# Historical (1850-1995) Nitrogen changes in UK catchments recorded by lake sediment $\delta^{15}N$.

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ABSTRACT

Rationale: The global nitrogen cycle has been fundamentally reconfigured by human activity in the last two centuries. This alteration has played out especially in freshwaters, where changes in nitrogen inputs have transformed whole lake and river ecosystems by boosting primary production in nutrient-limited systems and contributing to eutrophication in others. Global alteration of N is manifest in the nitrogen isotopic signature of organic material that moves through freshwater ecosystems. Lake sediments store organic material and can provide a unique historical, stratigraphic record of changes in nitrogen inputs that can be compared with modelled historical changes and contemporary monitoring.

Methodology: Lake sediment nitrogen isotopes ($\delta^{15}N$) were measured in archived lake sediment cores (n=90) at the well-resolved time intervals of 1850, 1900, 1980 and surface samples with a median age of 1995) determined by radiometric ($^{210}Pb$; $^{137}Cs$) dating. Total C, N and $\delta^{13}C$ were also measured to provide co-variables for assessment. Lake and catchment morphometries and environmental parameters were determined from open-access databases. Isotopic changes over time and space were investigated using geospatial and multivariate statistical analyses.

Results: The difference in $\delta^{15}N$ values between 1850 and 1980 in upland lakes (mean altitude of catchment; MAC) >300 m above sea level) are largely negative (median -0.75‰, SE 0.15), while lowland lakes with MAC <300 m show a positive difference (median 0.92, SE 0.3).

Discussion: Regional and local differences in the record of $\delta^{15}N$ in lake sediments are identified and investigated. Co-measured C, N and $\delta^{13}C$ and known characteristics of the lakes are used to indicate causes of the recorded differences. Limits to the spatial and temporal sampling approach used are identified and discussed; issues with bulk sediment analysis, effects of diagenesis and the operation of multiple, potentially conflicting global and local environmental drivers that become integrated to form lake sediment $\delta^{15}N$ records.

KEYWORDS nitrogen, sediment, isotopes, $\delta^{15}N$, lakes, $^{210}Pb$ dating

# INTRODUCTION

Bulk lake sediment $\delta^{15}N$ values provide an integrated and cumulative response to variations in both catchment, in-lake nitrogen (N) compounds and nutrient conditions (Jones et al., 2004). Nitrogen compounds from multiple organic and inorganic sources are incorporated into organic matter and waters in a catchment and then assimilated into littoral, planktonic and benthic ecosystems before burial in lake sediments. The isotopic composition of nitrogen compounds are fractionated during transport and in the water column due to multiple biogeochemical processes that affect the ratio of $^{15}N$ to $^{14}N$. For example, when oxygen is limited, microbial denitrification preferentially removes $^{14}N$, while phytoplankton preferentially uptake $^{14}N$ over $^{15}N$. Both processes lead to the residual nitrate pool becoming enriched in $^{15}N$, especially as eutrophication progresses. Measurement of the ratio of N isotopes $^{14}N/^{15}N$ ($\delta^{15}N$) in lake sediments therefore provides complementary data to biological (fossil) and other sedimentary proxies to assess past and current trophic conditions of lakes globally (Han et al., 2023; Herczeg et al., 2001; McCarthy et al., 2023; Vane et al., 2010; Wolfe et al., 2006). In the absence of long-term monitoring data, sediment $\delta^{15}N$ profiles provide a valuable spatial and temporal record of past N inputs to lake ecosystems.

Depletion of sediment $\delta^{15}N$ values from the mid-19th and 20th centuries have been reported from remote lakes in the Northern Hemisphere and ice cores in the Arctic (Heard et al., 2014; Holmgren et al., 2010; Holtgrieve et al., 2011) and signify the unprecedented global alteration of the N cycle due to anthropogenic emissions of reactive nitrogen (Nr) (Dean et al., 2014; Galloway and Cowling, 2002; Mason et al., 2023). Isotopic depletion of Nr in the atmosphere is attributed to several anthropogenic causes; fossil fuel emissions, synthetic fertiliser production (Bateman and Kelly, 2007) and/or an associated shift in partitioning caused by increasing atmospheric acidity (Geng et al., 2014). As a result of inter-catchment and inter-lake variation that affects the sequestration, cycling, and retention of Nr, and thus fractionation of $^{14}N/^{15}N$, the magnitude of the changes in $\delta^{15}N$ values observed vary. However, the timing of this depletion is largely consistent, having a c.1850 start and a mid-20th century acceleration, prompting the use of $\delta^{15}N$ trends as a stratigraphic expression and geological marker of the Anthropocene (Dean et al., 2014; Holmgren et al., 2010; Wolfe et al., 2013; Zalasiewicz et al., 2021).

By contrast, positive $\delta^{15}N$ trends of lake/wetland sediments in lower altitudes and latitudes are generally interpreted in terms of changes from land-use, nutrient enrichment and subsequent eutrophication (Brenner et al., 1999; Elliott and Brush, 2006; Hodell and Schelske, 1998; Lake et al., 2001; Vander Zanden et al., 2005). Previous studies of lake sediment $\delta^{15}N$ in the British Isles point to an upland-lowland divide; with the technique used to assess the ecological response to Nr deposition in the uplands (Curtis et al., 2012) and the effects of productivity changes and wastewater loads in lakes spanning the UK oligotrophic to eutrophic gradient (Rawcliffe et al., 2010; Vane et al., 2010; Woodward et al., 2012). Dissimilarities in sediment $\delta^{15}N$ values between upland and lowland lakes are not unexpected as there are many reasons to expect differences than just the effects of orographic rainfall and wet deposition (Curtis et al., 2007a; Metcalfe et al., 1999; Dore et al., 1992; Fowler et al., 1988).

Inconsistent lake sediment $\delta^{15}N$ trajectories exhibited in cores from lakes at multiple spatial scales, highlights the need to understand local and regional trends in sedimentary $\delta^{15}N$ (McLauchlan et al., 2013). This paper explores how the historical and global alteration of the N cycle by human activity is recorded in the N isotope ratio of lake sediments at a national scale, in this case, in $^{210}Pb$ dated sediment cores from lakes across the geographical and altitudinal range of UK catchments. Systematically measured, national scale datasets of N isotopic change in lake sediments spanning multiple catchments and waterbody types are rare. In the UK/British Isles, stable N and carbon (C) isotopes have been principally used alongside other high resolution paleoecological proxies in dated lake cores, e.g. with pigments and diatoms (McGowan et al., 2012; Moorhouse et al., 2014) and faecal markers (Vane et al., 2010) at a small numbers of sites, or have been measured at a regional scale in surface sediments along with other modern limnological parameters as analogues for past lake conditions (Jones et al., 2004; Woodward et al., 2012). A further study using high resolution lake sediment records of $\delta^{15}N$ from 19 lakes focused solely on remote upland sites in the UK (Curtis et al., 2012) using dual C and N isotope analysis. Here, 13 of the 19 mainly oligotrophic lakes demonstrated a timing and widespread alteration of N biogeochemistry comparable to Arctic and alpine lakes elsewhere (Botrel et al., 2014; Holtgrieve et al., 2011)

Here, we present a preliminary exploration of sediment $\delta^{15}N$ values from well-resolved time intervals (1850, 1900, 1980 and 1995) from a wider, national-scale selection of sites. These data are a novel compromise combining spatial and temporal differences; with reduced stratigraphic resolution balanced against information from a broader range and number of sites. However, such data remains essential to a better understanding of local and regional historical trends in N budgets and to trace the fate of deposited Nr in terrestrial and aquatic ecosystems (Bell et al., 2021; Davies et al., 2016; McLauchlan et al., 2013).

# METHODS

## Sampling of archived sediments

Lake sediment samples from the UCL Environmental Change Research Centre (ECRC) core archive were used. Core selection was an iterative process determined by the existence of a well-resolved $^{210}Pb$ core chronology and the availability of sufficient dried sediment from the chosen temporally defined intervals (below). The spatial distribution of lakes used in this study reflects the prevalence of lake acidification research conducted by the ECRC on UK upland waters from the 1980s, with continued and subsequent lake research by the group resulting in a broader geographical UK distribution (Figure 1a) as well as sites with catchments from across a spectrum of sizes and elevations (Figure 1b and 1c).

Sediment samples corresponding to dated intervals of 1850, 1900, and 1980 and 'surface' (median age 1995) were selected for stable isotope measurement. A 'top and bottom' approach using limited temporal core data to capture depositional changes in lakes has been used previously and is a valid one (Bennion et al., 2004; Ginn et al., 2007; Harris et al., 2006), as long as its limits are understood. The top and bottom approach (usually only using two-samples) can miss gradual/stepwise changes that have occurred between the past and present and so oversimplifies complex, non-linear processes. Intermediate samples (as in this study) add more detail, but it is a cost/effort decision between comprehensive analysis of fewer lakes, or as here, using dated sediment intervals from multiple lakes to capture broader landscape-scale changes.

For UK lakes and catchments and many others globally, the mid-nineteenth century (1850) broadly represents a time prior to or of only limited environmental impacts from fossil fuel emissions, industrialisation, and mechanised/intensive agriculture (Bell et al., 2021). Because of long-term landscape change by human activity, UK lake sediments from 1850 should not be viewed as representing pristine ecological settings (Battarbee et al., 2014). However, the choice of 1850 is also pragmatic as for many lake sediment cores analysed since the late 20th century, '1850' often represents the earliest dateable period due to the limits of unsupported $^{210}$Pb activity (Appleby, 2008).

The year 1900 was selected as the UK population approximately doubled (~20 to 40 million) between the mid-19th century and this time, concomitant with the growth of large industrial towns and cities, and an expanding national rail network fuelled by coal (Church et al., 1986; Mosley, 2013). From around 1900, traditional organic soil improvement methods were overtaken by the application of synthesised fertilisers (Brassley, 2000). The year 1980 was selected to equate to peak Nr deposition from fossil fuel combustion, that had, by this time, significantly affected UK aquatic systems (Fowler et al., 2005); via atmospheric transport and catchment hydrology. Nitrogen fertiliser consumption in the UK also peaked in the 1980s (1987, 1.6 x $10^6$ tonnes) (British Survey of Fertiliser Practice, 2021). The age of recent/surface sediments in the database ranges from cores collected between 1981 to 2010 (median 1995). Sediments representing the 'surface' were consistently taken from the adjacent depth interval below the surface for analysis to lessen the influence of fresh organic matter and loss of N due to rapid remineralisation with burial (Galman et al., 2009, 2008).

## 210Pb dating

All archived cores were $^{210}$Pb dated by direct gamma assay at the Environmental Radiometric Facility at UCL or Liverpool University Environmental Radioactivity Research Centre, using well-type coaxial low-background intrinsic germanium detectors. $^{210}Pb$ is determined via its gamma emissions at 46.5keV, and $^{226}Ra$ by the 295keV and 352keV gamma rays emitted by its daughter isotope $^{214}Pb$ following 3-weeks storage in sealed containers to allow radioactive equilibration (Appleby and Oldfield, 1978). Corrections are made for the effect of self-absorption of low energy gamma rays within the sample. Errors of $^{210}Pb$ dates increase with age due to the half-life of unsupported $^{210}Pb$ (22.3 yr); typical errors for 1850-1900 are in the order of ±15-25 years and 1980-present ±2 years. Further details on the core chronologies are provided in Supplementary Information (SI-1).

## Nitrogen and Carbon isotope measurements

Sediments were analysed simultaneously for $^{15}N/^{14}N$ and $^{13}C/^{12}C$, as well as total N and C, at the UC Davis Stable Isotope Facility, California, USA, via isotope ratio mass spectrometry on Hydra 20-20 or Anca-GSL isotope ratio mass spectrometers.

Bulk sediment was homogenised by a stainless-steel ball mill (Retsch™ MM200) from which ~10-12 mg of sediment was encapsulated in 9 x 5 mm tin capsules (Elemental Microanalysis) prior to combustion. Samples were interspersed during analysis with several replicates of laboratory standards. Elemental concentrations and stable isotope compositions were co-measured with nylon, bovine liver (SRM1577a), peach leaves (SRM1547) and Glutamic acid (USGS-41) reference materials. Sample values were finalised by correcting the values for the entire batch of samples based on the known values of the included laboratory reference material (https://stableisotopefacility.ucdavis.edu/carbon-and-nitrogen-solids).

The isotopic ratio of $^{15}N/^{14}N$ and $^{13}C/^{12}C$ is expressed using the delta (δ) notation, using $[(R_{sample}/R_{standard}] - 1] \times 1000$, where R is the $^{15}N/^{14}N$ or $^{13}C/^{12}C$ ratio in the measured sample or standard. The standard for N isotopes is the $\delta^{15}N$ of atmospheric N (commonly referred to as AIR), and for $\delta^{13}C$ the standard is Vienna Pee Dee Belemnite (VPDB).

As the aim of the study was to compare N isotopic changes, further bias was not introduced with the acidification of samples to remove inorganic C (Harris et al., 2001; Meyers and Teranes, 2001). Inorganic C in lake sediments comes from water chemistry (dissolved inorganic carbon) and geological-scale carbon fractionation (e.g. carbonate minerals). Inorganic carbon typically has higher $\delta^{13}C$ values due to equilibrium fractionation during carbonate precipitation/dissolution. Organic carbon has lower $\delta^{13}C$ values due to biological discrimination against $^{13}C$. The presence of inorganic C in lake sediments therefore limits the use of $\delta^{13}C$ as a proxy for changes in organic activity in the lake and catchment. This limitation is recognised in this paper where $\delta^{13}C$ values are used to interpret $\delta^{15}N$ changes.

$\delta^{15}N$ is often measured on untreated lake sediments, for example in upland oligotrophic lake systems where inorganic C/N sources are considered negligible (Battarbee et al. 2015, Jones et al. 2004, Moorhouse et al. 2014). Acidification treatments can also show significant non-linear patterns on measured $\delta^{13}C$ and $\delta^{15}N$ values, including no difference between different methods (Brodie et al., 2011).

GIS and other data sources

Lake and catchment morphometries were determined from Ordnance Survey Open Data Land-Form PANORAMA® raster data (50x50m cell) using ArcGIS (Hughes et al., 2004). Lake codes used in this paper correspond to ECRC sediment core codes assigned at the time of collection from the lakes. Lake names and associated codes are shown in SI-1.

Modern climate parameters (mean annual temperature and precipitation) were calculated in Arc GIS for each catchment polygon based on 5 km gridded data from UKCP09 (UK Met Office) data. Population density values for the lake catchment polygons were calculated for England and Wales (Office National Statistics, 2011). Population data for Scotland came from the 2001 Census Output Area data set (National Records of Scotland, 2001). Modern climate and population data are used here to compare with sediment $\delta^{15}N$ values. Human Footprint map data (1993 values) were used to compare UK lake sediment $\delta^{15}N$ with cumulative indicators of human impact (McLauchlan et al., 2013; Venter et al., 2016). ArcGIS (Spatial Statistics Toolbox) was used to calculate spatial autocorrelation (Global Moran's I) of $\delta^{15}N$ values. Z-score (standard deviation) and p-value (probability) from the autocorrelation calculation provides a numerical assessment of significant clustering or dispersion and distance from a random process. Generalised additive (mixed) models (GAMs) and Generalised Additive Models for Location, Scale and Shape (GAMLSS) were estimated using R (R Core Team, 2021) package mgcv (Wood, 2017; Wood et al., 2016). Isotope data are available open access from the NERC Environmental Information Data Centre (EIDC) (Turner and Rose, 2015).

# RESULTS

## Catchment-lake physiography

Lakes greater than 1 ha surface area are found from sea-level to 1215 m above sea level in the UK (UK Lakes Portal, https://eip.ceh.ac.uk/apps/lakes/) but lakes with water surface altitudes lower than 300m dominate (70%) our dataset (N = 90; Figure 1b). Mean catchment altitude (MCA) was considered to provide a more inclusive assessment of potential changing N sources to lakes in the UK, i.e. water bodies at the base of steeply glaciated catchments in Scotland and Wales. The dataset is largely split between lakes with an MCA less or greater than 300 m (n=48, 42 respectively; Figure 1c). In the UK, land above 300 m (1000 ft) altitude is broadly considered 'upland' with a cooler and wetter climate found in the north and west, compared to the warmer, drier 'lowland' in the south and east (Averis, 2004). This loose upland/lowland altitudinal divide in the UK is also marked by notable differences in vegetation, geology and historical land-use. Upland lakes in the UK are usually more remote, low nutrient systems, and sensitive to acid deposition due to thin soils and underlying geology with little buffering capacity. Lowland aquatic systems in the UK have a long history of being affected by far more intense land-use and subsequent nutrient enrichment/eutrophication as a consequence of being downstream and proximal to large populations. This lowland/upland division therefore provides a useful framing to observe how contrasting lake types have responded to human activity and global/national changes in historical atmospheric and nutrient N inputs.

### Spatial and temporal changes of $\delta^{15}N$

Sediment $\delta^{15}N$ values from all locations, ages, and depths vary between -1.6 and 13.3, although lakes with MCA >300m do not exceed 5.6. Lowland lake sediments deposited in 1850 exhibit $\delta^{15}N$ values comparable to upland sites. Spatial autocorrelation values (Table 1) show the 1850 $\delta^{15}N$ pattern is less spatially structured, representing pre-industrial, geographically dispersed, and variable N inputs into lakes. The 1900 *z*-score ($z = 2.18$, $p = 0.029$) indicates a more spatially clustered pattern than the 1980 value ($z = 2.91$, $p = 0.035$) with a <1% likelihood that $\delta^{15}N$ clustering is random indicating more spatially structured N drivers.

The frequency distribution of sediment $\delta^{15}N$ values in UK lakes sediments becomes more heavily tailed (Figure 2a) between 1850-1995 with the greatest difference between 1900 and 1980. Highly significant GAMLSS fits specifically in relation to altitude (Figure 2b) also show little difference between 1850-1900 and 1980-1995. This switch illustrates the known 20$^{th}$ century disruption to the global N-cycle, resulting in higher $\delta^{15}N$ values in lowland systems and lower $\delta^{15}N$ values in upland lakes.

Extreme low $\delta^{15}N$ values in the upland group from 1850 include Loughgarve (LGAR) in Northern Ireland and Llyn Glas (GLAS) in Yr Wyddfa, Wales. LGAR is a shallow (max depth 0.9 m) moorland lake with an upland bog catchment and is, or likely was N-limited (Gibson et al., 1995) while at GLAS low sediment $\delta^{15}N$ values also suggest nutrient-limitation due to a high flushing rate, lack of sewage/fertiliser and organic matter dominantly from lacustrine sources and low $\delta^{15}N$ catchment vegetation (Jones et al., 2004). These lakes are observed as having outlier N isotope values in both upland and lowland groups up to the present. The relationship between bulk sediment total N and $\delta^{15}N$ for all time interval samples from all 90 UK lake cores is poor ($r^2 = 0.007$, $p<0.1$), although an increase since 1850 in total N in lowland lakes is apparent (Figure 2d).

Comparison of past and current sediment $\delta^{15}N$ changes with co-measured C isotopes ($\delta^{13}C$) and the ratio of C:N provide more detail on temporal changes. Both clustering and dispersal of values over time is observed in plots of dual C/N isotope values (Figure 3a); a negative $\delta^{15}N$ shift of upland sites is apparent.

High $\delta^{13}C$ values are evident in more alkaline, lakes i.e., Hornsea Mere (HORN), Loch a Phuill (PHUI), Hawes Water (HAWE), Malham Tarn (MALH) and Upton Broad (UPTON) with significant inorganic C. These lakes have been historically affected by eutrophication (Ayres et al., 2007; Bennion et al., 2004; May et al., 2010; Rawcliffe et al., 2010) and so phytoplankton photosynthetic fractionation may have mediated sediment $d^{13}C$ values.

Sediments with lower C:N values in 1980 have a greater range of $\delta^{15}N$ values than lake sediments with a higher contribution from allocthonous (terrestrial) sources indicated by high C:N values (Figure 3b). Terrestrial organic C inputs to lakes with low and negative trending sediment $\delta^{15}N$ are seen in upland, peat abundant catchments e.g., Llyn Berwyn (BER), Loch Muick (MUIC), Loch na Gabhalach Nodha (NODH) and Grey Heugh Slack (GHEU). A negative shift in both sediment $\delta^{15}N$ and C:N has occurred in upland sites of GLAS, LGAR, MUIC and Llyn Clyd (CLYD).

Because of the age range in the surface samples (range 1981-2012, median 1995) and potential effects of sediment-water interface diagenesis, the difference between 1850 to 1980 values is here used to show the UK-scale change in lake sediment $\delta^{15}N$ trajectories during a period of unprecedented industrial and land-use change (Figure 4). The spatial distribution of changes shows both negative and positive historical trends. Negative trends are concentrated in upland areas of Scotland, Wales, NI, the Lake District, and northern England. Negligible to more positive differences occur scattered across the UK but noticeably in more lowland areas, that are the inverse of upland areas being warmer and with a higher population density (Figure 4 and 5a-c). The greatest positive differences (Table 2) in sediment $\delta^{15}N$ are observed in shallow, eutrophic lakes with historical nutrient inputs from urban and agricultural sources (Bennion et al., 2009, 2004; Gunn et al., 2013; May et al., 2011; Sayer et al., 1999).

Comparing $\delta^{15}N$ values with altitude indicates an effect of near sea-level lakes in high glaciated catchments. Positive value changes to the present, are seen in the higher mean catchment altitudes of Loch Lomond (LOMO), Loch Maree (MARE) and Loch Shiel (SHIE) in Scotland. Nutrient enrichment is suggested to have caused positive sediment $\delta^{15}N$ shifts in the uplands (e.g. in MALH and Llyn Fach (FACH)) but above 600m all sites show a negative change. (Figure 5b).

Magnitude and trajectory of change can also be determined by a best-fit regression between time intervals and $\delta^{15}N$ values for each of the lake cores; the slope values representing rate of change per year $a^{-1}$ and direction (+/-) of $\delta^{15}N$ change (Supplementary 2). This linear representation of change is only a guide. Mapped trajectories from 4-point regressions (Supplementary 2), show a similar spatial pattern as the difference in $\delta^{15}N$ values, but here also provides rate as well as a direction of change information.

## DISCUSSION

Changes in sediment $\delta^{15}N$ recorded in UK lakes are clearly a complex function of catchment and lake integration (Curtis et al., 2007). The spatial and temporal dataset of sediment $\delta^{15}N$

values presented here shows that global-scale historical N changes can be recognised, but considerable differences occur due to physiographic and anthropogenic factors and the biogeochemical complexity of soils, organic matter, in-lake and post-burial processes (Brahney et al., 2014; Meyers and Teranes, 2001). However, whilst recognising this complexity, it is also clear that despite using a low temporal resolution, opportunistic and iterative sampling process of available archived lake sediments, the dataset validates and communicates very well the distinct ecosystem change in water bodies across upland and lowland Britain that has occurred due to unprecedented human activity.

Our data here show that sedimentary $\delta^{15}N$ values should always be first considered on an individual core basis, within a local and regional context, as knowledge of the unique isotopic signature of the N inputs into lakes is critical (Botrel et al., 2014). Physiographic and anthropogenic influences have clearly influenced sediment $\delta^{15}N$ trends (Figure 5,6); with cool, high elevation (MCA>300m), oligotrophic lakes showing negative $\delta^{15}N$ shifts (up to -2.5) (Table 2), and warmer, low elevation lakes showing far greater increases in sedimentary $\delta^{15}N$ values (max 7.6). Low values of both $\delta^{15}N$ and C:N point to sediments in upland lakes (e.g. GLAS, LGAR, Round Loch of Glenhead (RLGH) and CLYD) having accumulated atmospheric-N directly by in-lake stimulation of autochthonous organic matter (lacustrine algae and plankton) ( Jones et al., 2004).

In lower altitude lakes the $\delta^{15}N$ history of eutrophication is not so uni-directional due to the variety and lesser/greater amount of N inputs in the recent historical past. For example, DISS, Marton Mere (MARM) and HOLTU received sewerage and wastewater inputs before 1850 (Peglar, 1993; Turner et al., 2013; Yang, 2010). Marine-derived N is proposed for the observed pattern seen at Gull Ponds (GULL) that was known for its large pre-World War 2 seagull colony (Hollom, 1940) as well as the near-coast MARM, that is likely to have had similar guano inputs to other UK lakes with gull colonies, such as Hickling Broad (Irvine et al., 1993). A marine/guano $\delta^{15}N$ sediment signal is also suggested to occur in near-coast, wildfowl rich lakes Monk Myre (MONK), Coldingham Loch (COD) and Loch Skene (SKEN) prior to fertiliser induced eutrophication. Increased $\delta^{15}N$ values certainly correspond with early and increasing 20th century eutrophication/hyper-eutrophication due to wastewater inputs at EDGB, Thoresby Lake (THOP), Fleet Pond (PFLE) and Hornsea Mere (HORN) (Bennion et al., 2018; Turner et al., 2013).

Due to their geographical location and relative isolation the negative shifts seen in small, woodland lakes Psygodlyn Mawr (PYSG) in South Wales and WAKE (Epping Forest, London) suggest the influence of atmospheric deposition of fossil fuel N from industrial/urban areas (Fowler et al., 2005). Supporting evidence from other indicators of fossil fuel atmospheric deposition (in WAKE, spheroidal carbonaceous particles, (Turner et al., 2013)) needs however to be considered against the inputs from the range of $\delta^{15}N$ values found in woodland soils, trees and leaf litter (Falxa-Raymond et al., 2014) as well as sedimentation in anoxic, tree-sheltered waterbodies. Low values of both $\delta^{15}N$ and $\delta^{13}C$ in WAKE suggest the selective preservation of $^{13}C$-depleted compounds and bacterial growth adding $^{15}N$-depleted biomass to the bulk sediment (Lehmann et al., 2002).

While a lack of a globally consistent trend in sedimentary $\delta^{15}N$ is reported (McLauchlan et al., 2013) due to local conditions, a national-scale trend in the UK since 1850 identified in this study indicate an increase in sedimentary $\delta^{15}N$ values due to population density (Figure 5c) and 'Human Footprint' (Venter et al., 2016) (Figure 6c).

*Other considerations*

Consistency of the $\delta^{15}N$ sediment record can be investigated by measurement of multiple dated cores in the same lake (Herczeg et al., 2001; Schelske and Hodell, 1995) and uncertainty reduced by measurement of trap sediments, seston and within-lake ecological compartments

(Jones et al., 2004; Owen et al., 1999). Similarly, increasing the number of replicates representing a particular time interval, or indeed increasing the stratigraphic resolution would improve confidence, but adds a significant workload to stratigraphic studies featuring large numbers of sites. This study was designed to contribute to the Long Term Large Scale (LTLS) Macronutrient Model for the NERC Macronutrient Cycles programme (2014-2017) that set out to simulate terrestrial and freshwater fluxes of nutrients at a broad scale (multiple catchments) over decades and centuries, rather than lake-specific changes. This compromise will be a continued feature of large-scale research always requiring more detail spatially and temporally.

Furthermore, the bulk measurement of lake sediments, by their integrative nature, homogenise C and N from a broad range of organic sources, that are a significant source of uncertainty in $\delta^{15}N$ measurements. Small changes in organic composition must be considered with the mass spectroscopy method, for example the effect of microscopic tree leaf particles in an algal dominated sediment sample. $\delta^{15}N$ measurements on cladocera remains (Perga, 2011, 2010), fish scales (Ventura and Jeppesen, 2010) and specific compounds in lake sediments (Enders et al., 2008; Tyler et al., 2010) clearly provide more certainty than bulk sediment but add an extra level of sampling effort at the least. Because of the linkage between C and N in lake sediments, it is clearly advisable to increase analytical effort and replicate dual C/N isotope measurements on bulk samples that have been acidified, to reduce some of the uncertainty from inorganic carbon (especially when interpreting measurements across diverse geological landscapes).

Improved understanding, or at least greater recognition, of the effect of early diagenesis on core profiles, should reduce the ambiguity of what stable isotope values represent in bulk lake sediment samples. Post-depositional processes change N and C compounds and sediment records of their isotopes also reflect this (Brahney et al., 2014; Lehmann et al., 2002).

Understanding how important diagenetic processes are is problematic as local redox conditions and organic matter availability, like the spatial variability of pre-burial controls, will influence the extent of change in $\delta^{15}N$ values. With such potential variability, the consistent decline in $\delta^{15}N$ during the last 150 years measured in UK high and remote lakes nonetheless supports causality due to changes in atmospheric N inputs rather than diagenesis. In conjunction this atmospheric process (depletion of $\delta^{15}N$ values) must have also reduced the more positive $\delta^{15}N$ values in lowland lakes, when in receipt of comparable atmospheric N inputs.

This exploratory low temporal resolution analysis clearly shows a demand for more specific and detailed analytical and modelling techniques to disentangle deposition and post depositional effects on N isotope patterns (Galman et al., 2009, 2008) which needs to be resolved across a broader range of lake types and timescales. One clear aspect to resolve is the effect that diagenesis has on the $\delta^{15}N$ signal over a decadal/century scale as organic matter is buried and preserved in different lakes. A result of how long the ECRC has been working on UK lakes, indicates one method for future study, i.e. the repeat measurement of dated sediments collected at different times from the same lake. Two cores from Loch Shiel (SHIE2 and SHIE5) were collected in 1995 and 2006 respectively and analysed as part of this research. Applying a null modelling approach (Brahney et al., 2014), the effect of diagenesis on $\delta^{15}N$ values is inconclusive, with a divergence of values occurring in sediments at present and also 1850 (Supplementary 3). Little difference in $\delta^{15}N$ values from 1900 was observed and from the 1980 layer that had an extra 11 years in the lake the $\delta^{15}N$ difference was only a value of 0.2.

While the range of environmental processes and variables that determine bulk lake sediment $\delta^{15}N$ values are broad and in need of further scrutiny, $\delta^{15}N$ values reported in this study, nonetheless show a transformation of UK lakes by human activity in the last 150 years. An interesting consideration for future study would be to analyse these lakes again now and in 2050 to capture a full two centuries of impact and potential recovery, as well as potential issues of the preservation of the $\delta^{15}N$ record in lake and archived materials. Significant efforts have been made since the late 20th century to reduce N pollution; most directly through fossil fuel emission reductions and improved wastewater treatment, but inputs into aquatic systems due to residual nitrogen stored in soils and groundwater will continue to influence ecosystems for decades into the future.

## CONCLUSION

Both global and local patterns and processes have determined the trajectory of changing sediment $\delta^{15}N$ trends in UK lakes since 1850. Sedimentary $\delta^{15}N$ trends show that the technique is sensitive to measure regional physiographic and anthropogenic influences, not just global controls of environmental parameters (McLauchlan et al., 2013).

The unprecedented transformation of the global N cycle due to fossil fuel combustion, artificial fertilisers and wastewater into freshwaters is recognised in UK lake sediment records of $\delta^{15}N$. Because of the historical integration of N sources, a sediment $\delta^{15}N$ decrease, attributed to fossil fuel combustion/atmospheric deposition of Nr is most apparent in upland lakes with mean catchment altitudes above 300m. Sediment $\delta^{15}N$ in lowland UK lakes show that anthropogenic changes to N cycling also occurred simultaneously due to atmospheric, terrestrial biogeochemical changes and wastewater inputs; with modern sediment $\delta^{15}N$ values in some lakes showing amelioration or recovery from past nutrient loads. This integration of $\delta^{15}N$ signals is a key reason why other paleoecological techniques are essential to understand sources and drivers.

Determining the precise environmental drivers and timing of sediment $\delta^{15}N$ values requires lake by lake and individual core analysis, but when viewed at a UK scale, the variability and trajectory of sediment $\delta^{15}N$ changes are evidently associated with elevation (250-300 m) above sea level, which in the UK is synonymous with a distinct biogeochemistry, population density, climate and nature/intensity of catchment land-use.

$\delta^{15}N$ core profiles reflect these environmental gradients, but because of the integrating nature of lake sediment and the bulk nature of sampling, disentangling cause from effect on down-core changes, is not straightforward and evidence from sediment $\delta^{15}N$ requires support from site specific historical information (for example documented ecological, physical changes) and from other palaeoenvironmental proxies (e.g. palaeoecology, sediment environmental DNA).

Adherence to and reporting of methodological procedures used is clearly important for continued use of the $\delta^{15}N$ sediment technique, as well as access to data from previous studies. Considering the effects of using bulk sediment, different methods of removal of inorganic/organic components, sample sizes and mass spectroscopes, there is a continued need for standardising sample preparation, use of standards, analysis with other palaeoecological techniques and ring-testing of values generated between laboratories to reduce uncertainty and improve pan-regional $\delta^{15}N$ sediment research.

## Acknowledgments

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## Data Availability

The sediment, isotope and location data used in this paper are available open access from the NERC Environmental Information Data Centre (EIDC) archive.

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## Conflict of Interest

The authors declare no conflicts of interest.

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**Historical (1850-1995) Nitrogen changes in UK catchments recorded by lake sediment $d^{15}N$.**

# FIGURES

**Figure 1.** (a) Locations of lakes and frequency histograms (bins of 50m altitude) of (b) lake surface altitudes and (c) mean catchment altitudes calculated. Full names of lakes and locations are given in Supplemental 1. Shaded area on map indicates land >300 m altitude. Sites with black circles have mean catchment altitudes (MCA) >300m.

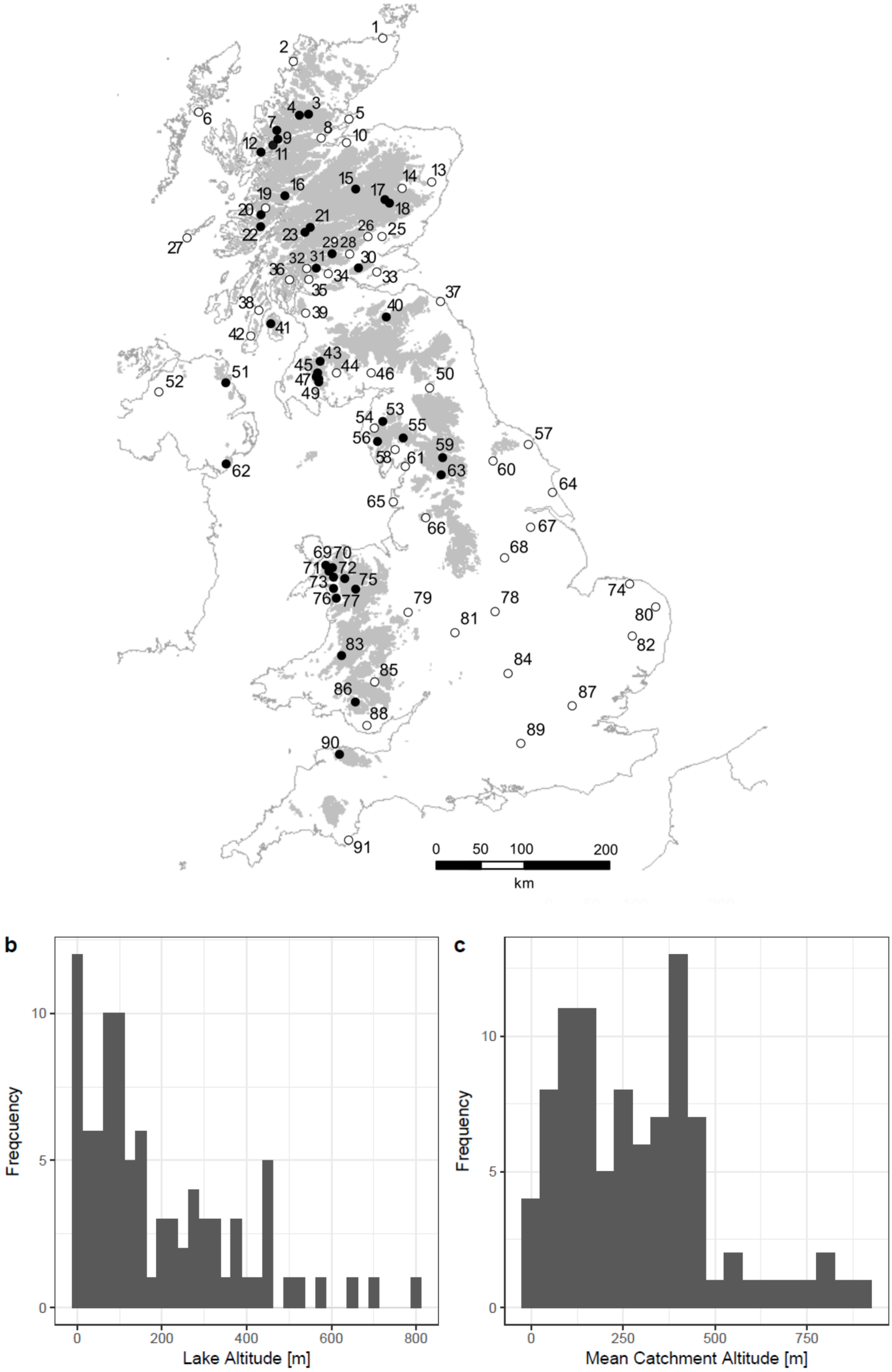


**Figure 2.** Lake sediment δ$^{15}$N values at 1850, 1900, 1980 and present (median 1995) (a) Frequency distribution (b) GAMLSS curved fits between sediment δ$^{15}$N values and mean catchment altitude, (c) box and whisker plot comparing lowland (LO) and upland (UP) sediment δ$^{15}$N values and (d) comparing sediment N. See Figure 1 for locations and names of outliers.

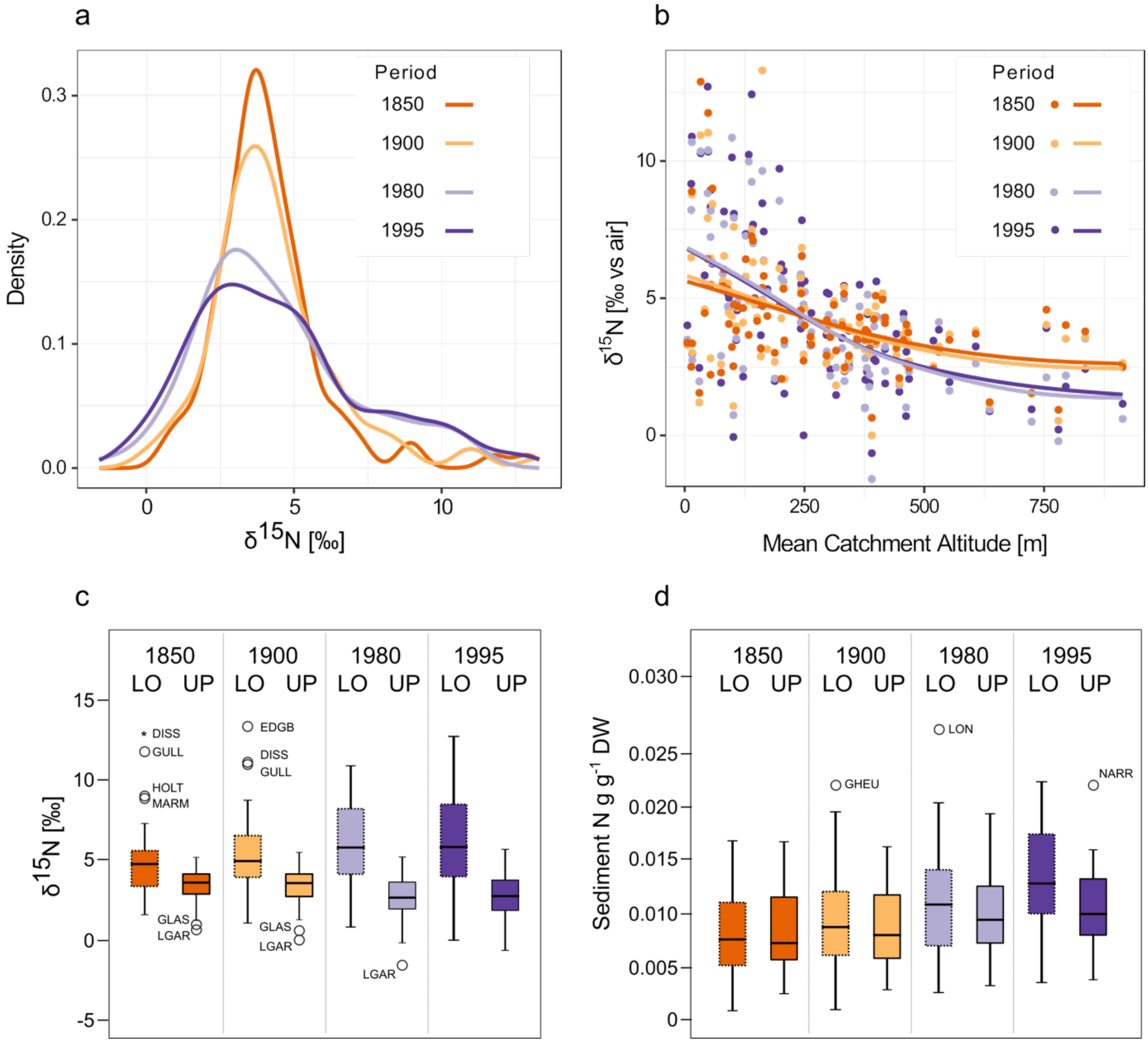


**Figure 3**. Dot and tail trajectory plots, Dots = 1980. End of tail = 1850. Circle = MCA <300m, Triangle = MCA >300m. (a) sediment $\delta^{15}N$ / $\delta^{13}C$ and (b) sediment $\delta^{15}N$ / C/N Codes for lakes are in Supplementary 1

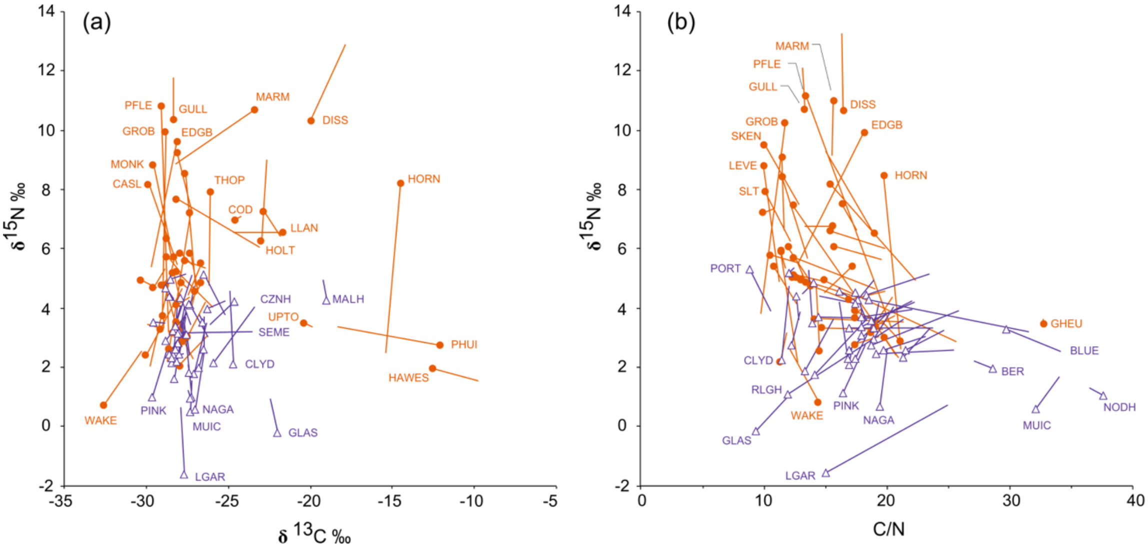


**Figure 4.** Difference in lake sediment $\delta^{15}$N between 1850 and 1980. Positive values indicate an positive change in $\delta^{15}$N from 1850 to 1980. Light green shading is UK land >300 m above sea level.

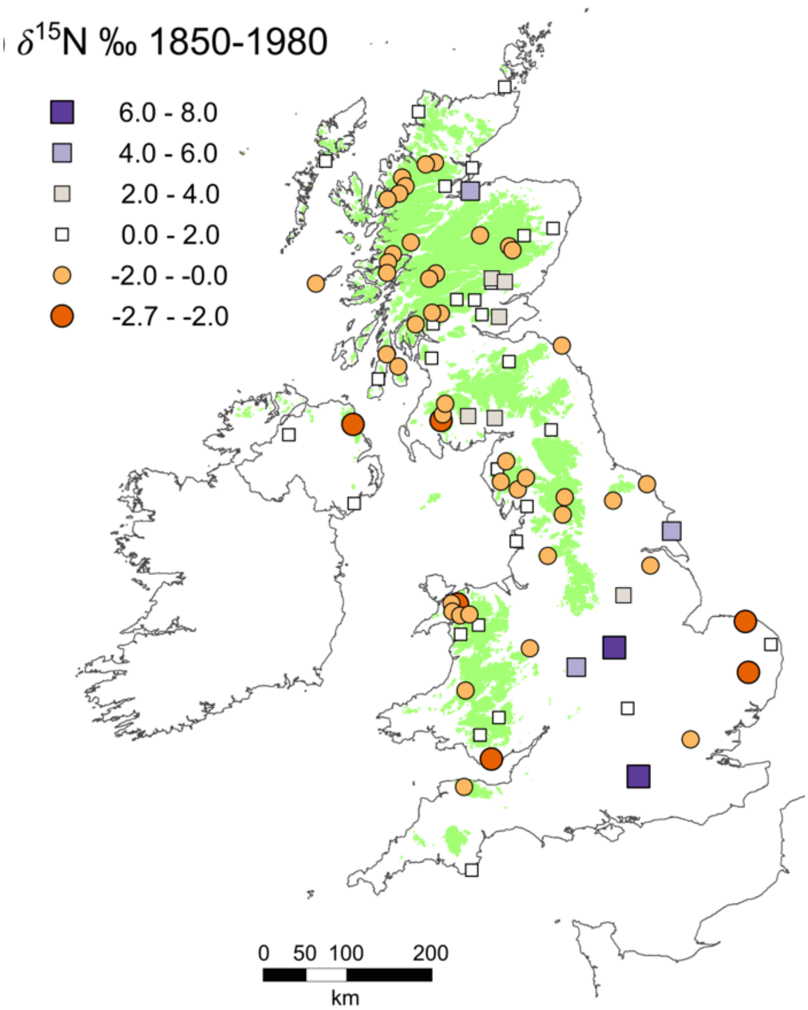


**Figure 5.** Change in UK lake sediment $\delta^{15}N$ from 1850 to 1980 in relation to environmental parameters (a) mean annual temperature (b) mean catchment altitude and (c) population density.

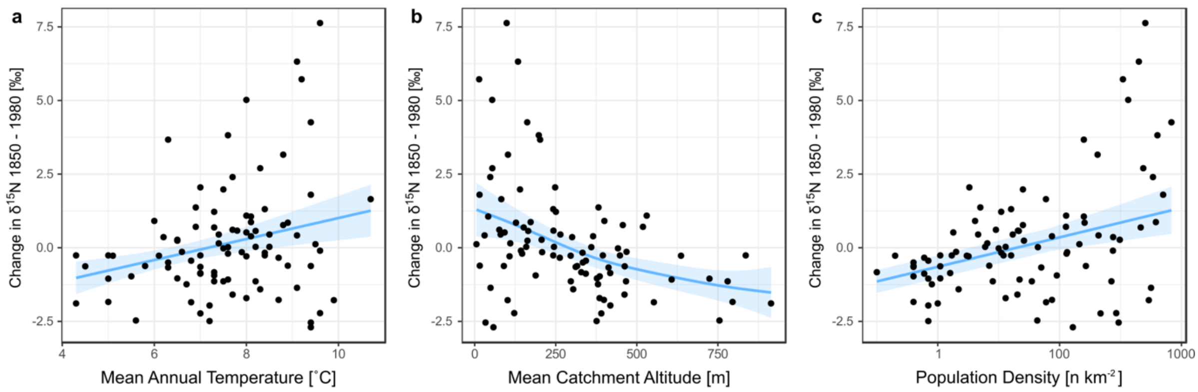
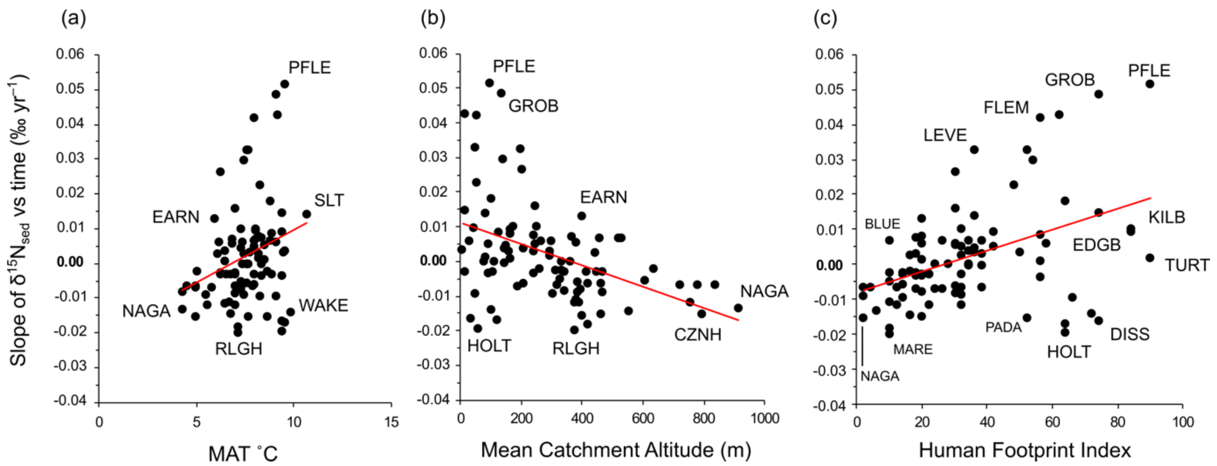



**Figure 6.** UK Lake sediment $\delta^{15}N$ trajectories from 1850 to 1995. Y-axis = slope of $\delta^{15}N$ vs time (‰ $yr^{-1}$) from 4-point linear regressions at individual sites (After McLauchlan et al. 2013). Lake trajectories in relation to (a) mean annual temperature (MAT) ($r^2 = 0.0775$ , $p < 0.01$), (b) mean catchment altitude (MCA) ($r^2 = 0.188$ , $p < 0.001$) and (c) Human Footprint Index (1993 values) from Venter et al. 2016. ($r^2 = 0.190$ , $p < 0.001$). Site codes see Supplementary 1.



# Historical (1850-1995) Nitrogen changes in UK catchments recorded by lake sediment $d^{15}N$.

## Tables

**Table 1.** Global Morans I Spatial Autocorrelation of $\delta^{15}N$ values

| | **1850** $\delta^{15}N$ | **1900** $\delta^{15}N$ | **1980** $\delta^{15}N$ | **1995** $\delta^{15}N$ |
|---|---|---|---|---|
| Moran's Index: | 0.024 | 0.126 | 0.180 | 0.147 |
| Variance: | 0.004 | 0.004 | 0.004 | 0.004 |
| z-score: | 0.556 | 2.181 | 2.919 | 2.384 |
| p-value: | 0.578 | 0.029 | 0.004 | 0.017 |
| Comments | Not significantly different than random | < 5% likelihood clustered pattern is result of random chance | < 1% likelihood clustered pattern is result of random chance | < 5% likelihood clustered pattern is result of random chance |
| *Conceptualization*: Inverse-Distance, *Distance Method*: Euclidean, *Row Standardization*: True | | | | |

**Table 2.** UK water bodies measured with the greatest positive and negative difference in sediment $\delta^{15}N$ between 1850 and 1980. Grouped by known lake histories.

| Change 1850 to 1980 $\delta^{15}N$ | Code | Water Body name and UK location | MCA (m asl) | Population (*n* $km^2$) |
|---|---|---|---|---|
| Positive shift (history of eutrophication) | | | | |
| +7.6 | PFLE | Fleet Pond, Hampshire. | 99 | 2250 |
| +6.3 | GROB | Groby Pool, Leicestershire. | 133 | 1998 |
| +5.7 | HORN | Hornsea Mere, Yorkshire. | 14 | 1094 |
| +5.0 | FLEM | Loch Flemington, Inverness. | 54 | 1336 |
| +4.2 | EDGB | Edgbaston Pool, Birmingham. | 162 | 6840 |
| +3.8 | LEVE | Loch Leven, Perth & Kinross. | 197 | 4036 |
| Negative shift (atmospheric deposition) | | | | |
| -1.85 | LLAG | Llyn Llagi, Snowdonia | 552 | 60 |
| -1.9 | NARR | Loch Narroch, Galloway. | 418 | 0.7 |
| -1.9 | NAG | Lochnagar, Cairngorms. | 914 | 1 |
| -2.2 | LGAR | Loughgarve, NI. | 395 | 470 |
| -2.5 | RLGH | Round Loch of Glenhead, Galloway. | 376 | 0.7 |
| -2.5 | CLYD | Llyn Clyd, Snowdonia. | 755 | 43 |
| *Negative (recovery from historical eutrophication - wastewater)* | | | | |
| -2.5 | DISS | Diss Mere, Suffolk | 33.4 | 930 |
| -2.7 | HOLT | Holt Hall Lake, Norfolk | 57.8 | 165 |

# Historical (1850-1995) Nitrogen changes in UK catchments recorded by lake sediment $\delta^{15}N$.

## Supplementary Information

## Supplementary 1

List of core codes, UK WBID (Waterbody identification codes – see UK Lakes Portal, UK Centre for Ecology & Hydrology, https://eip.ceh.ac.uk/apps/lakes/ NI = Northern Ireland, not included in WBID database), lake name and references for core chronology details.

| No. | Site Code | WBID | Lake Name | Core Code | Re |
|---|---|---|---|---|---|
| 1 | LON | 2077 | Long Loch | LON2 | Rose et al. 2011 |
| 2 | BRAC | 4229 | Loch nam Brac | BRAC1 | Rose et al. 2011 |
| 3 | NODH | 13616 | Loch na Gabhalach Nodha | NODH2 | Rose et al. 2012 |
| 4 | CZNH | 13758 | Lochan a Chnapaich | CZNH2 | Rose et al. 2012 |
| 5 | EYE | 14019 | Loch Eye | EYE1 | Bennion et al., 2004 |
| 6 | HUAM | 13354 | Loch Huamavat | HUAM1 | Clarke et al., 2007 |
| 7 | MARE | 14057 | Loch Maree | MARE1 | Bennion et al., 2004 |
| 8 | USSI | 16456 | Loch Ussie | USSI1 | Bennion et al., 2008 |
| 9 | CLAI | 16443 | Loch Clair | CLAI1 | Rose et al. 2011 |
| 10 | FLEM | 17013 | Loch Flemington | FLEM1 | Bennion et al., 2008 |
| 11 | LCFR | 17334 | Loch Coire Fionnaraich | LCFR1 | Pla et al. 2009 |
| 12 | ARR | 18209 | Loch Coire nan Arr | ARR5 | Juggins et al. 1993 |
| 13 | SKEN | 20757 | Loch Skene | SKEN1 | Bennion et al., 2004 |
| 14 | KINO | 21189 | Loch Kinord | KINO2 | Bennion et al., 2004 |
| 15 | EINI | 21191 | Loch Einich | EINI1 | Rose et al. 2011 |
| 16 | ARKA | 21490 | Loch Arkaig | ARKA1 | Clarke et al., 2007 |
| 17 | NAG | 21723 | Lochnagar | NAG27 | Dalton et al. 2000 |
| 18 | MUIC | 21790 | Loch Muick | MUIC2 | Rose et al. 2011 |
| 19 | SHIE | 21925 | Loch Shiel | SHIE5 | Clarke et al., 2007 |
| 20 | DOI | 22308 | Loch Doilet | DOI2 | Battarbee et al. 1989 |
| 21 | LAI | 22839 | Loch Laidon | LAI4 | Flower et al. 1996 |
| 22 | UIS | 22963 | Loch Uisge | UIS1 | Flower et al. 1993 |
| 23 | ACH | 23361 | Loch nah'Achlaise | ACH2 | Rose et al. 2011 |
| 24 | BUTT | 23531 | Butterstone Loch | BUTT3 | Bennion et al., 2004 |
| 25 | MONK | 23610 | Monk Myre | MONK1 | Bennion et al., 2008 |
| 26 | LOWE | 23559 | Loch of the Lowes | LOWE2 | Bennion et al., 2004 |
| 27 | PHUI | 23618 | Loch a Phuill | PHUI1 | Bennion et al., 2008 |
| 28 | MONZ | 24171 | Lake Monzievaird | MONZ1 | Bennion et al., 2008 |
| 29 | EARN | 24132 | Loch Earn | EARN1 | Rose et al. 2011 |
| 30 | AWE | 49001 | Loch Awe South | AWE2 | Bennion et al., 2004 |
| 31 | TINK | 24745 | Loch Tinker | TINK1 | Battarbee et al. 1989 |
| 32 | LOMO3 | 49002 | Loch Lomond North | LOMO3 | Bennion et al., 2004 |
| 33 | LEVE | 24843 | Loch Leven | LEVE11 | Bennion et al., 2004 |
| 34 | MENT | 24919 | Lake of Menteith | MENT2 | Bennion et al., 2004 |
| 35 | LOMO4 | 49003 | Loch Lomond South | LOMO4 | Bennion et al., 2004 |
| 36 | ECK | 24996 | Loch Eck | ECK4 | Bennion et al., 2004 |
| 37 | COD | 26072 | Coldingham Loch | COD2 | Rose et al. 2011 |
| 38 | NGAD | 26482 | Loch nan Gad | NGAD1 | Bennion et al., 2008 |
| 39 | KILB | 26566 | Kilbirnie Loch | KILB1 | Bennion et al., 2004 |
| 40 | PORT | 26720 | Portmore Loch | PORT1 | Rose et al. 2011 |
| 41 | TAN | 26916 | Loch Tanna | TAN3 | Rose et al. 2012 |
| 42 | TANG | 27234 | Tangy Loch | TANG1 | Bennion et al., 2008 |
| 43 | DOON | 27604 | Loch Doon | DOON3 | Rose et al. 2011 |
| 44 | RLD | 27824 | Round Loch of the Dungeon | RLD1 | Rose et al. 2011 |
| 45 | CASL | 27899 | Castle Loch | CASL1 | Bennion et al., 2004 |

**Supplementary 1 (continued)**

| No. | Code | WBID | Lake Name | Core Code | Ref |
|---|---|---|---|---|---|
| **46** | NARR | 27912 | Loch Narroch | NARR3 | Rose et al. 2011 |
| **47** | RLGH | 27927 | Round Loch of Glenhead | RLGHK5 | Allot, 1992 |
| **48** | LDE | 27948 | Loch Dee | LDE3 | Rose et al. 2011 |
| **49** | CRAZ | 28220 | Crag Lough | CRAZ2 | Turner et al. 2013 |
| **50** | LGAR | NI | Loughgarve | LGAR1 | Davidson et al. 2008 |
| **51** | LASH | NI | Lough Ash | LASH1 | Rose et al. 2011 |
| **52** | BASS | 28847 | Bassenthwaite Lake | BASS1 | Bennion et al 1997 |
| **53** | LOWS | 28986 | Loweswater | LOWS1 | Bennion et al., 2000a |
| **54** | SMAL | 29155 | Small Water | SMALL1 | Simpson, 2018 |
| **55** | WAST | 29183 | Wastwater | WAST1 | Bennion et al 1997 |
| **56** | GHEU | 29245 | Grey Heugh Slack | GHEU | Battarbee et al. 2015 |
| **57** | ESTH | 29328 | Esthwaite Water | ESTH1 | Bennion et al 1997 |
| **58** | SEME | 29479 | Semer Water | SEME1 | Bennion et al 1997 |
| **59** | GORM | 29545 | Gormire | GORM3 | Yang & Rose, 2005 |
| **60** | HAWE | 29647 | Hawes Water | HAWE3 | Rose et al. 2011 |
| **61** | BLUE | NI | Blue Lough | BLUE5 | Rose et al. 2011 |
| **62** | MALH | 29844 | Malham Tarn | MALH2 | Rose et al. 2011 |
| **63** | HORN | 30244 | Hornsea Mere | HORN1 | Rose et al. 2011 |
| **64** | MARM | 30553 | Marton Mere | MARM1 | Turner et al. 2013 |
| **65** | TURT | 31202 | Turton & Entwistle Reservoir | TURT1 | Yang & Rose, 2005 |
| **66** | GULL | 31749 | Gull Ponds | GULL1 | Yang & Rose, 2005 |
| **67** | THOP | 33316 | Thoresby Lake | THOP1 | Turner et al. 2013 |
| **68** | PADA | 33730 | Llyn Padarn | PADA2 | Bennion et al. 2010 |
| **69** | CLYD | 33843 | Llyn Clyd | CLYD1 | Rose et al. 2011 |
| **70** | GLAS | 34044 | Llyn Glas | GLAS1 | Rose et al. 2011 |
| **71** | LLAG | 34319 | Llyn Llagi | LLAG3 | Rose et al. 2011 |
| **72** | CON | 34400 | Llyn Conwy | CON4 | Rose et al. 2011 |
| **73** | HOLTU | 34756 | Holt Hall Lake Upper | HOLTU2 | Turner et al. 2013 |
| **74** | BALA | 34987 | Llyn Tegid | BALA1 | Bennion et al., 2003 |
| **75** | EIB | 35035 | Llyn Eiddew Bach | EIB2 | Patrick et al. 1987 |
| **76** | MYN | 35578 | Llyn Cwm-mynach | MYN6 | Rose et al. 2011 |
| **77** | GROB | 36536 | Groby Pool | GROB4 | Davidson et al 2005 |
| **78** | SCM2 | 36566 | Betton Pool | SCM27B | Bennion et al 1997 |
| **79** | UPTO | 36202 | Upton Broad | UPTO1 | Bennion et al 1997 |
| **80** | EDGB | 37758 | Edgbaston Pool | EDGB2 | Turner et al. 2013 |
| **81** | DISS | 37921 | Diss Mere | DISS07 | Yang, 2010 |
| **82** | BER | 38907 | Llyn Berwyn | BER7 | Rose et al. 2011 |
| **83** | STOW | 39683 | Eleven Acre Lake | STOW91 | Bennion et al., 2010 |
| **84** | LLAN | 40067 | Llangorse Lake | LLAN3 | Bennion & Appleby, 1999 |
| **85** | FACH | 41210 | Llyn Fach | FACH1 | Yang & Rose, 2005 |
| **86** | WAKE | 41481 | Wake Valley Pond | WAKE1 | Turner et al. 2013 |
| **87** | PYSG | 42392 | Pysgodlyn Mawr | PYSG1 | Goldsmith et al. 2014 |
| **88** | PFLE | 43315 | Fleet Pond | PFLE2 | Turner et al. 2013 |
| **89** | PINK | 43906 | Pinkworthy Pond | PINK3 | Yang & Rose, 2005 |
| **90** | SLT | 46472 | Slapton Ley | SLT4 | Rose et al. 2011 |

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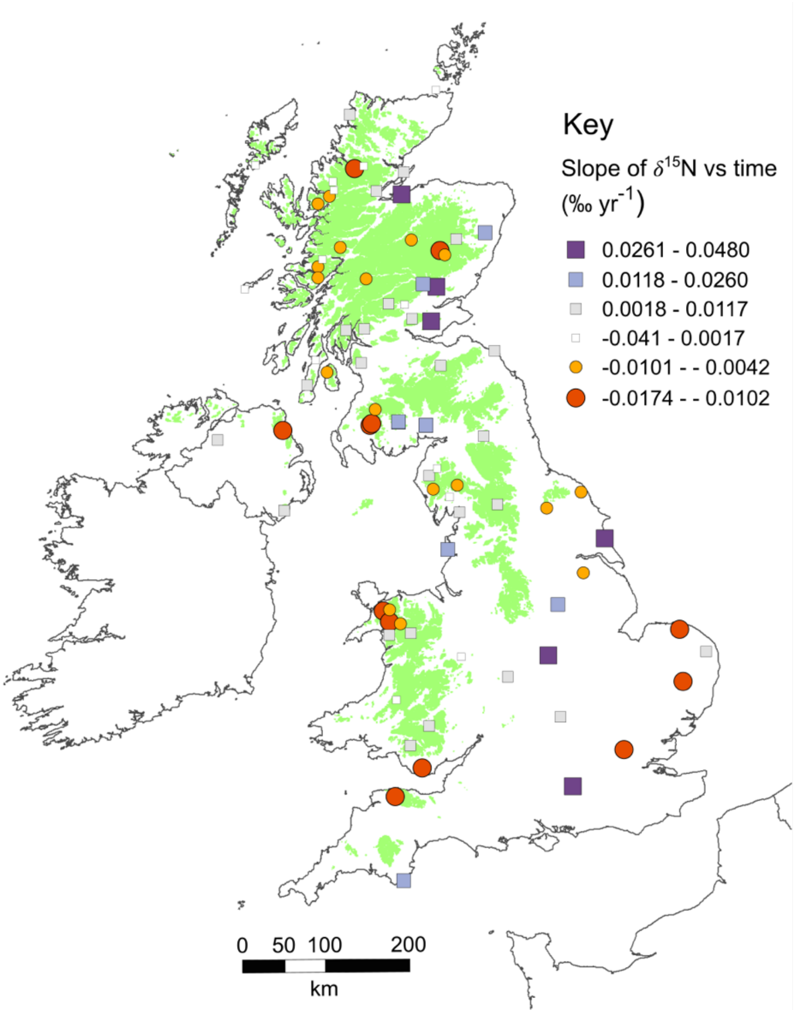
## **Supplementary 2**.

Regression slope values (4 point) showing difference in lake sediment d[15]N using 1850, 1900, 1980 and surface values. Area shading is UK land 300 m above sea level.



## Supplementary 3

Tracking diagenesis of $\delta^{15}$N signal and null modelling (after Brahney *et al.* 2014) to generate ‘corrected diagenesis’ $\delta^{15}$N values. Loch Shiel, Scotland. Lake area 2.5x$10^4$ ha, Lake surface 4m asl, MCA 262 m asl, Max catchment altitude 947 m asl)