High resolution sediment microfabric and geochemical analysis reveals seasonal scale redox mineralisation, anthropogenic environmental change and pollution in England's largest natural lake – Windermere

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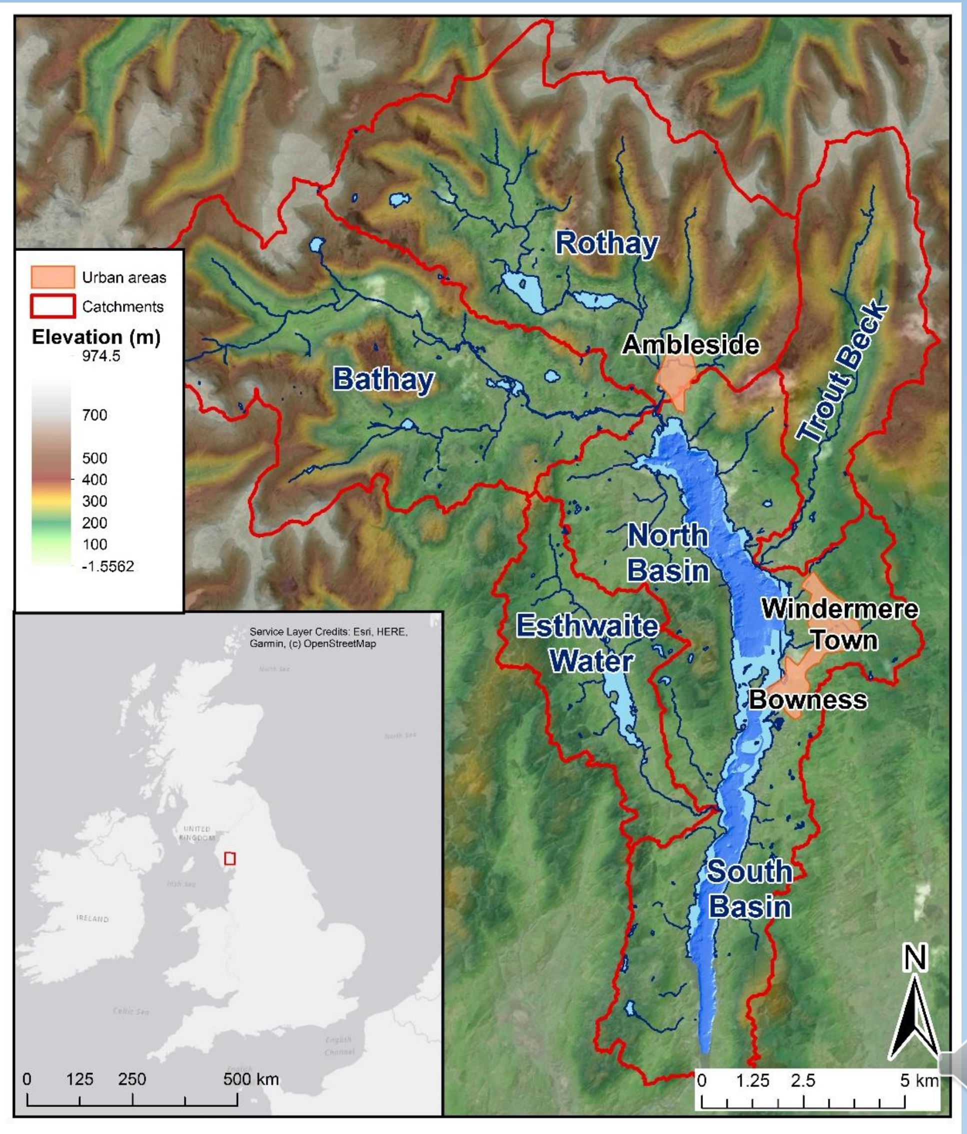
Study Site

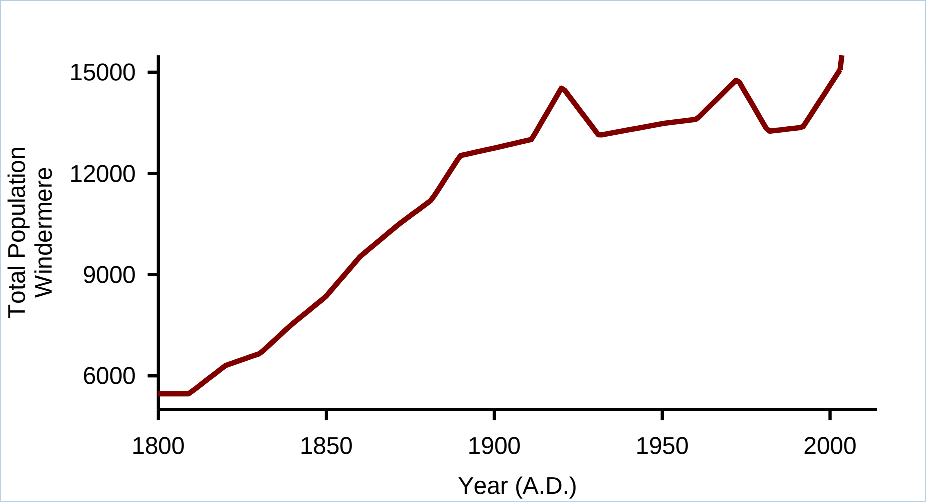
Located in NW England, Lake District National Park, Windermere is England's largest natural lake.

- 17km long, ~1km wide
- 2 Hydrologically distinct basin; deeper North Basin (max. depth: 64m) and shallower South Basin (max. depth: 42m)
- Urban Centres Ambleside (North) and Windermere Town/ Bowness (middle)
- Main rivers: Rothay, Brathay, Trout Beck (North), Cunsey Beck (South Basin)



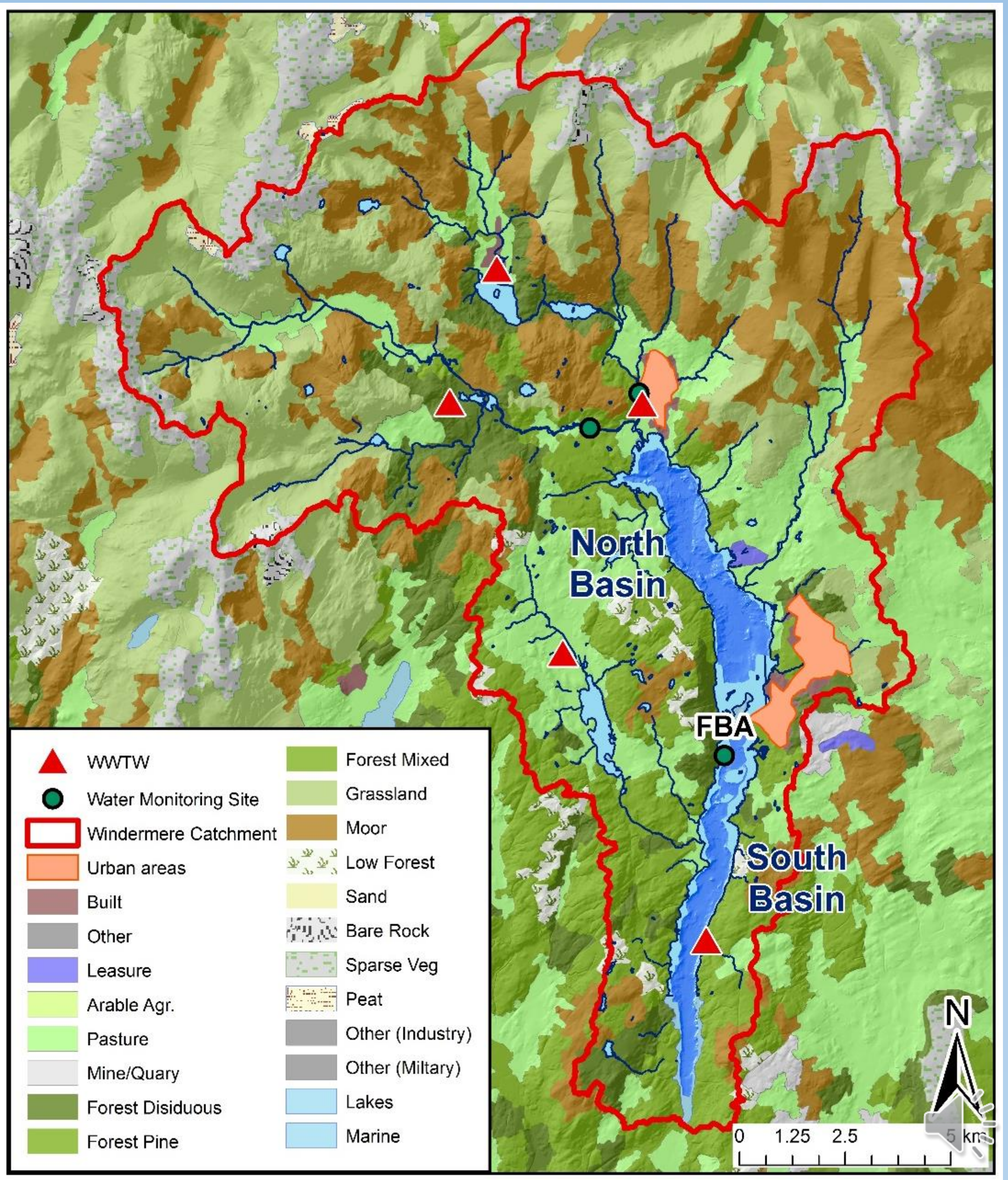
Population, land use and human impact

- Prominent tourist destination from late 18th century
- A protected rural landscape
- Variety of pollutants: excess nutrients (N,P,Si,K), toxic metals (Pb, As)
- Fresh Water Biology Association (FBA) water quality monitoring since the 1940s
- Currently mesotrophic – **eutrophic**
- **Anoxic at depth** during thermal stratification
- P stripping at water treatment works (WWTW) 1990, **BUT water quality remains poor - moderate** (EU-Water Framework Directive, 2016)



Left: Population estimates from UK census data from civil parishes within the Windermere catchment (Open access: *Population change through time.* GB Historical GIS / University of Portsmouth)

Right: Land use, waste water treatment and water monitoring sites (Open access data: data.gov.uk).



Coring

Study objectives

- Extent of anthropogenic pollution in the catchment before monitoring began?
- Impact on lake sediments?

Methods

- Palaeolimnology highlighted as an essential tool for catchment management (Saulnier-Talbot et al., 2016
- Multi-proxy geochemical and sediment fabric investigation
- Four gravity cores collected 2014 (right)

Radiochronology ^{210}Pb, ^{137}Cs, ^{14}C

Element geochemistry

- WD-XRF

- Core scanning XRF (itrax)

Organic Chemistry (TC, TN, C/N, δ^{13}C, δ^{15}N)

Scanning electron microscopy

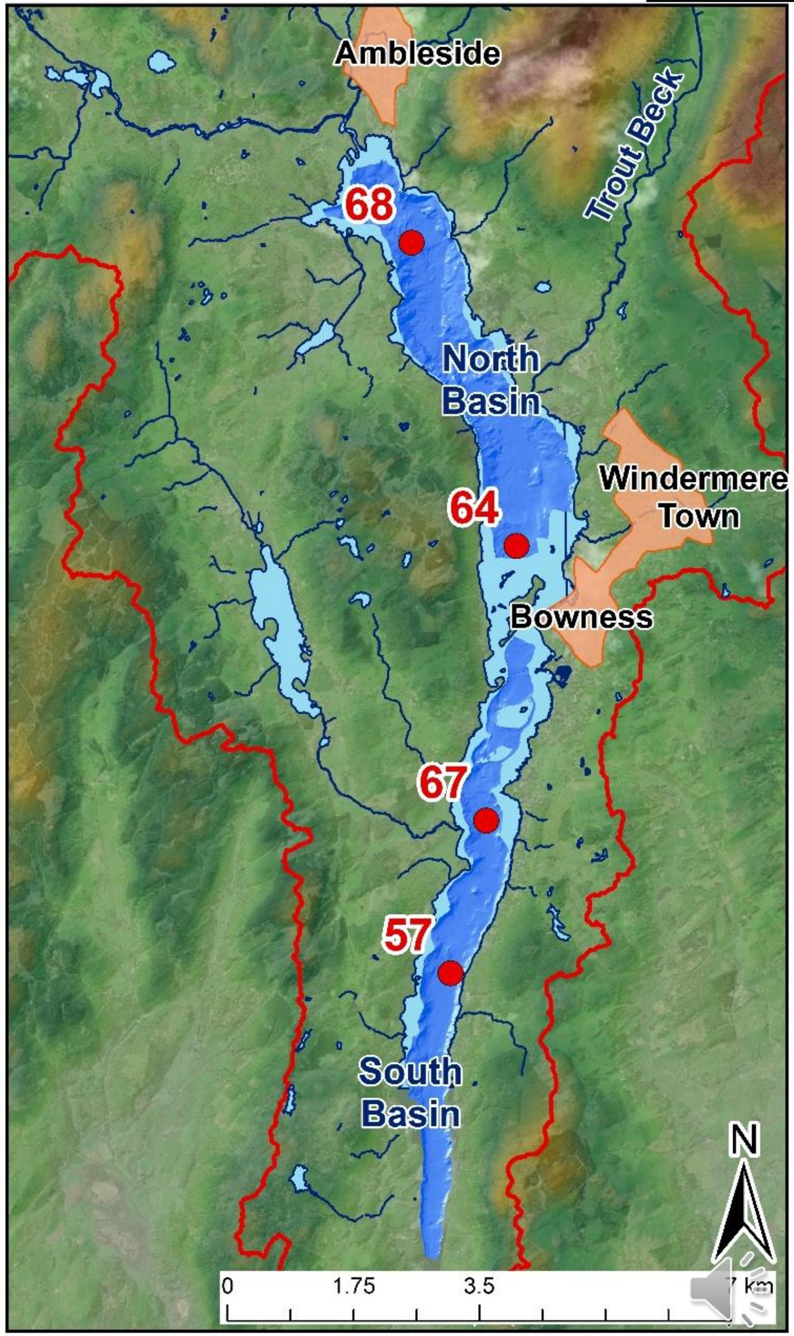
- Energy Dispersive Spectroscopy

Light microscopy

Core ID	Location	Water depth (m)	Length (cm)
68	Deep North Basin	53.9	40
64	Shallow North Basin	26.1	35
67	Shallow South Basin	29	30.5
57	Deap South Basin	39.1	35

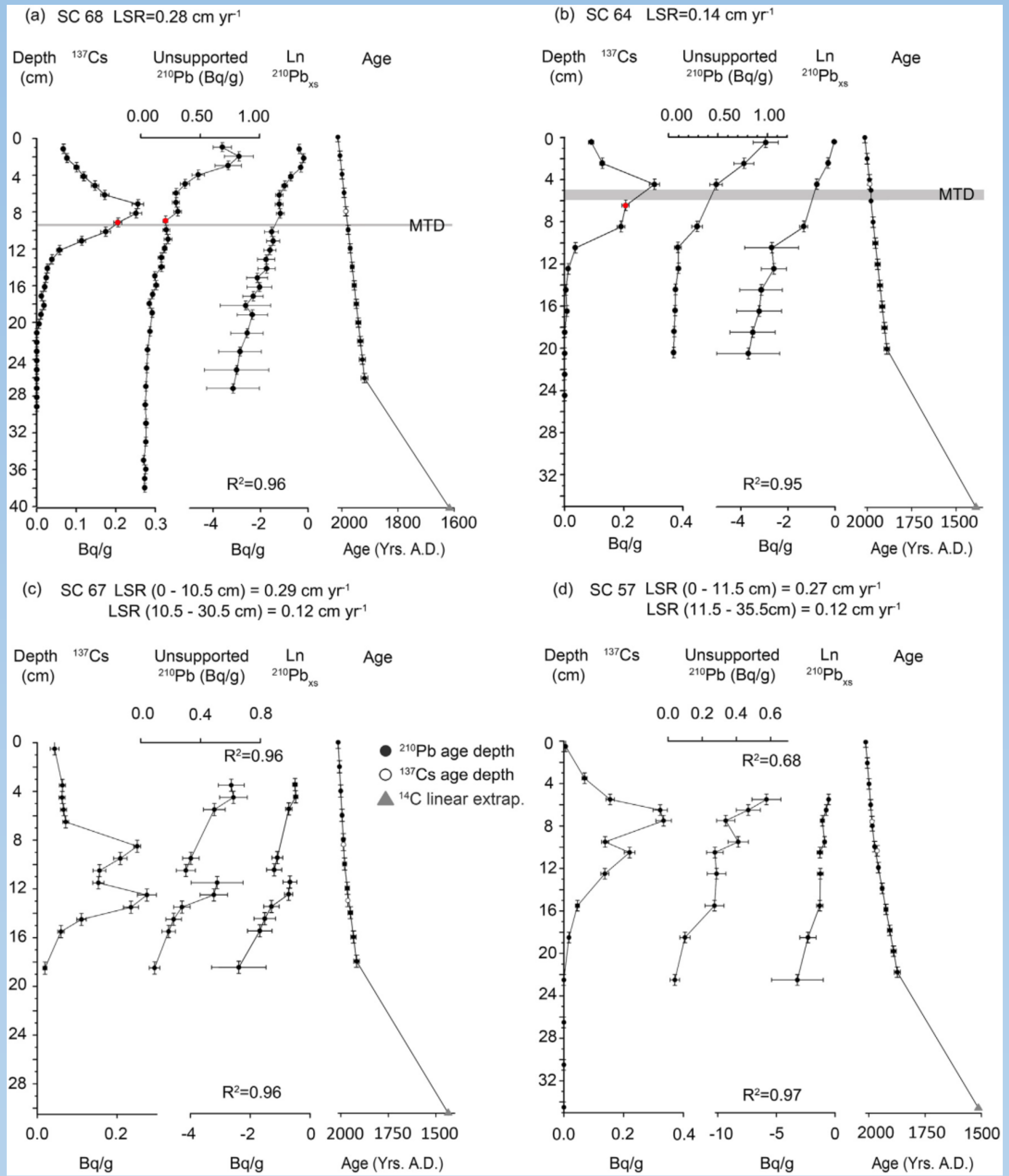
Above: Core data Left: Core location map

Below: Coring on WIndermere



Chronology and sedimentation rate

^{210}Pb and ^{137}Cs



Chronology and Linear Sedimentation Rate (LSR) – combination gravity core data (this presentation) and longer piston cores (up to 10 m) from corresponding sites (Miller et al., 2014).

Upper core (68 = 27 cm, 64 = 20.5 cm, 67 = 18.5 cm, 57 = 22.5 cm) dated by ^{210}Pb and ^{137}Cs, Constant Flux : Constant Sedimentation (Fielding et al.,2018).

Lower core dated by interpolation to radiocarbon date in the piston cores (Table below).

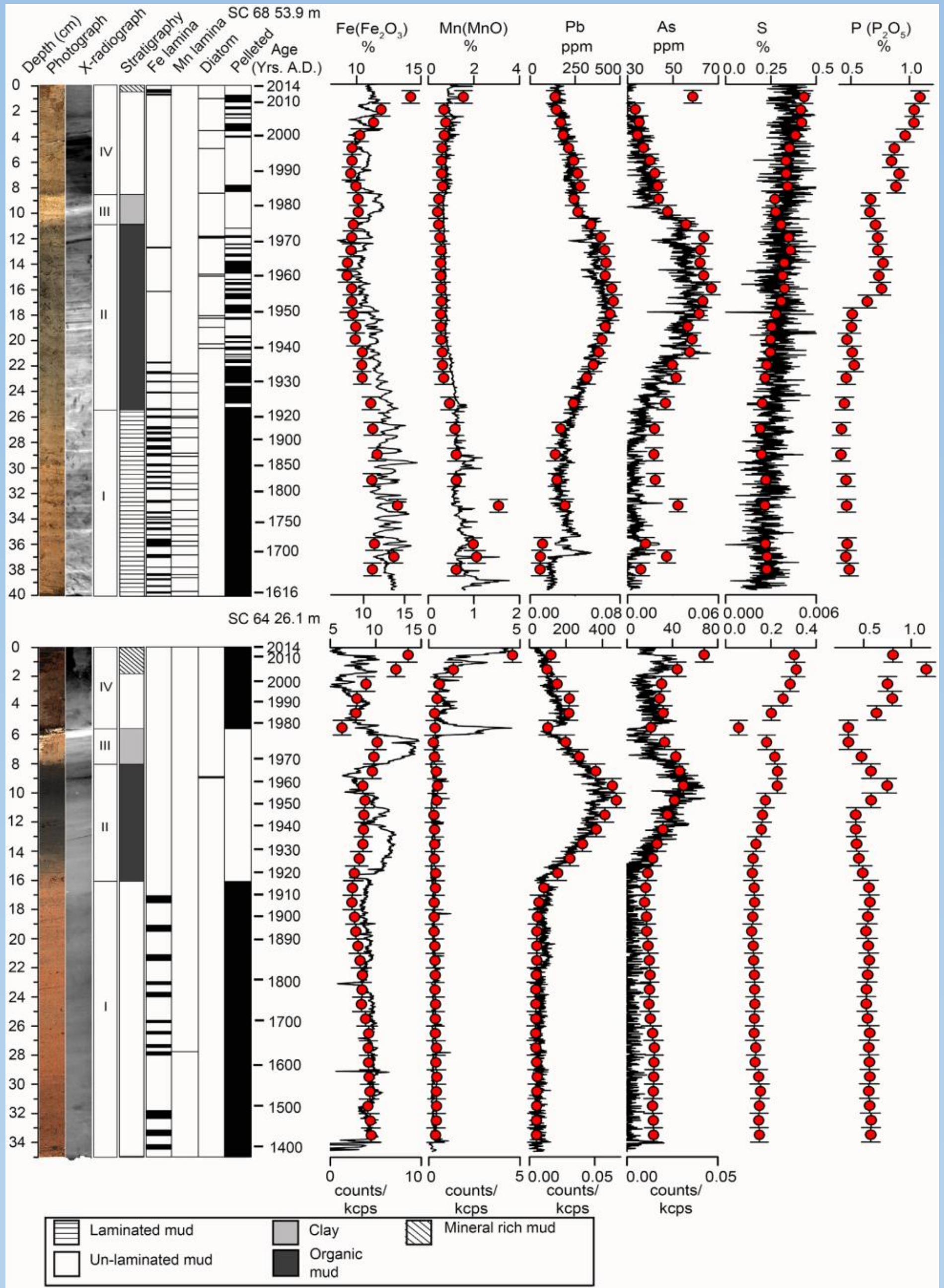
LSR an order of magnitude lower in the lower core.

Causes could include land erosion (agriculture) and increases in biogenic sediment (Sabater and Haworth, 1995; Schillereff et al., 2019).

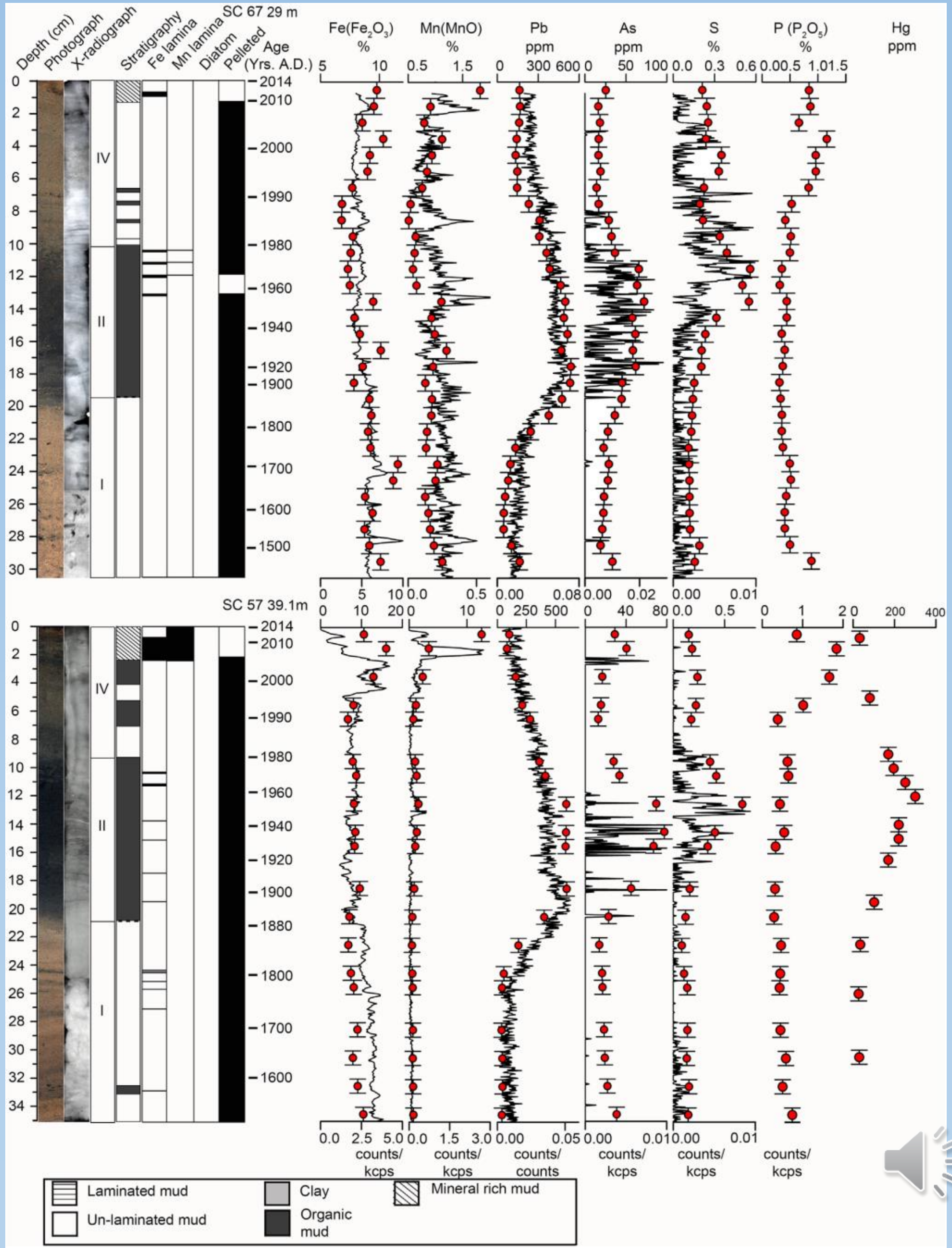
Core ID	Depth (cm)	Type	Mean age (yrs. b.p.)	2σ calibrated ages (yrs. B.P.)
68	69.5	Bulk	1020	1009-1125
64	92	Leaf	2544	2363-2620
67	48	Twig	1214	1083-1260
57	78	Wood	1651	1554-1732

Stratigraphy and geochemistry

North Basin



South Basin



Lithological units I – IV are defined by broad changes in all parameters. These are highlighted in slide 8 – 12.

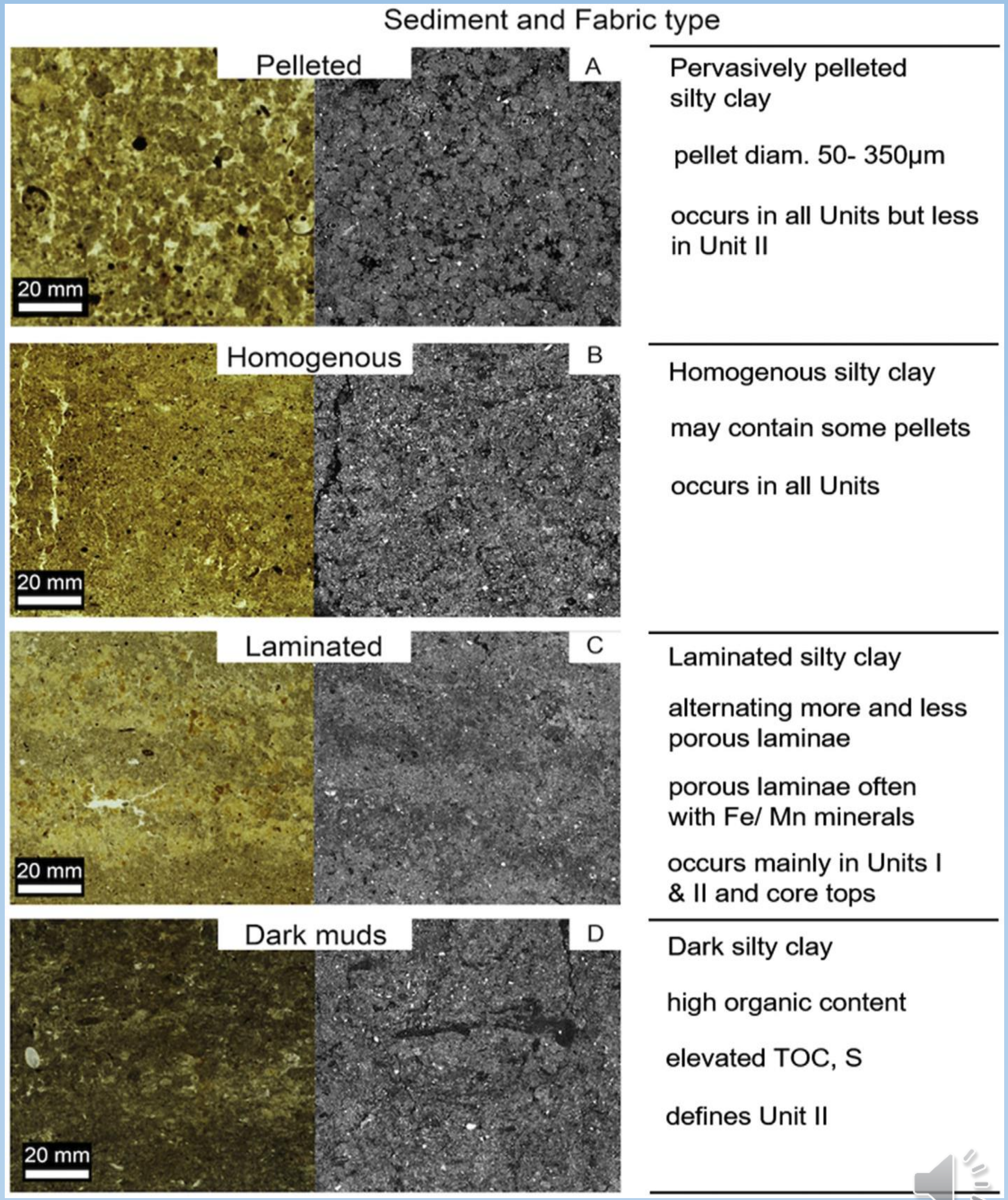
Interpretation of both geochemistry and stratigraphy follows this slide.

Black lines show Itrax ED-XRF (itrax core scanning equipment)

Red dots show discreet WD-XRF (Fielding et al, 2020).

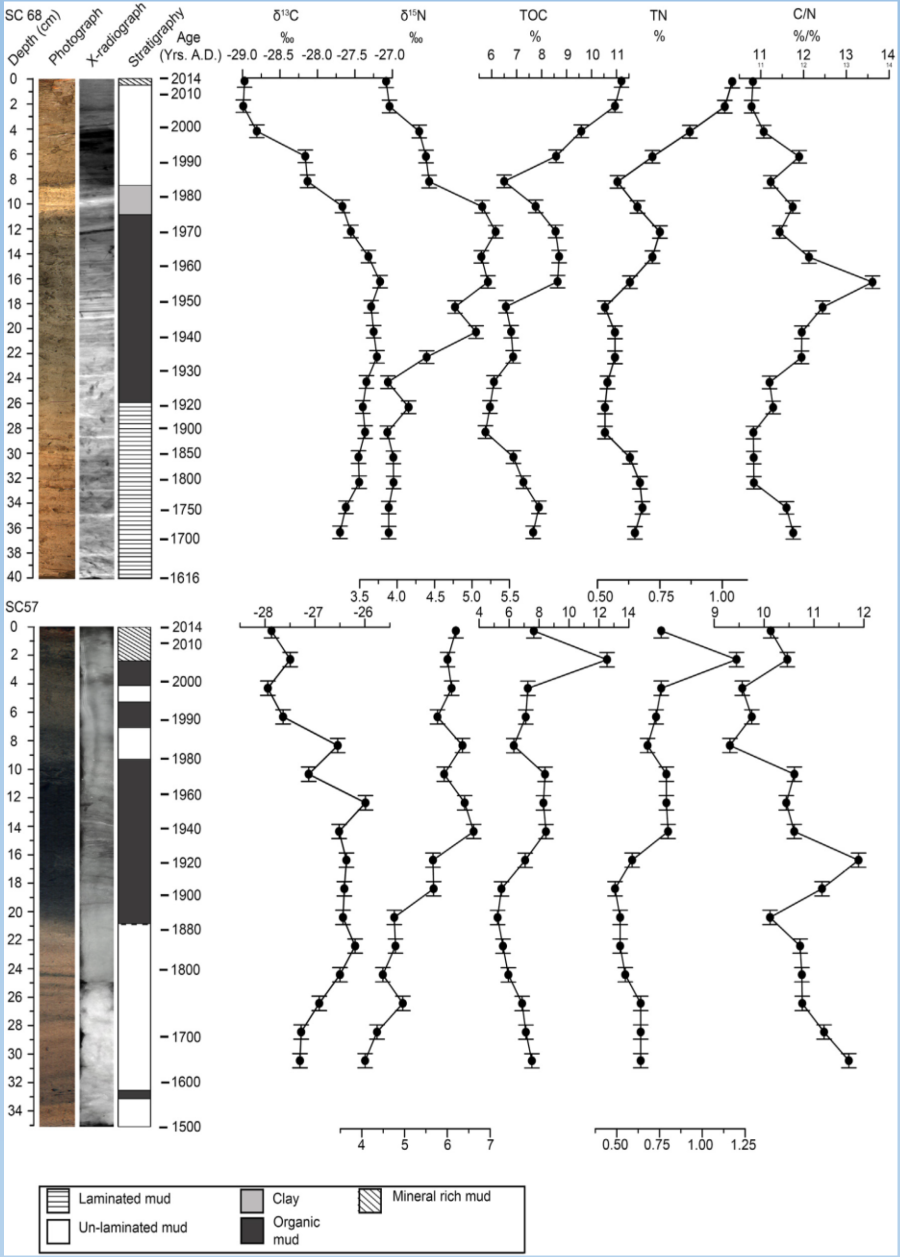
Interpreting the geochemistry and stratigraphy

Element	Environmental or climatic driver	Study
Fe, Mn, As, S	**Redox conditions of the water sediment interface:** Mn, Fe reduced in anoxic condition and (re)precipitate in oxic conditions. Fe oxidises more rapidly (and reduces more slowly) than Mn. Increased Mn accretion can only occur under prolonged oxic conditions. As is often sequestered by Fe and Mn oxyhydroxides. Sulphide formation occurs in lakes sediments due to the brake down of organic matter in anoxic conditions.	(Sugiyama et al. 1992; Davison 1993)
Pb, Zn, As, Hg, Cu	**Anthropogenic pollution:** Enrichment of Pb, Zn, As, Hg and Cu to be associated with Mining, fossil fuel combustion and sewage treatment output.	(Miller et al. 2014)
P	**Excess nutrient loading:** Increased levels of P are often found in excess in lake sediments affected by excess nutrient loading. P, along with N, is usually lacking in natural freshwater ecosystems, and thus is typically a controlling nutrient of productivity. Introduction of excess P can cause primary production to increase and lead to eutrophication.	(Søndergaard et al. 2003)



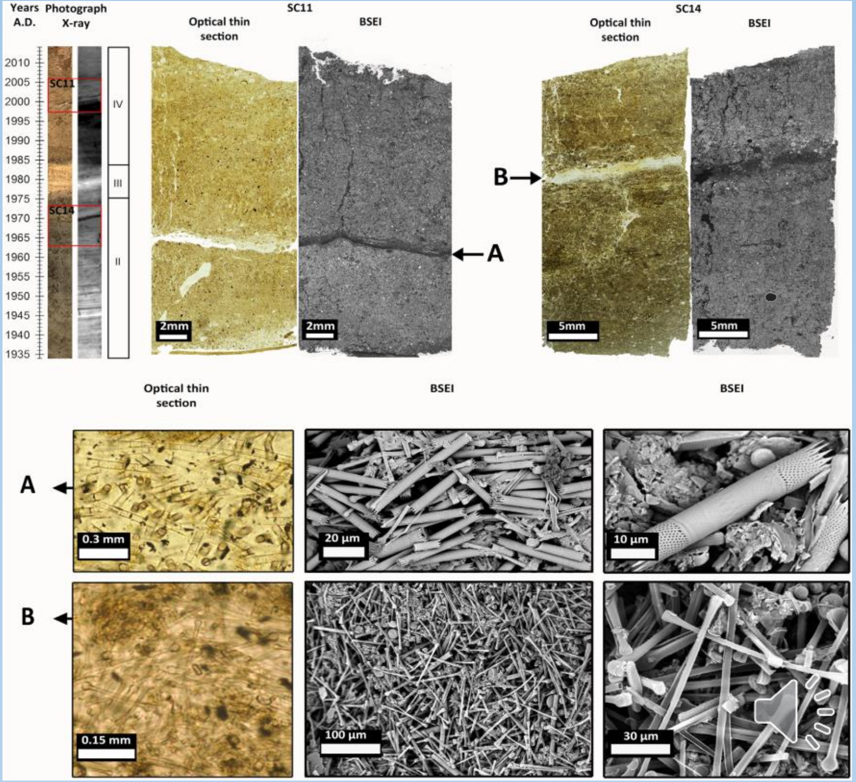
Right: Photograph and BSEI of sediment types and fabrics found through out the Windermere sediment, the occurrence of which are detailed in slide 5. Pelleting is the result of bioturbation by tubificid oligochaetes or chironomid lavae (McCall and Tevesz, 1982; Fielding et al, 2020) and are present in all but the most impacted sediments. Further details of other sediment types follow.

Organic chemistry and diatoms



	Low values	High Values
TOC	Lower organic productivity	Higher organic productivity
TN	Lower organic productivity	Higher organic productivity
δ^{13}C	Land plants	-25 ‰ to -30 ‰ lacustrine algea
δ^{15}N		> algal productivity, > primary sewage or farm runoff
C/N	Lacustrine algae 4-10	Plant matter >20

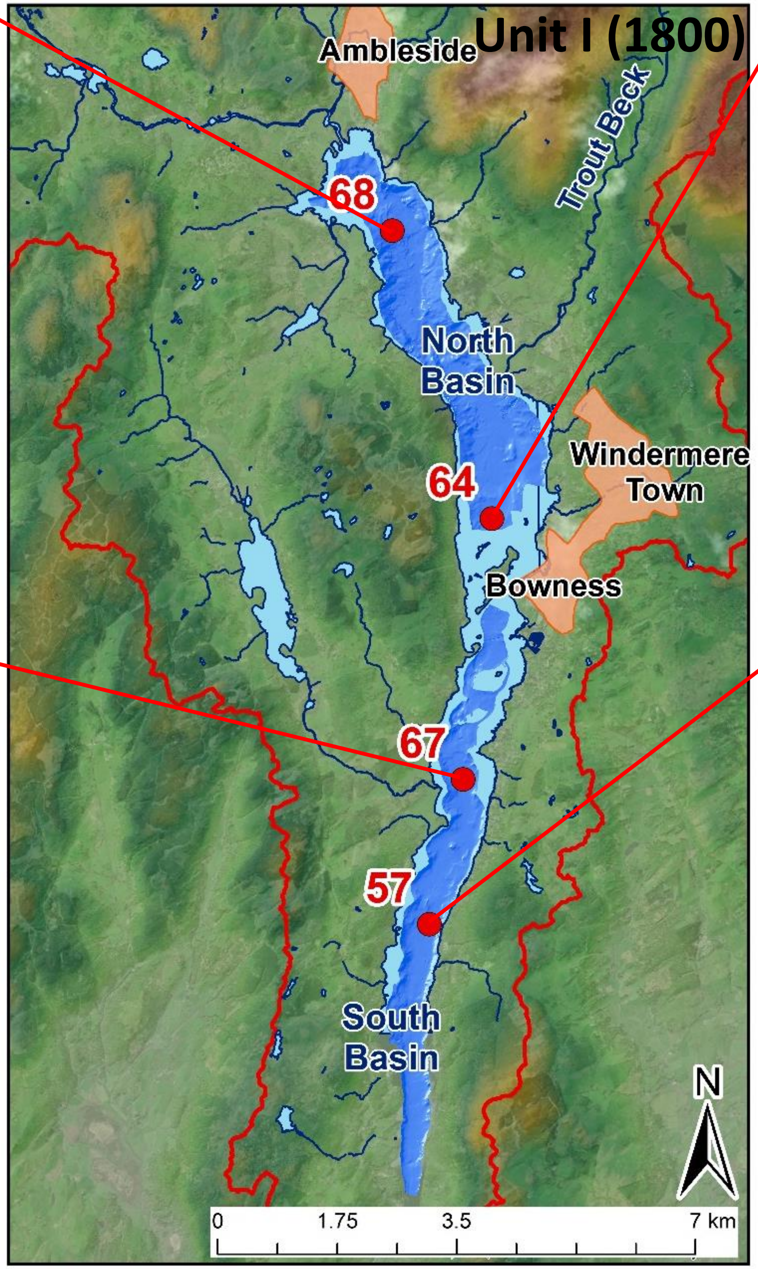
- Organic chemistry
- A) *Aulacoseira subarctica* (1997-98) and B) *Asterionella formosa* (1970-71) laminar in sediment. Both species are associated eutrophic conditions.



Early 19th century – Base line (Unit I)

Sediment	Values
Type	Continuous laminated, Pelleted
Mn & Fe	1-3 % & 11-13 %
Pb	149 - 194 ppm
As	42-52 ppm
P	0.46 %
TOC	7 %
$\delta^{13}C$	-27.4 ‰
$\delta^{15}N$	3.95 ‰
Status	Continuously varying oxygenation and trophic state at depth.

Sediment	Values
Type	Unlaminated, pelleted
Mn & Fe	0.8 % & 8 %
Pb	244 ppm
As	28 ppm
P	0.51 %
TOC	
$\delta^{13}C$	
$\delta^{15}N$	
Status	Well ventilated through out the year.



Sediment	Values
Type	Unlaminated, pelleted
Mn & Fe	0.4 % & 9 %
Pb	37 ppm
As	20 ppm
P	0.54 %
TOC	
$\delta^{13}C$	
$\delta^{15}N$	
Status	Well ventilated through out the year.

Sediment	Values
Type	Some lamination, pelleted
Mn & Fe	0.5 % & 7 %
Pb	55 ppm
As	16 ppm
P	0.53 %
TOC	6 %
$\delta^{13}C$	-26.56 ‰
$\delta^{15}N$	4.26 ‰
Status	Occasional varying oxygenation at depth.

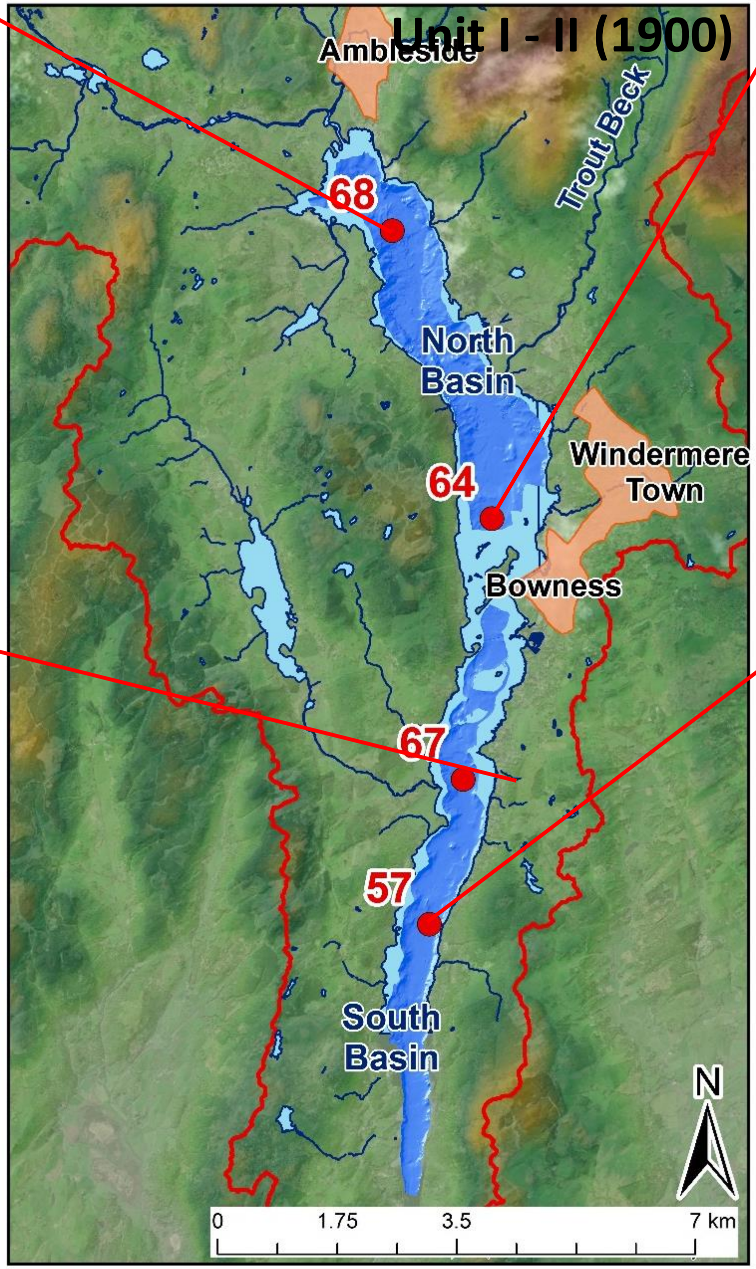
- At the start of the 19th century Windermere could be considered unaffected in a significant way by anthropogenic pollution.
- Sediments are pelleted suggesting good ventilation for much of the year.
- Laminated sediments in the deeper basin indicate seasonal oxygen depletion.
- Organic chemistry is consistent with a mixed algal – plant matter input.

Late 19th century – Onset of pollution (Unit I – II)

Sediment	Values
Type	Continuous laminated, Pelleted
Mn & Fe	1% & 12%
Pb	169 ppm
As	41 ppm
P	0.41 %
TOC	6 %
$\delta^{13}C$	-27.4 ‰
$\delta^{15}N$	3.87 ‰
Status	Continuously varying oxygenation and trophic status at depth.

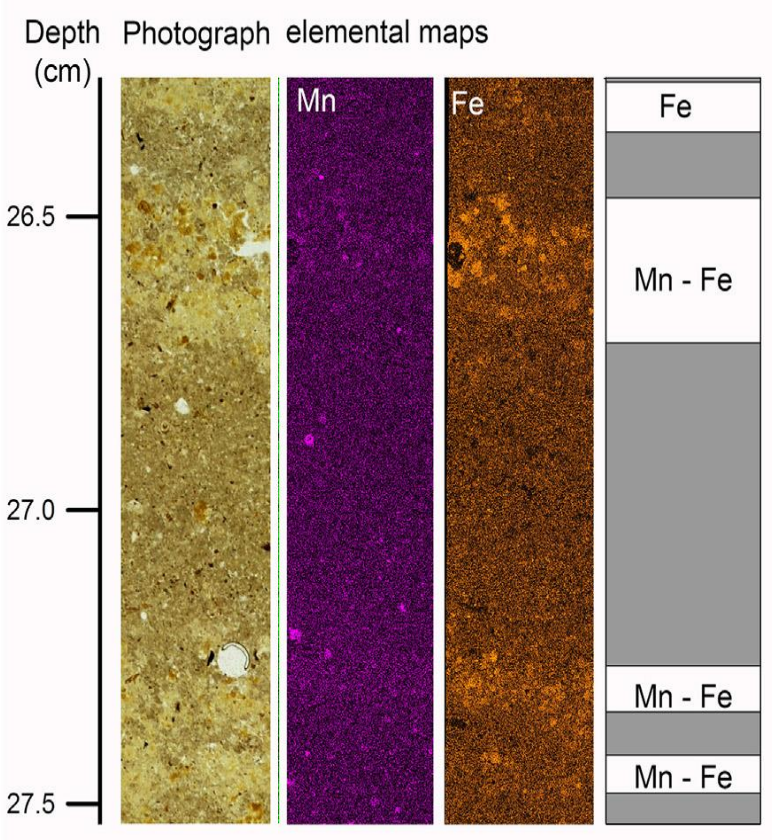
Sediment	Values
Type	Dark muds
Mn & Fe	0.8 % & 8 %
Pb	533 ppm
As	45 ppm
P	0.31 %
TOC	
$\delta^{13}C$	
$\delta^{15}N$	
Status	Poor ventilation, occasionally eutrophic

Lower: Higher:



Sediment	Values
Type	Unlaminated, pelleted
Mn & Fe	0.3 % & 8 %
Pb	44 ppm
As	17 ppm
P	0.52 %
TOC	
$\delta^{13}C$	
$\delta^{15}N$	
Status	Well ventilated through out the year.

Sediment	Values
Type	Dark muds
Mn & Fe	0.9 % & 10 %
Pb	597 ppm
As	45 ppm
P	0.31 %
TOC	5 %
$\delta^{13}C$	-26.47 ‰
$\delta^{15}N$	5.42 ‰
Status	Poor ventilation, occasionally eutrophic



Above: laminated Mn - Fe sediments in core 68 (date: 1905-1919), with optical thin section, Energy Dispersive Spectroscopy (EDS) elemental map. Resulting from preferential precipitation from the water column in over turning (Winter) oxygenated water following a period of dysoxic water (Summer/Autumn). Likely signifies 'usual' conditions and water quality.

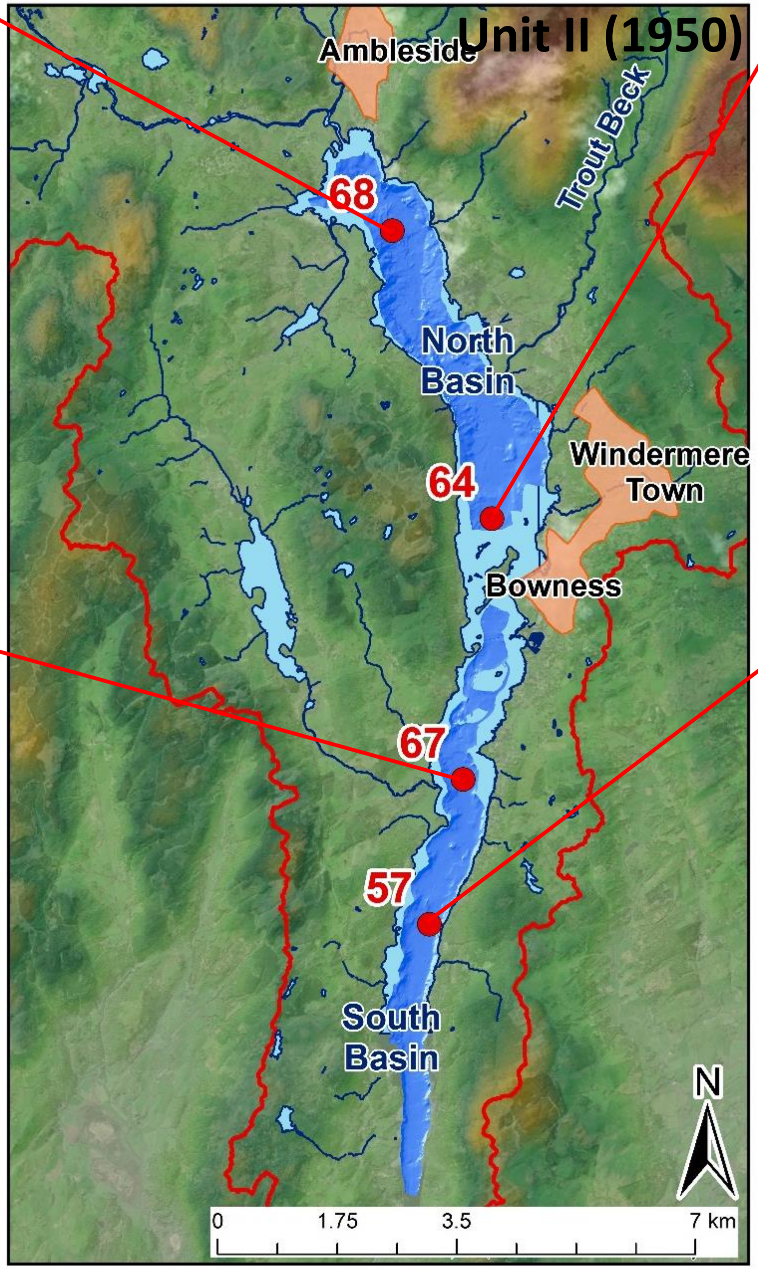
Left: Generally increasing toxic metals show the onset of pollution to the lake.

Mid-20th Century – Peak pollution and eutrophication (Unit II)

Sediment	Values
Type	Dark mud, diatomatious, discontinuous pelleting
Mn & Fe	0.6 % $ 10 %
Pb	465 ppm
As	63 ppm
P	0.64 %
TOC	7 %
δ13C	-27.28 ‰
δ15N	4.77 ‰
Status	Poor ventilation, eutrophic,

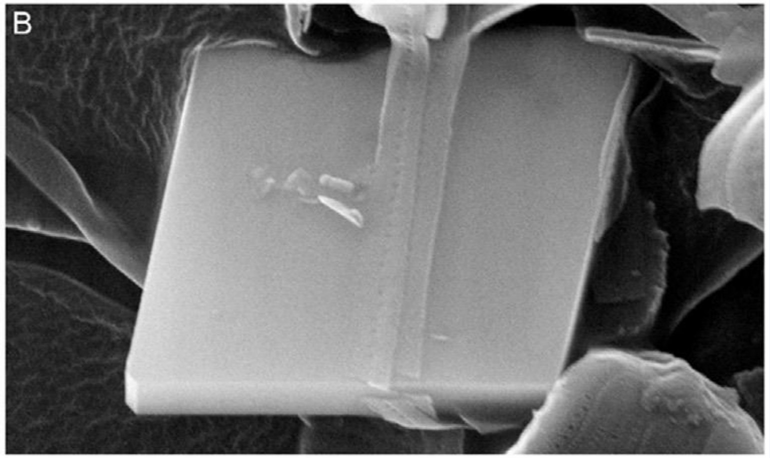
Sediment	Values
Type	Dark muds
Mn & Fe	1.1 % & 9 %
Pb	498 ppm
As	72 ppm
P	0.44 %
TOC	
δ13C	
δ15N	
Status	Poor ventilation, eutrophic.

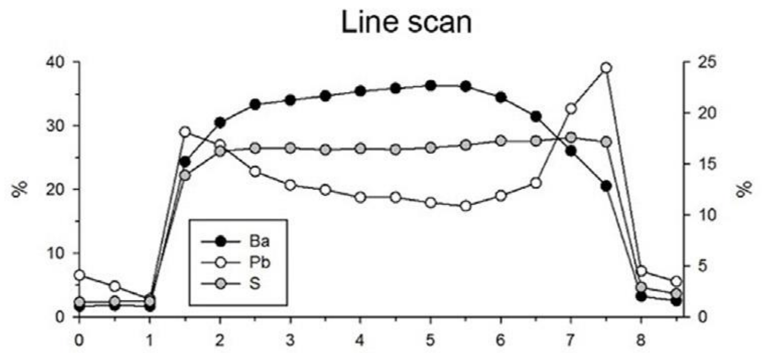
Lower: Higher:



Sediment	Values
Type	Dark mud,
Mn & Fe	0.4 % & 9 %
Pb	476 ppm
As	42 ppm
P	0.58 %
TOC	
δ13C	
δ15N	
Status	Poor ventilation, eutrophic.

Sediment	Values
Type	Dark muds
Mn & Fe	1.6 % & 8 %
Pb	593 ppm
As	69 ppm
P	0.43 %
TOC	5 %
δ13C	-26.06 ‰
δ15N	6.13 ‰
Status	Poor ventilation, eutrophic, increasingly polluted from sewage.





Above: Barite-anglesite mineral from unit II in 68. usually associated with mine waste and contaminated soils.

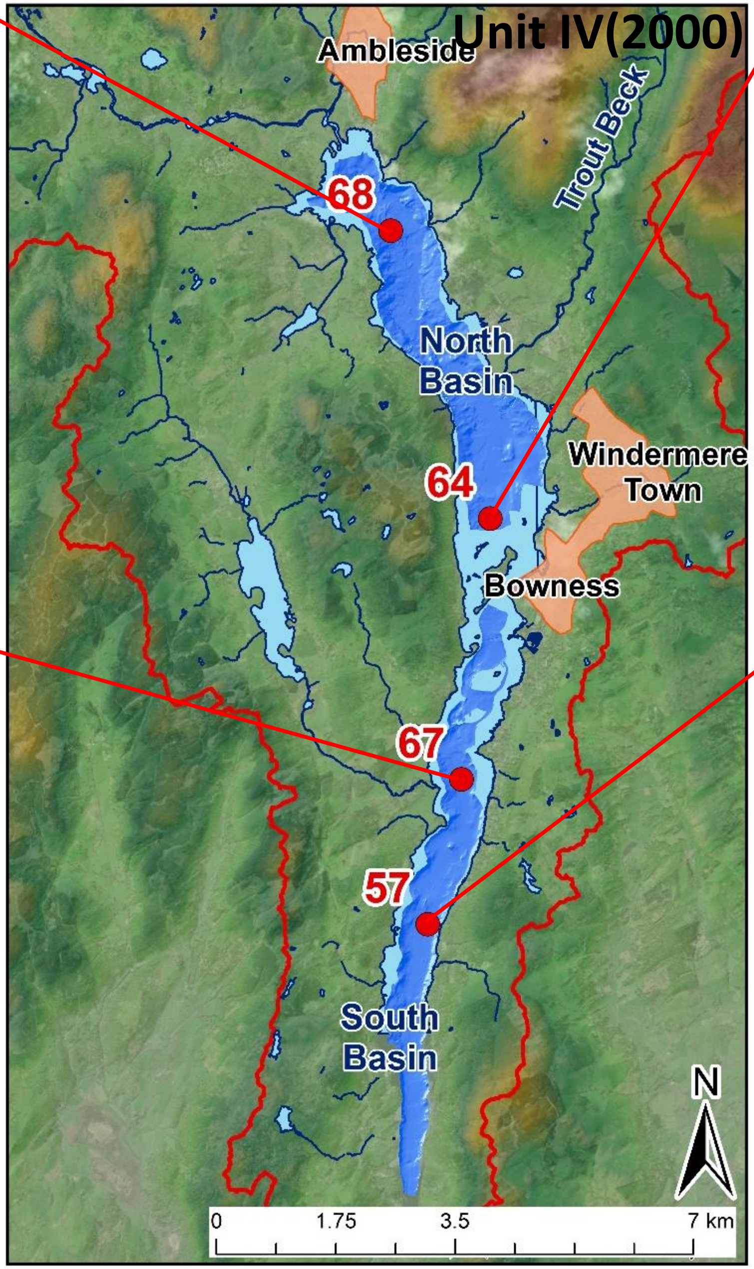
Left: Peak toxic metal concentration, low $\delta^{13}C$ indicative of high algal organic input, high $\delta^{15}N$ continued input sewage.

Late-20th century – Partial recovery (Unit IV)

Sediment	Values
Type	Unlaminated, pelleted, diatomatious
Mn & Fe	0.7 % $ 10 %
Pb	183 ppm
As	34 ppm
P	0.96 %
TOC	10 %
$\delta^{13}C$	-28.81 ‰
$\delta^{15}N$	4.29 ‰
Status	Well ventilation, continuing polluted from sewage.

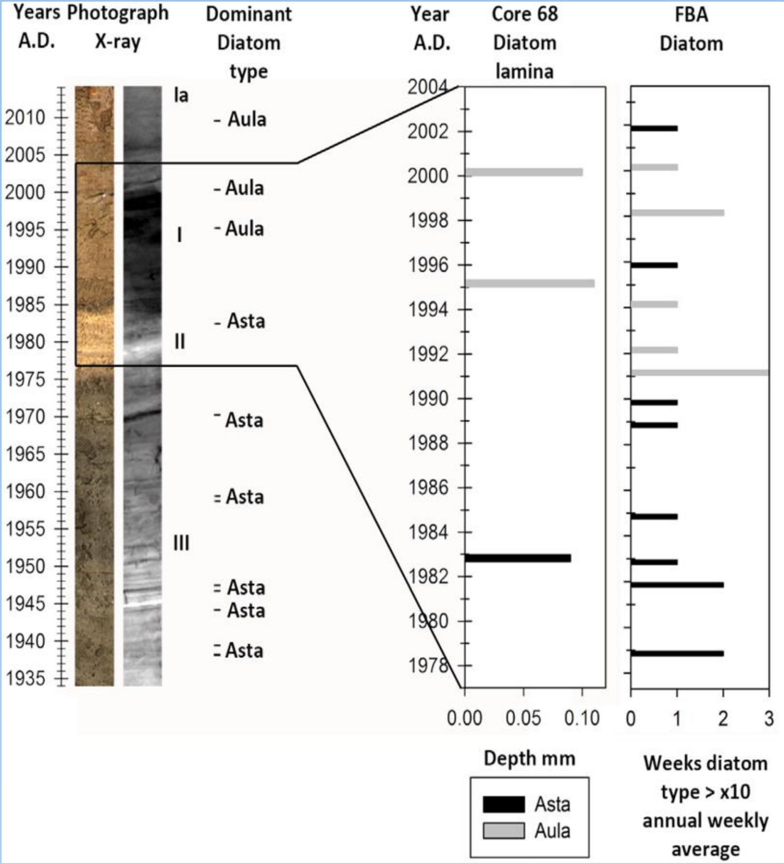
Sediment	Values
Type	Unlaminated, pelleted
Mn & Fe	0.9 % & 9 %
Pb	134 ppm
As	16 ppm
P	0.96 %
TOC	
$\delta^{13}C$	
$\delta^{15}N$	
Status	Well ventilated, continued excess nutrient impact

Lower: Higher:



Sediment	Values
Type	Unlaminated, pelleted
Mn & Fe	0.6 % & 9 %
Pb	151 ppm
As	30 ppm
P	0.75 %
TOC	
$\delta^{13}C$	
$\delta^{15}N$	
Status	Well ventilated, continued excess nutrient impact

Sediment	Values
Type	Dark muds
Mn & Fe	2.3 % & 16 %
Pb	157 ppm
As	17 ppm
P	1.66 %
TOC	7.2 %
$\delta^{13}C$	-27.6 ‰
$\delta^{15}N$	5.84 ‰
Status	Poor ventilation, eutrophic, continued polluted from sewage.



Above: Diatom lamina in 68 compared with FBA diatom bloom length and dominant species

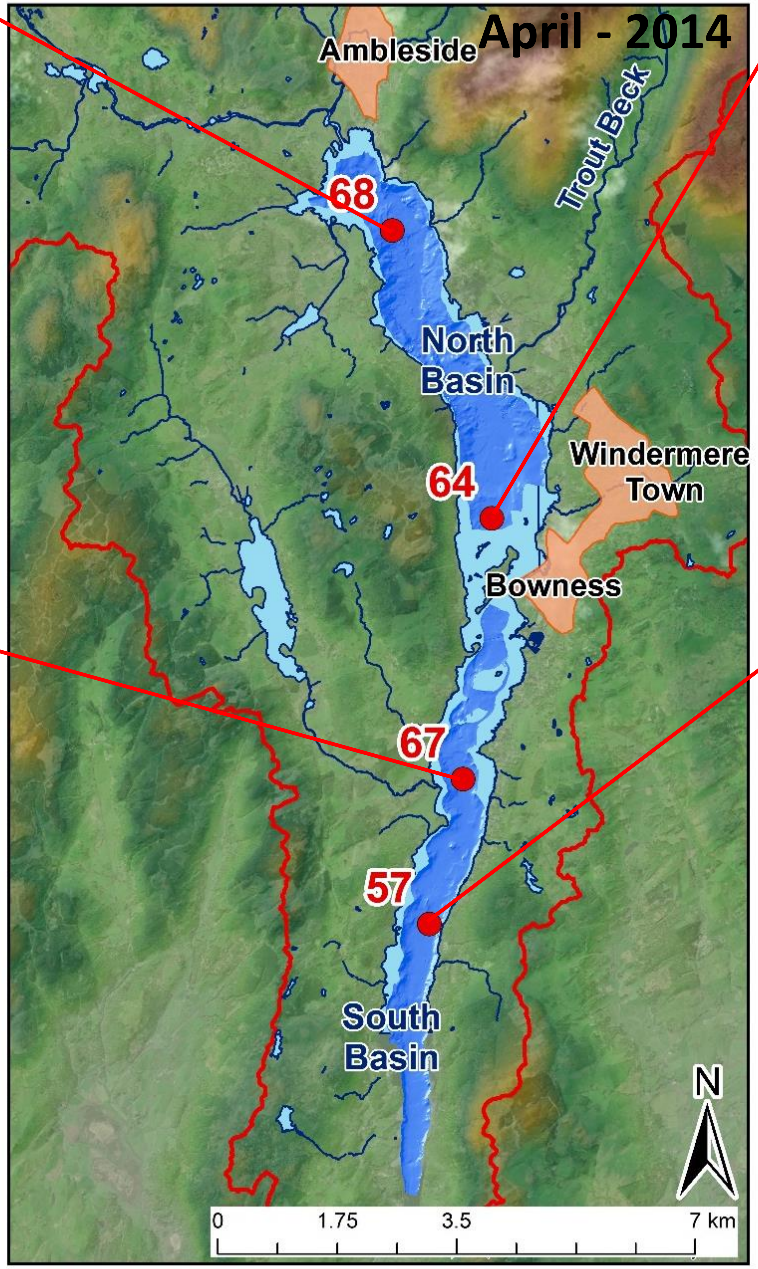
Left: Toxic metals decrease but the continuation of diatom blooms and high P indicates continued human impact.

Human impact at the water sediment interface

Sediment	Values
Type	Mineral rich
Mn & Fe	1. % & 10 %
Pb	138 ppm
As	58 ppm
P	1.08 %
TOC	11 %
$\delta^{13}C$	-28.97 ‰
$\delta^{15}N$	3.85 ‰
Status	Well ventilated, draw down of heavy metals and P by redox process.

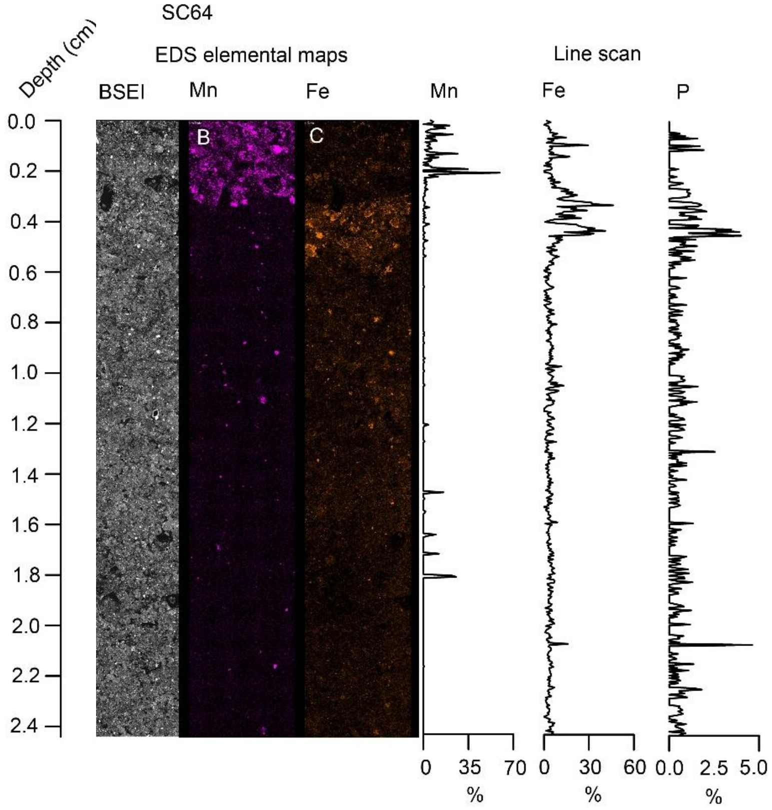
Sediment	Values
Type	Mineral rich
Mn & Fe	1.1 % & 10 %
Pb	163 ppm
As	25 ppm
P	0.84 %
TOC	
$\delta^{13}C$	
$\delta^{15}N$	
Status	Well ventilated, draw down of heavy metals and P by redox process.

Lower: Higher:



Sediment	Values
Type	Mineral rich
Mn & Fe	4.5 % & 13 %
Pb	117 ppm
As	68 ppm
P	1.15 %
TOC	
$\delta^{13}C$	
$\delta^{15}N$	
Status	Well ventilated, draw down of heavy metals and P by redox process.

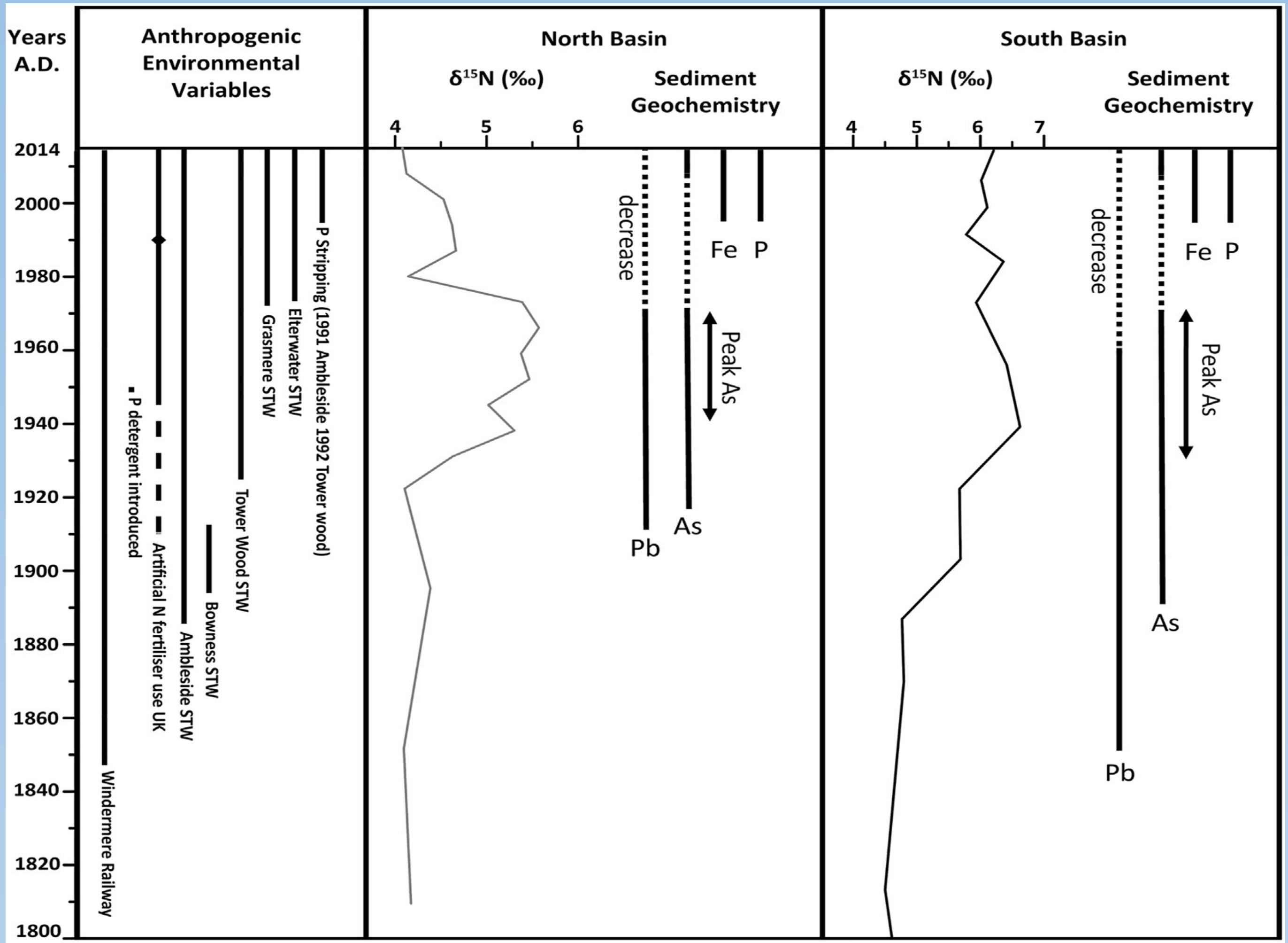
Sediment	Values
Type	Mineral rich
Mn & Fe	12.5 % & 11 %
Pb	102 ppm
As	29 ppm
P	0.85 %
TOC	7.6 %
$\delta^{13}C$	-27.89 ‰
$\delta^{15}N$	5.93 ‰
Status	Well ventilated, draw down of heavy metals and P by redox process.

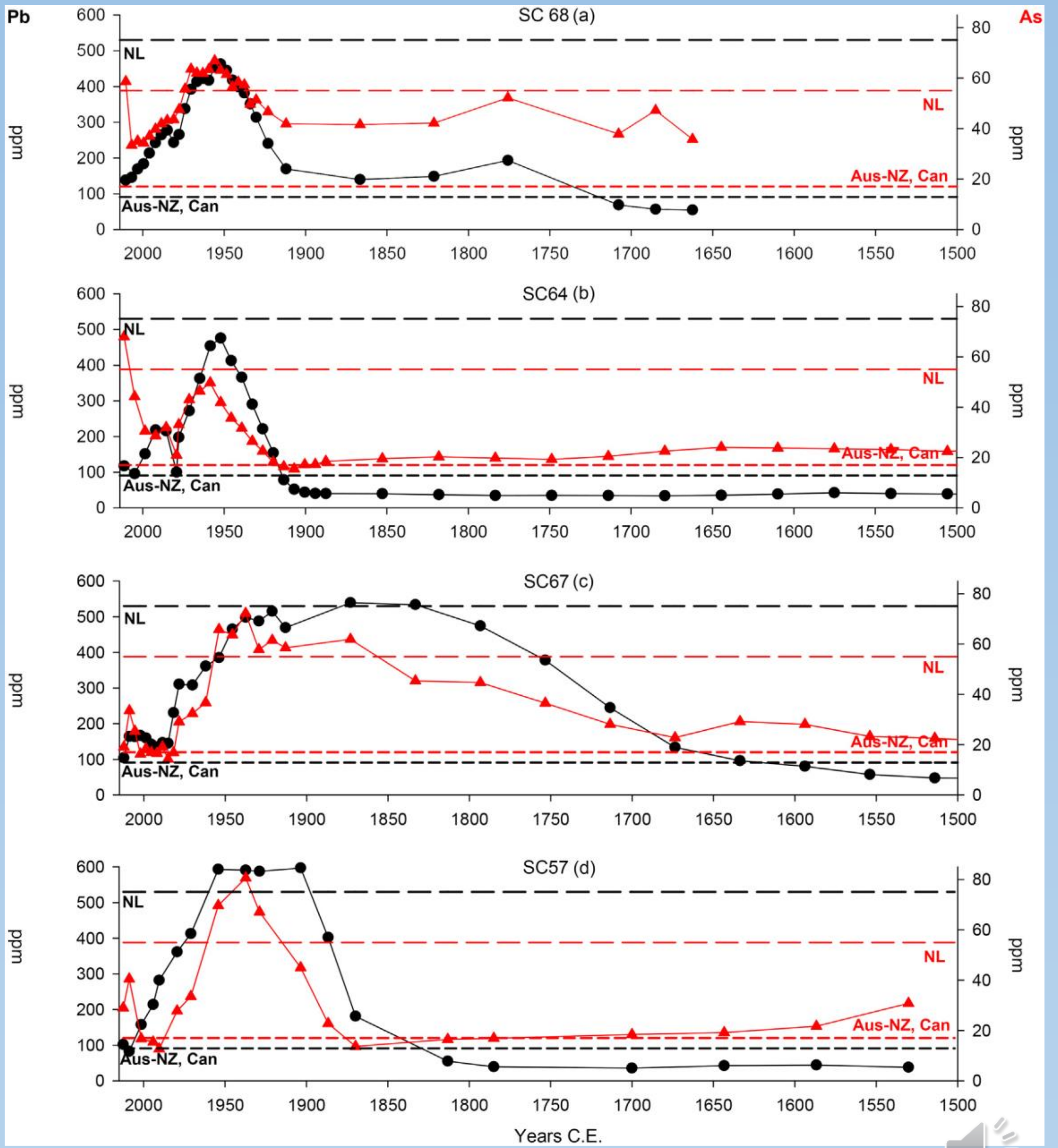


Above: BSEI, electron dispersive spectroscopy (EDS) elemental maps and EDS line scan data from the water sediment interface of core 64 . Fe and Mn which are precipitated in oxygenated waters at the water sediment interface are associated with P and other heavy metals (see left).

Left: Windermere is thermally stratified during Summer and Autumn causing the bottom waters to be depleted in oxygen. Under this scenario Fe along with P, As and Pb may be released in to the water column.

Human impact though time and continuing legacy





Above: Comparison of sediment geo and organic chemistry with a time line of human activity (STW = Sewage treatment works) (Fielding et al, 2020)

Right: Pb (black dots, left y-axis) and As (red triangles, right y-axis) concentrations over time in cores 68 – 57 compared to Australian-New Zealand, Canadian (short dashes) and Netherlands (long dashes) sediment quality standards (SQS) for Pb (black) and As (red). In addition to sediments being contaminated above international SQS, it is likely that toxic metals at the sediment surface which are bound to redox sensitive Fe and Mn will be released into the water column during anoxic conditions during thermal stratification in summer (Fielding et al, 2020).

Study Highlights Acknowledgments

- A multi-proxy investigation of sediment from Windermere, UK, yielded a detailed history of changing lake and catchment conditions over the past 300 years.
- Prior to the mid - 19th century in the lake's South Basin and from the 20th century in the North Basin, Fe and Mn rich laminae indicate regular, seasonal-scale ventilation of bottom waters.
- Following local population increases and associated increasing pollution input to the lake through the 19th century, Pb content in the sediment increases first in the South Basin and then the North Basin.
- At the same time increases in sedimentary $\delta^{13}C$, and the appearances of monospecific diatom ooze lamina, together with decreasing Fe and Mn lamina show a move to decreasing bottom water ventilation caused by eutrophication.
- Greater values of sedimentary $\delta^{15}N$ through the same period are also consistent with enhanced productivity coupled with increases in sewage discharge and farm runoff in to the lake.
- Through the middle of the 20th century benthic activity intermittently ceased in the deeper North Basin due to persistent strongly reducing conditions in the sediment and bottom waters, as indicated by the formation of unusual Pb-bearing barite mineralization.
- From 1980 there was a partial recovery, with bioturbated sediment reflecting increases in oxygenation of deep waters. However, elevated $\delta^{15}N$ of organic matter indicates continued impacts of sewage discharge.
- Oxidation at the Sediment Water Interface has caused significant enrichment of Mn, Fe, As, P and Ba in the surficial sediment and enrichment at the surface exceeds international Sediment Quality Standards. It would thus appear that despite mitigation measures being put in place pollution issues still remain in Windermere, including the possible mobilisation of toxic elements from the sediments in anoxic conditions.

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