

Stable Isotopes as Tools for Tracing Nutrient Sources and Biogeochemical Cycling:

A Case Study at Esthwaite Water

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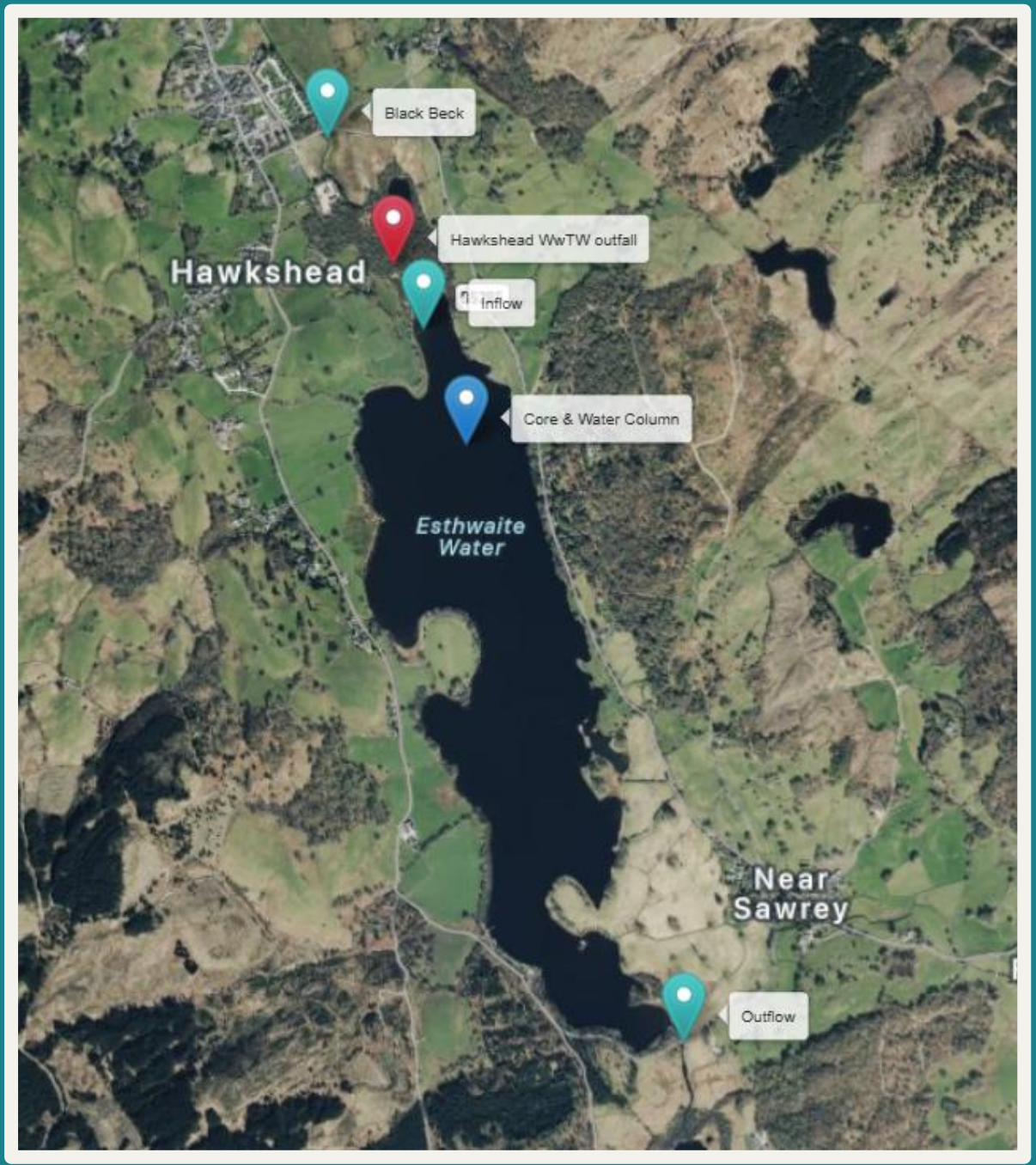
- Andrew Smith, British Geological Survey
- Ellie Mackay, UK CEH
- Gareth McShane, UK CEH

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Loughborough University

National Environmental Isotope Facility

NATURAL ENVIRONMENT RESEARCH COUNCIL



- Reduced external P load (by 55%,1992-2010; Maberly et al., 2011)
- But… recovery has been limited.

- → Internal nutrient loading from sediments

- Summer sediment P release with lake stratification.
  - 38-50 % summer SRP in wet years (2008 and 2014; Mackay et al. 2014)
  - 14 % of annual TP load (Anderson 2018).

- Winter nitrate also rose by ~70 % since 1970
  - attributed to catchment runoff, fish farm activity and atmospheric deposition.
  - Internal loading as well?



Limits of Current Methods

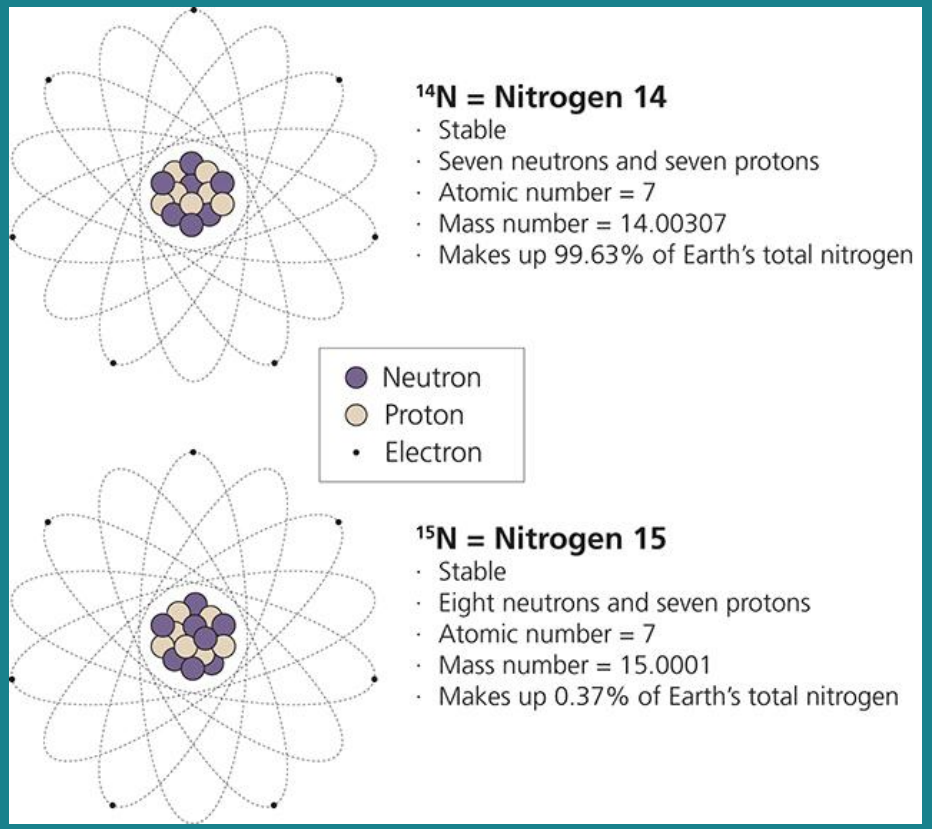
- Nutrient concentration measurements are highly sensitive to spatial and temporal variability.
- Outcome-focused methods that do not directly evaluate processes (that cause concentrations).
- Stable Isotopes as a solution…?

Overview of Stable Isotopes

- Stable isotopes are different forms of the same element.

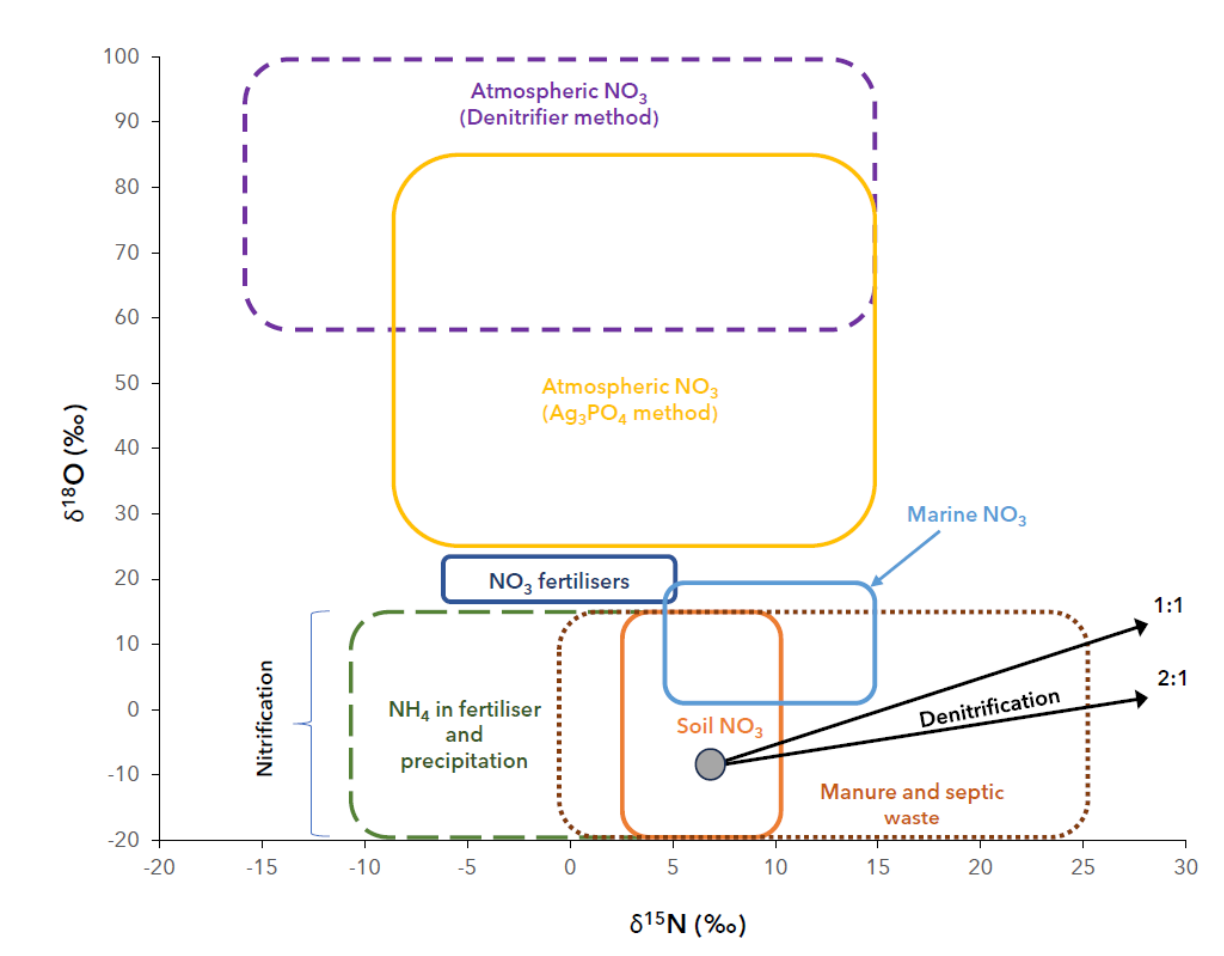
- Biogeochemical processes alter the amount of each isotope → fractionation

- E.g. Organisms will preferentially use up lighter N^{14} before heavier N^{15}
  - Ratio of N^{14} to N^{15} changes in cells/water
  - Higher $\delta^{15}N$ = greater utilisation



Stable Isotopes as Pollution Tracers

Stable isotope can be used to track the source and fate of nutrients



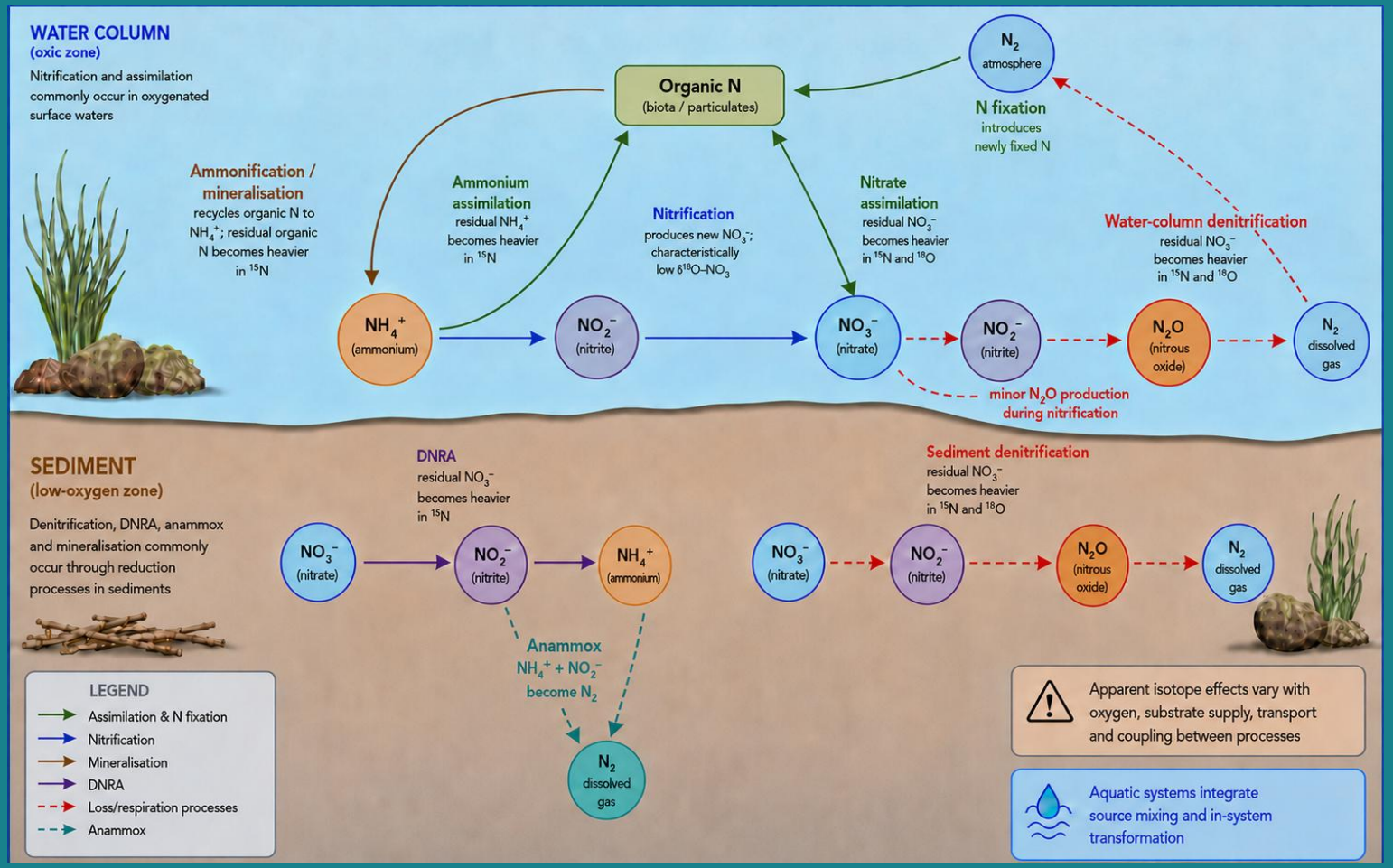
- Different sources have different "end-members"
- E.g. Dual nitrate (NO_3) isotope measurements: $\delta^{15}N$ and $\delta^{18}O$

Worne et al., (2026), modified from Kendall et al., (2007). *Stable isotopes in ecology and environmental science.*

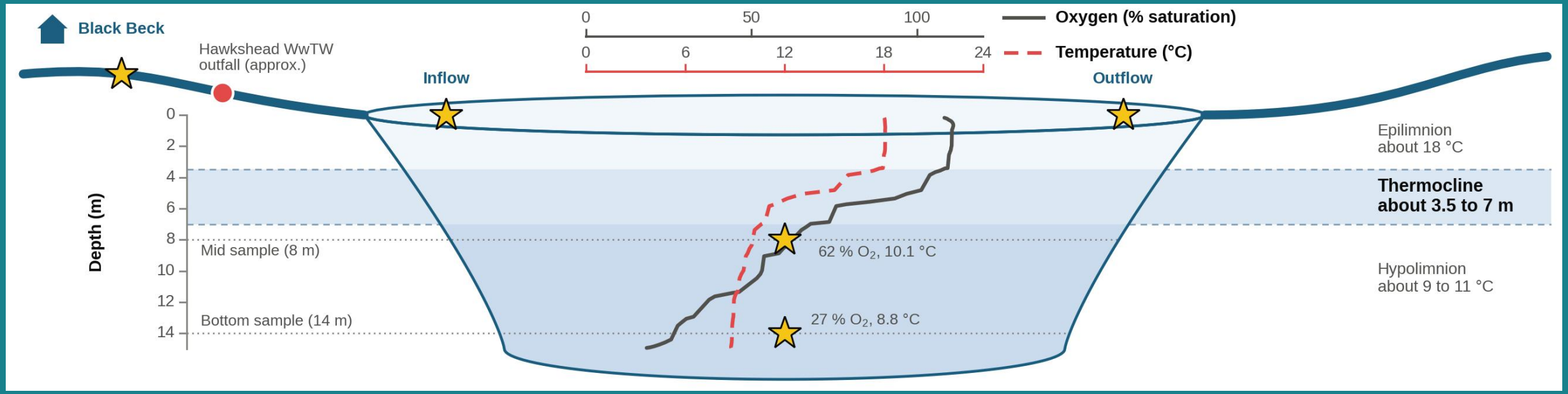
Stable Isotopes as Pollution Tracers

Stable isotope can be used to track the source and fate of nutrients

- Biogeochemical process have known fractionation effects
- Denitrification (anoxic) increases $\delta^{15}N$ and $\delta^{18}O$ of residual nitrate
- Nitrification (oxic) produces new nitrate with low $\delta^{15}N$ and $\delta^{18}O$

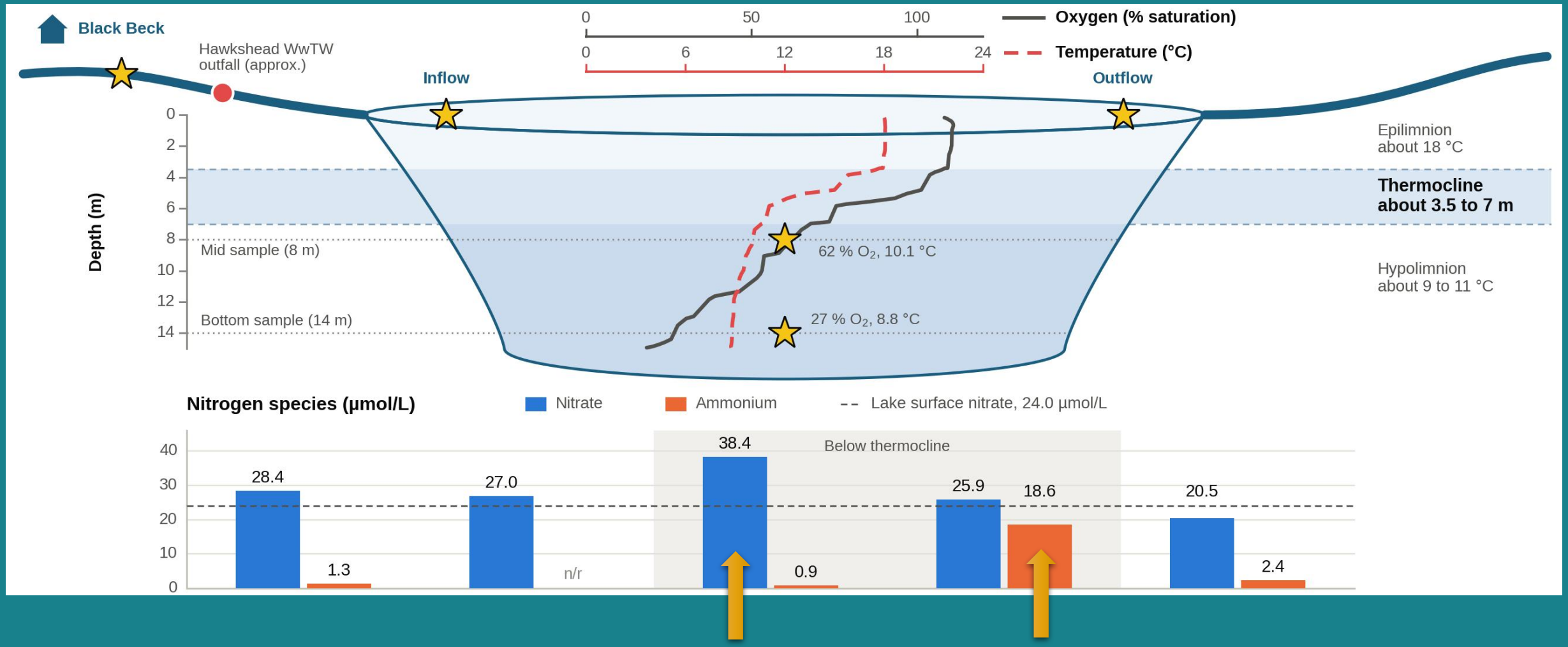


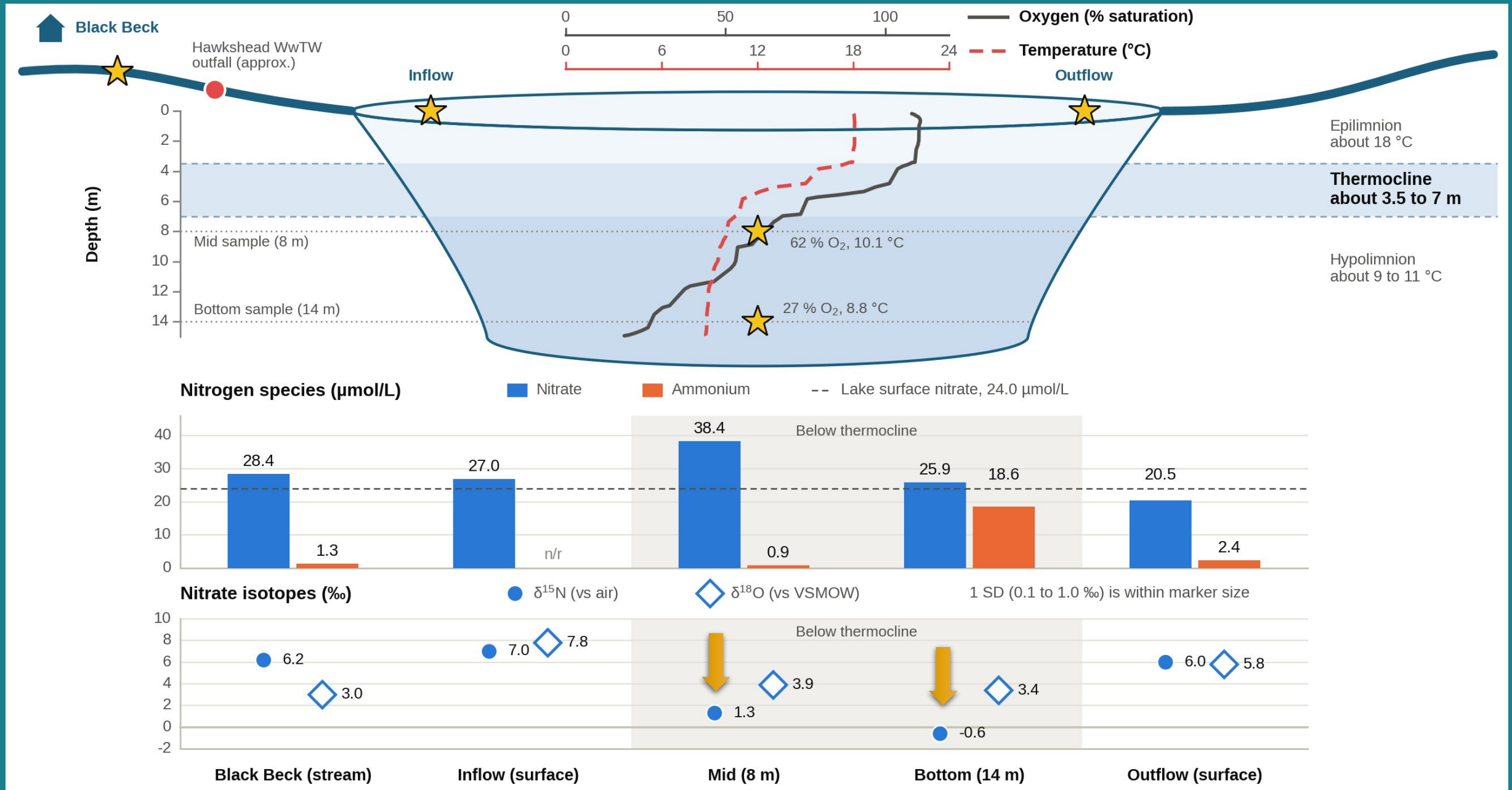
Worne et al., (2026). *Frontiers in Environmental Science.*



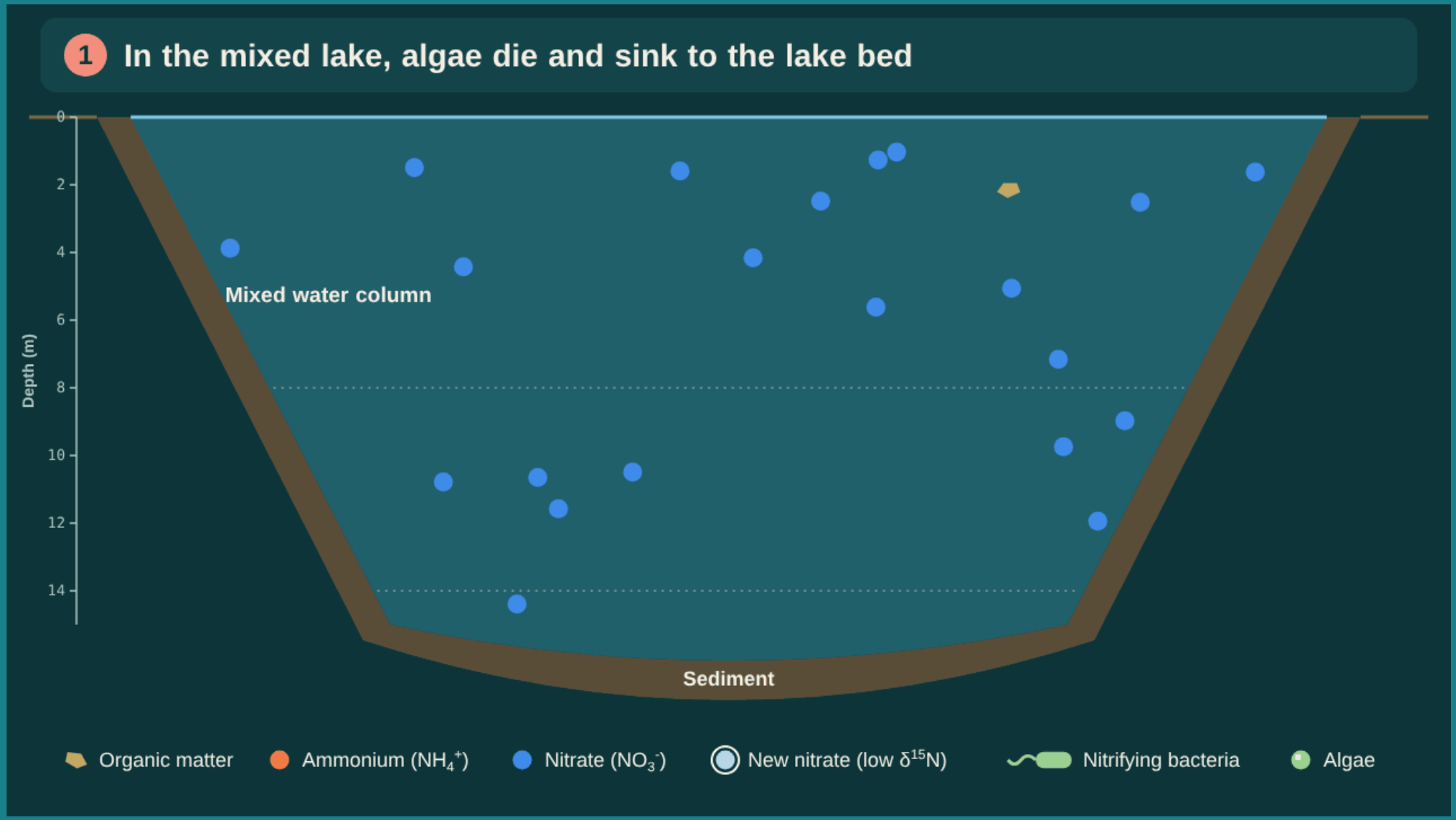
Pilot Study - May 2025

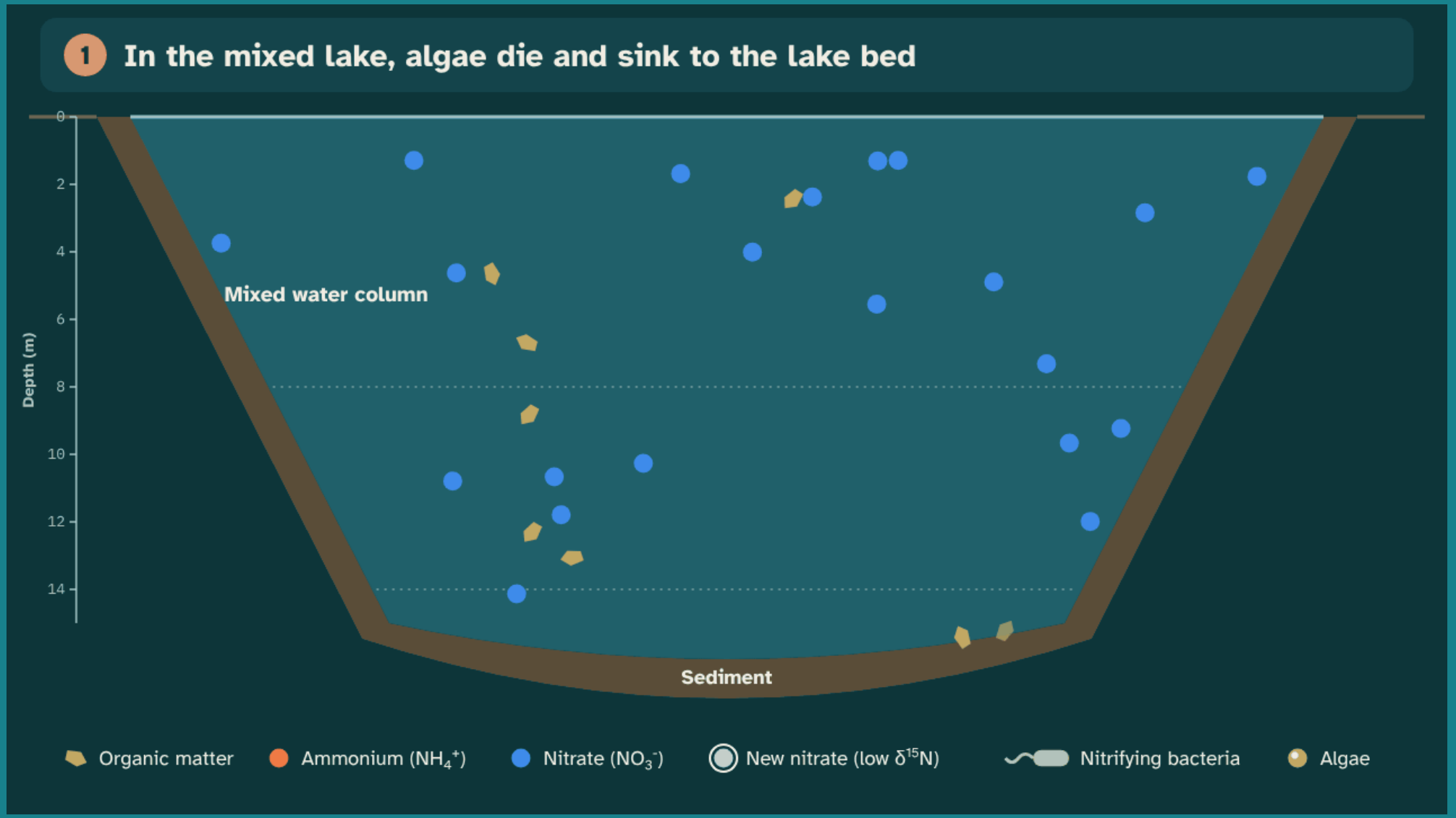
- Water samples in a transect from Black Beck (left), through the lake, to the outflow (right)
  - Samples at surface, mid-depth and bottom at the deepest part of the north basin
  - Black Beck sampled above WwTW (catchment signal)
- Measured the nitrate, nitrite and ammonium concentrations, and isotopes ($\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$, $\delta^{15}N\text{-}NH_4$)

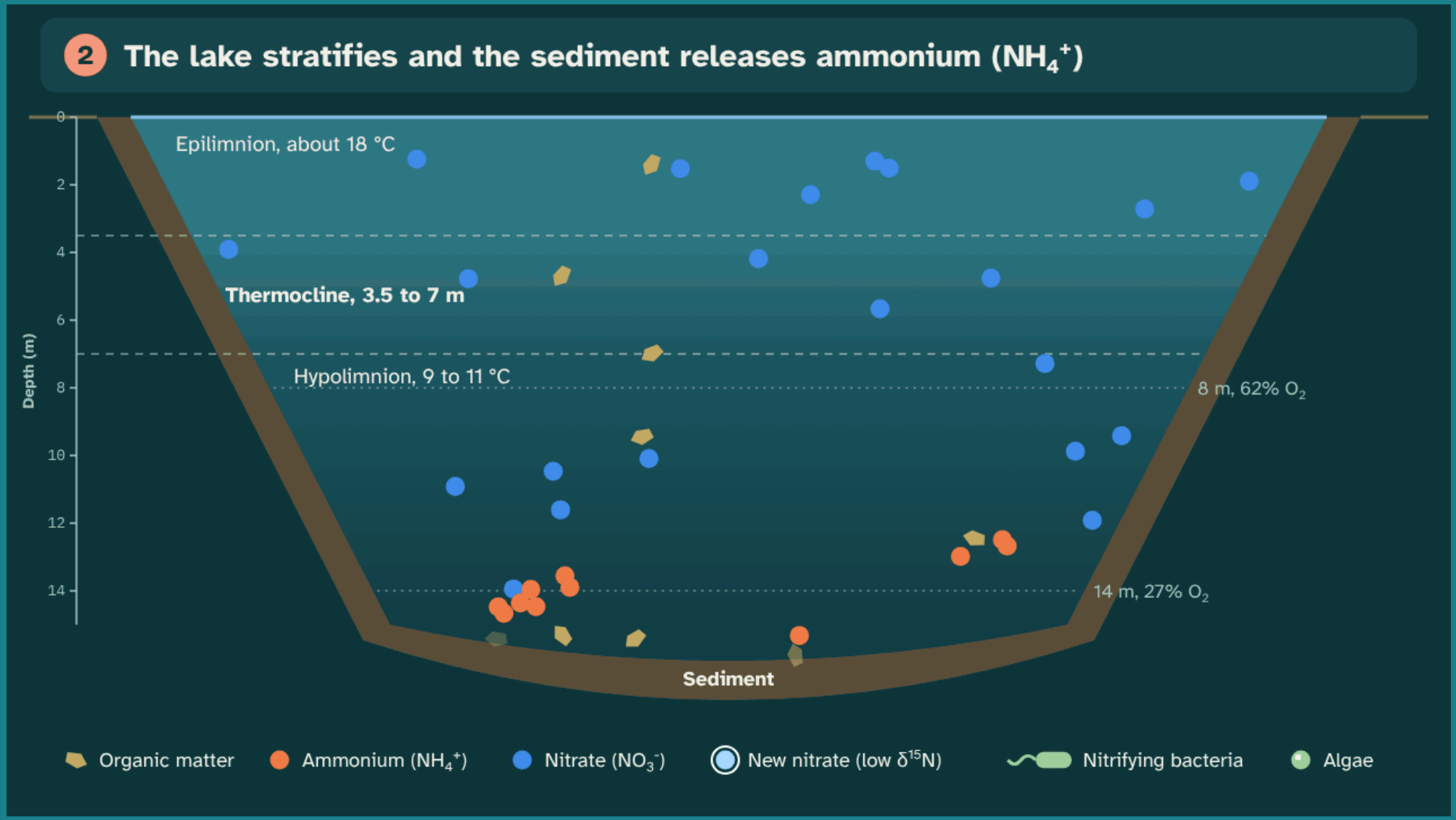

Black Beck
Hawkshead WwTW outfall (approx.)
Inflow
Outflow
0
50
100
Oxygen (% saturation)
0
6
12
18
24
Temperature (°C)
Depth (m)
0
2
4
6
8
10
12
14
Mid sample (8 m)
Bottom sample (14 m)
62 % O2, 10.1 °C
27 % O2, 8.8 °C
Epilimnion
about 18 °C
Thermocline
about 3.5 to 7 m
Hypolimnion
about 9 to 11 °C
Nitrogen species (µmol/L)
Nitrate
Ammonium
Lake surface nitrate, 24.0 µmol/L
40
30
20
10
0
28.4
1.3
27.0
n/r
38.4
0.9
Below thermocline
25.9
18.6
20.5
2.4

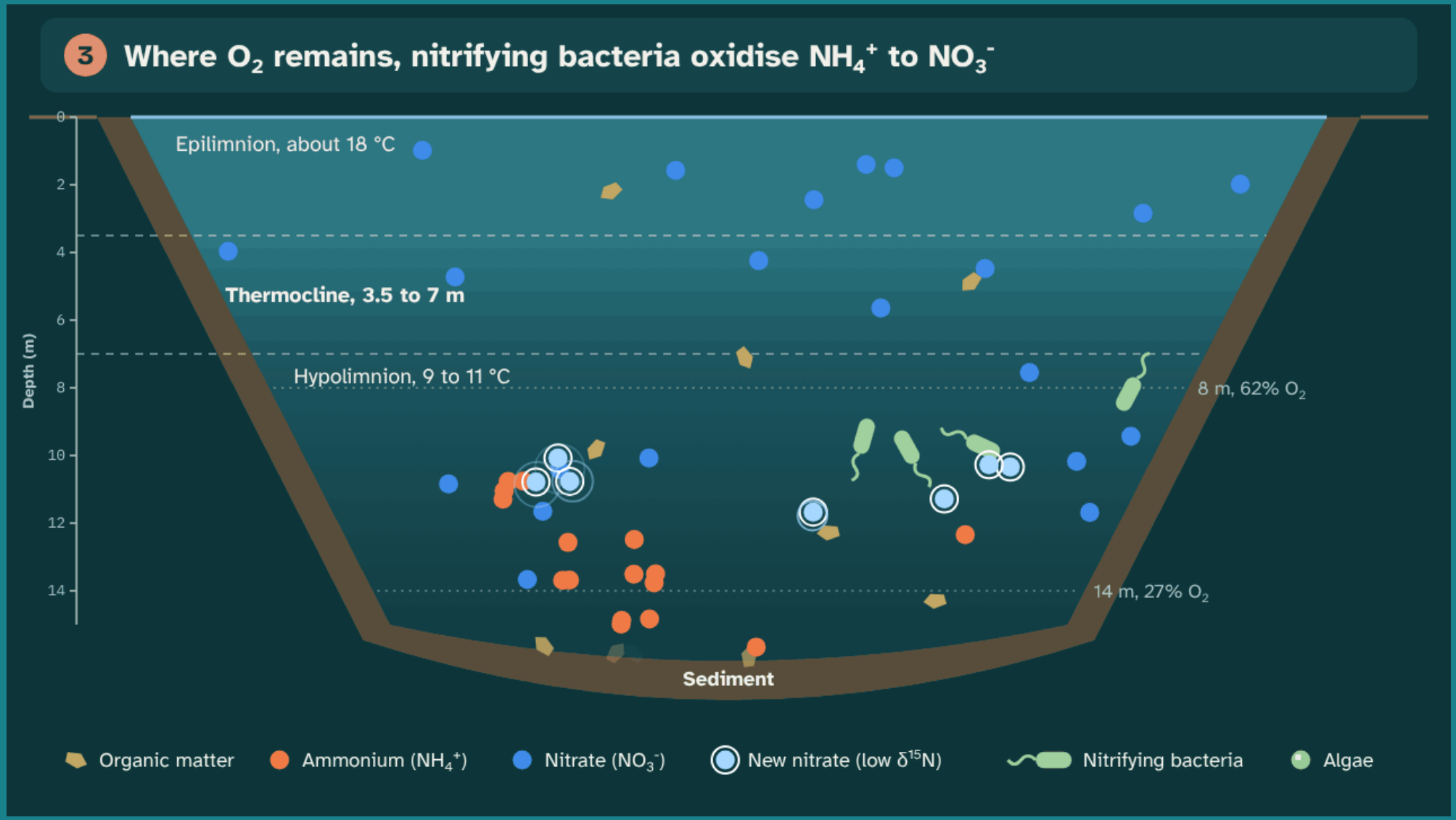


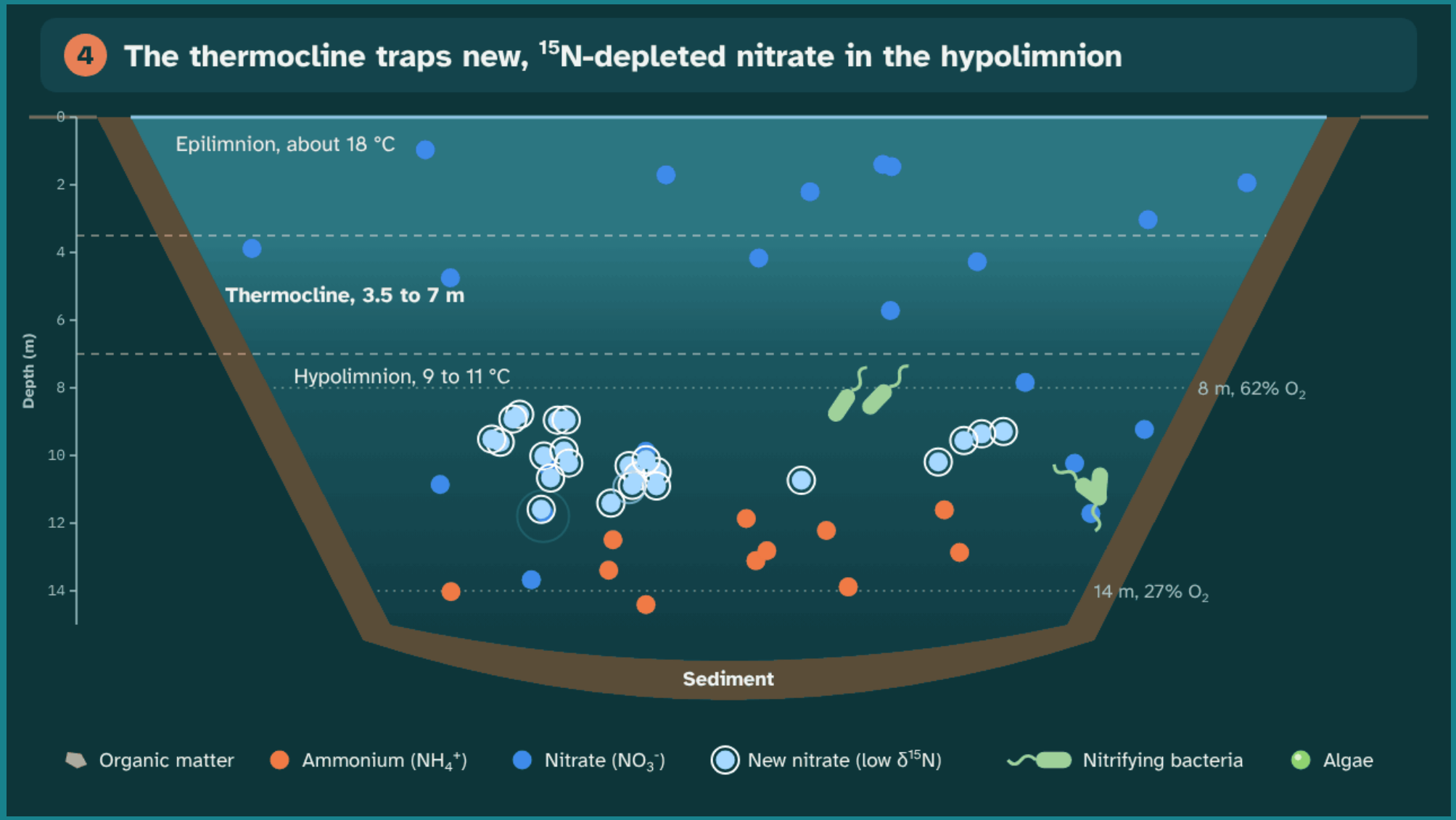
Esthwaite Water, 22 May 2025. Single sampling date; preliminary. Mid (8 m) and bottom (14 m) sample depths are approximate; horizontal scale is schematic.
Profile is the downcast only; oxygen at depth may be over-read by sensor lag (upcast: 14 to 18 % at the bottom). Thermocline: downcast gradient above 1 °C per m.
Nitrate and ammonium by ion chromatography (mg/L as NO_3^- and NH_4^+, converted to µmol/L); n/r, not reported. Isotopes are of nitrate. Red dot: approximate WwTW outfall.


1 In the mixed lake, algae die and sink to the lake bed
Depth (m)
0
2
4
6
8
10
12
14
Mixed water column
Sediment
Organic matter
Ammonium (NH_4^+)
Nitrate (NO_3^-)
New nitrate (low $\delta^{15}N$)
Nitrifying bacteria
Algae

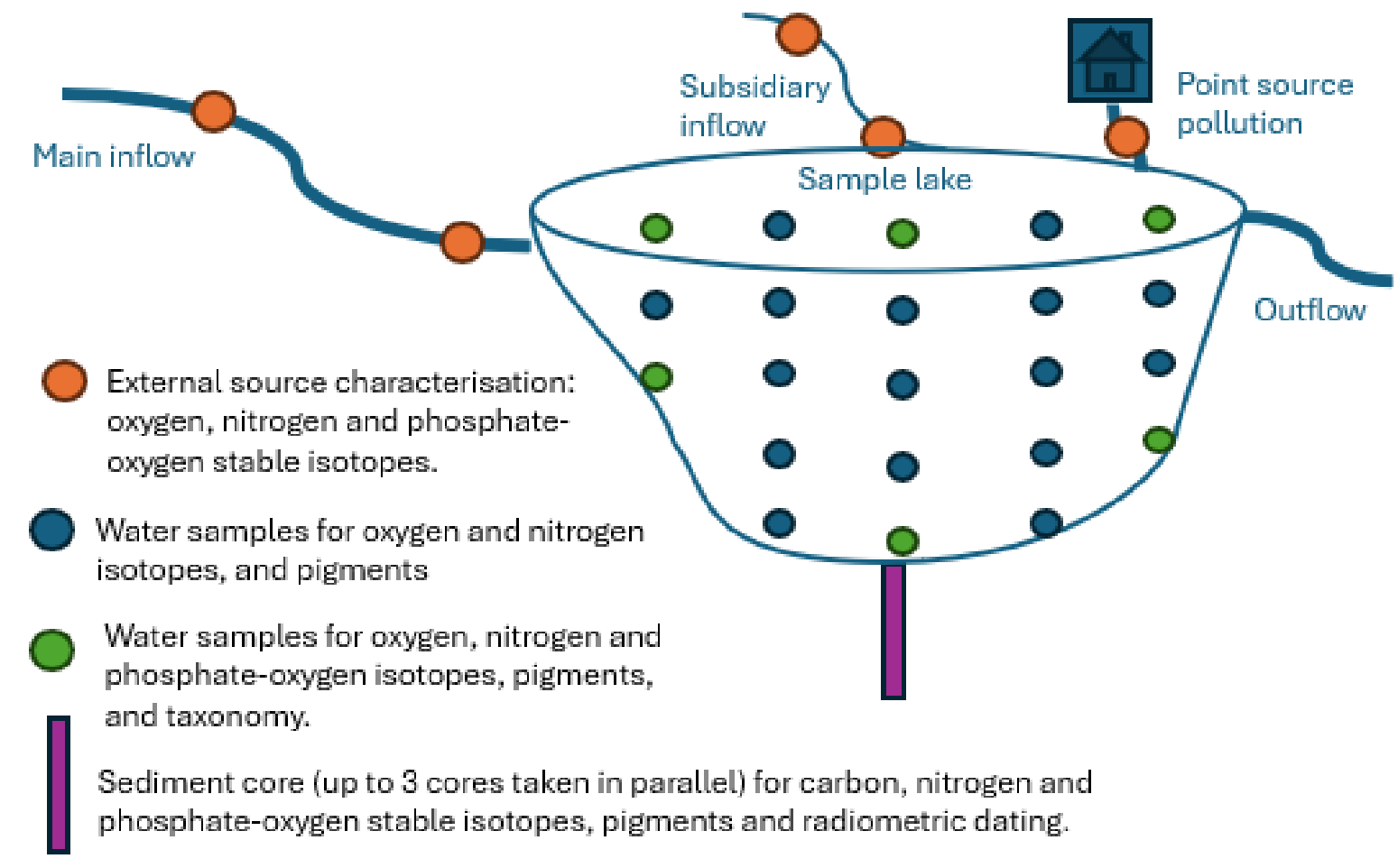

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Nitrate (NO_3^-)
New nitrate (low $\delta^{15}N$)
Nitrifying bacteria
Algae


2 The lake stratifies and the sediment releases ammonium (NH_4^+)
Depth (m)
0
2
4
6
8
10
12
14
Epilimnion, about 18 °C
Thermocline, 3.5 to 7 m
Hypolimnion, 9 to 11 °C
8 m, 62% O_2
14 m, 27% O_2
Sediment
Organic matter
Ammonium (NH_4^+)
Nitrate (NO_3^-)
New nitrate (low $\delta^{15}N$)
Nitrifying bacteria
Algae


3 Where O_2 remains, nitrifying bacteria oxidise NH_4^+ to NO_3^-
Depth (m)
0
2
4
6
8
10
12
14
Epilimnion, about 18 °C
Thermocline, 3.5 to 7 m
Hypolimnion, 9 to 11 °C
8 m, 62% O_2
14 m, 27% O_2
Sediment
Organic matter
Ammonium (NH_4^+)
Nitrate (NO_3^-)
New nitrate (low $\delta^{15}N$)
Nitrifying bacteria
Algae


4
The thermocline traps new, ^{15}N-depleted nitrate in the hypolimnion
Depth (m)
0
2
4
6
8
10
12
14
Epilimnion, about 18 °C
Thermocline, 3.5 to 7 m
Hypolimnion, 9 to 11 °C
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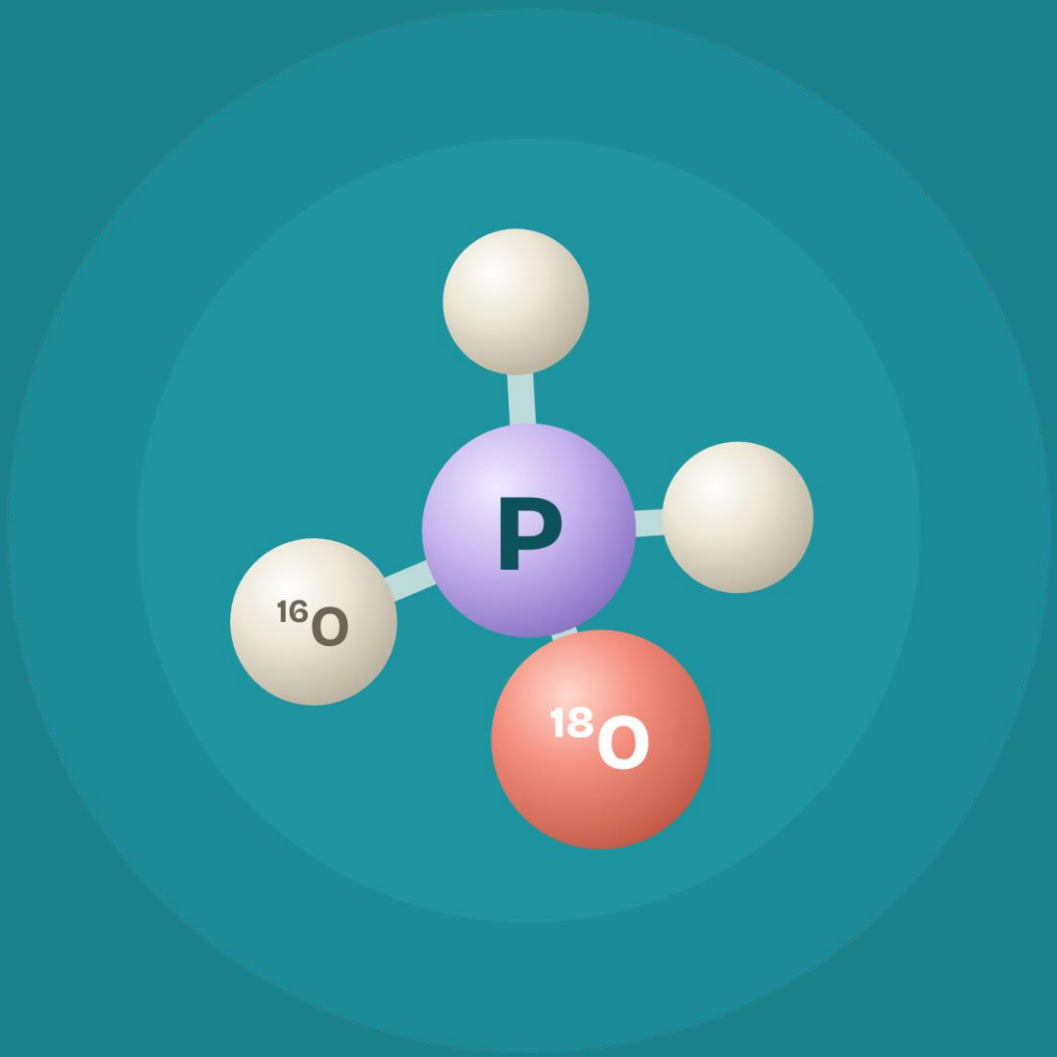
Next Steps



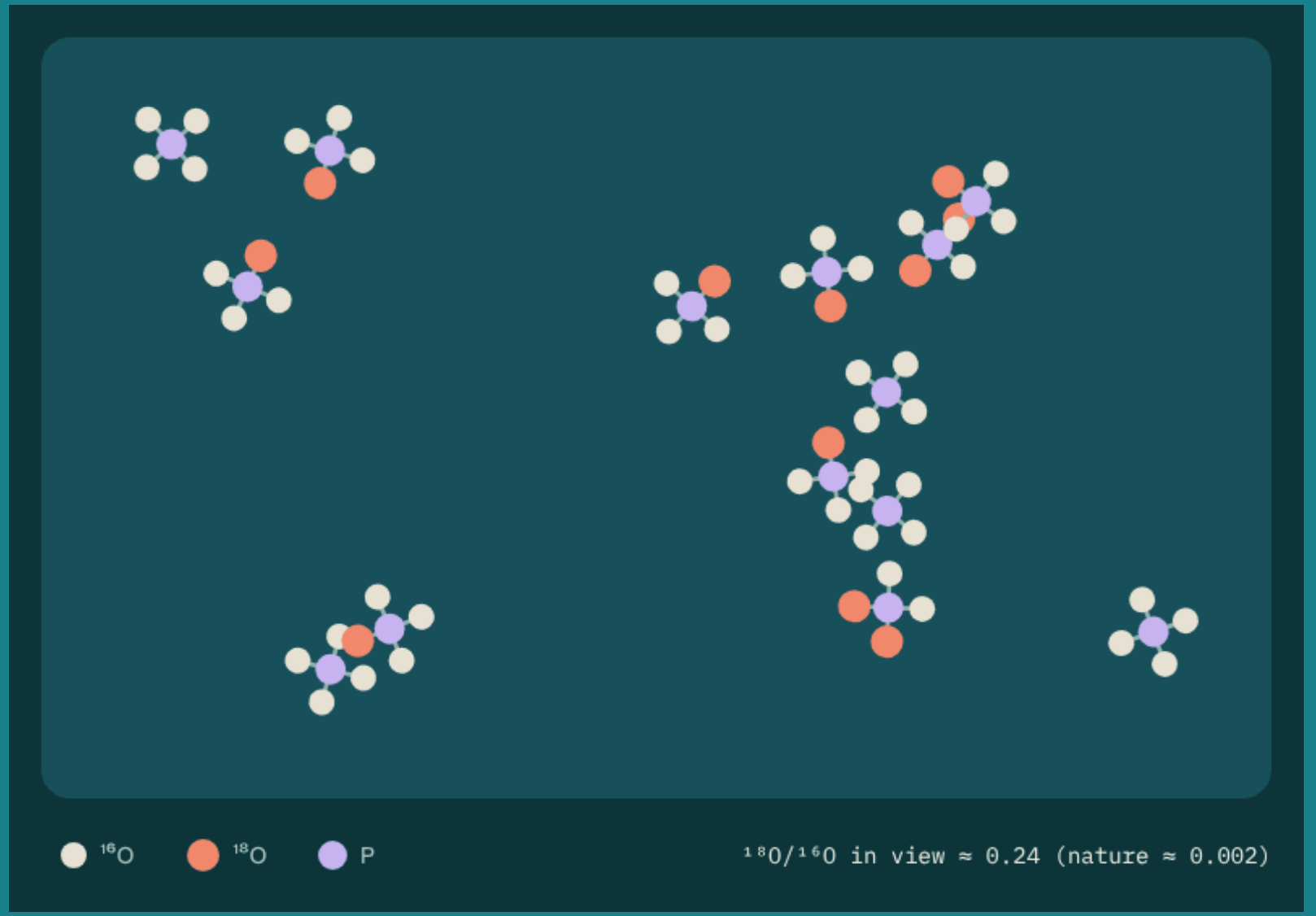
- **Repeat seasonal sampling**, at higher spatial resolution
- **End-member modelling** to quantify nitrate sources and processing
- **Ammonium isotopes, including porewaters** to Investigate internal loading

What about Phosphorus...

Phosphate oxygen isotopes ($\delta^{18}O$-PO_4)

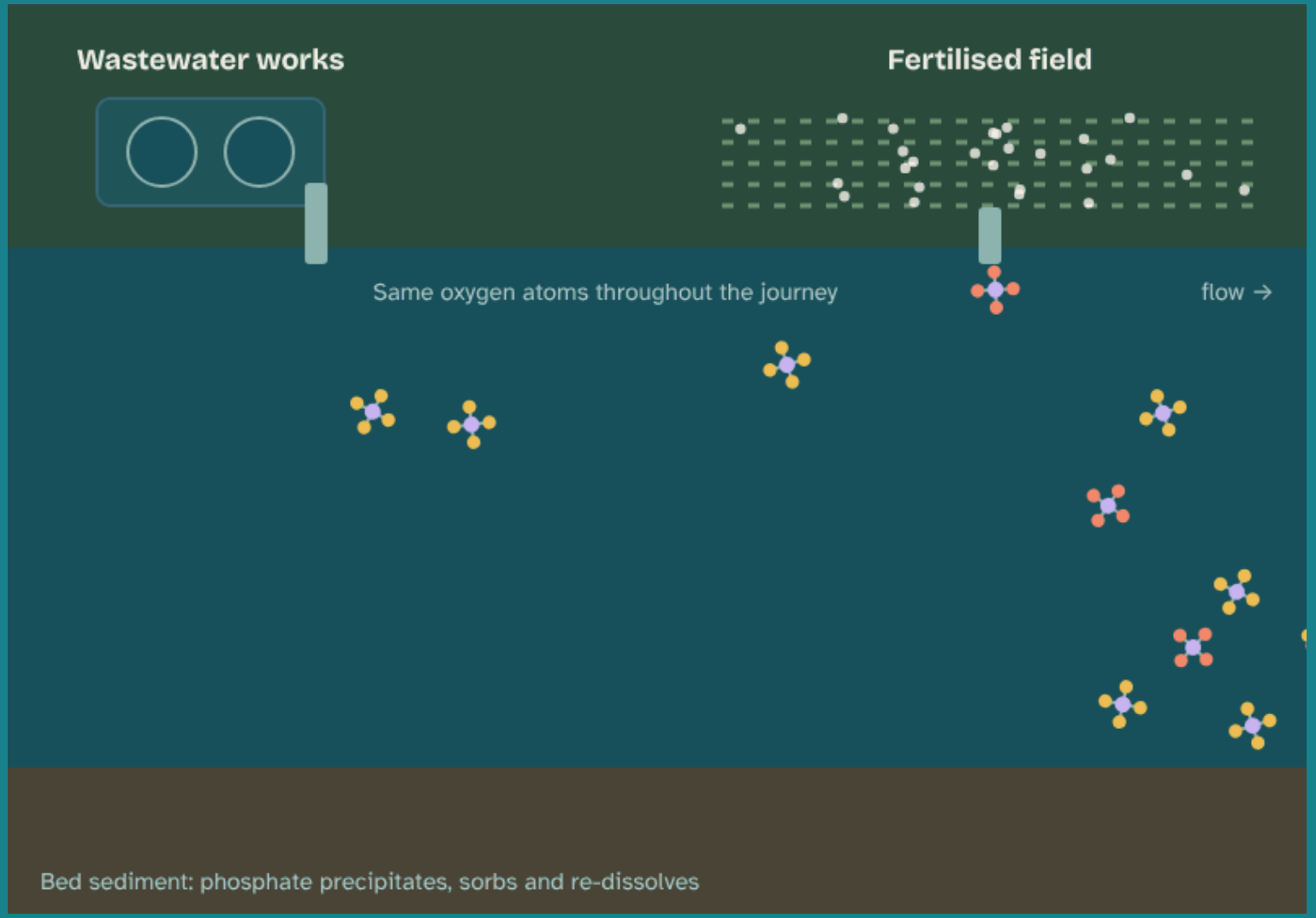


Measure the ratio of O^{16} to O^{18} in a PO_4 molecule



In waters or sediments

Different sources have different $\delta^{18}O\text{-}PO_4$ values



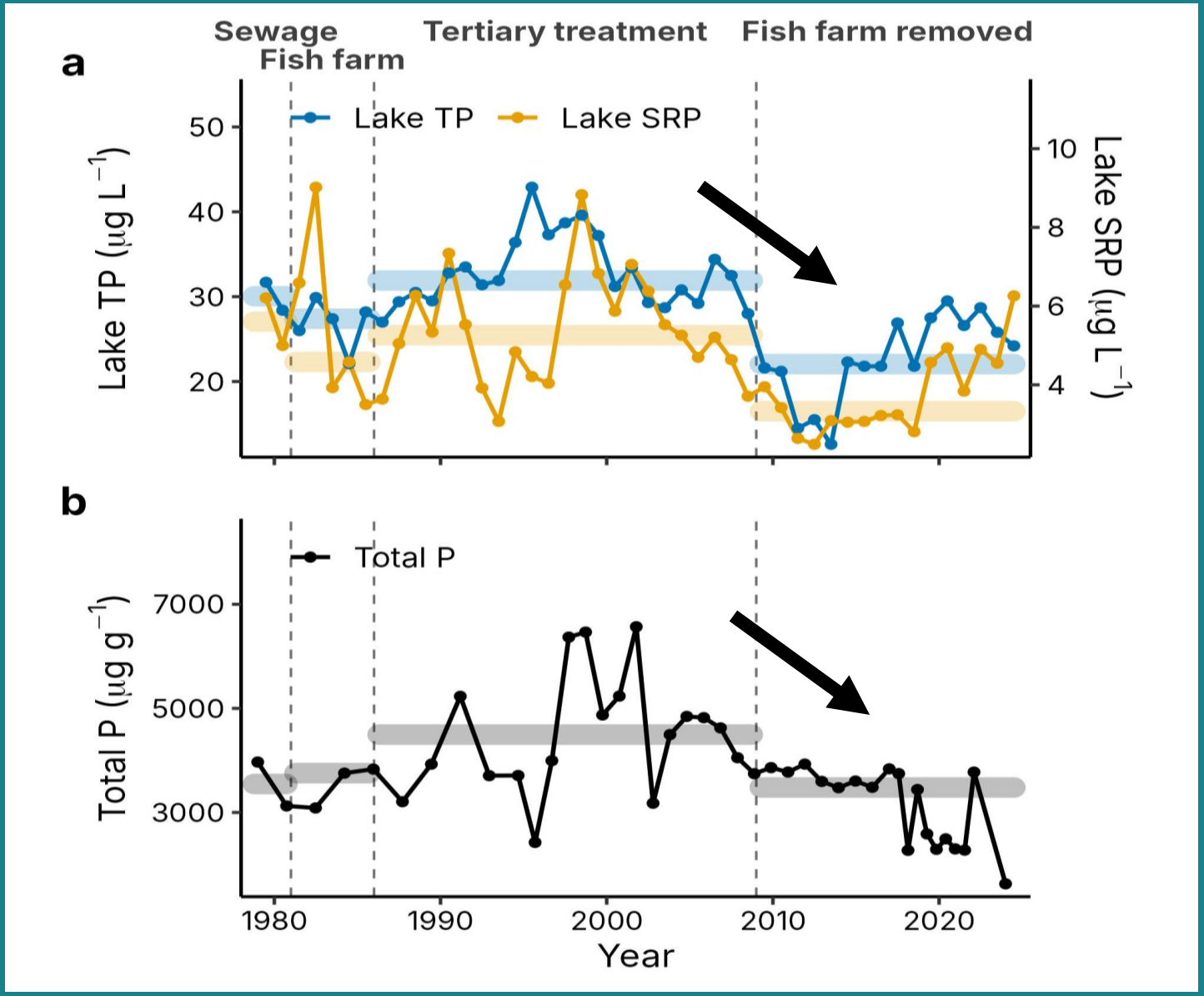
Chemical and physical processes don’t alter this value

Sediment Core Reconstruction

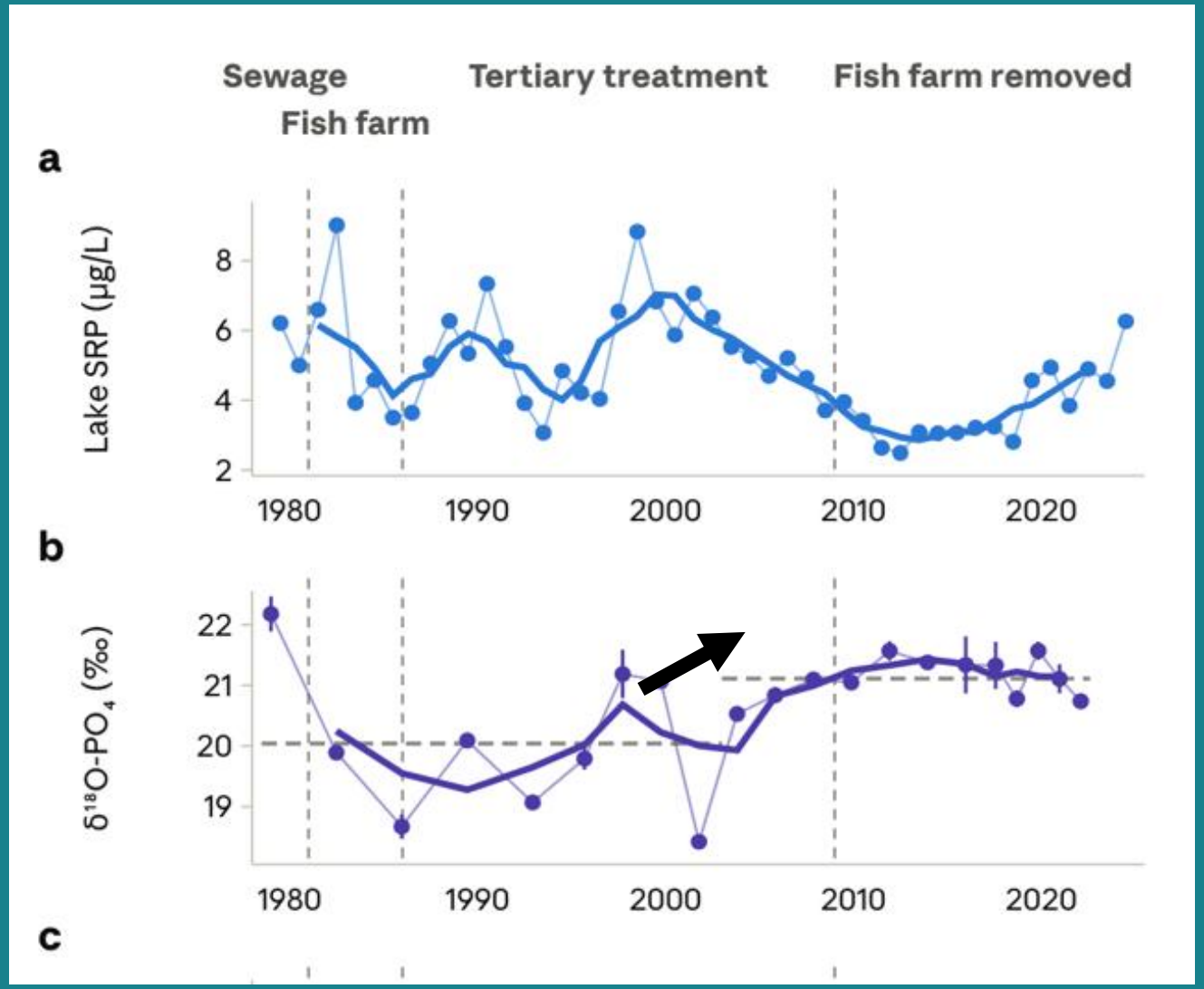
Can we use phosphate-oxygen isotopes to reconstruct P sources and cycling over time and how this changed with catchment management?



Monitoring vs Sediment P concentrations



- Total sediment P (black) aligns with monitoring TP and SRP which decline most notably after fish-farm removed in 2009.
- Measured phosphate oxygen isotopes on the mineral-P fraction (most stable, catchment-derived) to understand changing P sources.



- $\delta^{18}O\text{-}PO_4$ increases in mid-late 2000's as P concentrations decline

Possible explanations…

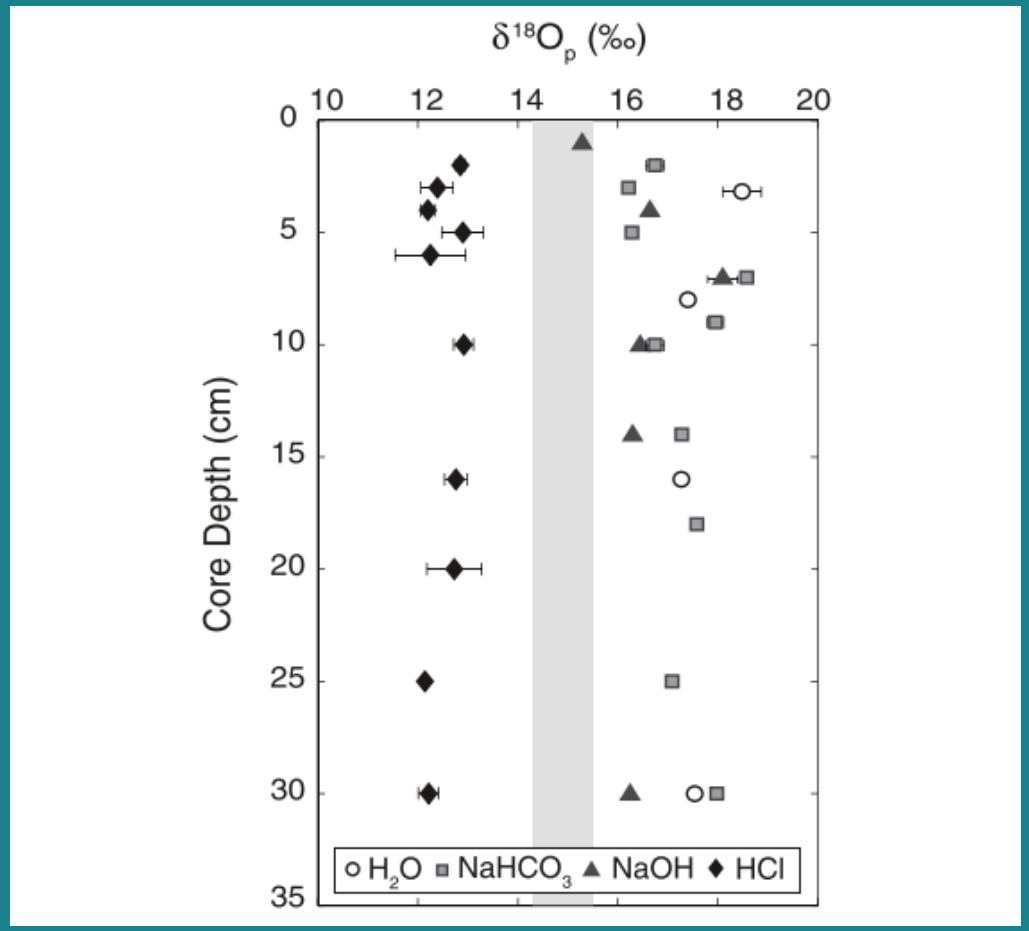
1. Increased relative input of catchment sources
   - Detrital apatite from weathering

   OR
   - Mineral fertiliser from runoff

   - Upcoming → site-specific end-members and XRF analysis.

2. Phytase breakdown of soil organic P, releasing heavier P in catchment, washed into the lake (e.g. von Sperber et al., 2015).
   - C/N and $\delta^{13}C$ don't suggest increased soil influx.

Next Steps



Paytan et al., (2017). *Sci. of Tot. Env.*

Catchment → Internal loaded

- Internal loading assessment → sediment Fe-P and Al-P $\delta^{18}O$-PO_4
- Biological P cycling → $\delta^{18}O$-PO_4 analysis of lake surface and bottom waters
- Spatial variability → additional cores from across the lake
- Loading potential of P and N → incubation experiments



Conclusions

- Stable isotopes are promising tools for:
  - Process-based water quality monitoring
  - Tracing biogeochemical cycling
  - Understanding nutrient limitation dynamics

- Lake sediment cores help us link long-term eutrophication to ecological response.

- Lots of upcoming work to build on pilot study.... Opportunities to collaborate!



THANK YOU FOR LISTENING
ANY QUESTIONS?

GET IN TOUCH!

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