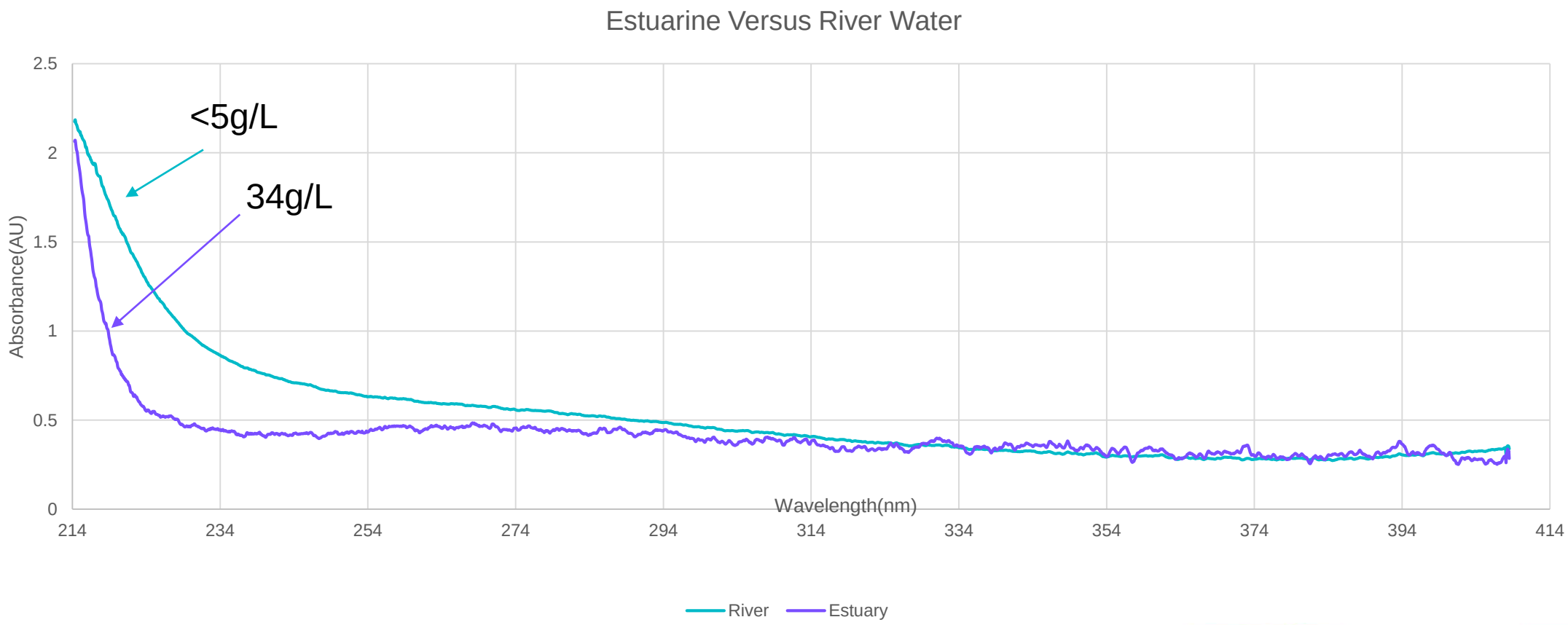
Sea Water / River Water



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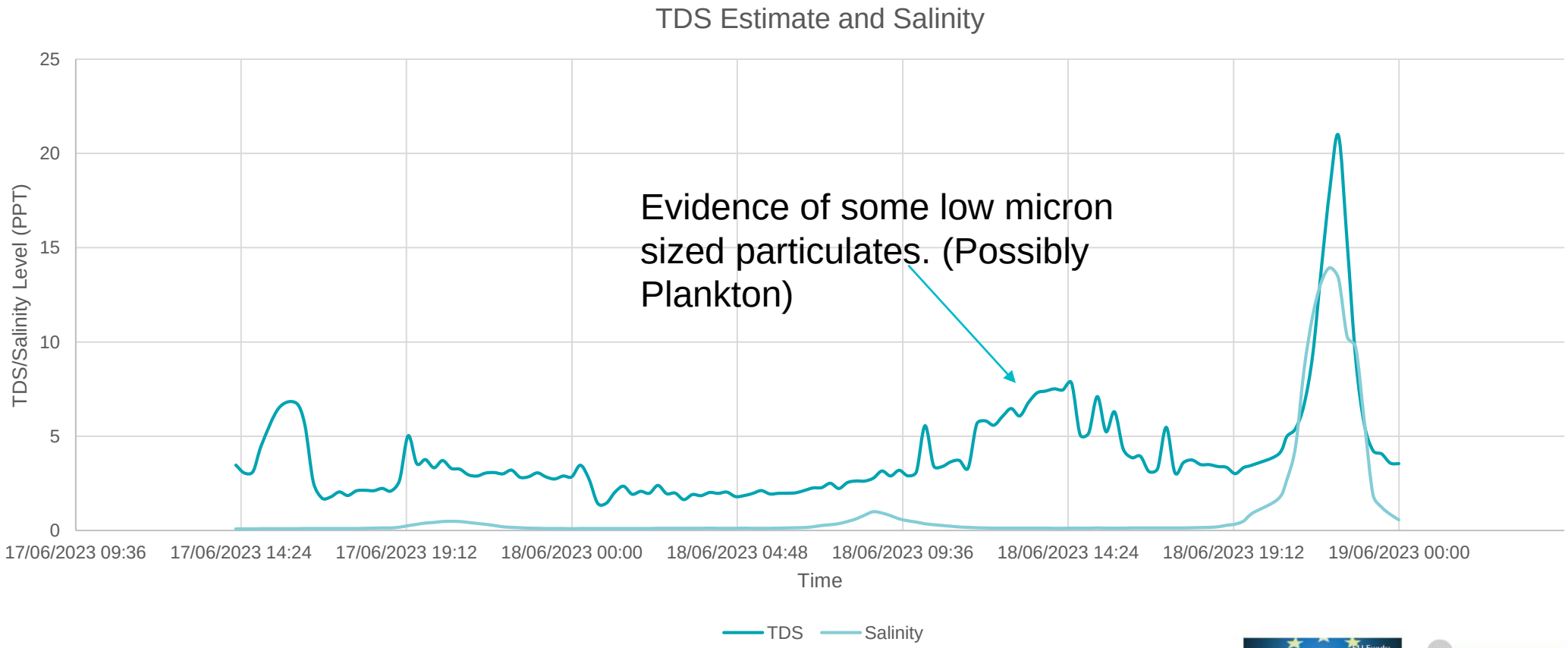
TDS relates to the slope of the short Wavelength Absorbance



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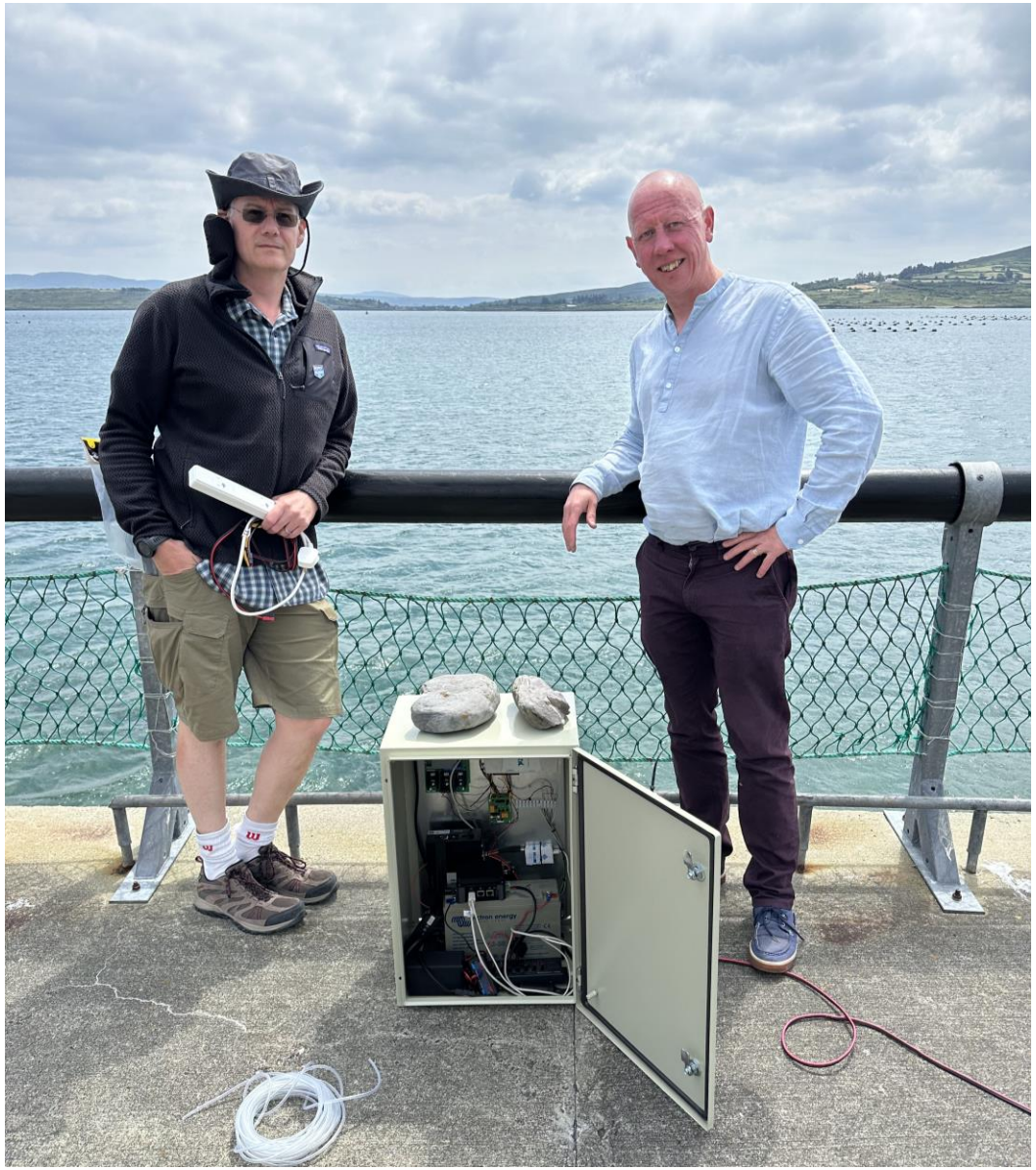

Castletownbere

- Energy Harvested Solution
- Sample pumped to sample flow cell
- Tidal Variation ~2.5m

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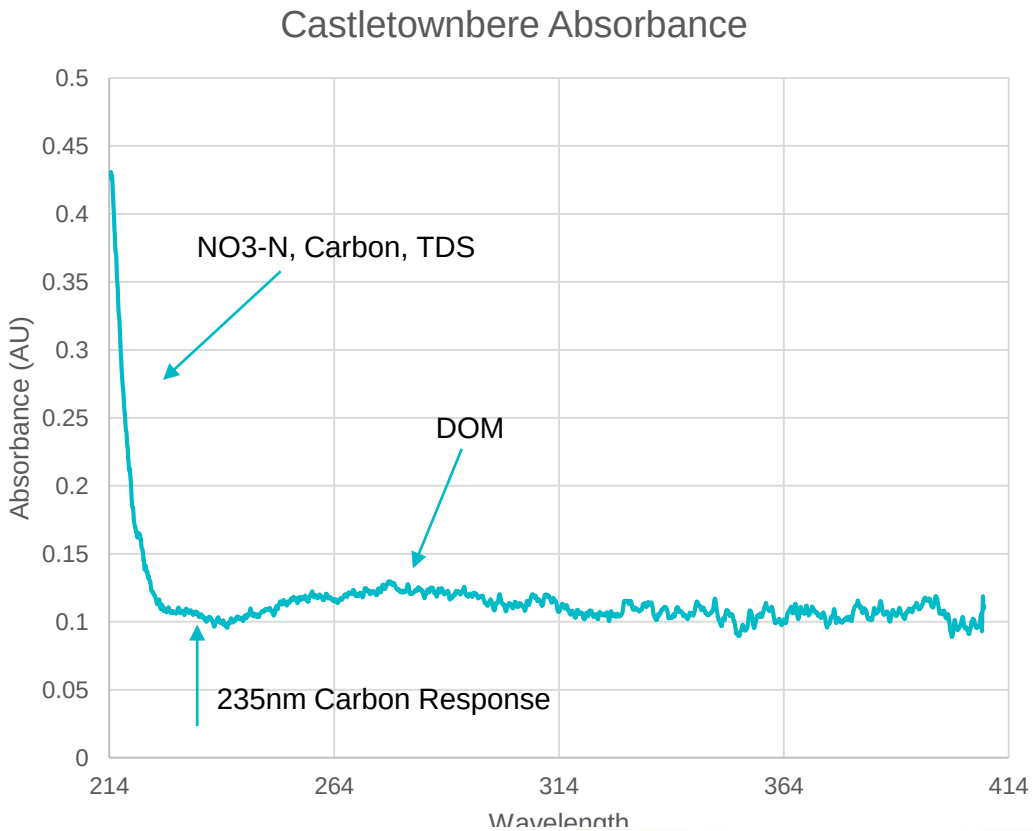
Castletownbere Absorbance

- As there is no slope to the data set in the region 250nm to 360nm we need a different method to determine Carbon Contribution to Nitrate Signal.
- We also have a low but measurable response at 235nm which is noise limited.
- Strong curvature at 275nm provides a measurable DOM component.
- Much steeper slope at Left-Hand peak due to zero Nitrate and High Salinity



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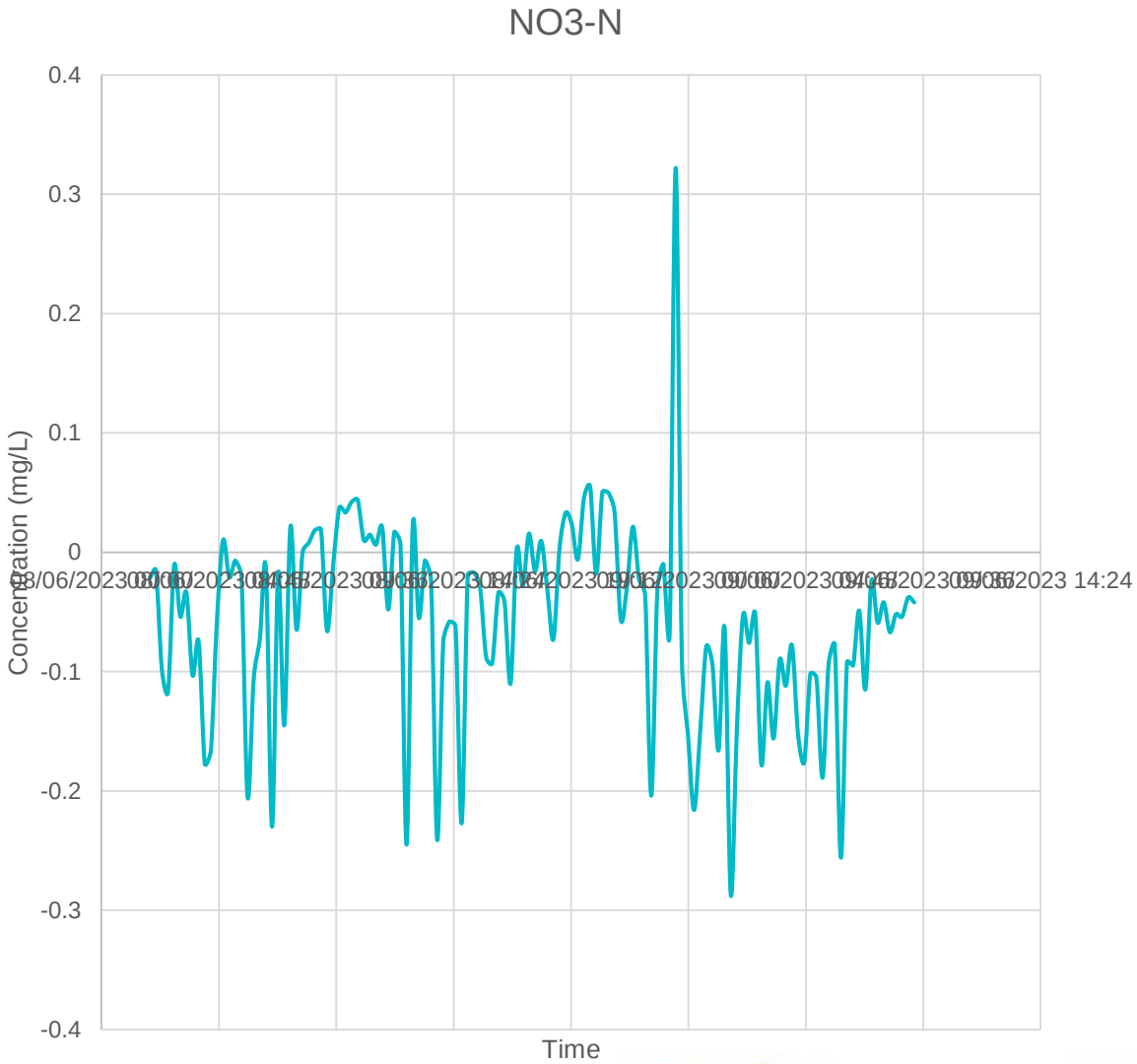
NO3-N

Concentration of Nitrate-N at Castletownbere should be close to zero.

Negative going values are due to an overestimate of the Carbon correction value for the site.

The indication is that there is almost zero nitrates in the sample – which is to be expected.

Correction of the algorithm will allow for a more sensitive reading at Castletownbere and other sites.



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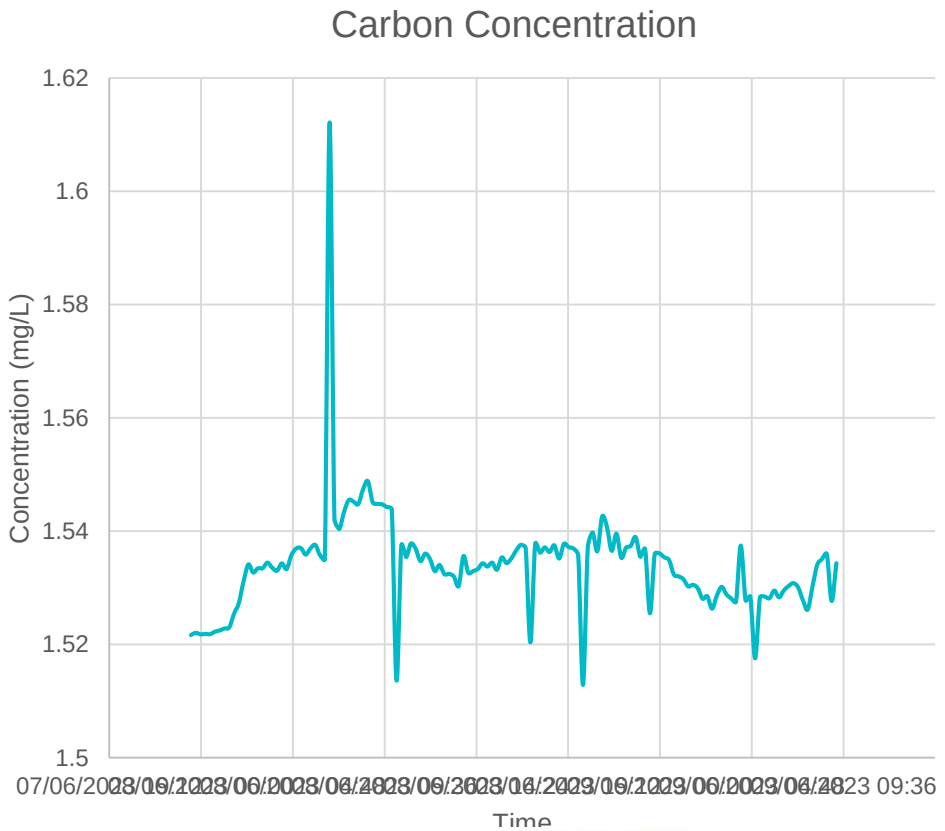
Carbon

- Carbon is calculated from the Absorbance ratio at 270nm to 350nm
- This provides a very accurate measurement of Carbon in salt-water environments.
- Carbon Concentration shows a tidal variation – decreasing at high tide.
- The system is very stable with very low changes in carbon recorded.



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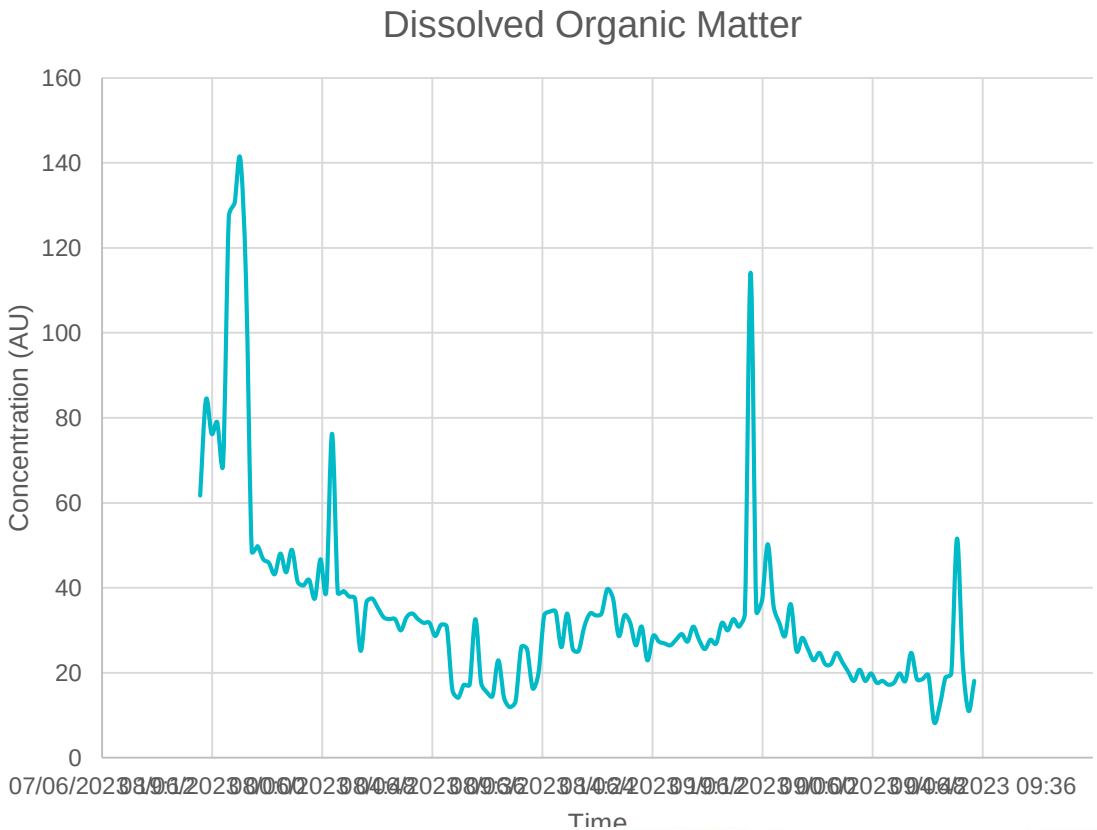
CDOM – Slope Method

- Strong DOM signal recorded at low tide.
- DOM concentrations << River DOM
- Wellington Bridge site shows a DOM signal that is more than 10 times that of Castletownbere.



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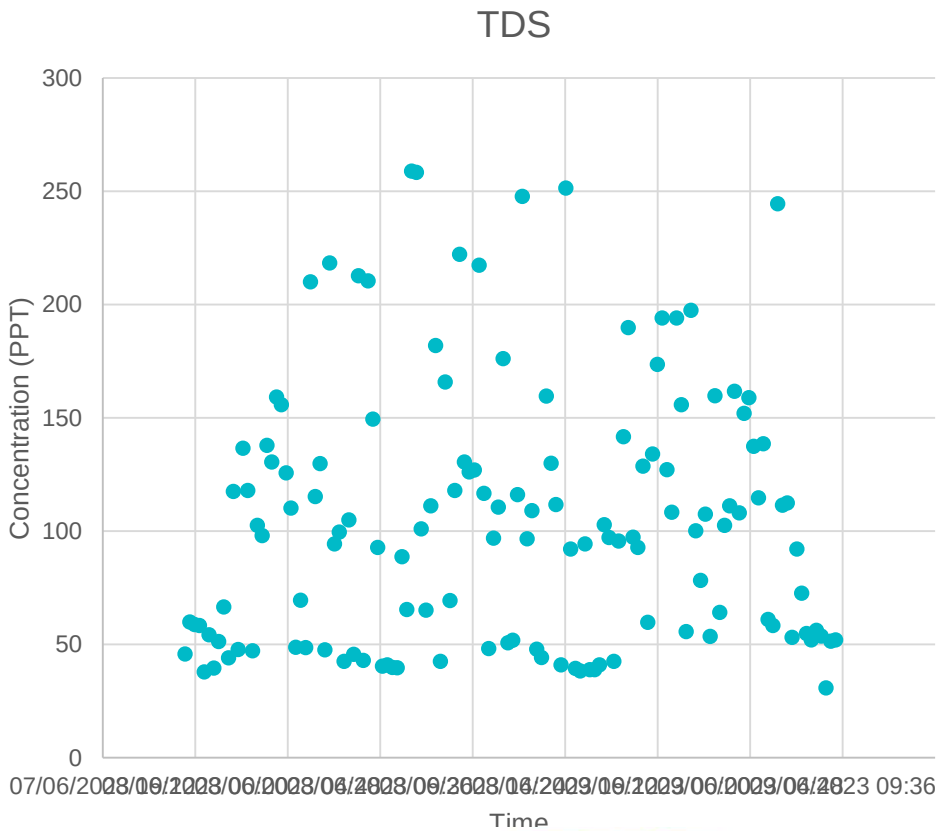
TDS – An Unexpected Result

- Baseline ~35-PPT indicative of the environment.
- Significant scatter in the data – indicative of small particles.
- These particles are most likely Phytoplankton with a cross-section of ~10 to 20 microns.
- Results indicate a healthy population of Phytoplankton.



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Conclusion

- Spectral Sensing works well for Nitrate and Carbon determination
  - Filed Trials indicate a refinement of the algorithms are required to optimise the results.
- TDS measurements provide indicative information for rivers and can be used in highly saline waters.
  - Where small particles exist, the base line will provide the TDS equivalent and the scatter is measurement of the prevalence of these particles.
- DOM can be determined directly from UV data however determination of the types of DOM requires further work.
  - The curvature as seen in the Castletownbere plot – provides a mechanism for this and the peak wavelength as identified from a Gaussian fit to this data – may provide greater information.

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Other Sensors

01

3-Wavelength Nitrate-N and Carbon Sensor

02

Nanostructured Array Sensor for extra-cellular toxin identification.

03

Posters can be seen in the breakout room.

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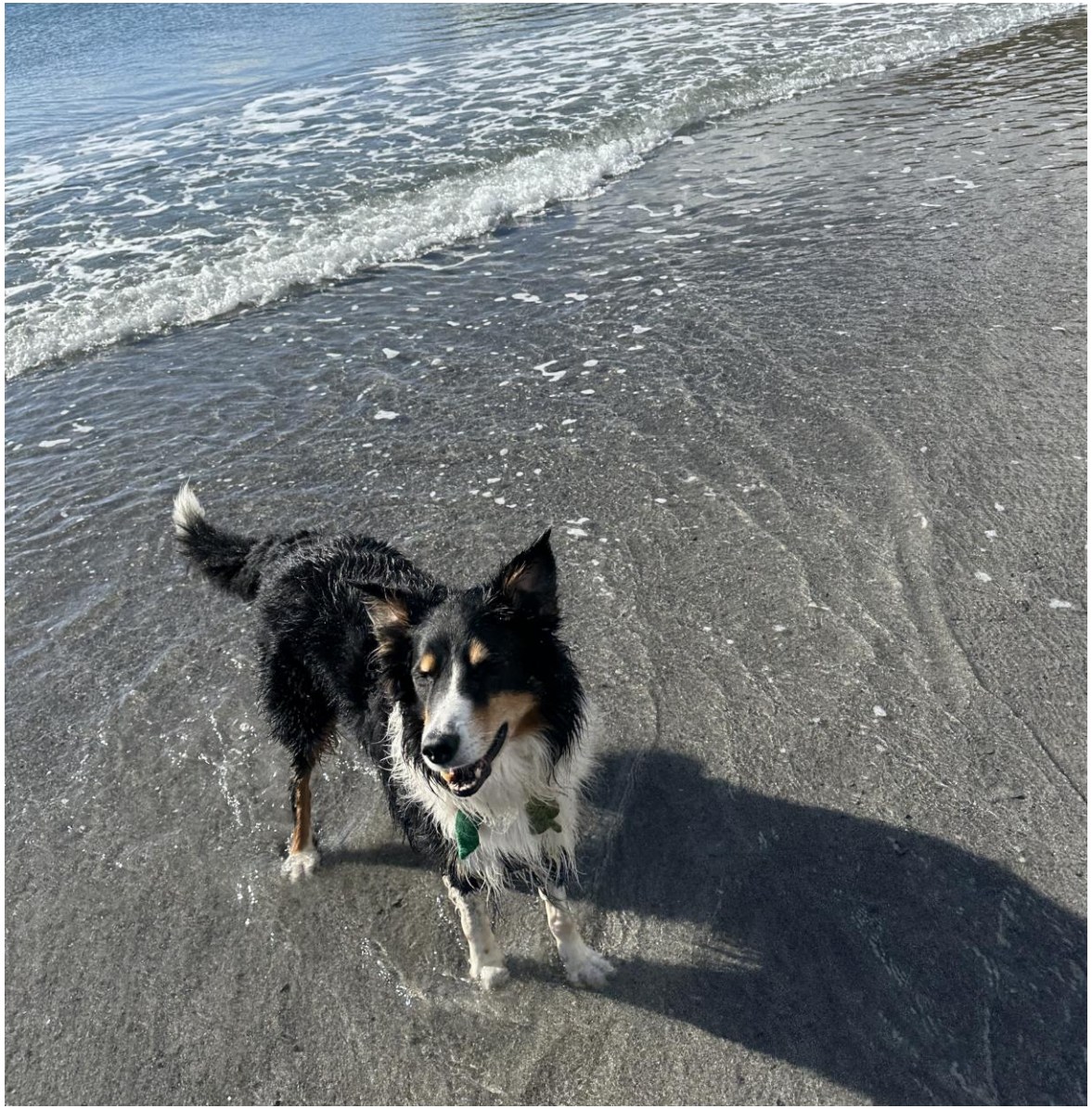

Thank You

- Benyuan, John, Mitra, Ronan & Neidin.
- The Ireland Wales Programme

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