

A bright yellow kayak is positioned on a river. On the kayak, there is a white rectangular box, a blue vertical sensor or pump assembly, and a white antenna. The kayak has 'UKCEH' printed on its side. In the background, several swans are swimming in the water near a grassy bank.

Resolving sequential storm-driven pollutant pulses
using novel hydrochemical measurements within a
reactivity-hydrodynamic workflow.

Chris Pessa

Rameshwaran Ponnambalam (UKCEH), Andrew Wade (University of Reading), Nick Everard (UKCEH)



University of
Reading



UK Centre for
Ecology & Hydrology



Scenario
DOCTORAL TRAINING PARTNERSHIP

The Problem



The
Confluence
and How We
Sampled it

What the Strom
Revealed

What This
Means for
Monitoring

Key Takeaways

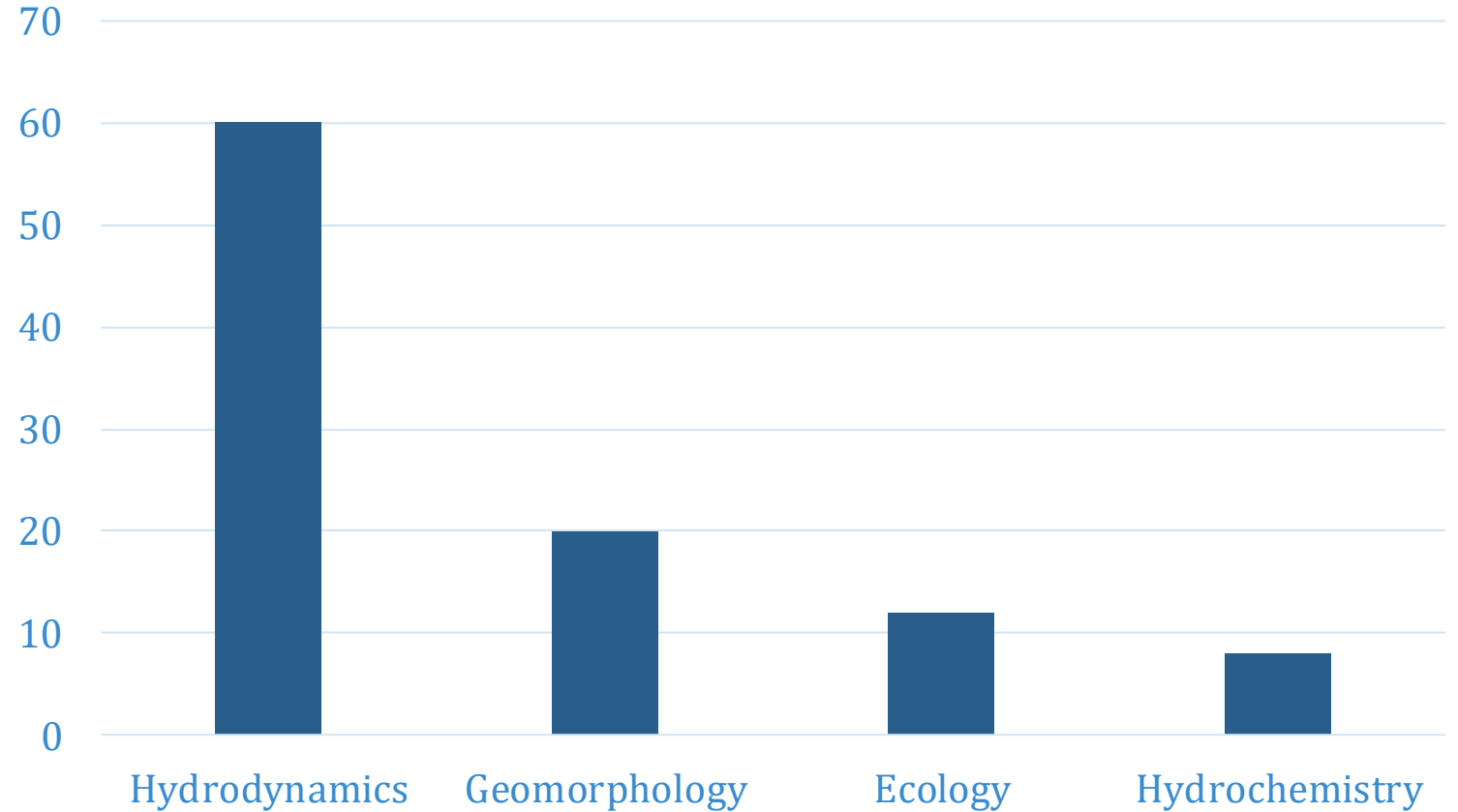
c.d.pesso@pgr.reading.ac.uk;
chrpes@ceh.ac.uk



The Problem

Why is hydrochemistry understudied?

Focus of River Confluence Research (%)

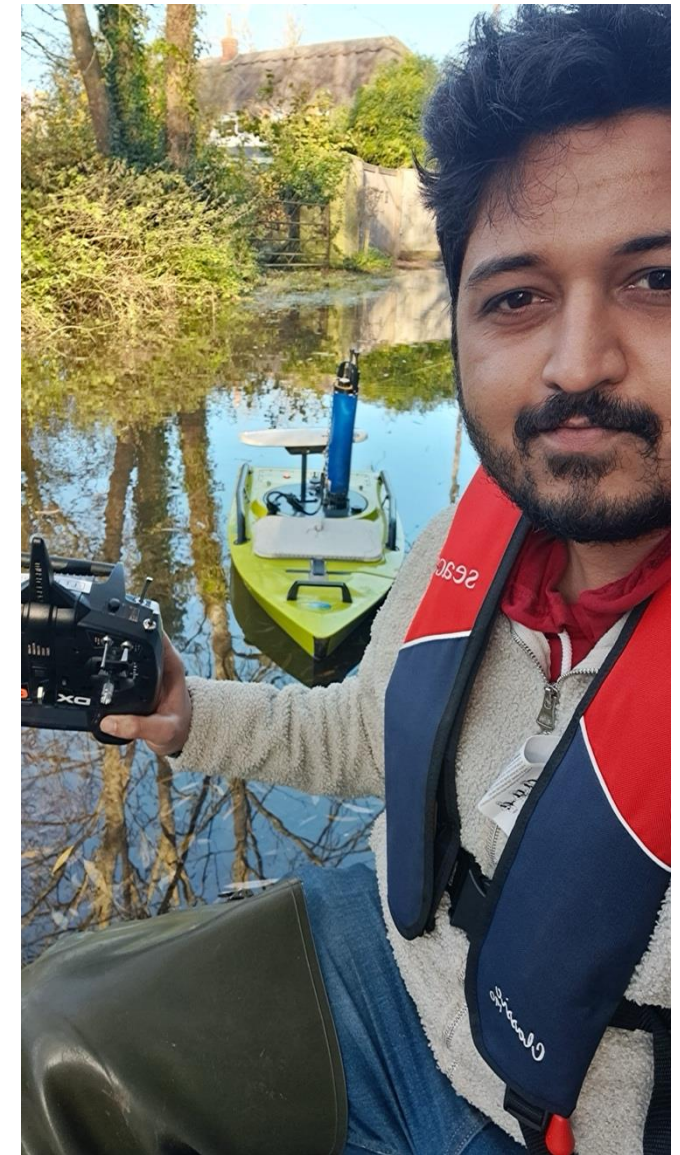


(Based on a review of 140 research papers)



The ArcBoat

The Confluence and How We Sampled it





EXO (YSI) Sonde

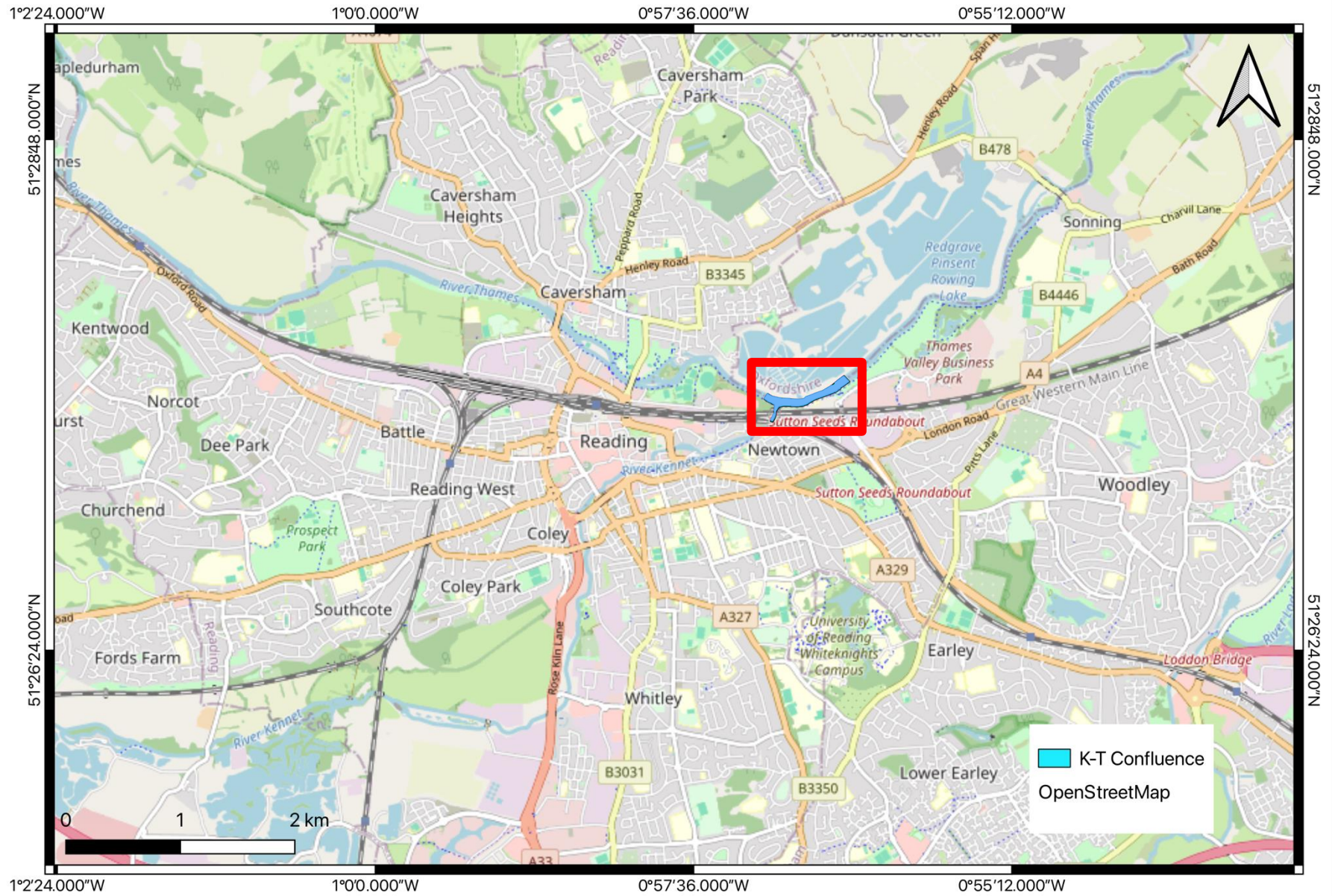
GPS

ADCP (beneath GPS)



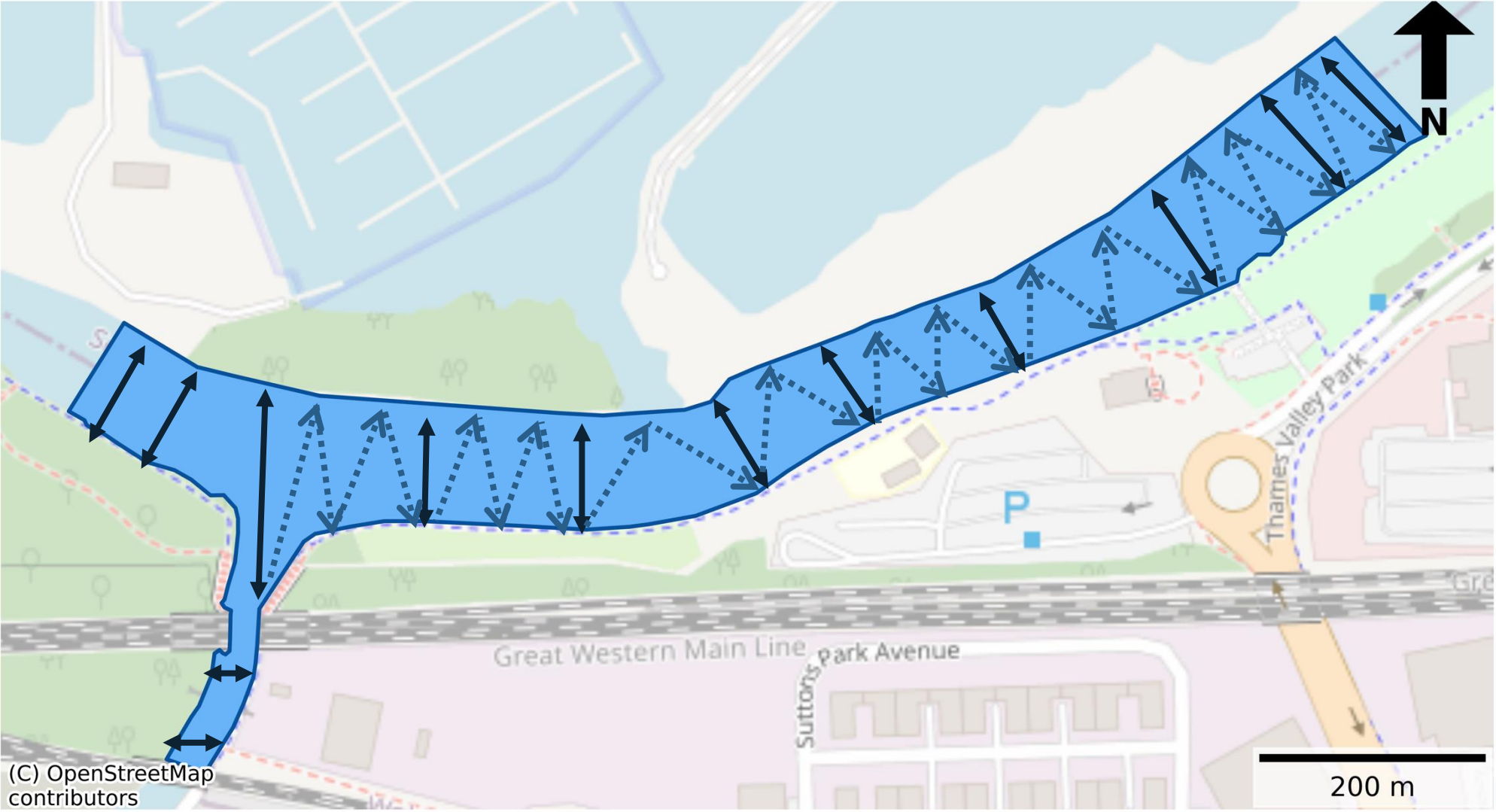


Study Area



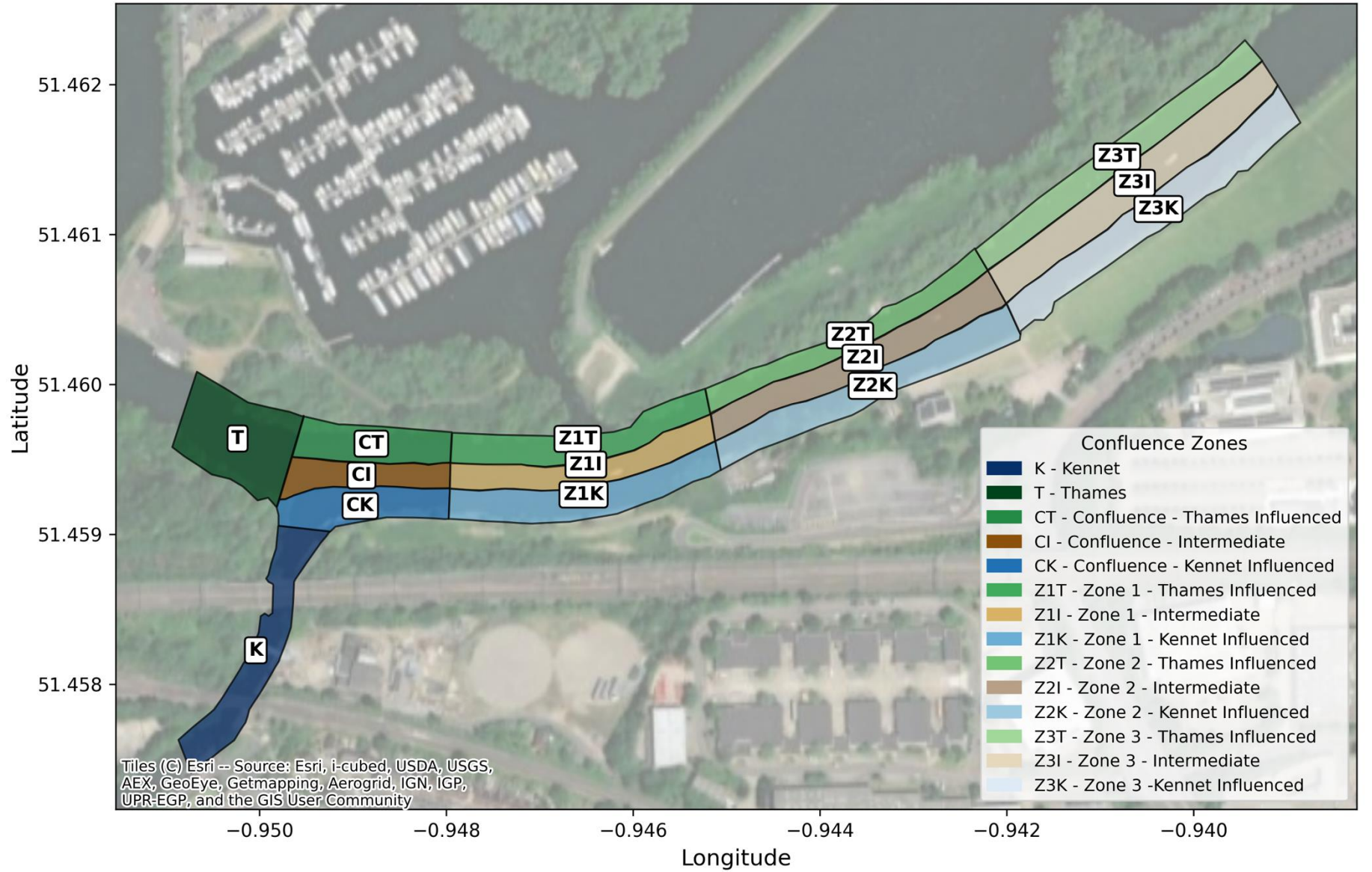
Kennet-Thames Confluence

Monitoring Strategy

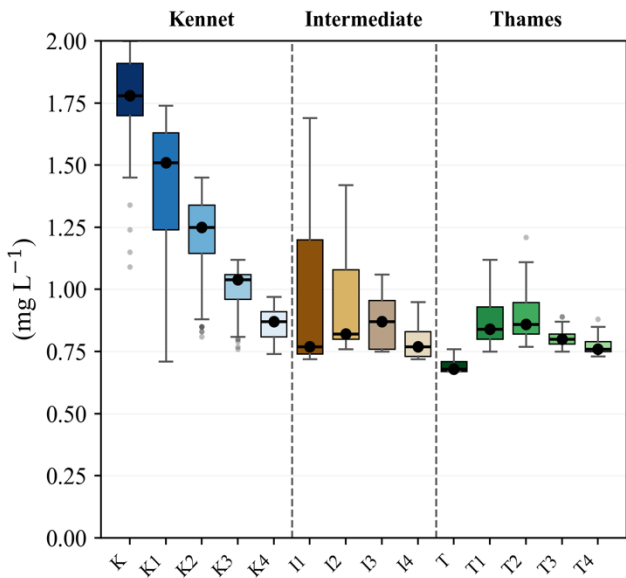


Confluence Zone Map

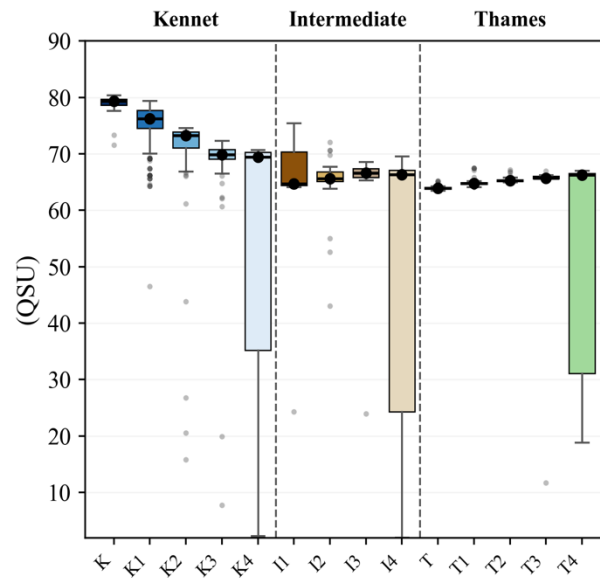
Zoning Scheme



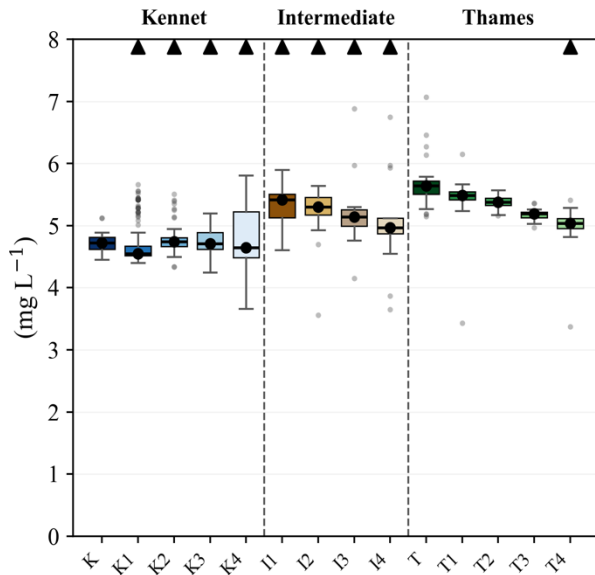
$\text{NH}_4^+ \text{-N}$



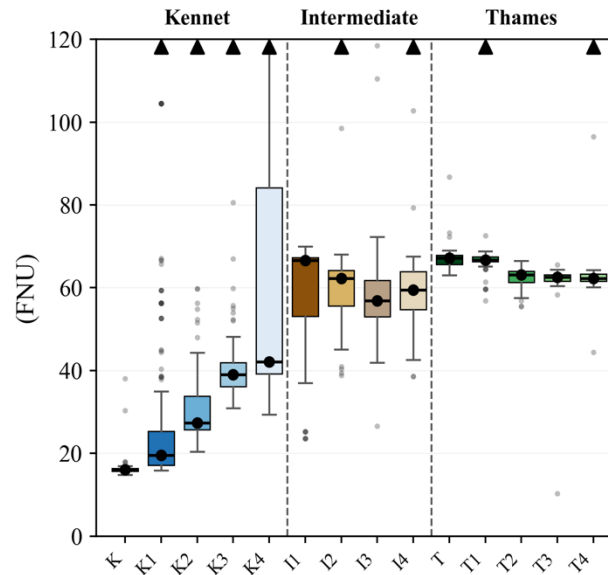
fDOM



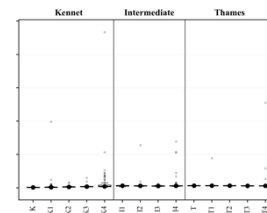
$\text{NO}_3^- \text{-N}$



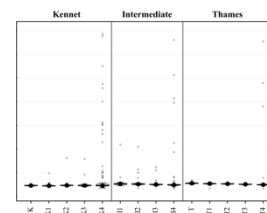
Turbidity



Turbidity ▲



$\text{NO}_3^- \text{-N}$ ▲



Spatial Distribution of Water Quality

All variables:
 Kruskal-Wallis $P < 0.0001$
 Effect size (ϵ^2): 0.48 – 0.86

Dunn's post-hoc pairwise tests with false discovery rate (FDR) correction showed that 69.5% zone pairs differed significantly, with 90.2% of those significant pairs showing large effect sizes (Cliff's Delta, $|\delta| > 0.5$)

■ K ■ K1 ■ K2 ■ K3 ■ K4 ■ I1 ■ I2 ■ I3 ■ I4 ■ T1 ■ T2 ■ T3 ■ T4



River Thames

Field Conditions

Spatial Distribution of
Water Quality

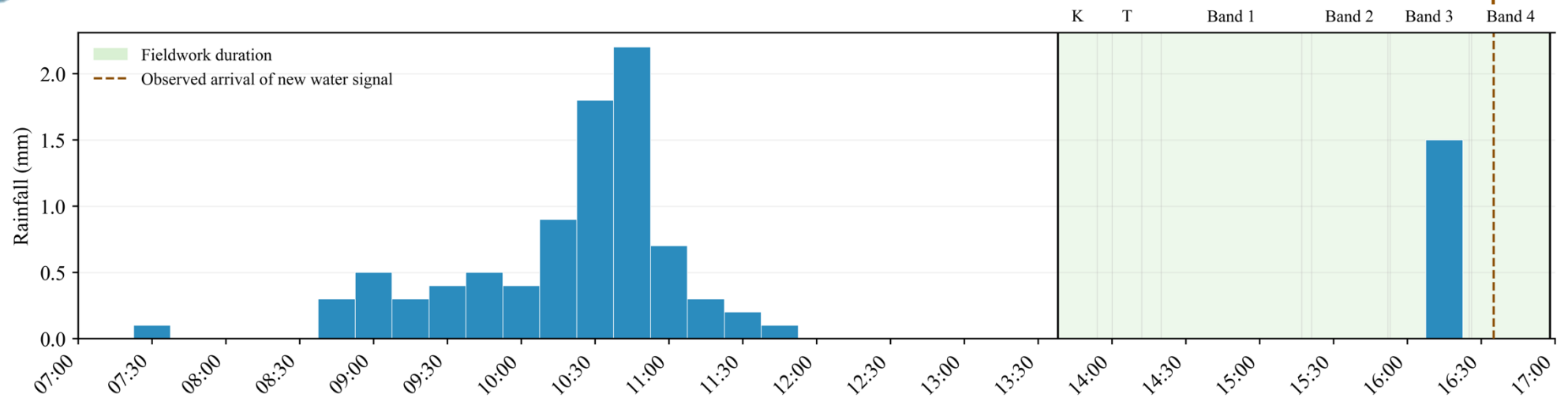
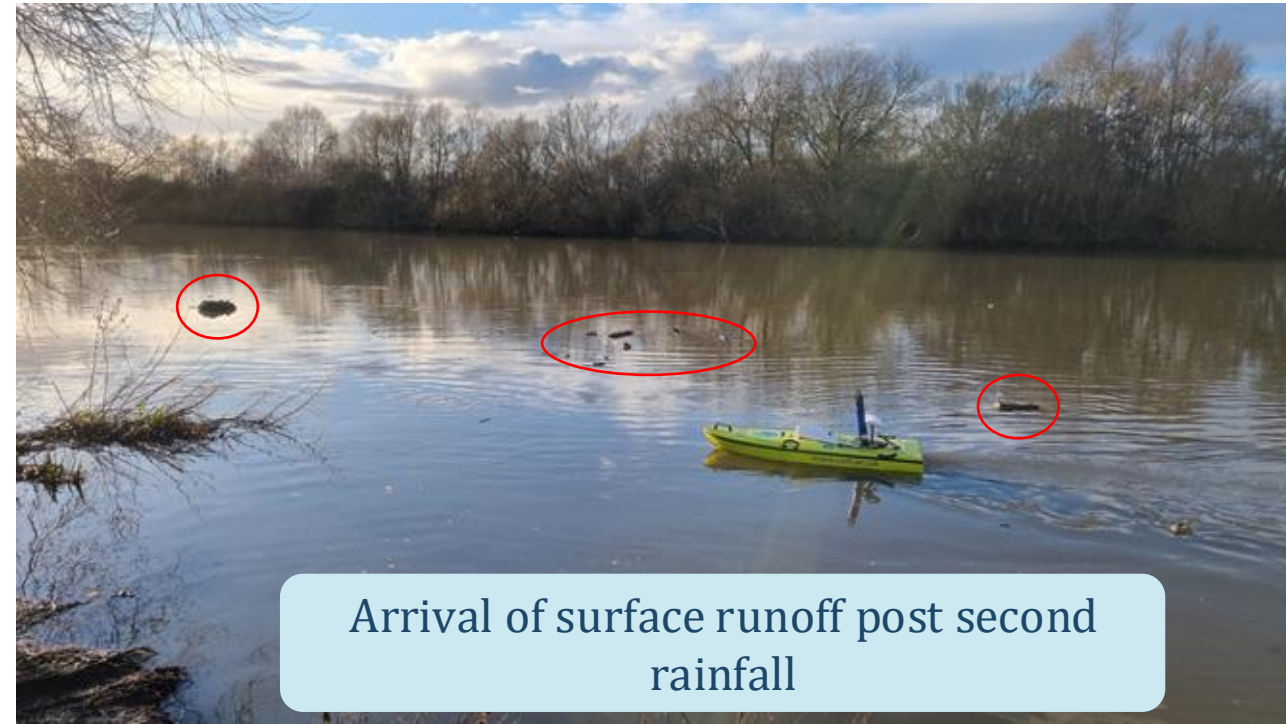
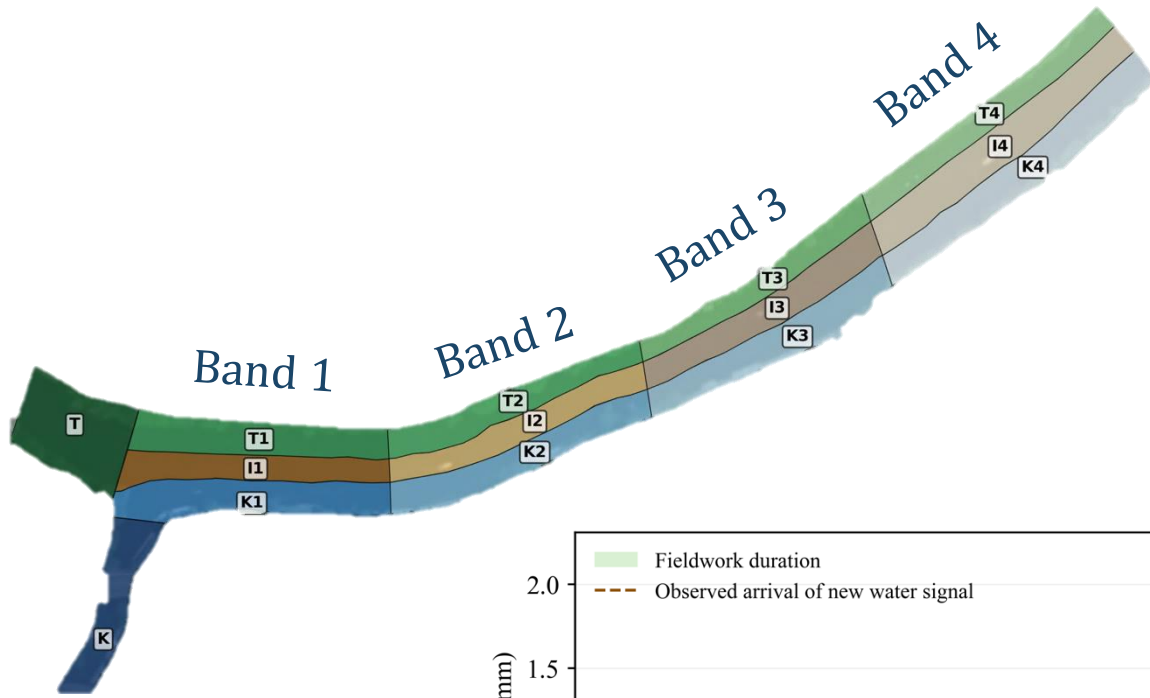
Disentangling the
Nutrient Signals

Bridging Hydrodynamics
and Hydrochemistry

River Kennet



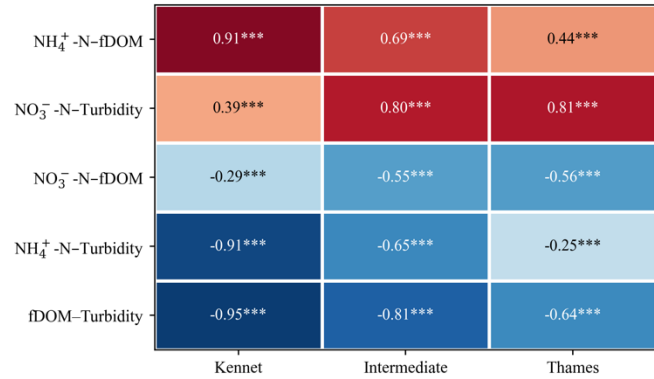
Field Conditions



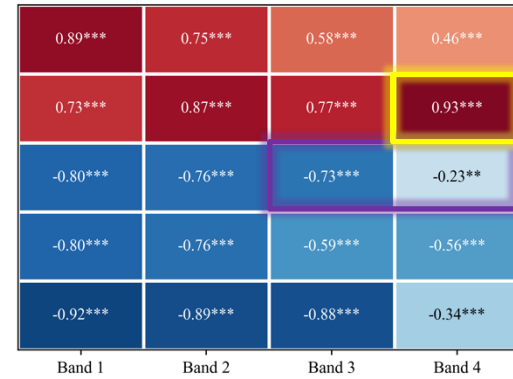


Disentangling the Nutrient Signals

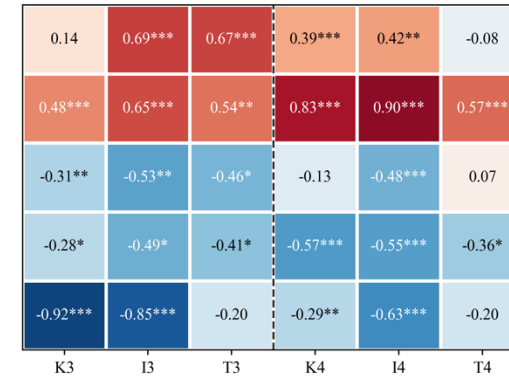
a Spearman correlation across lateral corridors



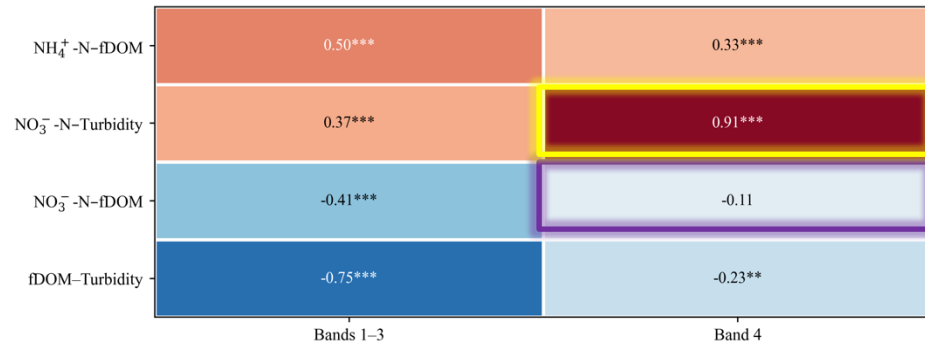
b Spearman correlation along downstream bands



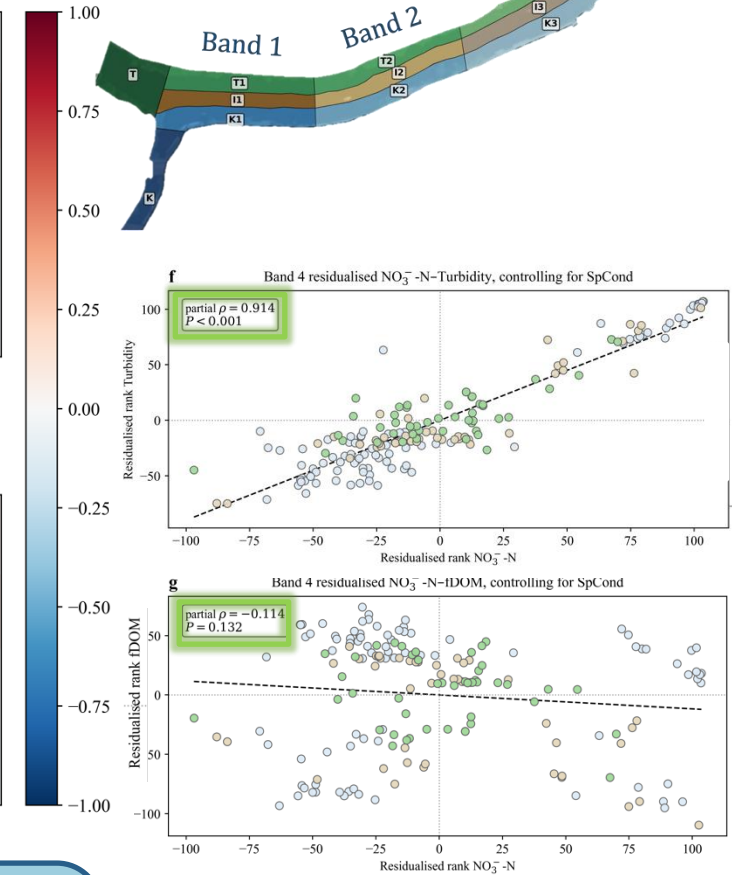
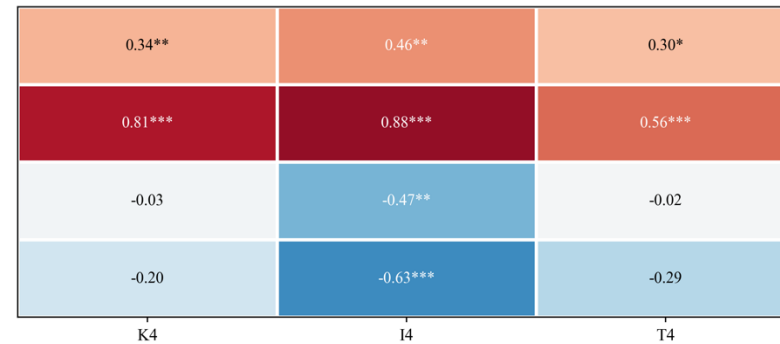
c Spearman correlation across transition zones



d Partial correlation contrast between Bands 1–3 and Band 4, controlling for SpCond



e Partial correlation within Band 4 zones, controlling for SpCond



- i. After controlling for conservative mixing (SpCond), the NO_3^- -N-turbidity relationship in Band 4 held firm (partial $\rho = 0.91$), indicating the relationship was not a product of mixing.
- ii. The NO_3^- -N-fDOM relationship collapsed to non-significant confirming the late nitrate signal was distinct from the earlier dissolved NH_4^+ -N-fDOM signal.

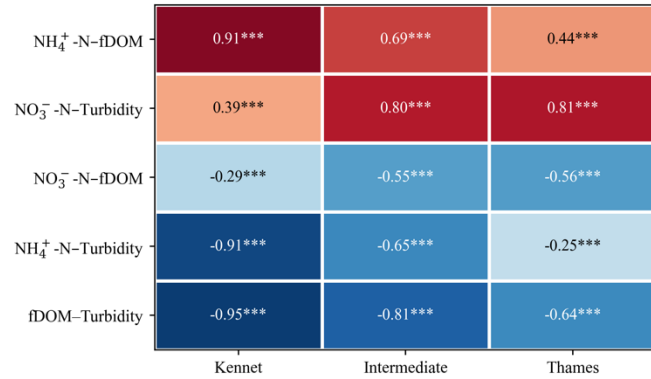
* $P < 0.01$, ** $P < 0.001$, *** $P < 0.0001$

Start of Section

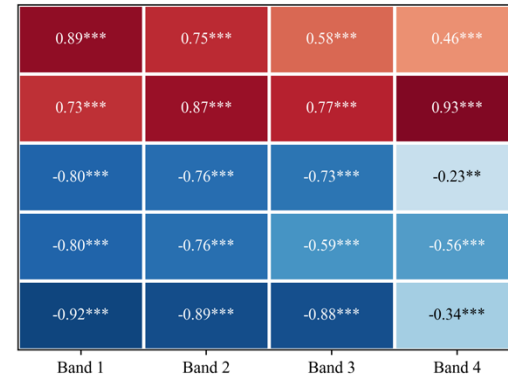


Disentangling the Nutrient Signals

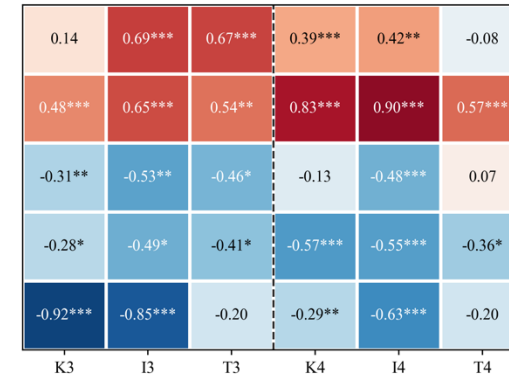
a Spearman correlation across lateral corridors



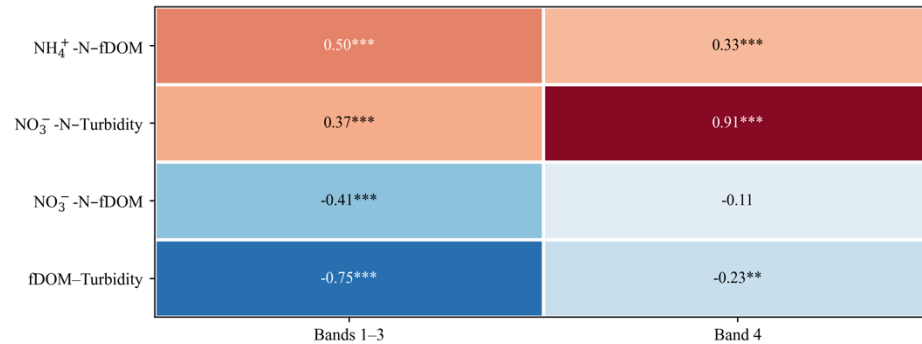
b Spearman correlation along downstream bands



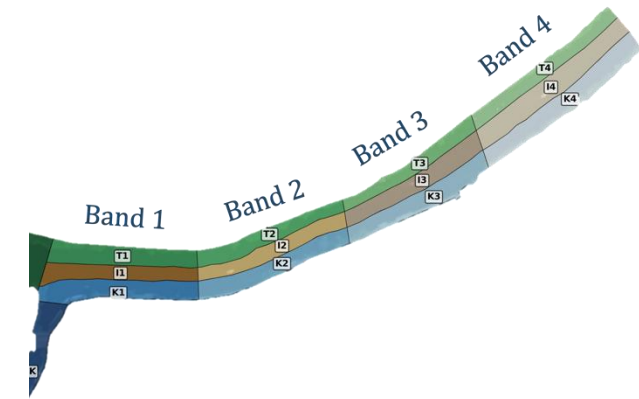
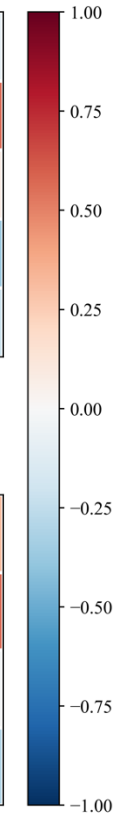
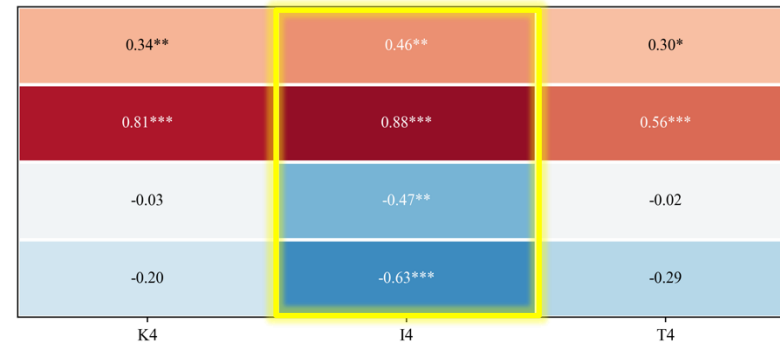
c Spearman correlation across transition zones



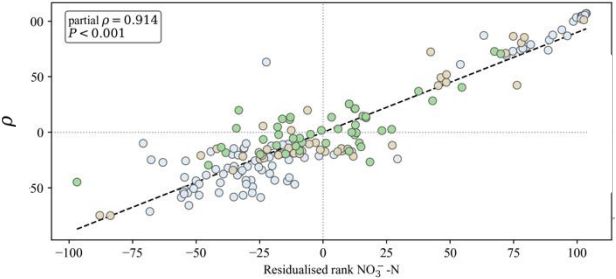
d Partial correlation contrast between Bands 1–3 and Band 4, controlling for SpCond



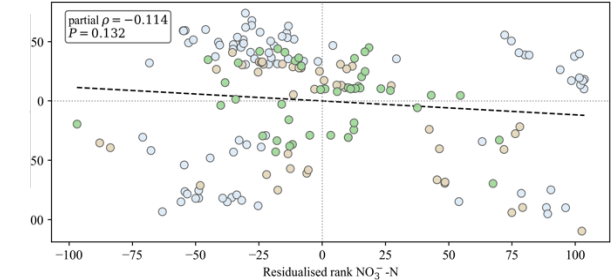
e Partial correlation within Band 4 zones, controlling for SpCond



f Band 4 residualised NO_3^- -N-Turbidity, controlling for SpCond



g Band 4 residualised NO_3^- -N-fDOM, controlling for SpCond



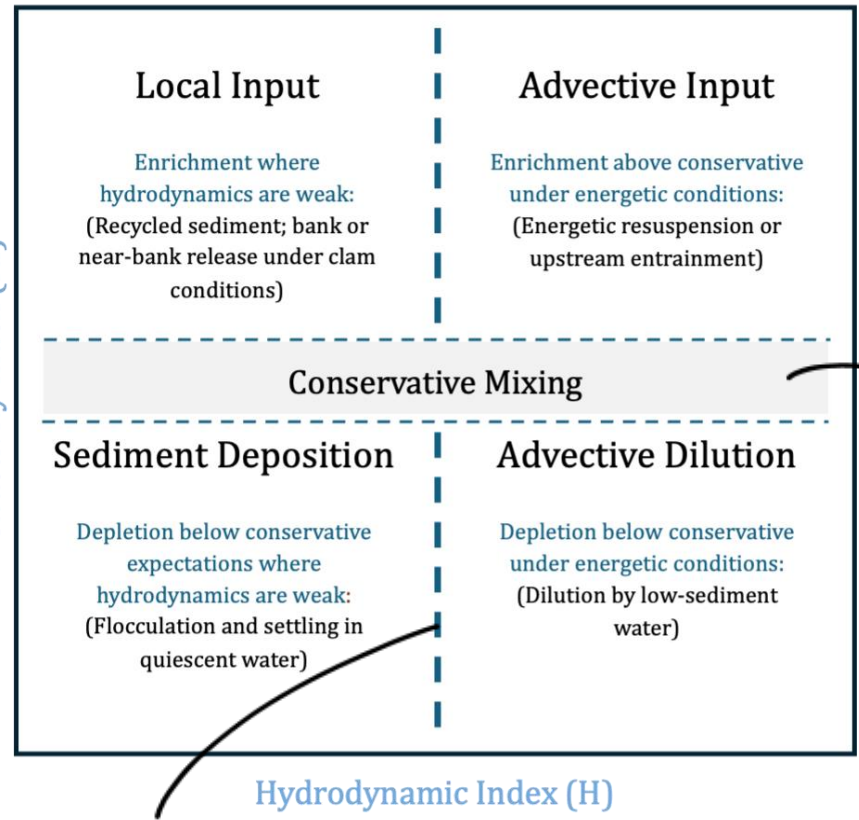
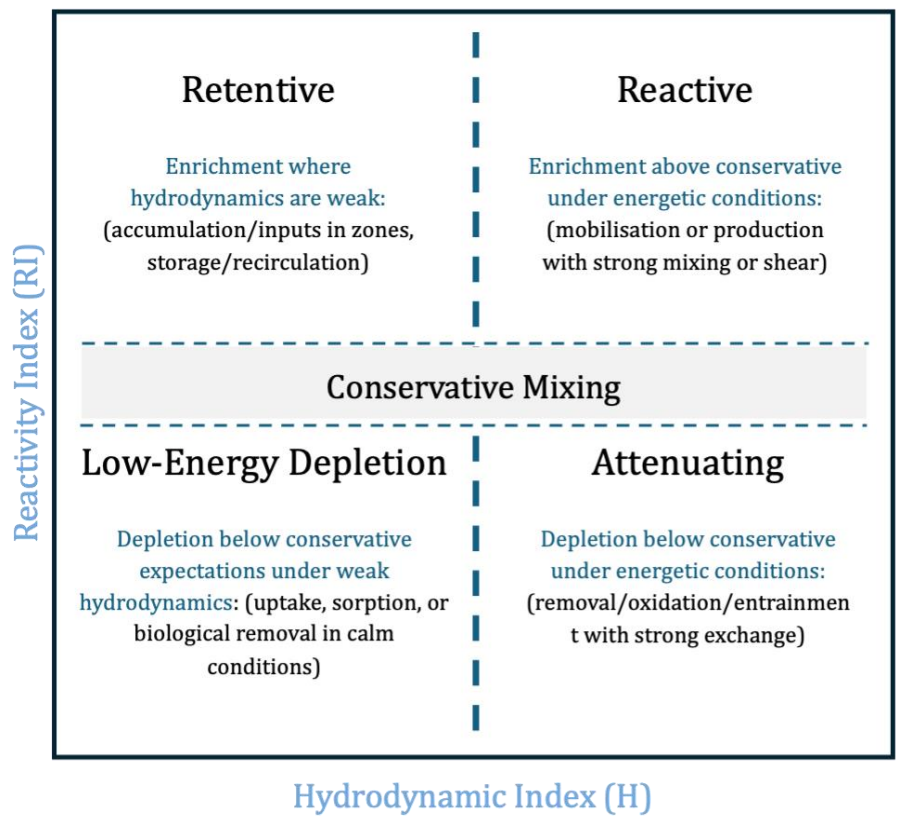
○ K4 ○ I4 ○ T4

- i. Within Band 4, I4 expressed the strongest relationships among the different variables.
- ii. I4 showed a clear juxtaposition of the earlier dissolved signal (NH_4^+ -N-fDOM) and the post-storm pulse (NO_3^- -N-turbidity).
- iii. Here, lateral mixing and the temporal overlap of distinct chemical signals converged at the same location at the same time.

*P < 0.01, **P < 0.001, ***P < 0.0001

Start of Section





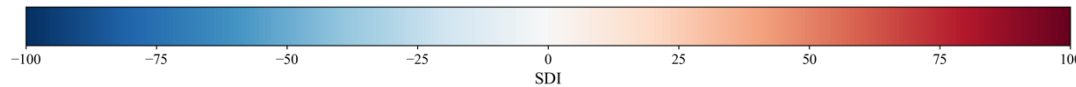
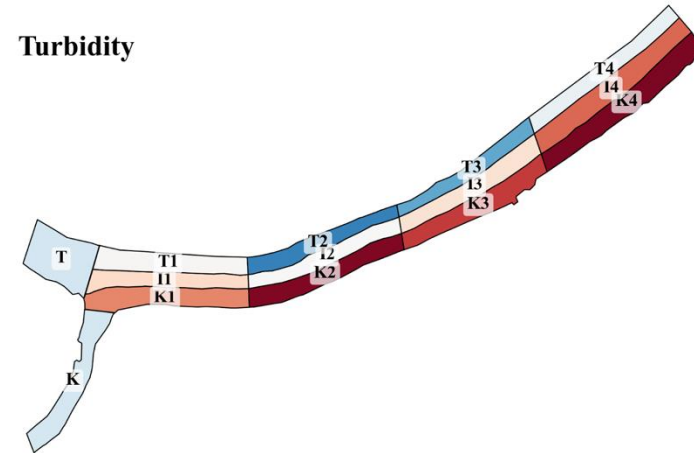
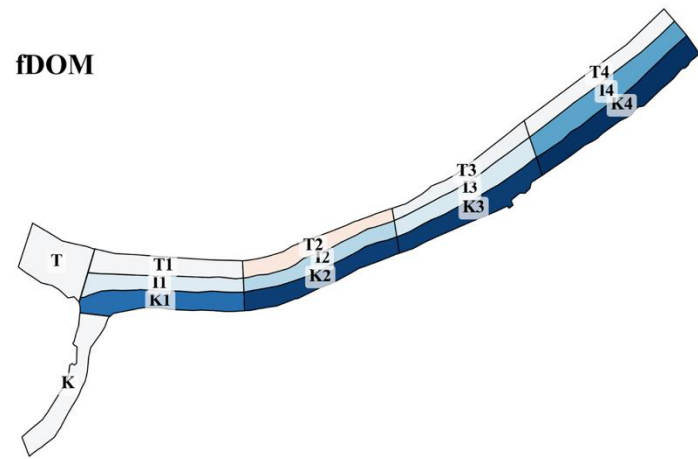
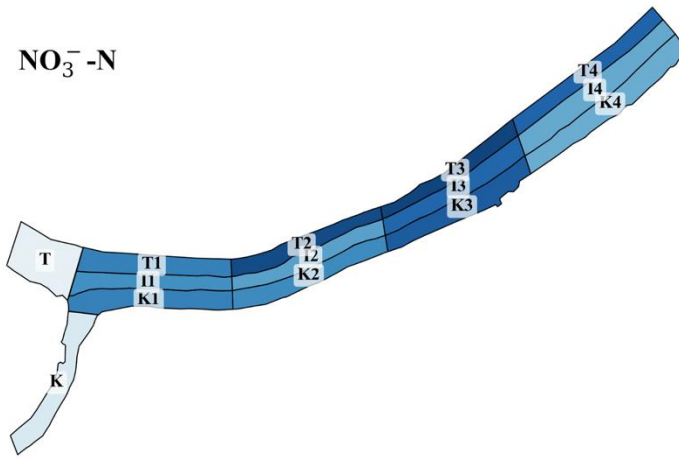
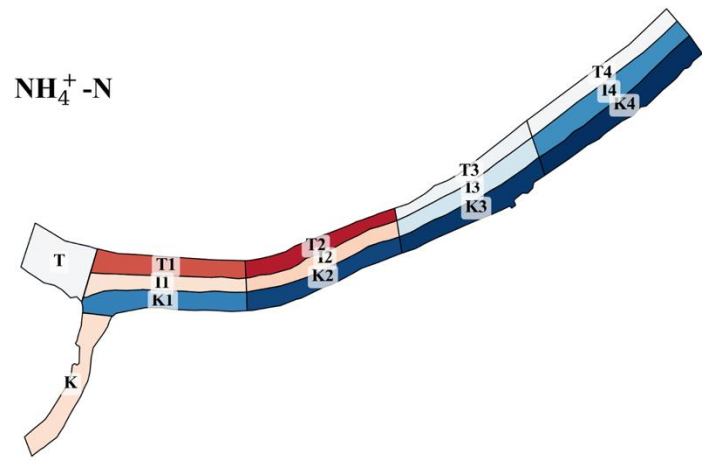
Bridging
Hydrodynamics
and
Hydrochemistry

α – Band (Conservative Threshold)

H^* (Median H across the survey)

The Reactivity –
Hydrodynamic
Index (RI-H)
workflow.

The RI-H workflow classifies each observation by both the direction of its chemical departure from the conservative mixing line and the intensity of near-surface flow. This approach links the chemical nature of water to how it is moving physically.



Source-Sink Dominance Index (SDI)

Through the RI-H workflow, mosaics of source-like and sink-like behaviour (with respect to the mixing line) can be mapped.

$$SDI_{solute} = (Retentive \% + Reactive \%) - (Attenuating \% + Low\ energy\ depletion \%)$$

Environmental Act 2021, UK

Monitoring quality of water potentially affected by discharges

- (1) In Chapter 4 of Part 4 of the Water Industry Act 1991, after section 141DA insert—
- “141DB Monitoring quality of water potentially affected by discharges from storm overflows and sewage disposal works**
- (1) A sewerage undertaker whose area is wholly or mainly in England must continuously monitor the quality of water upstream and downstream of an asset within subsection (2) for the purpose of obtaining the information referred to in subsection (3).
- (2) The assets referred to in subsection (1) are—
- a storm overflow of the sewerage undertaker, and
 - sewage disposal works comprised in the sewerage system of the sewerage undertaker,
- where the storm overflow or works discharge into a watercourse.
- (3) The information referred to in subsection (1) is information as to the quality of the water by reference to—
- levels of dissolved oxygen,
 - temperature and pH values,
 - turbidity,
 - levels of ammonia, and
 - anything else specified in regulations made by the Secretary of State.
- (4) The duty of a sewerage undertaker under this section is enforceable under section 18 by—
- the Secretary of State, or
 - the Authority, with the consent of or in accordance with a general authorisation given by the Secretary of State.

EU Water Framework Directive 2000

1.3.2. Design of operational monitoring

Operational monitoring shall be undertaken in order to:

- establish the status of those bodies identified as being at risk of failing to meet their environmental objectives, and
- assess any changes in the status of such bodies resulting from the programmes of measures.

The programme may be amended during the period of the river basin management plan in the light of information obtained as part of the requirements of Annex II or as part of this Annex, in particular to allow a reduction in frequency where an impact is found not to be significant or the relevant pressure is removed.

Selection of monitoring sites

Operational monitoring shall be carried out for all those bodies of water which on the basis of either the impact assessment carried out in accordance with Annex II or surveillance monitoring are identified as being at risk of failing to meet their environmental objectives under Article 4 and for those bodies of water into which priority list substances are discharged. Monitoring points shall be selected for priority list substances as specified in the legislation laying down the relevant environmental quality standard. In all other cases, including for priority list substances where no specific guidance is given in such legislation, monitoring points shall be selected as follows:

- for bodies at risk from significant point source pressures, sufficient monitoring points within each body in order to assess the magnitude and impact of the point source. Where a body is subject to a number of point source pressures monitoring points may be selected to assess the magnitude and impact of these pressures as a whole,
- for bodies at risk from significant diffuse source pressures, sufficient monitoring points within a selection of the bodies in order to assess the magnitude and impact of the diffuse source pressures. The selection of bodies shall be made such that they are representative of the relative risks of the occurrence of the diffuse source pressures, and of the relative risks of the failure to achieve good surface water status,
- for bodies at risk from significant hydromorphological pressure, sufficient monitoring points within a selection of the bodies in order to assess the magnitude and impact of the hydromorphological pressures. The selection of bodies shall be indicative of the overall impact of the hydromorphological pressure to which all the bodies are subject.

Water Act 2007, Australia

45. Measurements of Water Quantity and Quality

The Authority must establish, maintain and operate an effective and uniform system:

- for making and recording continuous measurements of -
 - the flow of the River Murray, and tributaries of the River Murray within the boundaries of each State; and
 - the volume of stored water,at such locations as the Authority deems necessary to determine the volume of the intake from the several portions of the drainage area of the River Murray, the flow at selected locations along the River Murray and the losses from selected reaches of the River Murray, with their positions and modes of occurrence;
- for making and recording continuous measurements of all diversions, whether natural or artificial, or partly natural and partly artificial, from the River Murray and its tributaries; and
- for measuring and monitoring the quality of -
 - River Murray water;
 - water in tributaries of the River Murray at such locations at or near the confluence of each of those tributaries with the River Murray as the Authority, after consultation with the appropriate authorities of each of the Contracting Governments, deems necessary; and



Capturing the two Nutrient Signals



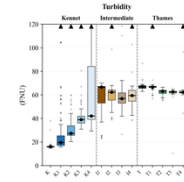
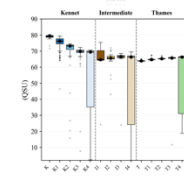
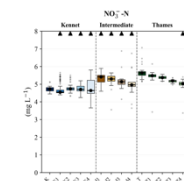
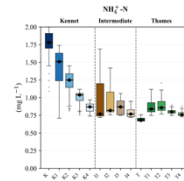
Two chemically independent nitrogen signals from the same tributary, an ammonium pulse and a storm-derived nitrate signal, coexisted in the same downstream cross-section.

e Partial correlation within Band 4 zones, controlling for SpCod

	K4	I4	T4
K4	0.34**	0.40**	0.30*
I4	0.01***	0.83***	0.25***
T4	-0.05	0.27**	-0.02
	K4	I4	T4
	-0.26	-0.63***	-0.29

Confluence Corridors

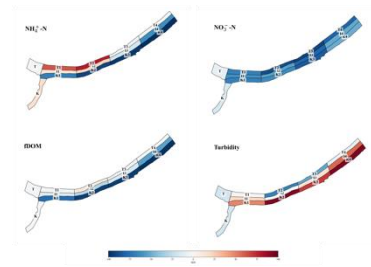
Persistence of laterally distinct hydrochemical corridors.



Legend for confluence corridors: K1, K2, K3, K4, I1, I2, I3, I4, T1, T2, T3, T4

The RI-H Workflow

Our study has resolved source and sink behaviour coexisting simultaneously for the same variable, within the same reach of the river.



Monitoring Regulations at Confluences

Existing regulatory frameworks do not specify which bank to monitor at river confluences.

45. Measurements of Water Quantity and Quality

The Authority must establish, maintain and operate an effective and uniform system:

- (a) for making and recording continuous measurements of -
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 - (ii) the volume of stored water,

at such locations as the Authority deems necessary to determine the volume of the intake from the several portions of the drainage area of the River Murray, the flow at selected locations along the River Murray and the losses from selected reaches of the River Murray, with their positions and modes of occurrence;

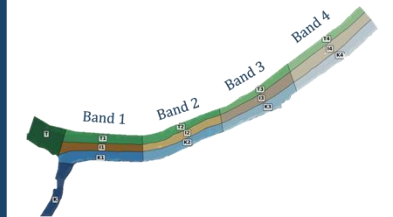
- (b) for making and recording continuous measurements of all diversions, whether natural or artificial, or partly natural and partly artificial, from the River Murray and its tributaries; and

- (c) for measuring and monitoring the quality of -

- (i) River Murray water;
- (ii) water in tributaries of the River Murray at such locations as or near the confluence of each of those tributaries with the River Murray as the Authority, after consultation with the appropriate authorities of each of the Contracting Governments, deems necessary, and

The Framework

Our framework provides a transferable diagnostic approach to screen potential zones for further hotspot and hot moment studies.



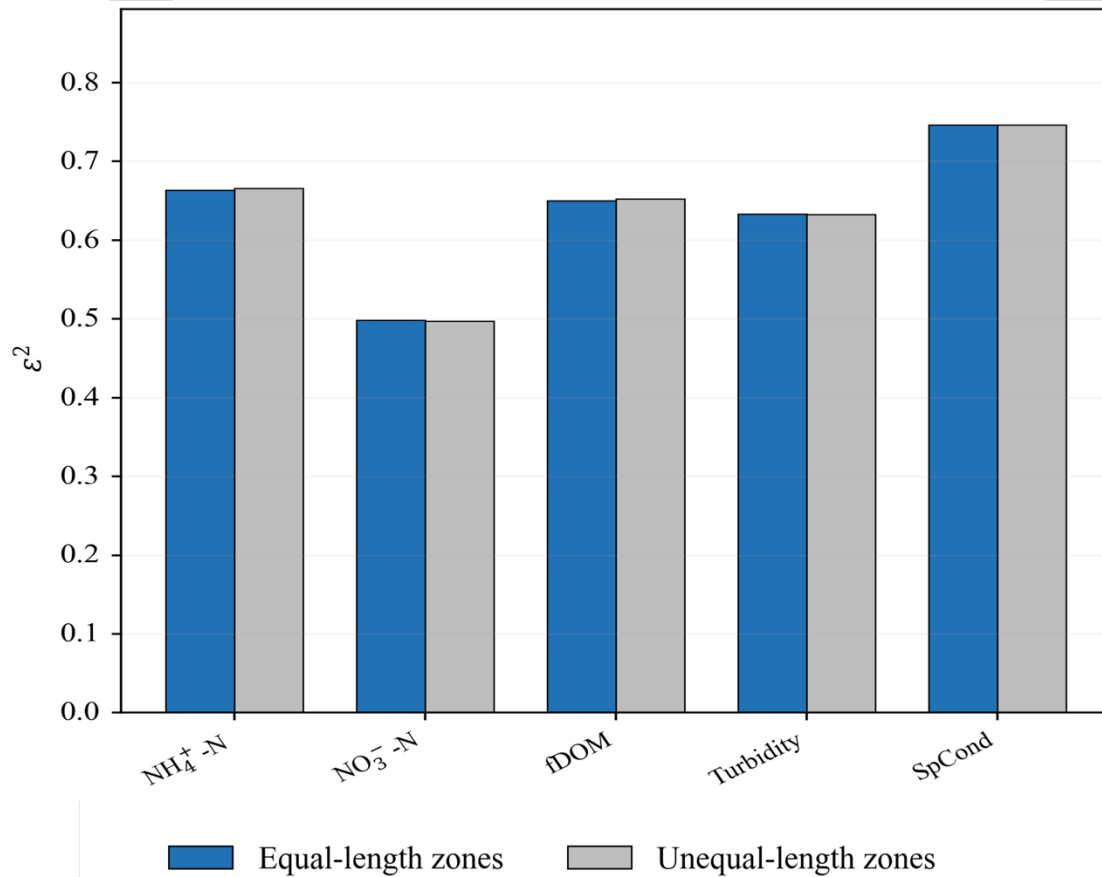
Supplementary Information

Sensitivity Analysis

The main findings of this study rest on three analytical choices: the definition of the conservative band (α) width around $RI = 0$, the hydrodynamic threshold used to separate energetic and quiescent conditions for observations, and the ADCP bin pair used to derive the near-surface hydrodynamic index. A fourth check tested whether the spatial distribution of the four variables (Ammonium, Nitrate, fluorescent Dissolved Organic Matter (fDOM), and Turbidity) captured by the zone scheme depended materially on the choice of downstream band lengths.

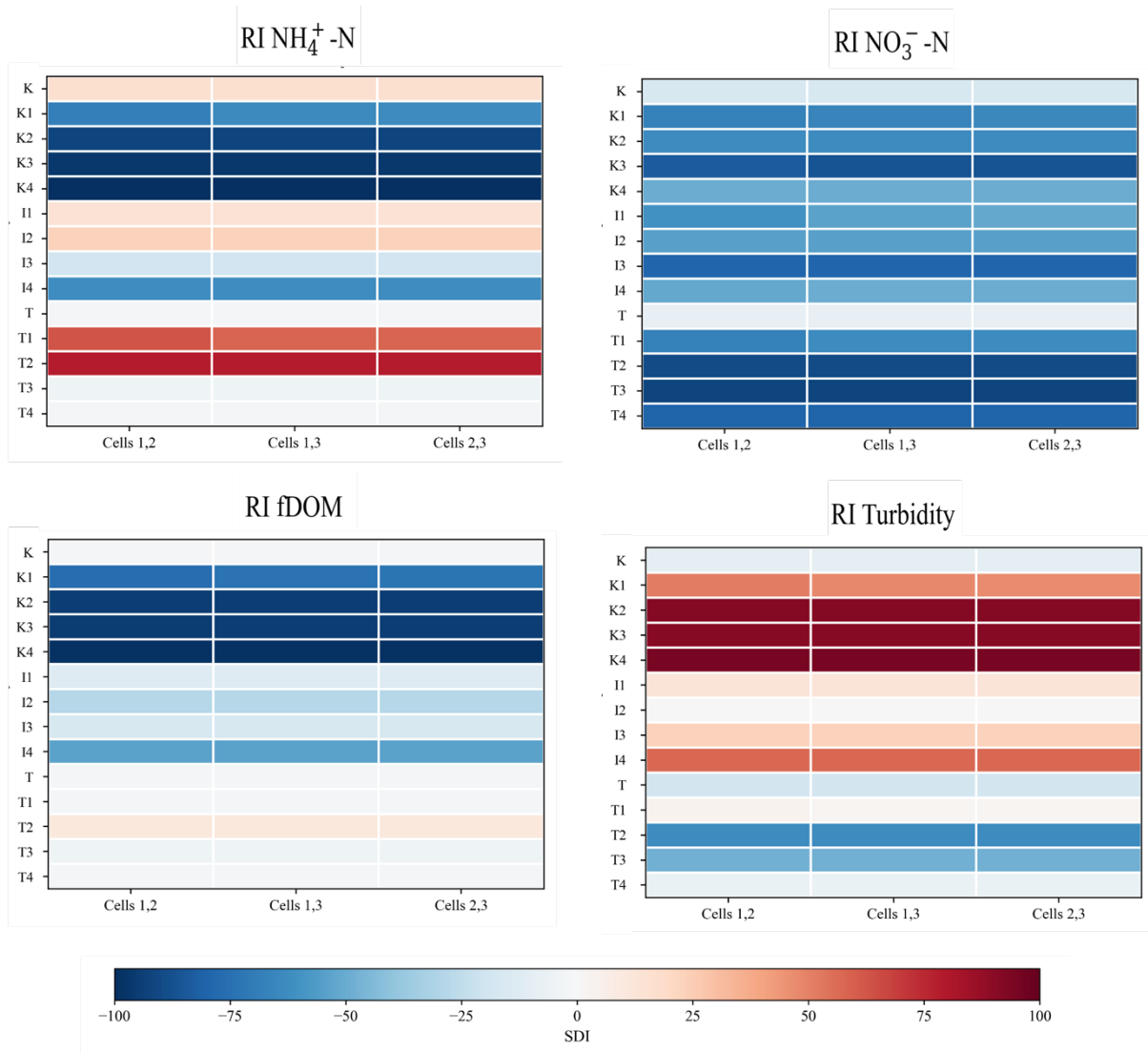
The framework was robust to the hydrodynamic threshold choice and to the zone scheme comparison, with negligible changes in the Source-Sink Dominance Index (SDI) across alternative thresholds. ADCP bin-pair sensitivity was generally modest and did not alter the main spatial patterns, noting that Cells 1 and 2 were selected as the primary bin pair because they most closely matched the deployment depth of the YSI EXO2 water quality sonde. The main uncertainty was concentrated in the conservative band width, where turbidity classifications remained highly stable but some dissolved variable classifications in marginal zones, particularly the Thames corridor, where NH_4^+ -N and fDOM, shifted or changed sign at the narrowest band width choice for k when calculating the conservative band (α).

Equal-length vs unequal-length zone schemes



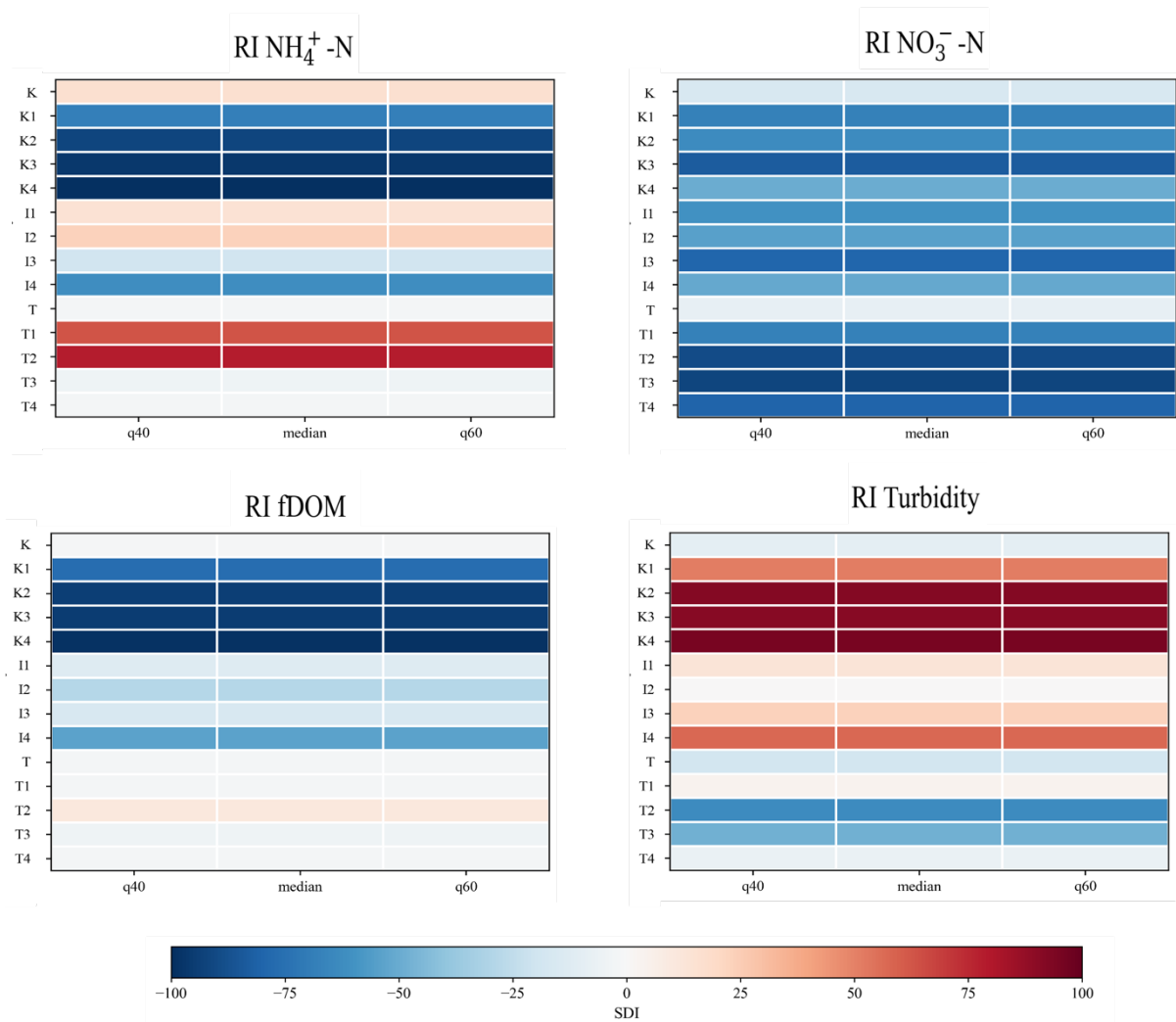
Supplementary Fig. S1 | Sensitivity of spatial organisation of water quality to choice of zoning scheme.

Kruskal-Wallis effect size (ϵ^2) compared between the adopted equal-length zone scheme and an alternative unequal-length zone scheme for $\text{NH}_4^+ \text{-N}$, $\text{NO}_3^- \text{-N}$, fDOM, turbidity and specific conductivity (SpCond) on 26 February 2025. Higher ϵ^2 indicates stronger separation among zones. Differences between the two schemes were small across all variables, therefore lateral hydrochemical organisation did not depend on the choice of downstream band lengths.



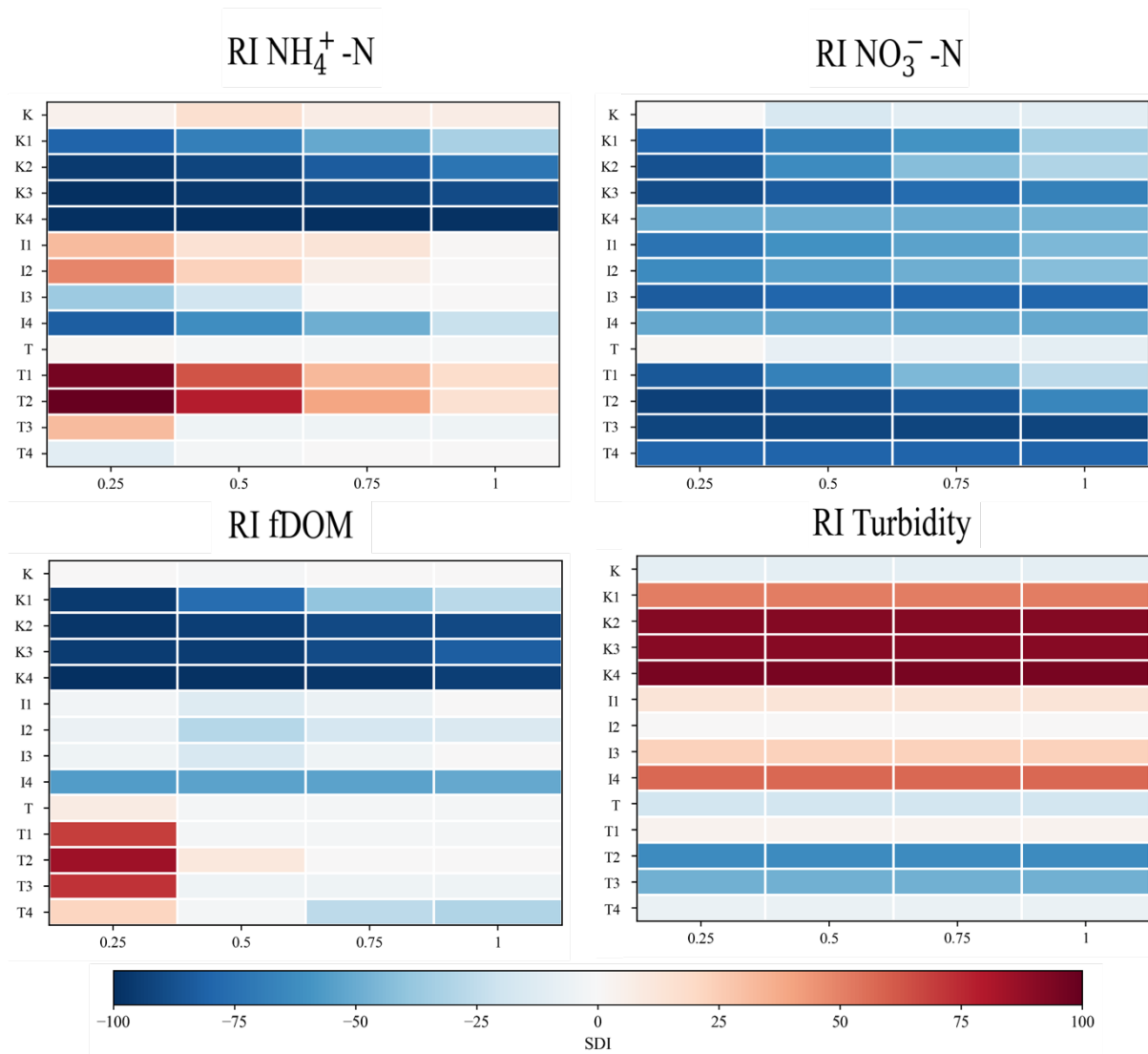
Supplementary Fig. S2 | Sensitivity of SDI to ADCP bin-pair selection.

Source-sink dominance index (SDI) across three tested ADCP bin-pair combinations: Cells 1 and 2 (primary), Cells 1 and 3, and Cells 2 and 3. Panels show results for $\text{NH}_4^+ \text{-N}$, $\text{NO}_3^- \text{-N}$, fDOM and turbidity respectively. Bars are coloured by zone. The primary bin pair (Cells 1 and 2, corresponding to approximately 0.3 m depth) was selected because it most closely matched the deployment depth of the YSI EXO2 multiparameter sonde. SDI values were generally consistent across bin-pair combinations.



Supplementary Fig. S3 | Sensitivity of SDI to the hydrodynamic threshold (H*).

SDI was calculated across three alternative hydrodynamic thresholds: the 40th percentile, the campaign median and the 60th percentile of the hydrodynamic index H. Panels show results for NH₄⁺-N, NO₃⁻-N, fDOM and turbidity respectively. Bars are coloured by zone. SDI values were negligibly sensitive to the choice of threshold across all four variables



Supplementary Fig. S4 | Sensitivity of SDI to the conservative band width (α).

SDI was calculated across four values of the conservative band width multiplier k (0.25, 0.50, 0.75 and 1.00), which controls the width of the band around $\text{RI} = 0$ within which observations are classified as conservative. Panels show results for $\text{NH}_4^+ \text{-N}$, $\text{NO}_3^- \text{-N}$, fDOM and turbidity respectively. Bars are coloured by zone. Turbidity classifications were highly stable across all k values. For dissolved variables, K4 and I4 showed moderate stability, while Thames zones, particularly T4 for $\text{NH}_4^+ \text{-N}$ and fDOM, showed greater sensitivity at the narrowest band width, with some zones shifting sign at $k = 0.25$. Results at $k = 0.50$, the primary analysis setting, are consistent with those at $k = 0.75$ and 1.00 for all zones.