Continuous Fluorescence Monitoring of River Organic Matter

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Fluorescence spectroscopy – pros & cons

- Fast
- Sensitive
- Small quantities of sample
- No sample pretreatment
- Correlates with standard parameters (BOD, TOC)

- Qualitative
- Influenced by external factors
- Only organic contamination

Fluorescence spectroscopy

Main application:

- Water quality monitoring;
- waste / drinking water treatment process control.

reduce costs

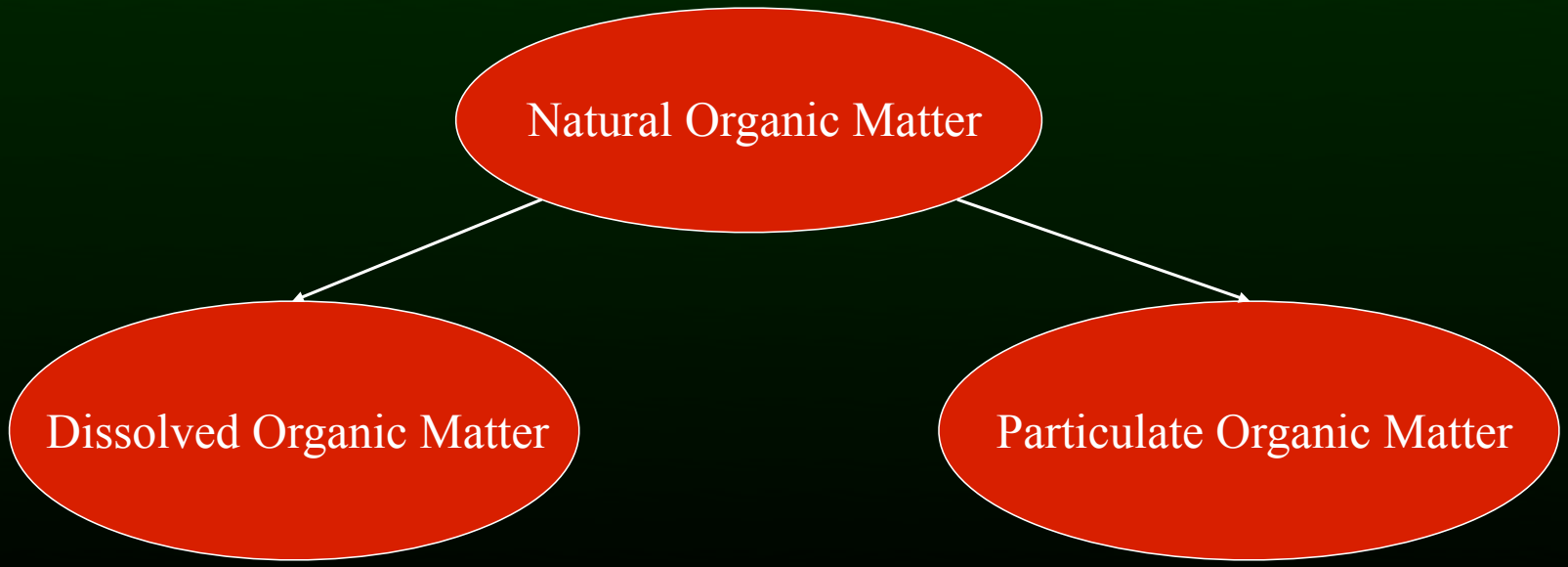
timely action

chlorine + organic matter  chlorination by-products (trihalomethanes (THMs) & haloacetic acids (HAAs))

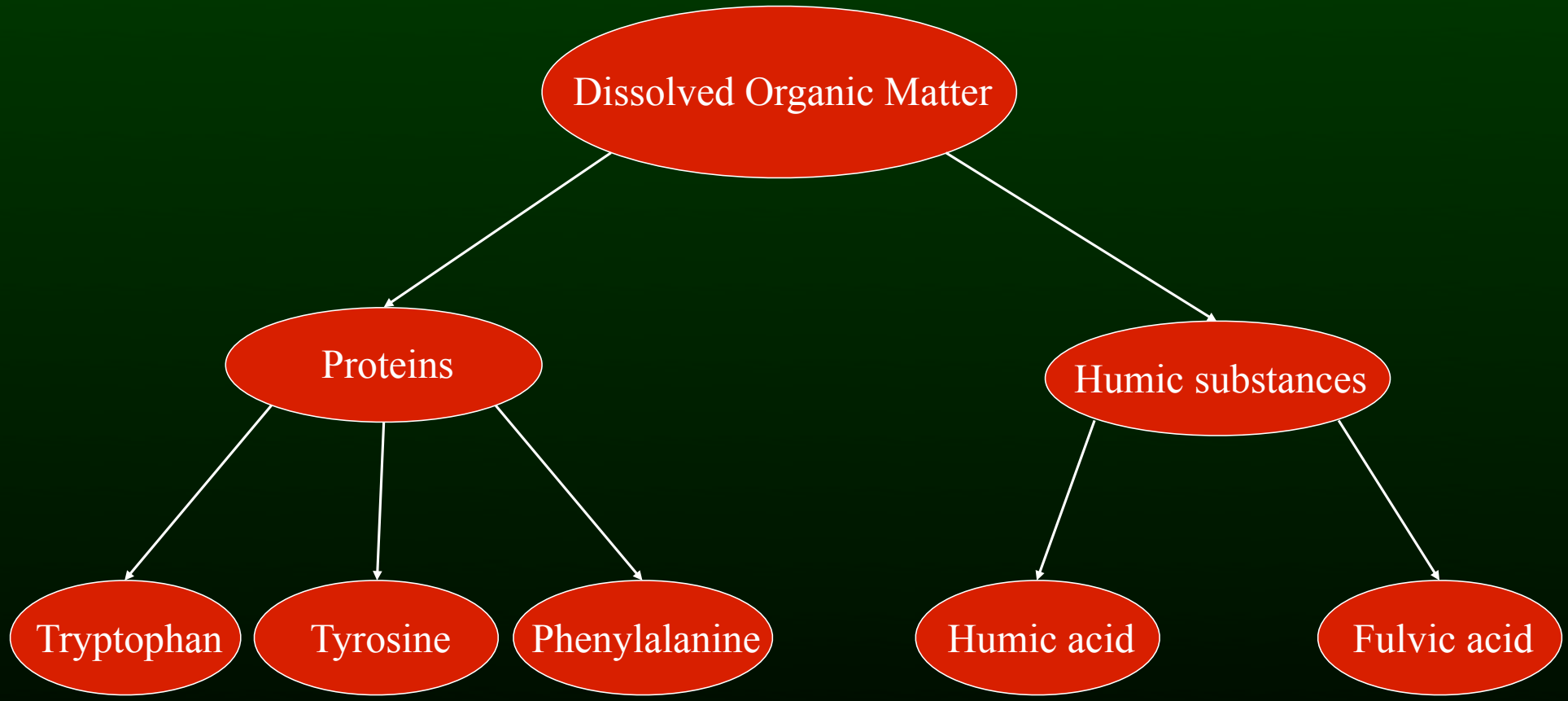
Ates et al., 2007

Natural Organic Matter (NOM)

- comprises the decay products of animal and plant matter.
- **NOM:**
  - Autochthonous – microbially derived
  - Allochthonous – terestrially derived

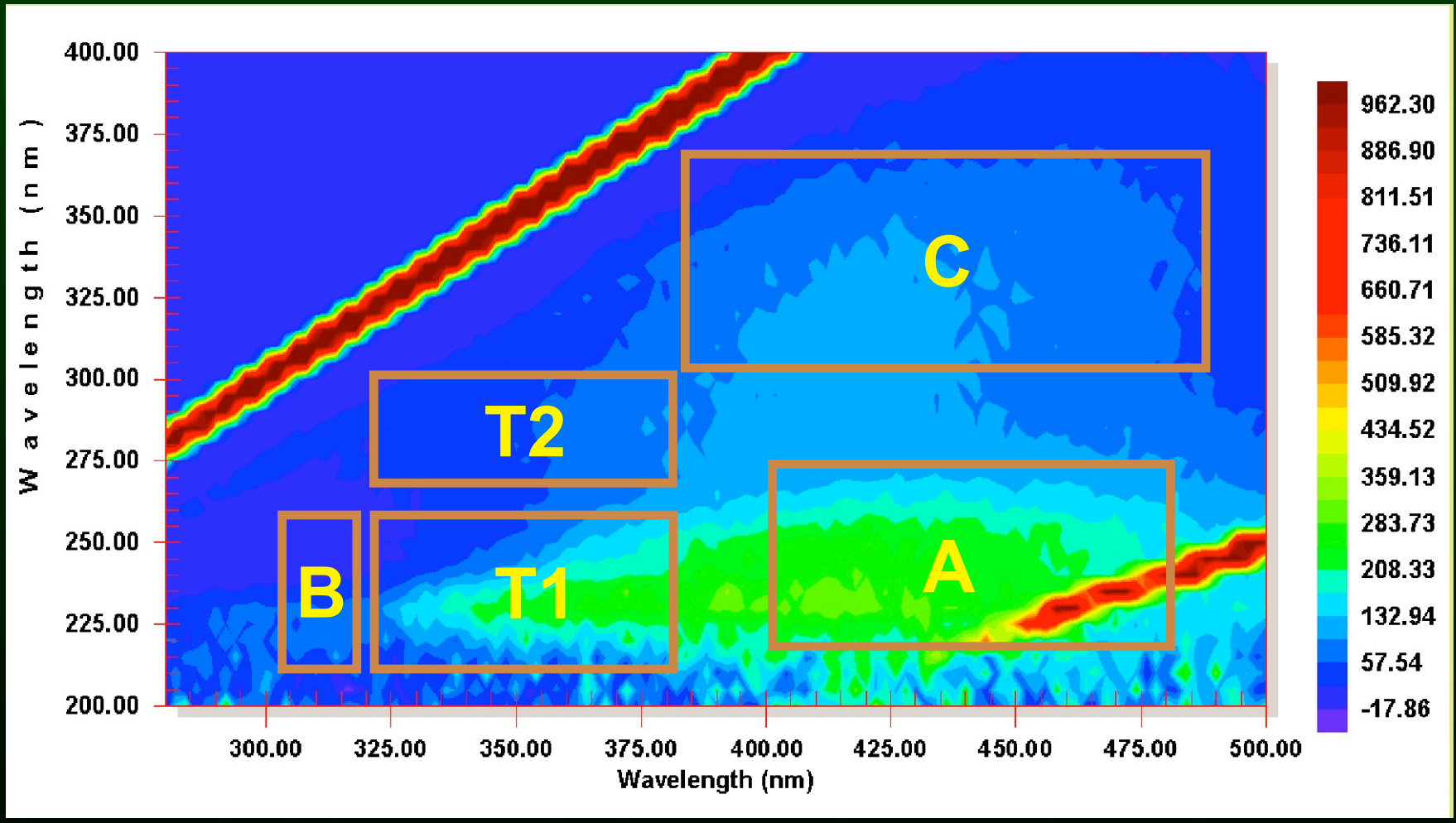


NOM Fluorescence



λ_{ex} = 230/ 290 nm λ_{em} = 350 nm	λ_{ex} = 230/ 275 nm λ_{em} = 310 nm	λ_{ex} = 260 nm λ_{em} = 282 nm	λ_{ex} = 230 nm λ_{em} = 400 - 500 nm	λ_{ex} = 300 - 350 nm λ_{em} = 400 - 500 nm

NOM Fluorescence

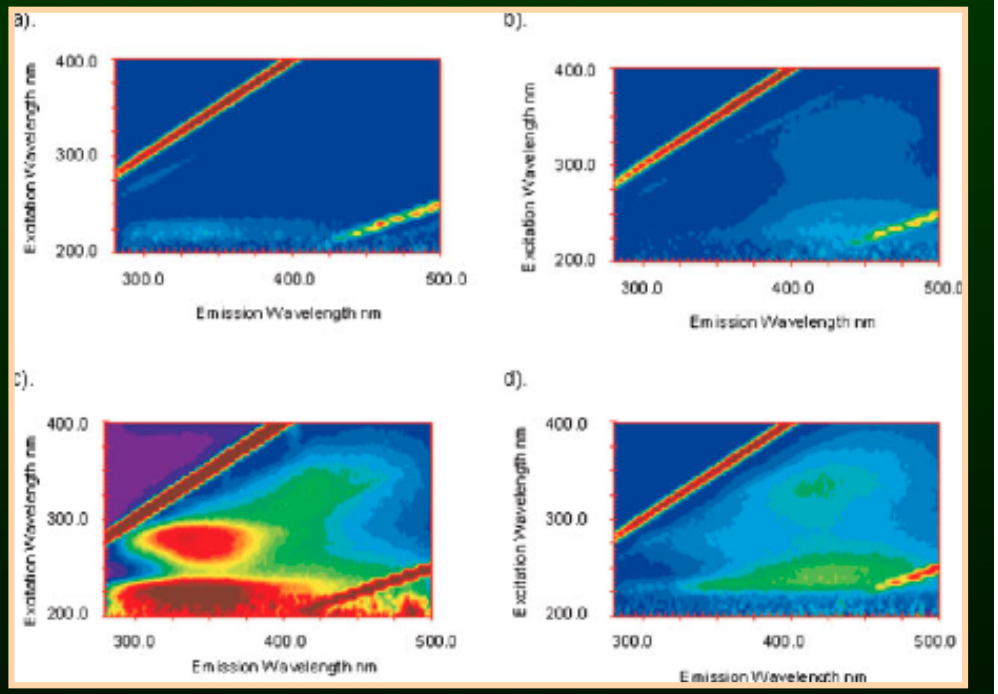


A – humic acid
C – fulvic acid

T1 & T2 – tryptophan
B – tyrosine

Spatial and temporal variability

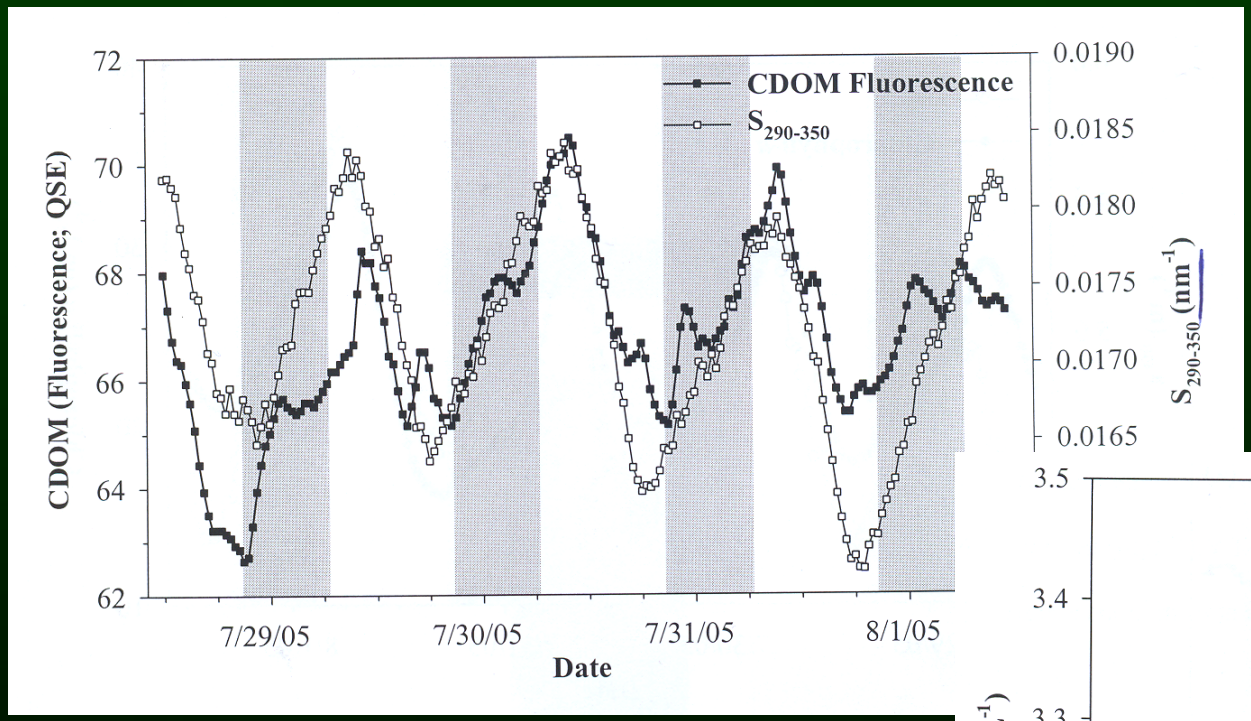
Water sample	Excitation wavelength (nm)	Emission wavelength (nm)
Rivers	340	448
Humic substances	310	423
Coastal waters	342	442
Marine, surface waters	299	389
Marine, deep waters	340	438
Groundwaters	320	407
Lake	330	437



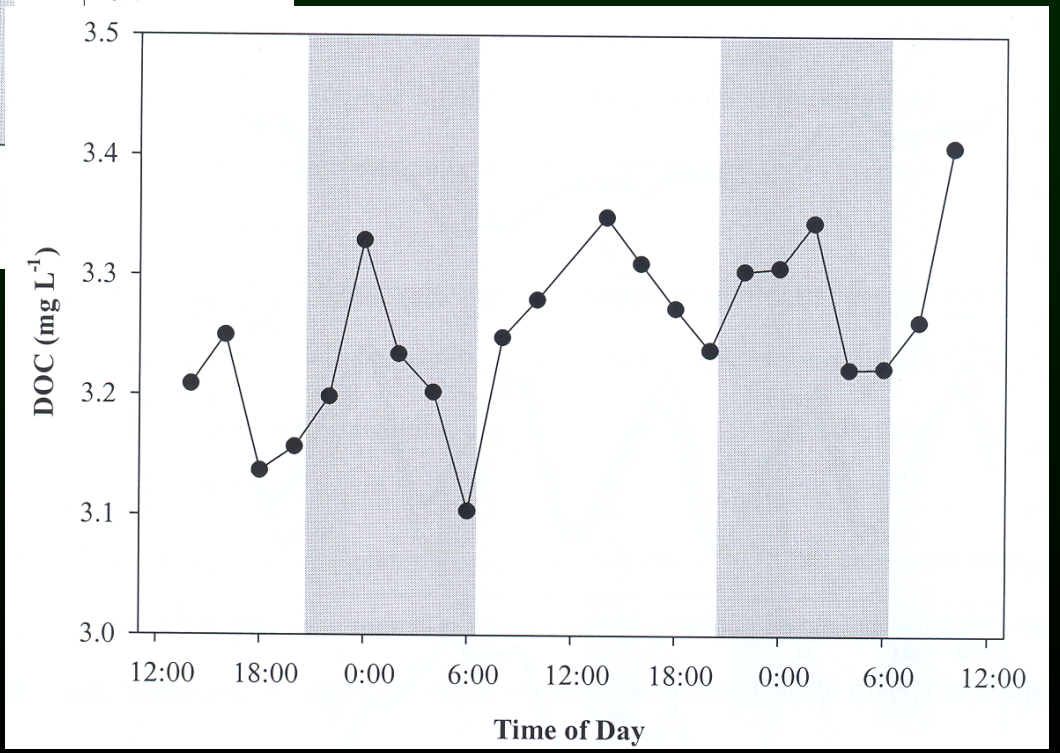
Coble (1996)

Hudson et al. (2007)

Spatial and temporal variability

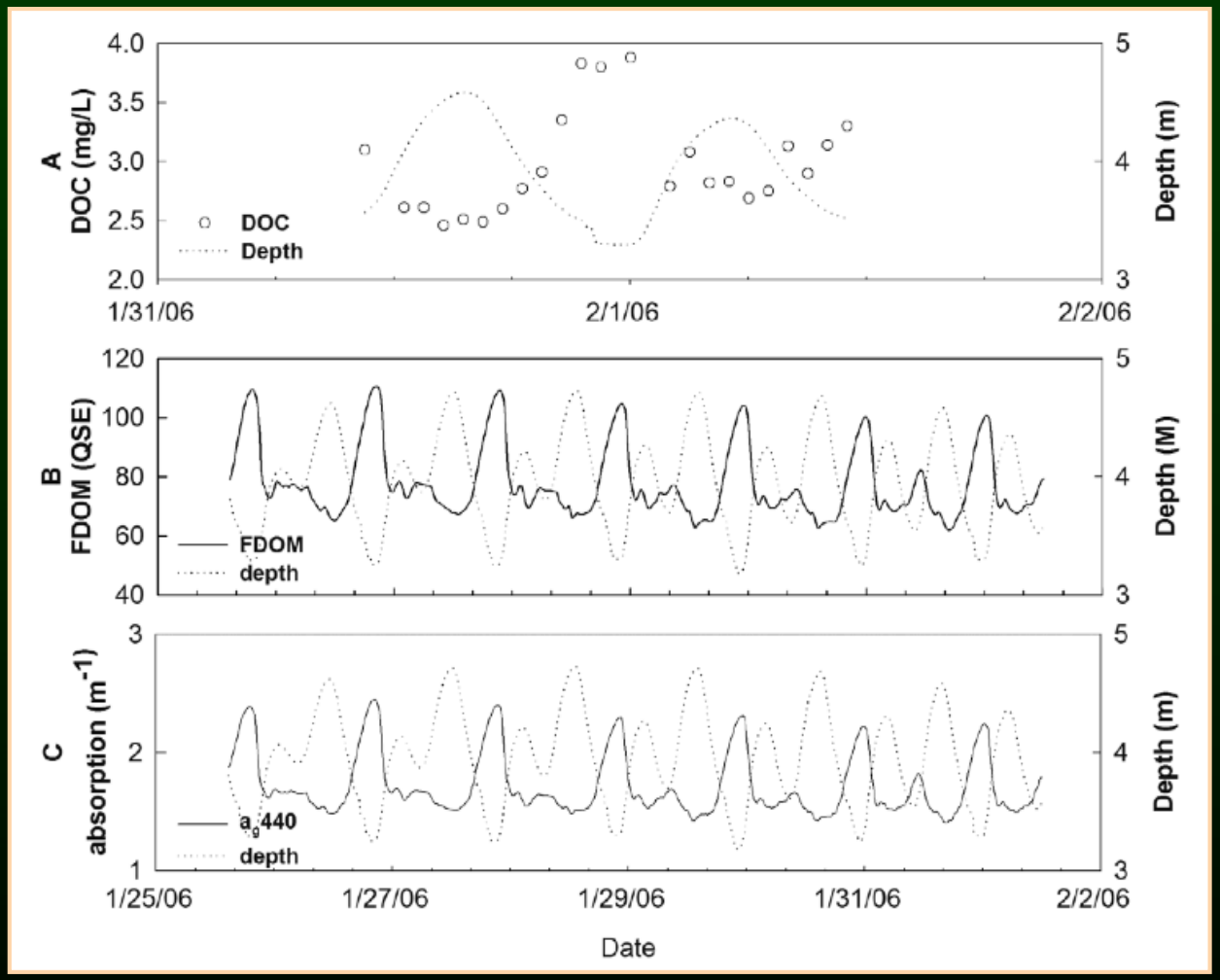


- In situ measurements using a WET Labs WETStar
- Single-band excitation-emission in situ fluorometer 370 nm excitation / 460 nm emission



Spencer et al., 2007

Spatial and temporal variability



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Downing et al., 2009

Spatial and temporal variability

HYDROLOGICAL PROCESSES
Hydrol. Process. **23**, 1937–1946 (2009)
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Continuous fluorescence assessment of organic matter variability on the Bournbrook River, Birmingham, UK

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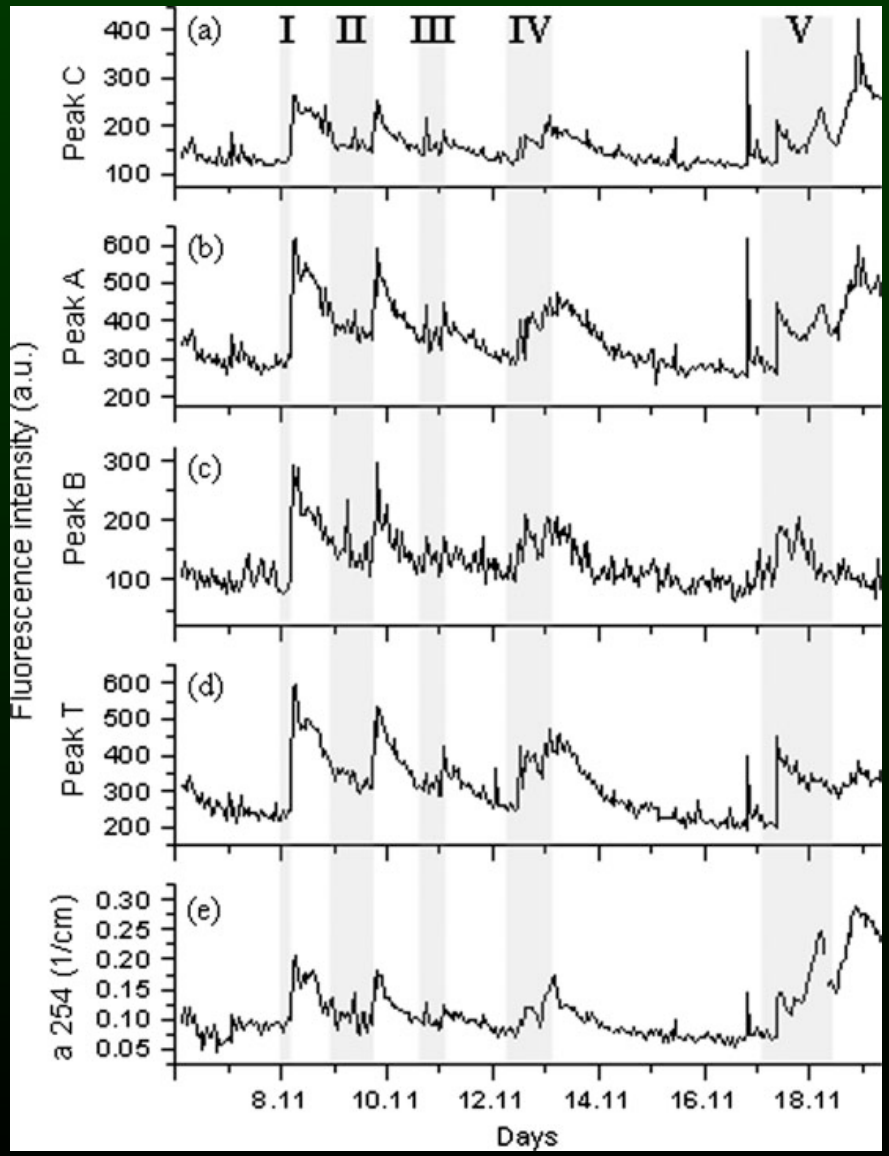
Abstract:

Continuous monitoring of dissolved organic matter (DOM) character and concentration at hourly resolution is rare, despite the importance of analysing organic matter variability at high-temporal resolution to evaluate river carbon budgeting, river water health by detecting episodic pollution and to determine short-term variations in chemical and ecological function. The authors report a 2-week experiment performed on DOM sampled from Bournbrook, Birmingham, UK, an urban river for which spectrophotometric (fluorescence, absorbance), physiochemical (dissolved organic carbon [DOC], electrical conductivity, pH) and isotopic (D/H) parameters have been measured at hourly frequency. Our results show that the river had sub-daily



Methodology

- Varian Cary Eclipse spectrofluorometer, scan rate 9600 nm/min, integration time 0.0125 s, both excitation and emission slits at 5 nm
- Mean value of Raman peak intensity 7 arbitrary units.
- Excitation wavelength range 225 nm - 400 nm, 5 nm step
- Emission wavelength range 280 nm -500 nm, 2 nm step.
- Water pumped to Cary Eclipse Fluorescence Spectrometer (20ml /min).
- Fibre-optic probe with 1 cm path-length liquid probe tip measures fluorescence EEMs every 3 minutes in a 20 ml sample chamber.
- Samples also taken every hour from both river and sample chamber for fluorescence, UV absorbance, pH, electrical conductivity, hydrogen isotopic composition, and total organic carbon.
- Water temperature monitored using a Tinytag T logger. River stage recorded every hour.

Sampling site

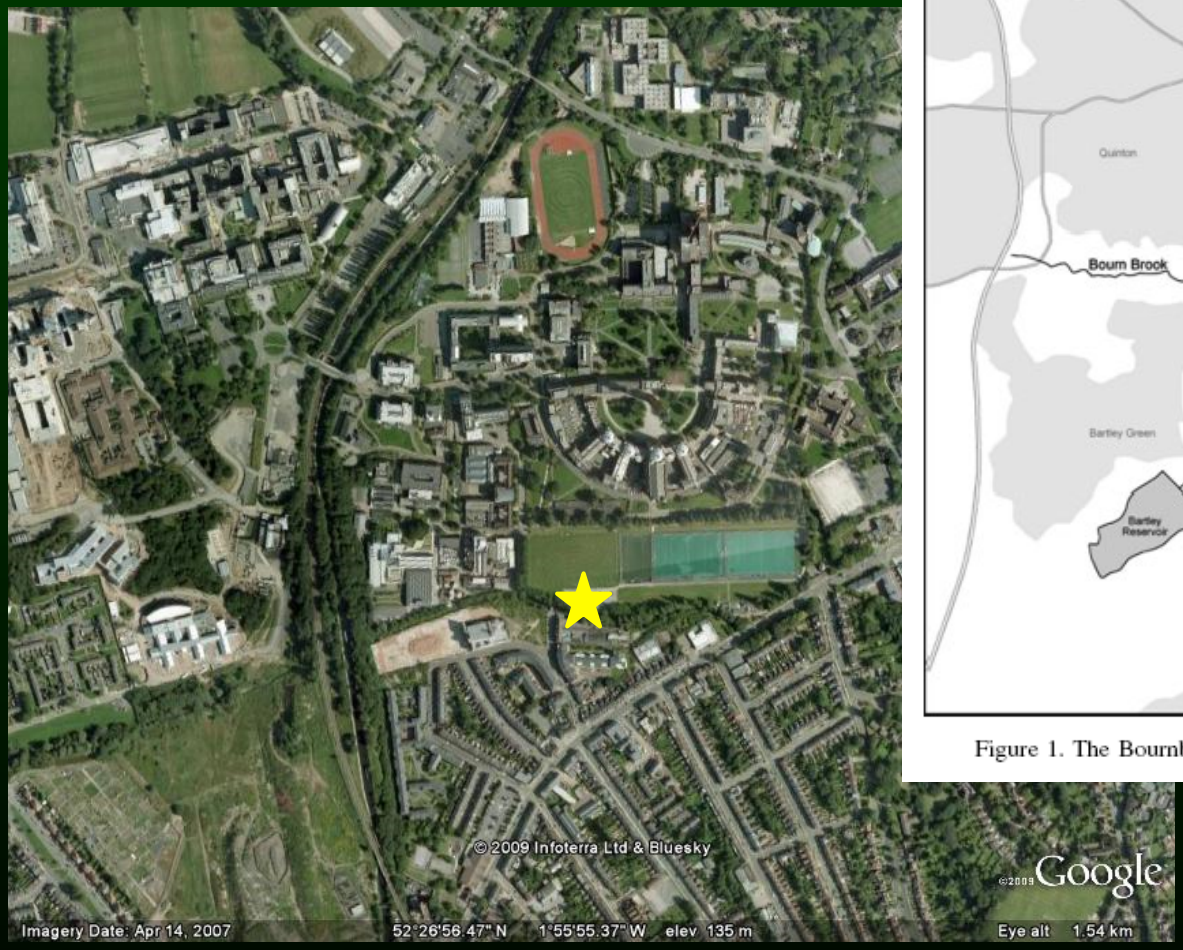
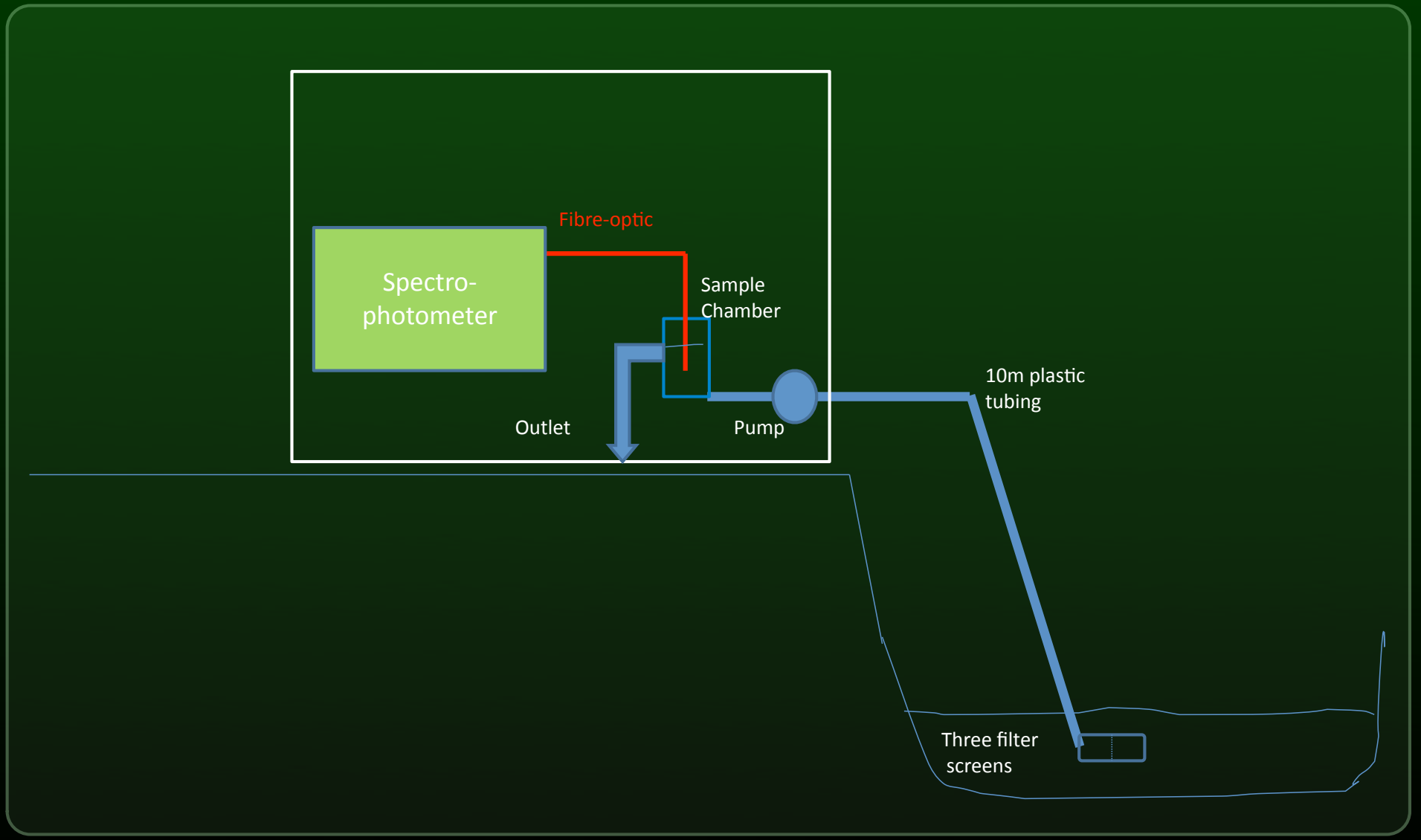
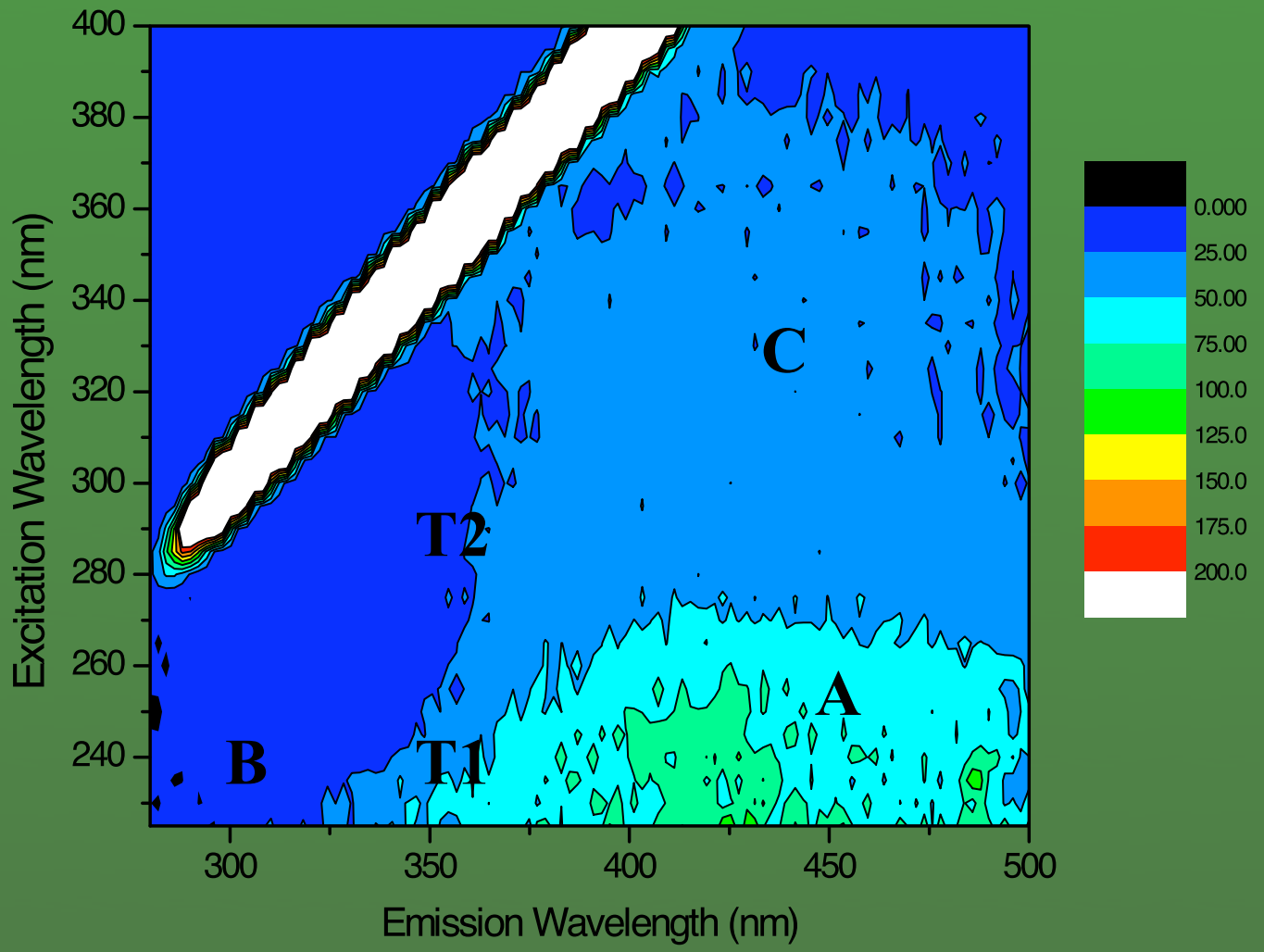


Figure 1. The Bournbrook catchment; sampling site and

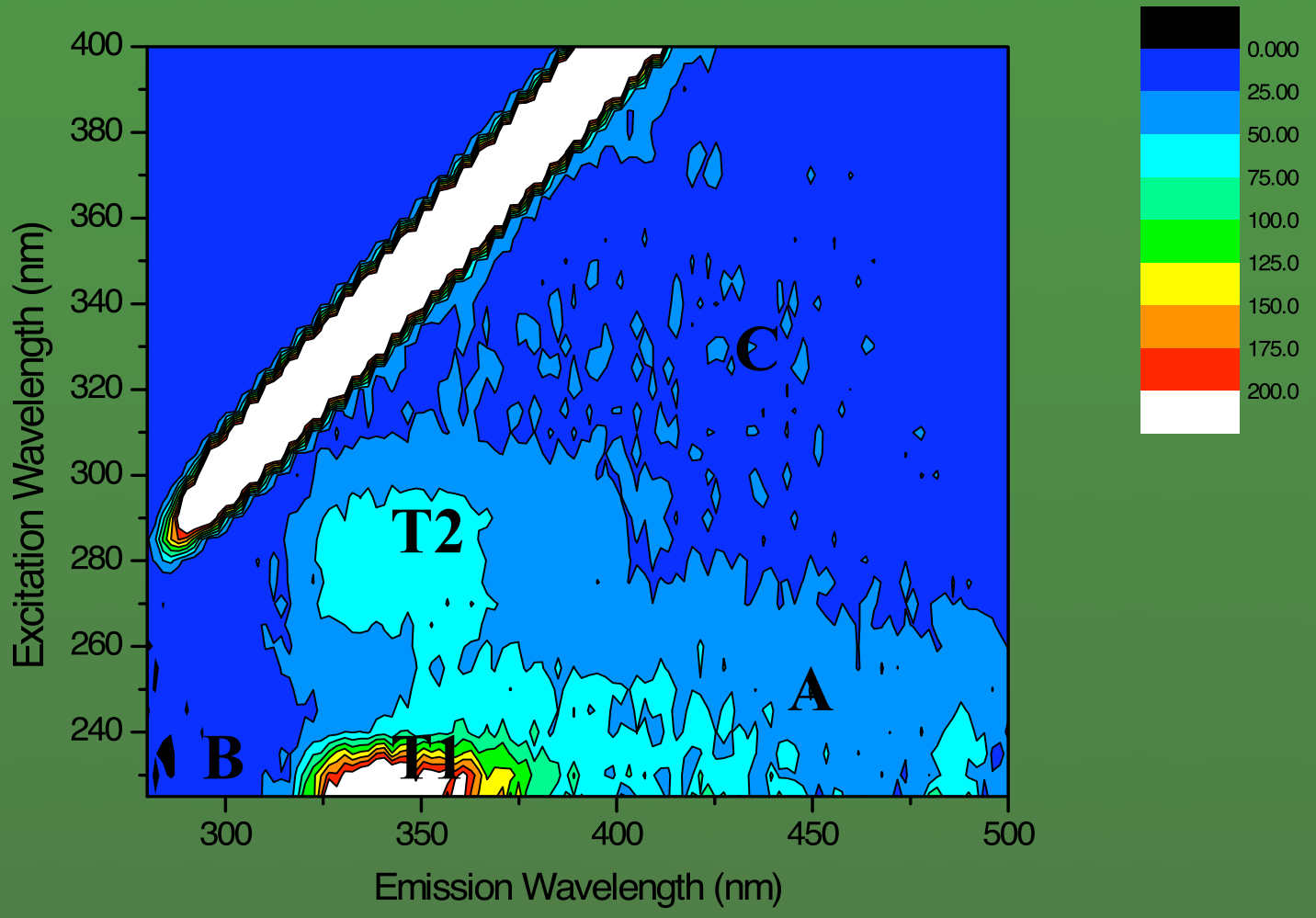
Set-up


Fibre-optic
Spectro-
photometer
Sample
Chamber
10m plastic
tubing
Outlet
Pump
Three filter
screens

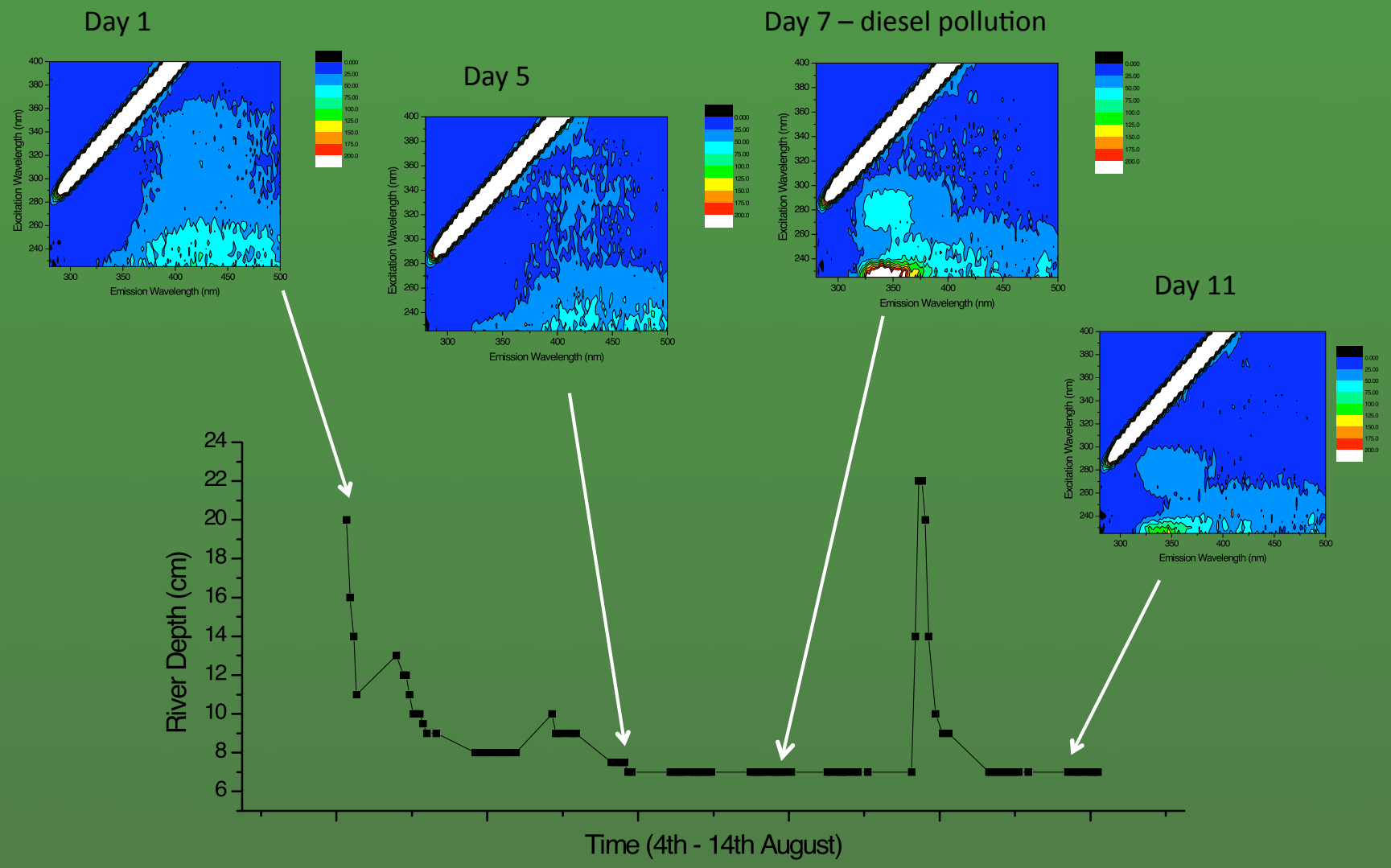
Fluorescence EEMs



Fluorescence EEMs



Continuous fluorescence data



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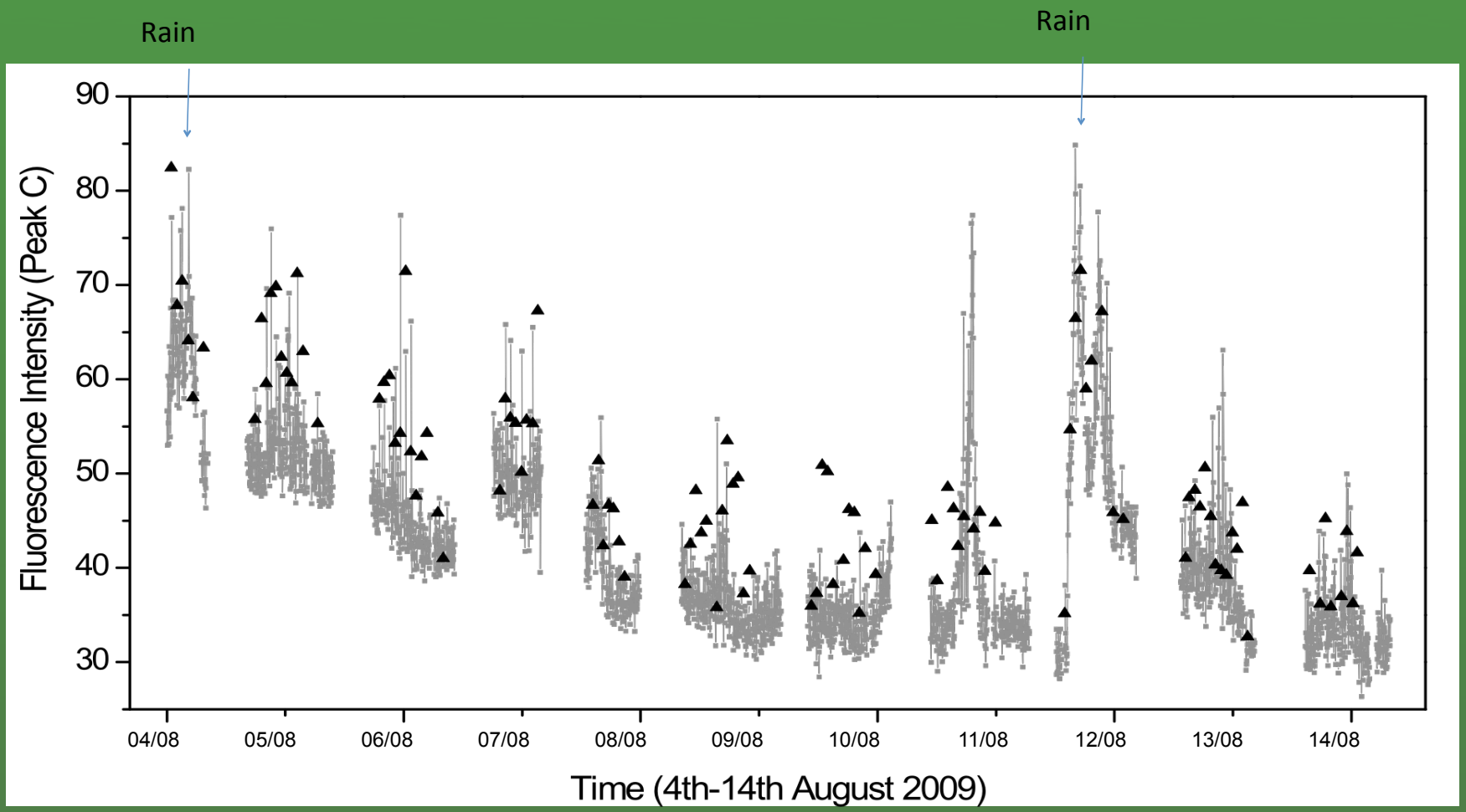
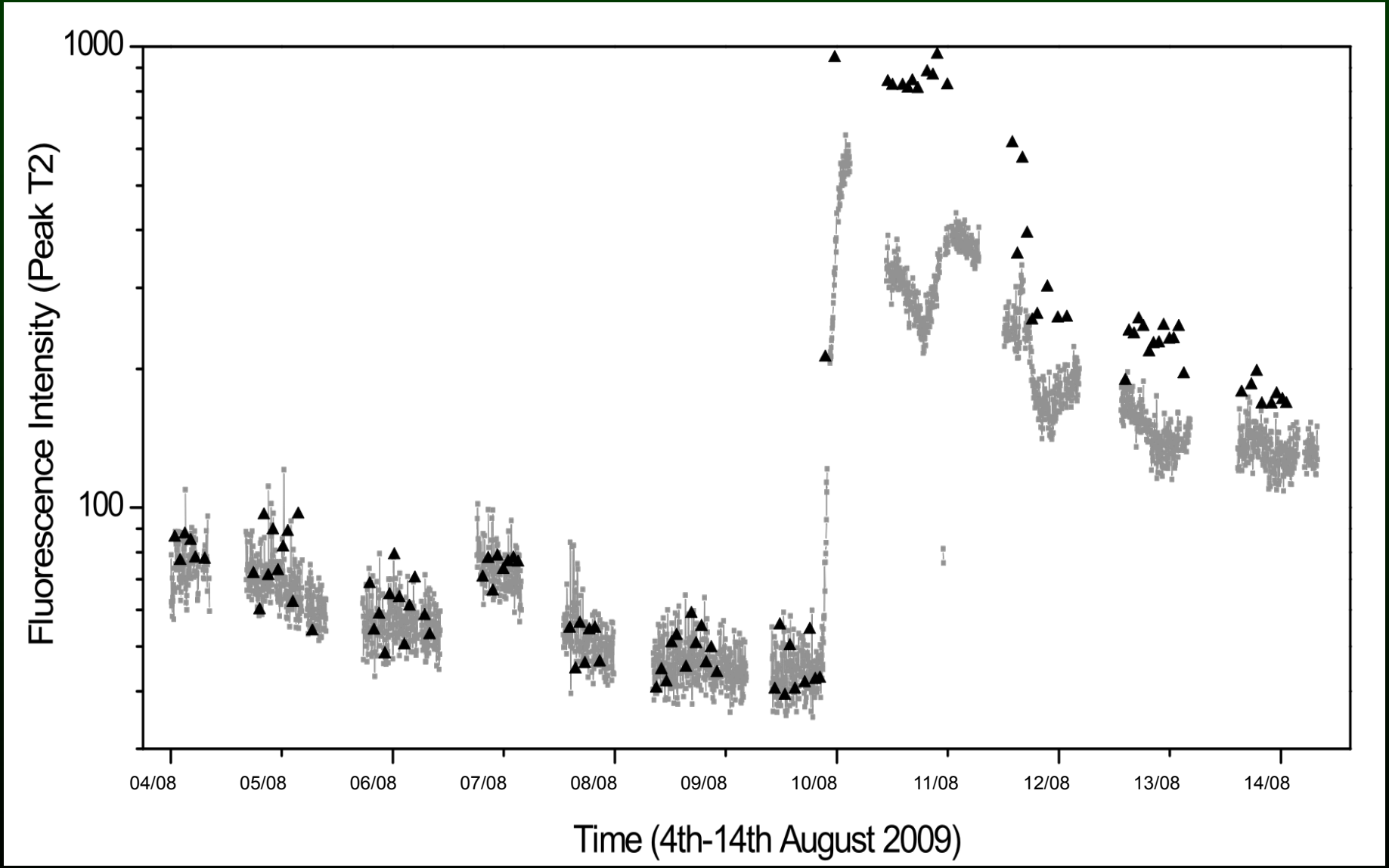


Continuous fluorescence data



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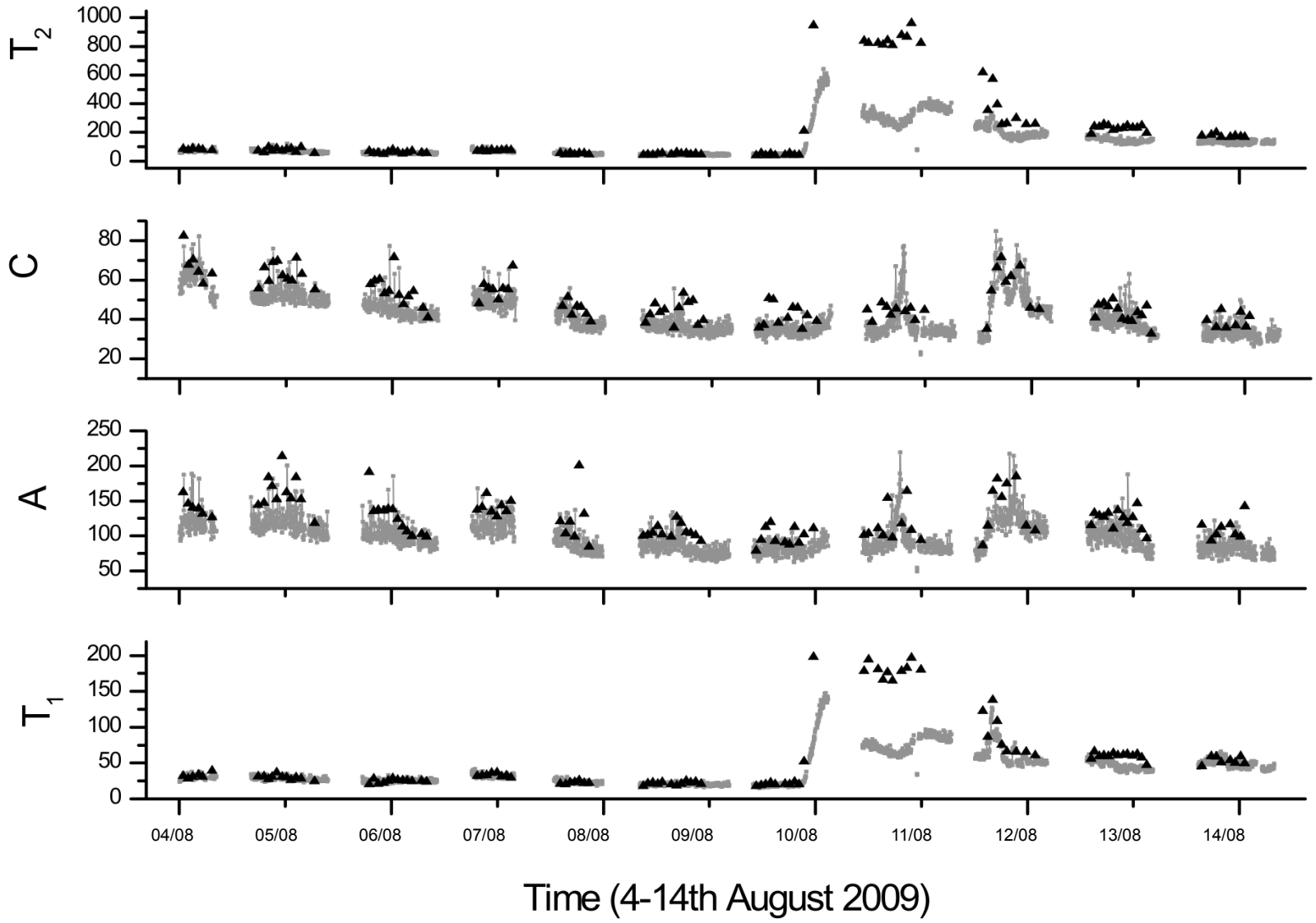
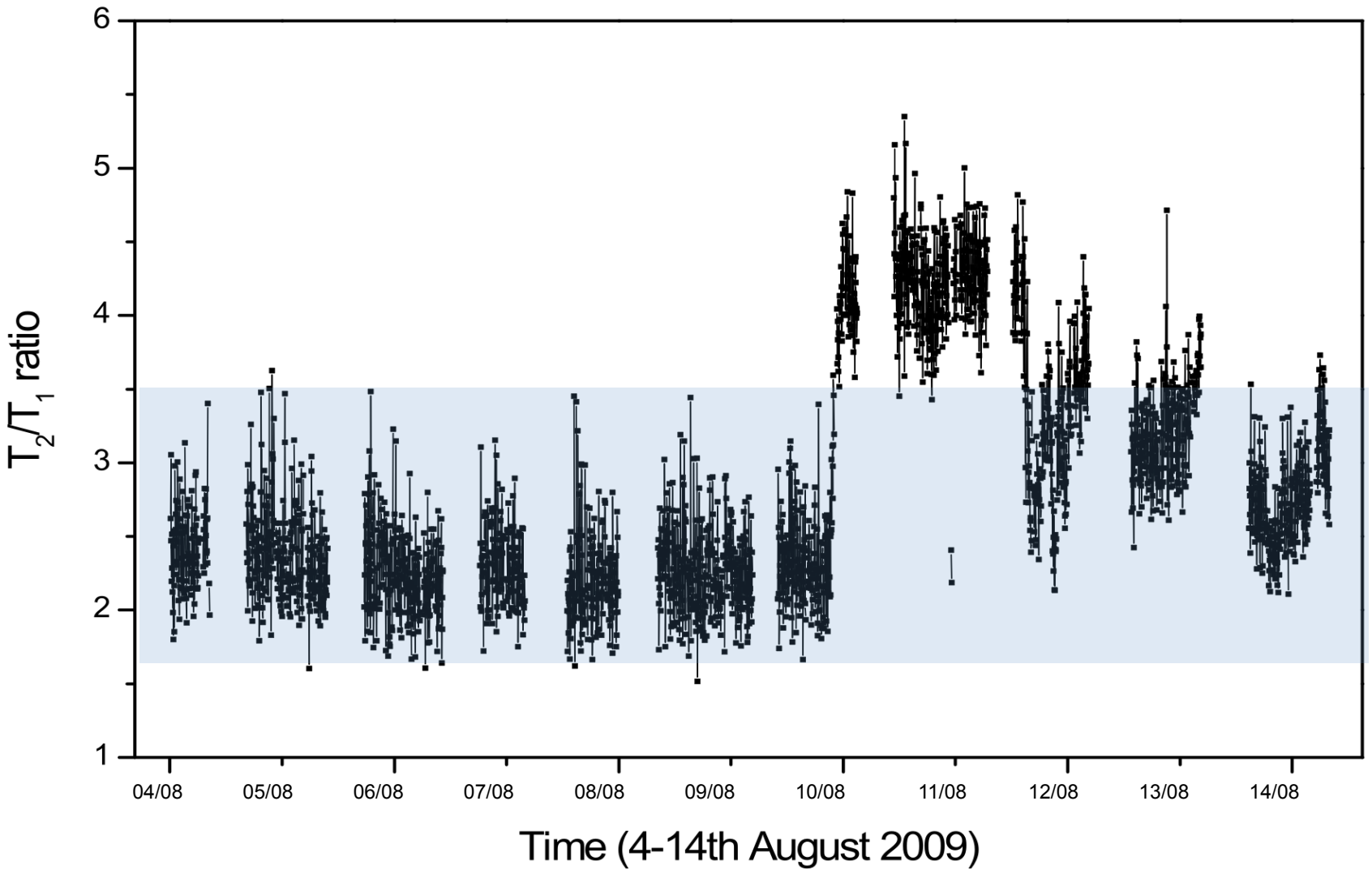
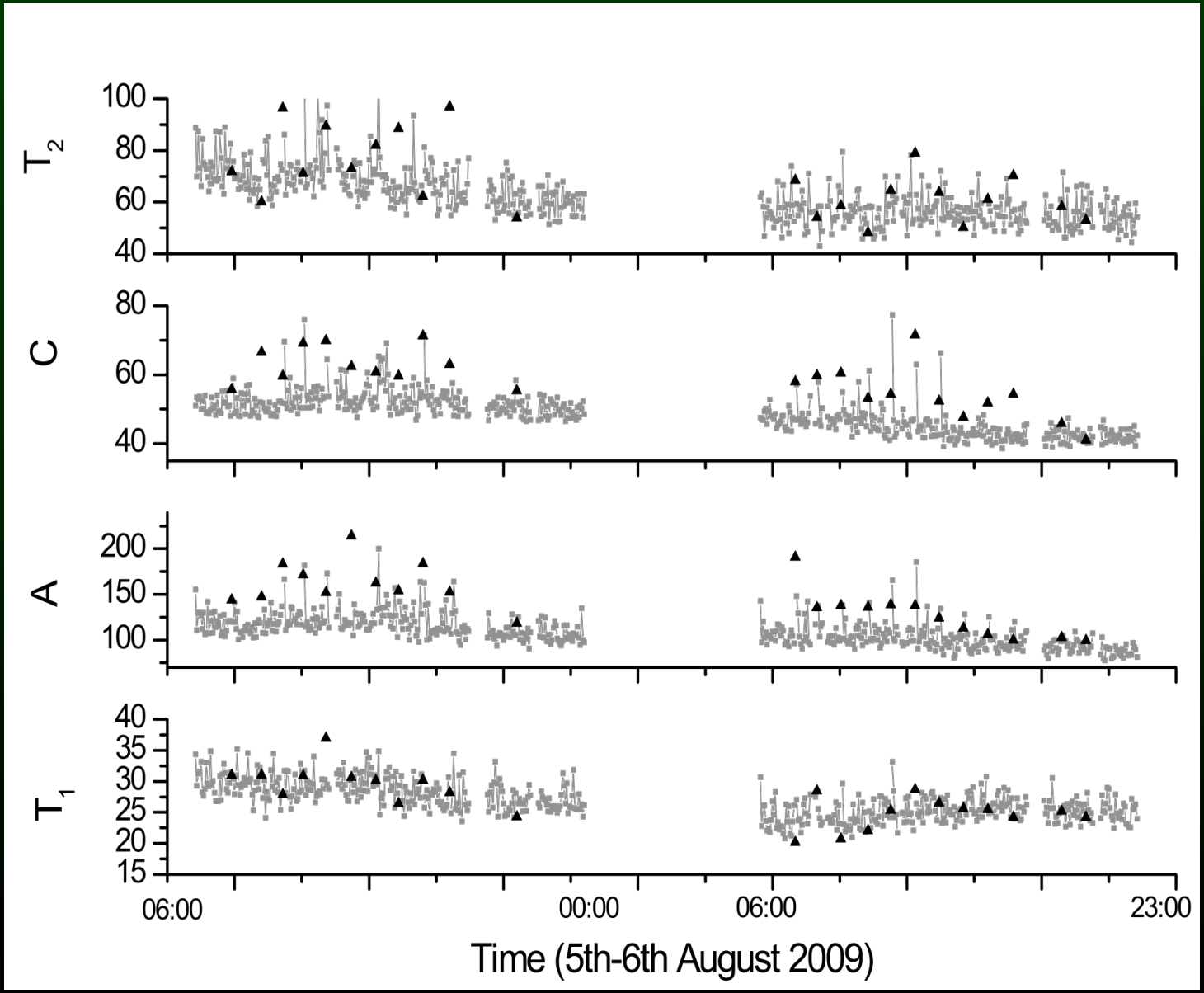


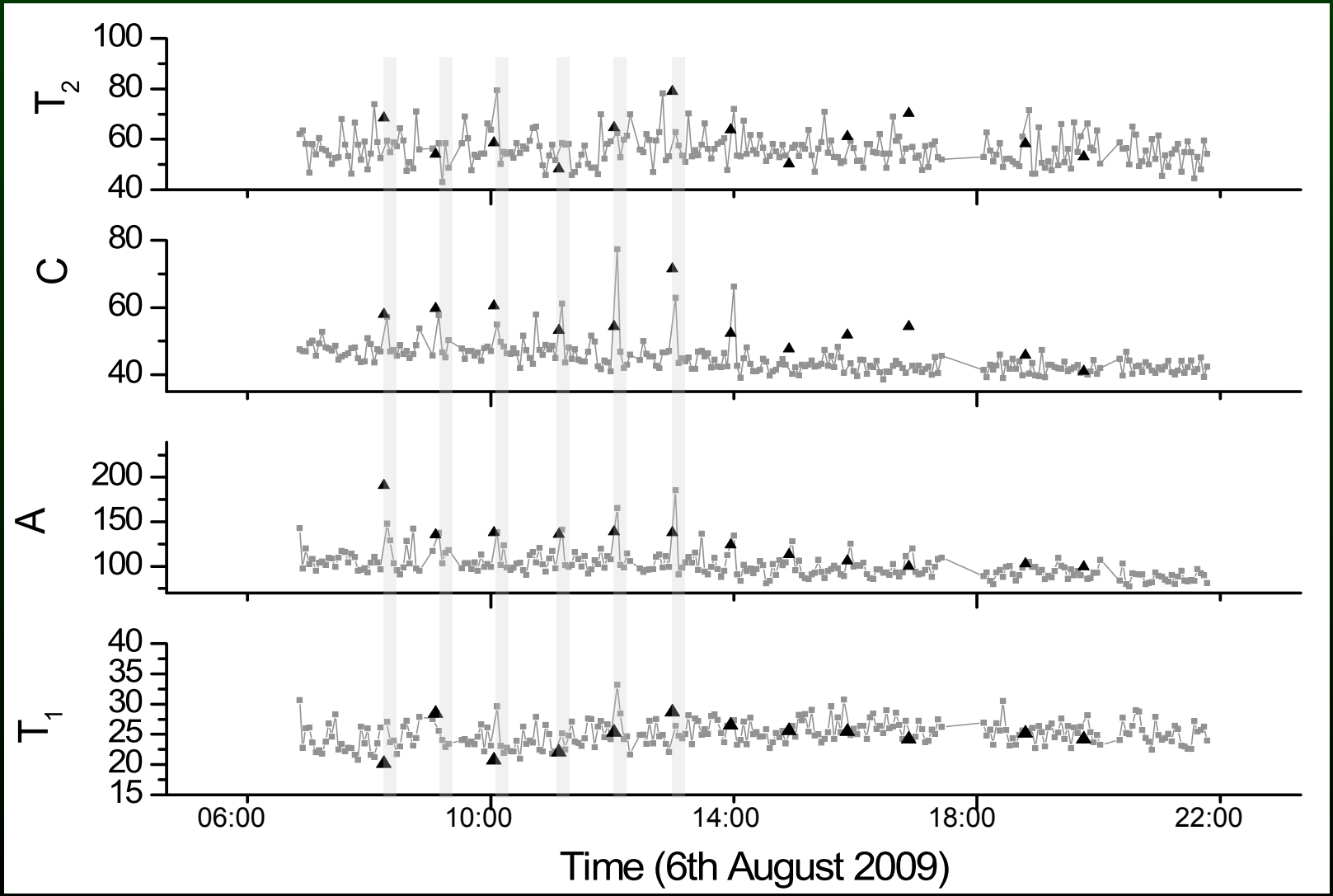
Continuous fluorescence data



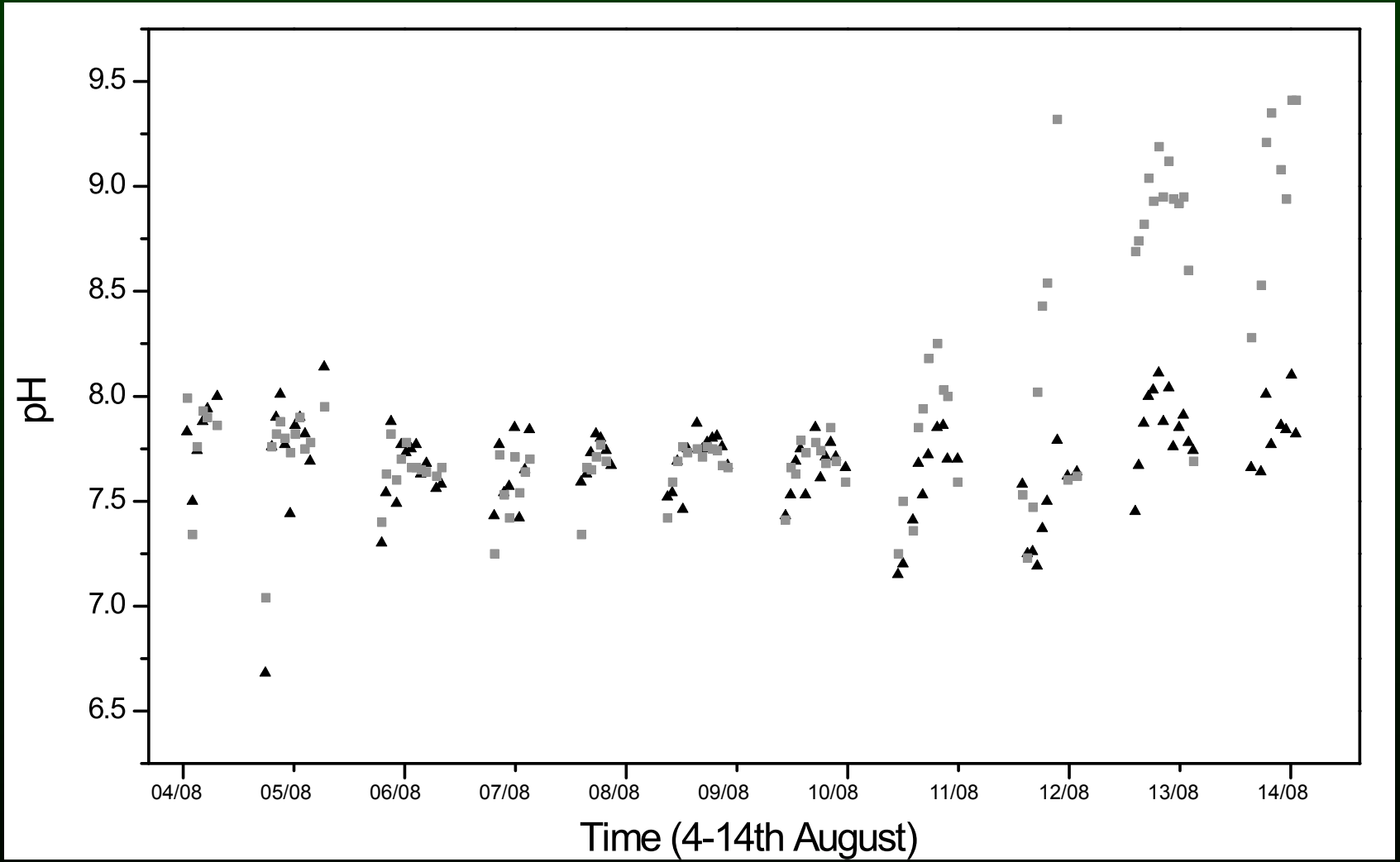
Continuous fluorescence data



Continuous fluorescence data



Continuous fluorescence data



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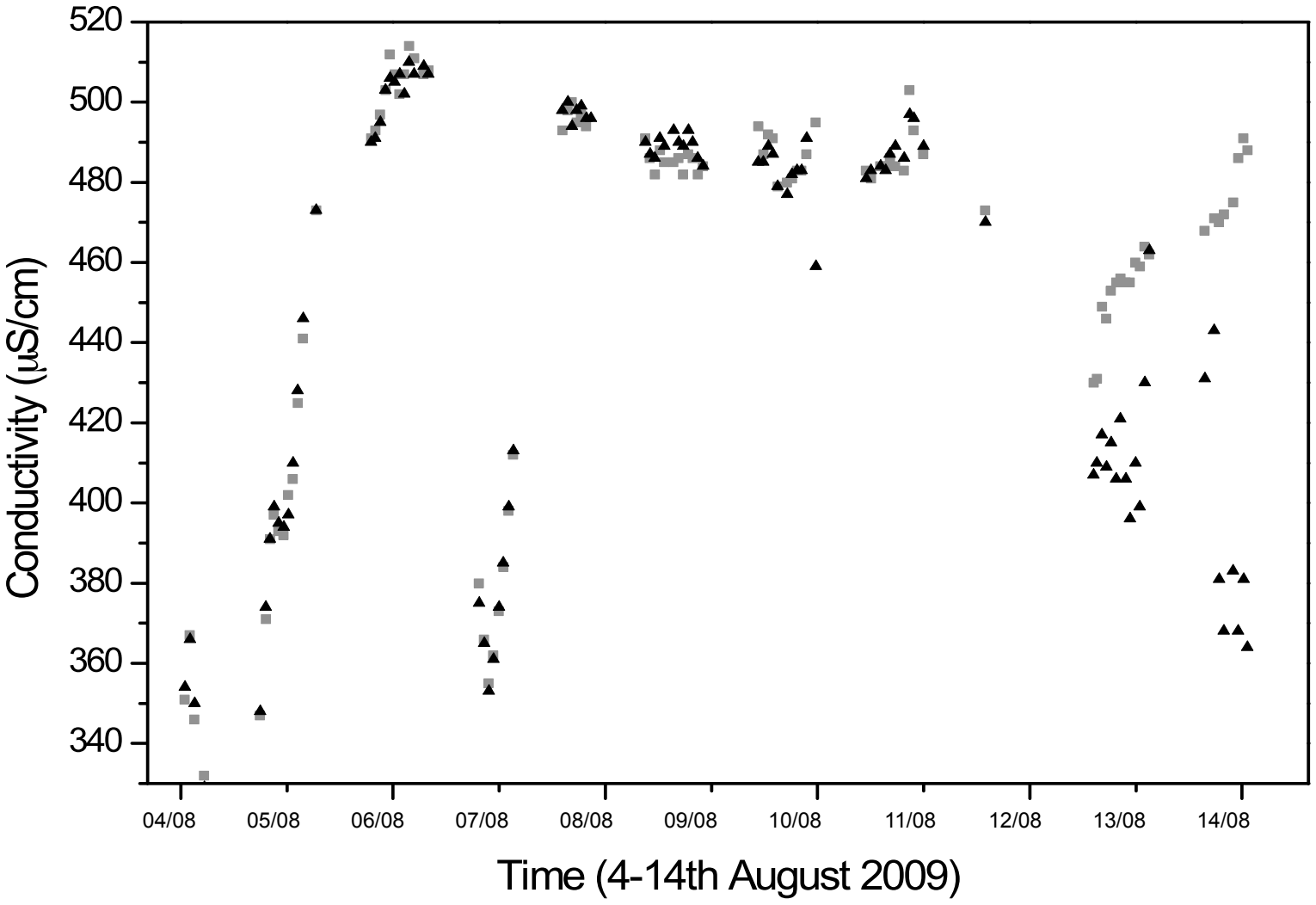

Conclusions

- First continuous EEM data for any application.
- Successful optical protocols (slits, filters, scan speeds, etc.).
- Data gaps due to software bugs.
- Ten days of continuous data collection until generator failure.
- No drift or calibration issues over the ten days.
- Identification of major diesel pollution event.
- Identification of ~ hourly minor pollution pulses from cross connections.
- Unanswered question – how long could continuous EEMs be collected for?