Palaeo-perspectives on surface water brownification

Thesis submitted in accordance with the requirements of the University of Liverpool for the degree of Doctor in Philosophy

By

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August 2020

ABSTRACT

‘Brownification’, or increases in surface water Dissolved Organic Carbon (DOC) concentrations across the northern Hemisphere, are often regarded as upland waters responding to declining atmospheric acid deposition. Discriminating between this and alternative hypotheses requires data sets longer in duration than monitored records. Palaeoenvironmental approaches provide a solution and this thesis iterates through method development, applications to UK sediments, and explores the implications for understanding of changes in surface water DOC.

A new approach to interrogating Near Infra-red Spectra (NIRS) was developed that avoided the empirical chemometric statistical procedures and used the direct fitting of spectra for known end member materials to spectra of samples using multiple regression (EMS-MR). This approach avoids the need for building training sets and produces simultaneous estimation of multiple sediment components. Throughout, data generated by NIRS EMS-MR were compared with parallel independent sediment burial flux data from loss-on-Ignition, geochemistry and sediment chronology measurements to corroborate the reconstructions. The stages were:

I) The EMS-MR method was developed and trialled for end members including total organic matter, biogenic silica, and mineral matter. For Loch Grannoch (SW Scotland), analysis of the Holocene sediments showed and corroborated changes in biogenic silica, organic and mineral content over 11,500 years.

II) Motivated by the methodological successes, the NIRS EMS-MR approach was applied to a stratigraphy dominated by fluctuations in humic acid (DOC) using an ombrotrophic peatland, Holcroft Moss (NW England). This allowed direct quantification of the organic matter fractions associated with DOC, using International Humic Substances Society (IHSS) humic and fulvic acid and other standards. There, the approach struggled to differentiate between plant taxa due to the similarity of different end member spectra and a strong sensitivity of NIRS to plant decomposition. The approach showed more success in the rapid non-destructive characterisation of humic acid concentrations and peat humification.

III) Records of DOC concentrations were inferred from the sediments at four lakes in the UK Upland Waters Monitoring Network (UK-UWMN). Using a simple process model, the aqueous DOC concentration was calculated from the DOC sediment burial flux. Those DOC concentrations agreed well with the monitoring record (1988-2016) for DOC in the water ($r^2 = 0.78$). DOC increases recorded in the sediment predate lake acidification and it appears enhanced terrestrial productivity may have driven brownification. The timing is broadly consistent with fertilisation of upland soils by enhanced atmospheric N deposition, though other land use factors and recent climate warming are likely contributing factors.

IV) Lake water DOC throughout the Holocene was reconstructed for dystrophic Loch Grannoch and oligotrophic Llyn Cwm Mynach to explore the controls over DOC at longer timescales. The results show significant variation in the DOC flux, in the early Holocene driven predominantly by climate and catchment vegetation cover, but from 5000 BP human activity drives the flux of terrestrial materials showing importance of land management in limiting carbon loss from soils. DOC flux declines with cooler climate of the past 2000 BP, but without falls in total organic matter suggesting changes in either supply or in the processing of organic matter.

In summary, climate and vegetation cover have been strong drivers of terrestrial organic matter supply to surface waters through the Holocene, and although it is widely accepted that recovery from acid deposition may have enhanced DOC flux during the late 20th century, my findings conclude that this is not responsible for these recent rises, which are driven instead by increasing terrestrial productivity related to warming. Future increases in DOC flux are likely given expected future climate warming, but careful management of catchment land cover change could mitigate surface water “brownification”.

ACKNOWLEDGMENTS’

It has a been a long journey, filled with incredible experiences, wonderful opportunities, kind and inspiring people and lots of hard work.

It goes without saying that I owe so much to my supervisors Richard Chiverrell and John Boyle who have continued to support me through not just my PhD, but previously in my Masters and undergraduate programmes. Providing academic, financial, field support and guidance throughout. Without their encouragement and belief in me I wouldn’t have dreamt of even applying to complete a PhD, let alone hand one in (finally).

I also owe thanks to the many academics of the Geography Department at Liverpool who over the years have taught and guided me. There are simply too many to mention individually, testament to the kind and supportive environment that exists at Liverpool.

My line manager Lis Rushworth has been an incredible support to myself and my fellow University Teacher Simon Martin. I am incredibly grateful that Lis and Simon have been there throughout my time working and studying, it wouldn’t have been the same without you both!

From tea breaks, field support, after work drinks and simply always having someone to talk to when you need a lift, my fellow PhD students have helped in making my PhD experience enjoyable, insightful and fun. I would like to thank my fellow office mates, Karen Halsall and Charlotte Lyddon. My house mates, Rachael Lem and Hazel Phillips. Danielle Alderson, a good friend whose Master’s Thesis (data and samples) were the starting point for this project. The Simons (Clark and Martin). And finally, my fellow 8th floor corridor PhD students and good friends Maddy, Ai, Hannah, Celestine, Chris, and Grace.

A special thanks goes out to my ‘breast’ friend, Jenny Bradley (forever Mobbs in my mind). I know that we will be friends for life, but it’s hard to believe that I won’t see you every day in the Roxby Building/teaching labs or fieldwork. We will make up for it!

Most of all I would like to thank my parents, Deb and Pete. I don’t think there are words to express what your support means to me, not just regarding my time at University, but in everything I take on. You are behind my love for the environment have always kept me going when my belief in myself has wavered. Thank you!

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1 INTRODUCTION

1.1 RATIONALE

1.1.1 RECENT TRENDS IN DISSOLVED ORGANIC MATTER IN SURFACE WATERS

Over the last three decades monitoring programmes distributed across the Northern Hemisphere, have recorded increases in concentration of dissolved organic carbon (DOC) in surface waters (Worrall *et al.*, 2003; Kernan *et al.*, 2010). These increases parallel in part observations of an increased brown colouration of surface waters, e.g. lakes, reservoirs, ponds and rivers (Hongve *et al.*, 2004; Worrall *et al.*, 2010). The term brownification has been defined as a process that increases the yellow-brown colour in lake and stream water (Figure 1.1), and is typically caused by dissolved humic matter or dissolved organic matter being more abundant in the water column (Graneli, 2012).

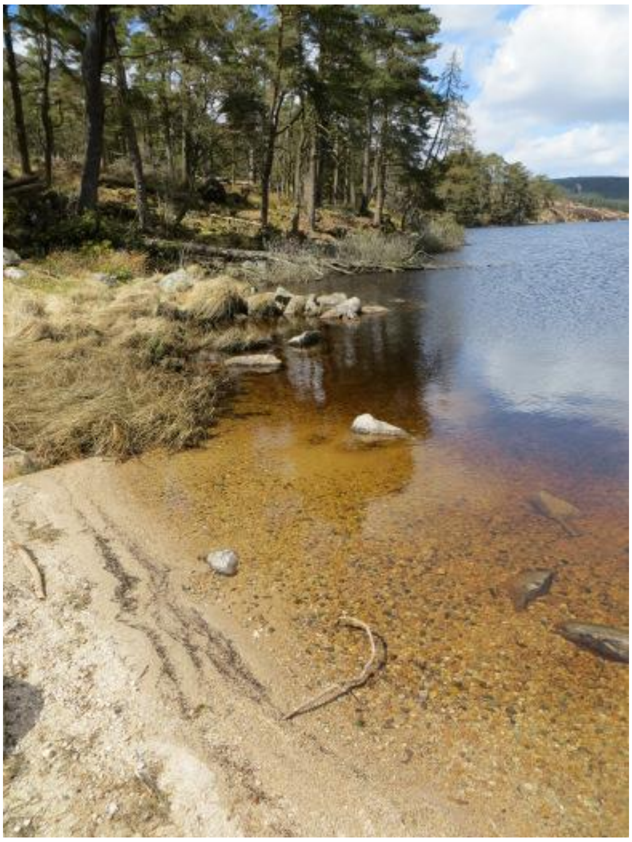


Figure 1.1 Brown surface waters in November 2015 at Loch Grannoch, SW Scotland, part of the UK-UWMN.

This organic component in surface waters is typically of a terrestrial and/or wetland origin and must reflect either greater production and/or efficient release to watercourses. Brown surface waters are a concern because of the impacts on ecosystem functioning and because of knock-on impacts on water treatment costs. Brownification of rivers and lakes in NW Europe and in N America (Forsberg, 1992; Hongve *et al.*, 2004; Evans *et al.*, 2005; Roulet *et al.*, 2006; Vuorenmaa *et al.*, 2006) has in places doubled in a few decades (e.g. Figure 1.2), and parallels lower level increases in DOC. Thus, brownification of lakes in part relates to the quantity of DOM and DOC, but it also reflects the quality of DOM delivered from terrestrial catchments and may include a contribution from increases in Fe content of surface waters.

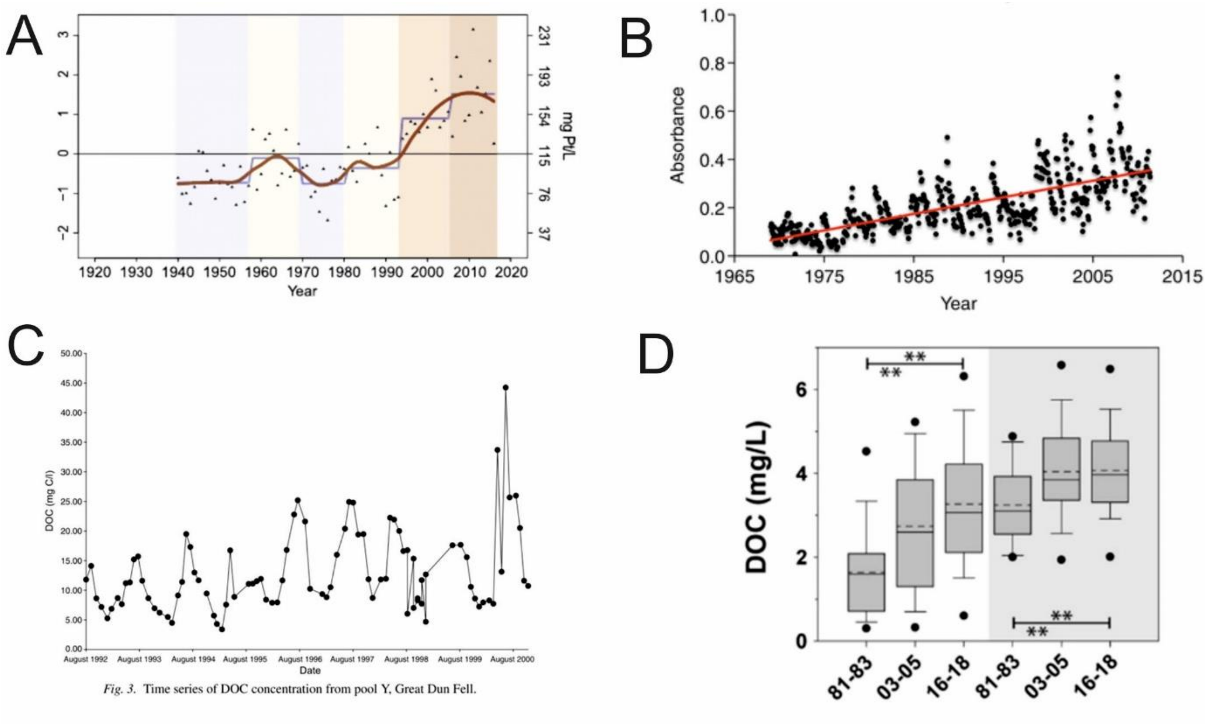


Figure 1.2 Water colour and DOC trends from UK, Europe and North America. A) Variation in water colour, values on right y-axis (Škerlep *et al.*, 2020). B) Increases in brown colouration, measured as light (420nm) absorbance, recorded for filtered waters from the River Helge at Lake Hammar, Scania, south Sweden (Graneli, 2012). C) Time series of DOC concentrations from poll Y, Great Dun Fell(Worrall *et al.*, 2004). D) Boxplots of DOC at acid sensitive and reference lakes from the Sudbury region (1981-2018) (Meyer-Jacob *et al.*, 2020)

Many causal mechanisms have been proposed as explanations for increases in surface water DOC concentrations. These include land-use or climate changes, but the most widely quoted explanation attributes the current increases in DOC for UK lakes to the recovery from past DOC suppression caused by mid-twentieth century acid rain and sulphur deposition (Evans *et al.*, 2006; Monteith *et al.*, 2007; Battarbee, Shilland, *et al.*, 2014; Sawicka *et al.*, 2017). The recent trends in DOC concentrations appear linked temporally to the phenomena of 'acid rain', which became a major environmental concern in the 1970s due to the associated acidification of land and waters through deposition of sulphur and nitrogen (Evans *et al.*, 2005; Monteith *et al.*, 2007; Pagano *et al.*, 2014;

Sawicka *et al.*, 2017). The subsequent recovery from acidification appeared to parallel the increasing trend in DOC.

Monitoring networks recording these changes were set up for a myriad of water quality purposes, e.g., assessing trends in acidity, nutrient status and potability. For the most part such programmes were set up in order to monitor how landscapes and surface waters responded to environmental legislation reducing SO_2 emissions to the atmosphere that aimed to reduce atmospheric acid deposition ($SO_2 + H_2O$), the primary driver of acidic rainwater (Battarbee, Shilland, *et al.*, 2014). The UK Acid Waters Monitoring Network (UK-AWMN) was established in 1988 (Monteith *et al.*, 2005) funded by the Department for Environment, Food and Rural Affairs (DEFRA). From 2013 the network was replaced with the UK Acid Upland Waters Monitoring Network (UK-UWMN), continuing to collect data on 14 water-courses and 12 lakes (Kernan *et al.*, 2010). These monitoring programmes, with durations limited to 30-40 years of data, document strong and convincing relationships between atmospheric acid deposition, pH and DOC. For the 12 UK-UWMN lakes the trends in monitored DOC, measured by continuous flow analyser, thermo-oxidation and TOC-Vcph analyser (dependent on lab capability), found increases in DOC concentration across the entire extent of the monitoring period (Kernan et al. 2010a - Figure 1.3). They also show that rate of increase in lake water DOC concentration varies across the natural gradients from dystrophic to oligotrophic conditions. The multifaceted interaction between forcing parameters hampers attempts to understand how these drivers influence DOC flux, making it difficult to differentiate between or isolate the relative importance of individual factors (Moss, 2012). It is possible that the correspondence between factors, for example declining SO_2 deposition and increasing DOC, are simply coincidence, and that there are other underlying causes such as changes in climate or land use.

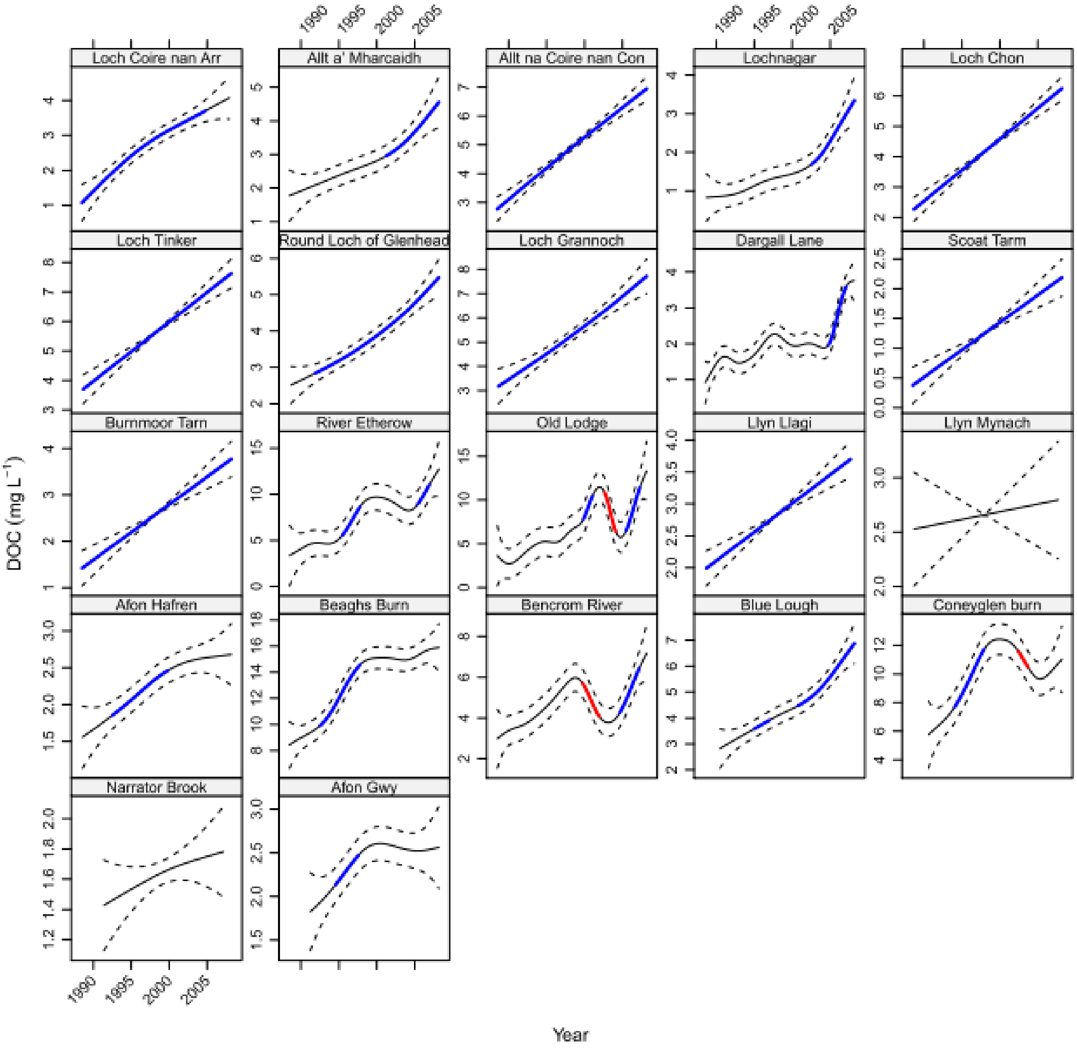


Figure 1.3 Fitted trends in DOC (mg l^{-1}) at UK-UWMN lake and stream sites. Blue indicates increases in trend, red indicates decreases determined by derivative analysis. From (Kernan *et al.*, 2010)

The DOC transported in surface waters, particularly lakes, is important with respect to the global carbon cycle. Although they have been much overlooked, understanding what drives and controls whether a lake is a sink or source for carbon will help to understand further the role of lakes in the carbon cycle. The amount of carbon supplied to lakes is set to change as climates alter. This is due to effects on in lake processes and changes to the DOC supply from catchments. The balance between carbon sequestration in sediments and evasion of carbon to the atmosphere is complex and dependent on many variables. It has been suggested that the burial of carbon in lakes and other inland waters combined, exceeds that of burial on the ocean floor (Tranvik *et al.*, 2009), which emphasises the importance of lakes in the carbon cycle. Numerous researchers have now attempted to quantify the amount of DOC sequestered into inland water sediment and evaded to atmosphere, including suggestions that inland waters transport, mineralise and bury approximately 2.7 PgC yr^{-1}

equating to the estimated quantity of anthropogenic emissions sequestered in the terrestrial biosphere (Battin *et al.*, 2009). With the brownification and increasing DOC of surface waters, the key implications are increases to the 0.9 PgC yr^{-1} carried in rivers and lakes, potentially greater burial flux (0.2 PgC yr^{-1}) and greater evasion by freshwater outgassing ~ 1 PgC yr^{-1} (CO_2 and CH_4) (Shields, 2004)

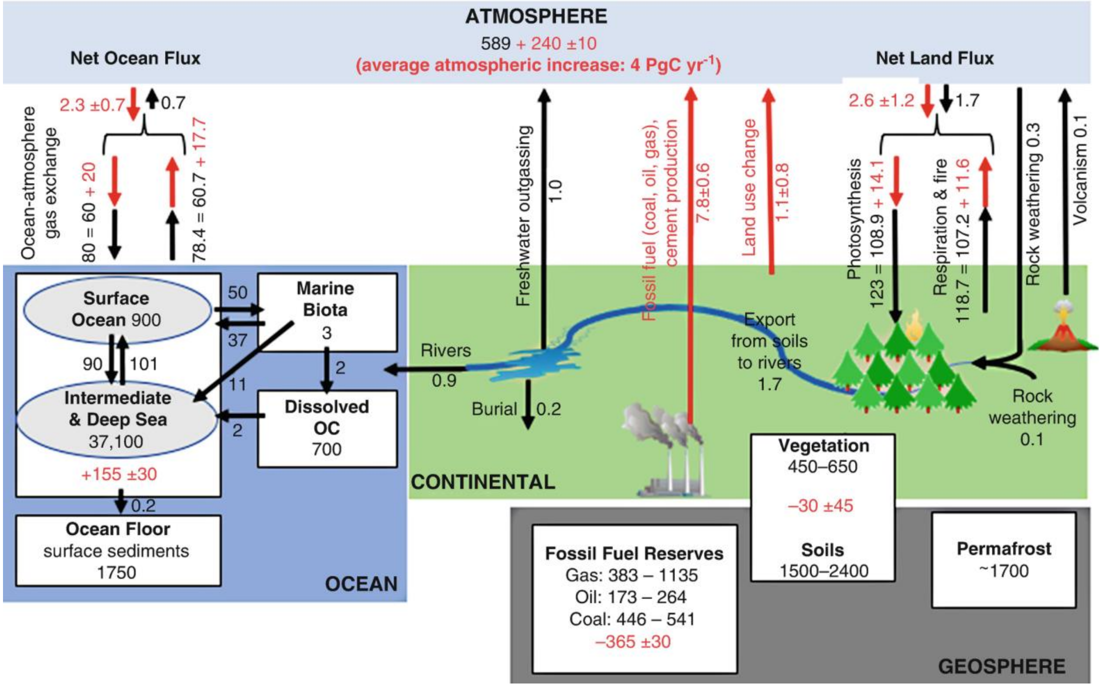


Figure 1.4 Simplified schematic of the global carbon cycle, with a focus on the relatively fast-cycling reservoirs. Numbers represent reservoir mass, also called "carbon stocks" in PgC and annual carbon exchange fluxes (in PgC yr^{-1}). Numbers and arrows indicate reservoir mass and exchange fluxes estimated for the time prior to the Industrial Era (~1750). Red reservoir numbers denote cumulative changes of anthropogenic carbon over the Industrial Period 1750–2011. Red arrows and numbers indicate annual anthropogenic fluxes averaged from 2000 to 2009. By convention, a positive cumulative change means that a reservoir has gained carbon since 1750. Unless otherwise specified, these values pertain to total C, while values in the text are provided for organic and inorganic C pools (Figure adapted from (Ciais *et al.*, 2013) and references therein. https://link-springer-com.liverpool.idm.oclc.org/referenceworkentry/10.1007/978-3-319-39193-9_175-1)

The development of longer records of dissolved organic matter for water courses and lakes could contribute to this debate, because the longer duration palaeorecord preserved in lake sediments would contain greater variety in land use and climate changes. The past also contains examples of previous changes in water acidity, trophy and catchment-to-lake sediment load. Parameters like trophic status, water acidity and nutrients have proven more easily tractable, because of the diatom methods developed for reconstructing past changes (Hall *et al.*, 1996). Changes in catchment-to-lake sediment fluxes can be discerned from geochemical and environmental magnetic signals (Dearing, 1991; Boyle, 2001). Catchment land use histories can be quantified from pollen-based reconstructions of land cover (Hellman *et al.*, 2007). Thus, lake sediments provide a basis for developing long-term multivariate datasets on ecosystem functioning and for exploring the linkages between histories, e.g. vegetation changes and catchment erosion. Quantifying the concentrations of major organic components preserved in lake sediments is more challenging (Malley *et al.*, 2000, 2014; Pearson *et al.*, 2014), which is in part a function of both autochthonous and allochthonous materials contributing to the sediment record. To address questions using a palaeorecord for DOM/DOC flux from the sediments that accumulate in lake basins requires appropriate analytical methods, ones that can distinguish allochthonous from autochthonous materials. For the purposes of this research, it is necessary to quantify the signal of allochthonous DOC that is preserved in the lake sediment. The processes of flocculation and coagulation are important in the sedimentation of DOC (von Wachenfeldt *et al.*, 2008), a process known to be impacted by UV radiation, microbial respiration (Von Wachenfeldt *et al.*, 2009), and lowered pH (Maignan, 1983). This is important because in boreal lakes a substantial fraction of the sediment organic carbon is derived from flocculated allochthonous DOC (von Wachenfeldt et al., 2008; 2009).

The integration of multi-decadal monitoring and the analysis of the recent lake sedimentary records has provided important environmental information. Using the 12 UK-UWMN lakes, Battarbee et al. (2014a) tracked the recovery of UK lakes from acidification by combining diatom data from sediment cores and sediment trapping. Their data show the evolution in water quality from pre-acidification (before ca. 1850 AD) with initial acidification in the 19th century, becoming further acidified through the 20th century and a recovery shown by the diatom flora in sediment trap materials 1991 to 2008 and onwards (Battarbee, Shilland, *et al.*, 2014). These changes in diatom flora parallel declining concentrations of non-marine sulphate and monitored increases in alkalinity, rising pH, falling Al concentrations and rising DOC concentrations (Monteith *et al.*, 2014).

1.1.1 POTENTIAL INFLUENCES OVER DOC SUPPLY

Acid rain: In addressing the implications of these water quality changes, Evans et al. (2006) argue that during times of high atmospheric acid deposition soil water pH would have declined resulting in suppression of DOC solubility and ionic strength, limiting the amount of DOC available/labile that could potentially make its way to water courses. With declines in the levels of acid deposition, DOC concentrations have increased leading to suggestions that soil pH or ionic strength may limit the DOC supply from the catchments (Krug *et al.*, 1983). The recovery from lake acidification is not unique to the UK, with similar changes observed in other countries including Sweden (Futter *et al.*, 2014;

Kritzberg, 2017), Canada (Clair *et al.*, 2011; Meyer-Jacob *et al.*, 2020), and the USA (Driscoll *et al.*, 2003; Skjelkvåle *et al.*, 2005).

An indirect benefit of the UK-UWMN research has been the collection of a comprehensive data set on increasing DOC concentration in lakes over 20-30 year timescales, permitting assessment of potential forcings. Possible drivers of DOC fluctuations include the above mentioned SO_2 deposition linked to acid rain, but also nitrogen deposition, which has continued throughout the last few decades, increasing atmospheric carbon dioxide levels, hydrological changes, temperature change and human interactions with landscapes. Nitrogen deposition is likely to continue as result of agricultural, vehicle and power station activities. The deposition of nitrogen can lead to fertilization of catchment soils resulting in a greater pool of available carbon and therefore enhanced DOC formation and transport (Sawicka *et al.*, 2017).

Temperature: Processes of physical and chemical weathering controlled by temperature influence soil formation and erosion, vegetation type and extent, which ultimately influence the type and quantity of carbon entering surface waters. Temperature exerts control over organic matter decay rates, temperature influences DOC flux particularly since much of the DOC supplied to surface waters is recently fixed carbon from decompositional processes (Sawicka *et al.*, 2017) .

Hydrological conditions (precipitation, storm events and floods): Wetzel (2001) suggests that soil type and hydrological conditions are the main controls over DOC flux to lake. This is supported by Schindler et al. (1997) who found droughts to be important in relation to declines in terrestrial inputs of DOC to lake water associated with low stream flow. Therefore, changes in hydrological flows will alter the transport of DOC into surface water environments.

Land use: Intensity and extent of land use can impact transport and mobilisation of organic materials. For instance, forestry development can impact the level of acidification in a catchment through the interception of pollutants by the forest canopy leading to enhanced acidification when compared to similar non forested sites (Miller *et al.*, 1991).

Local characteristics: Local environment characteristics are important, particularly in terms of DOC export. Peat environments are estimated to export 10.3-95.6 tonnes km^{-2} yr^{-1} whilst sites with forested catchments are estimated to export 1.5-5.3 tonnes km^{-2} yr^{-1} (Moody *et al.*, 2013), evidencing how important managing activities in sensitive catchments is to managing release of soil carbon stores. Lake characteristics will alter the dynamics of carbon processing within the water column, for example lake morphology and size can influence turbidity and water residence time impacting the sedimentation of materials (Battin *et al.*, 2008).

1.1.2 TRAJECTORY OF DOC

Various predictions have been made for future trends in surface water DOC based on assumed drivers of flux. For example, if DOC increases are linked to atmospheric acid deposition then we may expect increase to cease as deposition fluxes trend toward zero. On the other hand, it is possible that continued nitrogen deposition could promote primary productivity, resulting in continued enhanced flux, possibly leading to DOC concentrations in surface waters exceeding levels observed pre-industrial era (Sawicka *et al.*, 2017). The validity of these suggested theories explaining the DOC flux variation clearly have implications for the temporal trajectory of DOC flux from terrestrial areas to waters and therefore the burial rates and mineralization of carbon to the atmosphere.

1.1.3 WATER QUALITY IMPLICATIONS OF INCREASING DOC IN SURFACE WATERS

DOC is identified as a major source of energy in aquatic ecosystems as well as an effective screen for protecting aquatic organisms from harmful UV rays (Rae *et al.*, 2001). However, there are impacts to surface water relating to ecological functioning and human activities that occur with increasing DOC concentrations that are often considered to be negative. These include impacts such as declines in fish population (Hedström *et al.*, 2017) and reduced primary productivity (Karlsson *et al.*, 2009) and negative public perception of water quality occur as a result of the increased brown colour of waters (associated with increased organic matter content). Importantly for the water treatment industry is the costly and time consuming process of treating waters containing organic carbon (Ledesma *et al.*, 2012). The concentration of DOC in surface waters also has implications for the processing of carbon and its fate (i.e. evaded to atmosphere, deposited, or transported downstream). For example, evidence shows that when lakes have low DOC concentration coupled with high total phosphorus (TP) they are more likely to be sinks of carbon from the atmosphere (Hanson *et al.*, 2011), whereas higher DOC linked to increased microbial processing results in evasion of carbon to the atmosphere (Tranvik *et al.*, 2009).

1.2 UK UPLAND WATER MONITORING NETWORK AND STUDY SITES

The UK-UWMN, consisting of 12 lakes and 14 streams, provides a unique opportunity to investigate the drivers of organic flux from catchment to lake across a range of geological and spatial regions of the UK uplands. DOC (mg l^{-1}) has been measured since 1988 along with a suite of biological and chemical water quality indicators such as diatom species and labile Al. The lake core records at these sites offer a rare opportunity to compare surface water DOC concentrations with contemporaneous sedimentary materials. This will enable two things: 1) to directly compare the concentration of DOC monitored in surface waters with the quantity of DOC estimated by a new near infra-red spectroscopy (NIRS) end member multiple regression method (EMS-MR) applied to the contemporary lake sedimentary record, and 2) if we accept that the NIRS EMS-MR method is successful at reconstructing the concentration of DOC in the sedimentary record it would be possible to reconstruct whole Holocene DOC flux profiles for lakes and their catchments.

For the purpose of this study four of the lake sites (Loch Chon, Loch Grannoch, Scoat Tarn and Llyn Cwm Mynach) were chosen based on several criteria including a wide range of present-day DOC concentrations and recent trends, trophic status, range of afforested and forested catchments, varied spatial (North to South) and geological settings. Multiple short gravity cores were obtained from each site providing several hundred years of sedimentary record, and full Holocene profiles were obtained from Loch Grannoch and Llyn Cwm Mynach. Although radiocarbon dates have not been measured for these cores, a comprehensive geochemical record, providing detail on the Pb contamination profile, allows corroboration with previously dated cores from each site or suitable nearby sites.

1.3 METHODS DEVELOPMENT

Many techniques exist for measuring the concentration of DOC in waters. However, in order to determine past lake-water DOC concentrations from their deposited signal in a sedimentary record we require a wholly different approach. Particles formed in the lake water column from DOC by flocculation or coagulation settle to the lake bed and become incorporated into the sediment record. If we can measure the concentration of the DOC-derived particles, and calculate their accumulation rate, then we have a basis for directly calculating the average past lake water DOC concentration.

This method is not the approach taken by previous investigations. Rosén (2005), and other studies, have not attempted to directly measure the DOC-derived organic matter in the sediment; instead, they have trained a statistical Near Infrared Spectroscopy technique to associated water measurments for a suite of lakes with the spectra of their sediments. Often training these using lake water TOC measurements, there is a gap in capability to quantify DOC concentration in sedimentary records and therefore understand how DOC has varied prior to monitoring programmes. This indirect approach has the further disadvantage of being empirical with no means of assessing whether the inference models are consistent with any underlying theory.

Our alternative approach uses NIRS to measure the DOC-derived organic matter directly. It achieves this using multiple regression where spectra are obtained for individual end-member materials which can then be regressed in combination against sediment sample spectra. This use of NIRS negates the need for a training set. It does, however, need an end-member material to represent the DOC-derived material. Attempts to obtain DOC end-member materials for this purpose included extraction of organic matter from waters draining peat sediments, and acquisition of commercially available International Humic Substances Society (IHSS) humic compound standards (Suwannee River) since humic and fulvic acid are the predominant components of DOC. Figure 1.5, showing the derivative end-member spectra for these materials, illustrates the similarity in these materials. Based on the assumption that the filtered dry water samples from peatlands may contain some contaminants the decision to progress this study using a 50:50 mix of humic acid and Fulvic acid was taken.

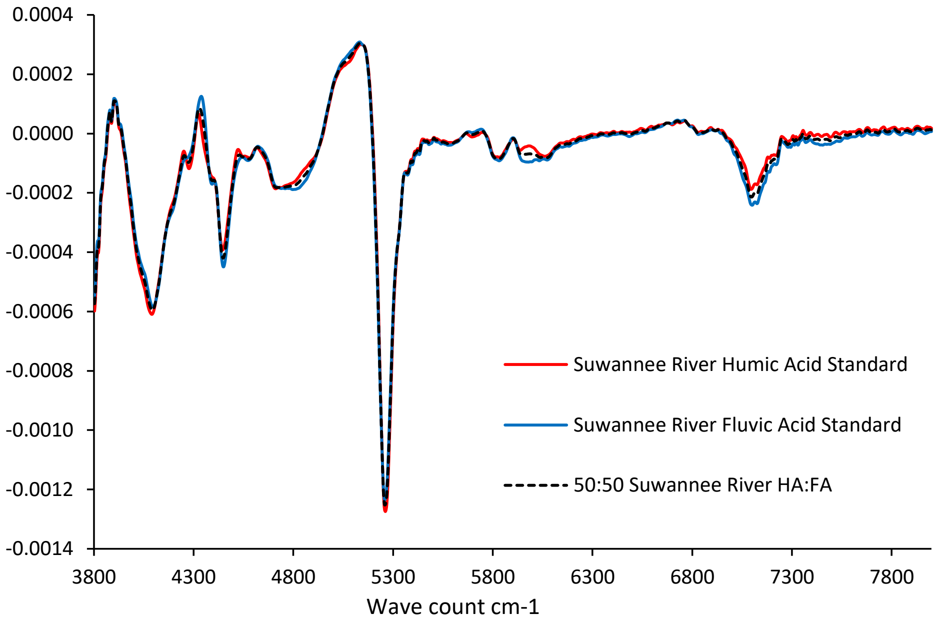


Figure 1.5 1st Derivative NIR Spectra of Suwannee River (IHS) Humic Acid and Fulvic Acid Standards III and a 50:50 mixture

The NIRS multiple regression method produces an estimate for each chosen end member expressed as concentration in sediment (as a simple mass fraction) which in Chapter 3 we convert to % for clarity. In Chapter 4 our aim is to use NIRS multiple regression in an environmental system predominantly controlled by humification processes, with limited external allochthonous influences and where the stratigraphical sequence was dominated by variations in humic acid content. In terms of end-member reconstruction, the approach is no longer quantifying the fraction of carbon that is dissolved, but one that exhibits the same chemical characteristics and in the appropriate conditions would be the dissolved fraction of carbon. Therefore, in all situations where we aim to quantify material associated with DOC (aqueous (mg l^{-1}), burial flux (g cm^{-2} yr^{-1}) and humified proportion (weight %) we have chosen to use a 50:50 mixture of humic and fulvic acid standard reference material (Suwannee River) as the representative end-member. In Chapter 5, the aim was to produce a record of DOC concentration using sediment records that can be directly compared with surface water DOC concentration. Therefore, in Chapter 5 we present weigh t% (concentration in g $100g^{-1}$) which we are then able to convert to aqueous DOC concentrations by first calculating burial flux (g cm^{-2} yr^{-1}) and converting to dissolved DOC concentration (mg l^{-1}) using a simple lake mass balance model. In Chapter 6, we move away from reconstructing aqueous DOC and focus on fluxes to sediment, using weight% and MAR to calculate burial flux (g cm^{-2} yr^{-1}) over long Holocene time scales.

1.4 THESIS AIM AND STRUCTURE

The format for this thesis is a series of four journal articles, supported by an introduction, review of the relevant literature and a concluding synthesis. The aim of this thesis is to develop methodologies and apply a framework for assessing the potential of the DOC palaeorecord preserved in Holocene lake and peat sequences, and then to use the longer perspective afforded by the palaeorecord to address the drivers and forcing of recent increased concentrations of DOC in surface waters. This aim was tackled by addressing four key objectives.

- Develop new analytical application of Near Infrared spectra (NIRS) and quantitative methods for measuring the quantity of major sediment components in lake and other sediments and using geochemistry and loss-on-ignition data as independent validation measures.
- Apply a novel end member multiple regression (EMS-MR) of NIR spectra to materials composed predominantly a mixture of subfossil plant remains and humic compounds, quantifying them in peat and thereby testing the performance of MIRS EMS-MR approaches to reconstructing humic acid or DOC concentrations.
- Develop, apply, and evaluate the performance of NIRS EMS-MR to reconstructing concentrations of dissolved organic carbon (DOC_{NIRS}) using the recent sediments records from four UK Upland Water Monitoring Network lakes for comparison with the monitored records at each location.
- Apply the DOC_{NIRS} methodology to the short (300 year) and long (whole Holocene) lake sediment records to evaluate the drivers and forcing of longer-term patterns of DOC in surface waters using the palaeorecord.

In order to address these overall aims, the thesis is broken down into the following chapters, which include a literature review (Chapter 2), four papers presenting the results (Chapters 3-6) and a synthesis that identifies future research priorities. At the time of submission, one paper is published, one is under revision and two are in manuscript form. The author contribution, summary objectives of the contributions and status are as follows:

CHAPTER 2 LITERATURE REVIEW FOCUSED ON DISSOLVED ORGANIC CARBON IN LAKES

Author contributions:

Russell, F.E. - Author, conducted the literature review, and wrote the manuscript.

CHAPTER 3 NIRS QUANTIFICATION OF LAKE SEDIMENT COMPOSITION BY MULTIPLE REGRESSION USING END-MEMBER SPECTRA

Russell, F.E., Boyle, J.F. & Chiverrell, R.C. NIRS quantification of lake sediment composition by multiple regression using end-member spectra. Journal of Paleolimnology 62, 73–88 (2019). https://doi-org.liverpool.idm.oclc.org/10.1007/s10933-019-00076-2

Author contributions:

Russell, F.E. - Lead author, collected, processed and interpreted the data and wrote the manuscript.

Boyle, J.B. - Collected sediment cores, in-depth discussions and detailed manuscript review.

Chiverrell, R.C. - Collected sediment cores, GIS expertise, in-depth discussions and detailed manuscript review.

Manuscript submitted 12 April 2018, accepted 21 March 2019, Published Online 28 March 2019, with an Issue Date 01 June 2019.

AIM: The chapter develops and tests a novel method for quantifying sediment components, e.g. biogenic silica, organic or mineral matter, from near infrared (NIR) spectra based on fitting by multiple regression of measured spectra for end-member materials. The multiple regression end member approach (EMS-MR) has wider utility in other spectroscopy techniques. The paper shows that component NIR spectra are additive, a prerequisite for use of multiple regression to un-mix the compound spectra and show that a number of environmental materials make suitable end-members for this analysis. The approach is applied a postglacial sediment sequence from Loch Grannoch (SW Scotland) and reveals down-core patterns of varying dominance by biogenic silica, organic and mineral content from the late glacial to present.

CHAPTER 4 RECONSTRUCTING PEAT COMPOSITION FOR THE HOLCROFT MOSS OMBROTROPHIC PEATLAND USING NEAR INFRARED SPECTROSCOPY (NIRS)

Author contributions:

Russell, F.E. - Lead author, collected, processed, and interpreted the data and wrote the manuscript.

Boyle, J.B. - In-depth discussions and detailed manuscript review.

Chiverrell, R.C. - Collected sediment cores, co-wrote the ^{14}C dating application, conducted TGA/DSC analyses, in-depth discussions, and detailed manuscript review.

Kirby, J. - Collected sediment cores, led the ^{14}C dating application, discussions, and manuscript review.

Valentine, J. – Collected sediment cores, conducted peat humification and plant macrofossil analyses for the Holcroft Moss peat deposits.

Manuscript not submitted to date,

Aim: Development of a new multiple regression end member approach (EMS-MR) (Russell et al. 2019) using near infrared spectra (NIRS) offered the potential to quantify sediment components (e.g. humin). Here, the approach is applied to a lowland ombrotrophic raised mire peat sequence from north Cheshire, UK. These peats are dominantly organic and contain little or no mineral matter or biogenic silica, instead they are dominated by well-preserved subfossil plant remains and a series of humic compounds. Using a 50:50 mix of IHSS (International Humic Substances Society) Fulvic Acid standard III and Humic Acid standard III from Suwannee River as an end member in our EMS-MR equivalent to dissolved organic carbon we test the capacity of the approach to distinguish a DOC signal in the 5000 year peat profile. Comparison of information in the NIRS with independent measures for plant remains, peat humification, geochemistry and pyrolysis properties provided an assessment of utility of the technique in quantifying major components of peat. Success in the reconstruction of patterns in DOC or humic/fulvic component in materials like peat with its organic dominated characteristic, formed a basis for subsequent applications to more heterogeneous lake sediments.

CHAPTER 5 DECIPHERING THE DRIVERS OF A 300 YEAR RECORD OF SEDIMENT INFERRED DOC CONCENTRATIONS AT FOUR UK LAKES

Russell, F.E., Boyle, J.F. & Chiverrell, R.C., Deciphering the drivers of a 300-year record of sediment inferred DOC concentrations at four UK lakes. Journal of Paleolimnology under review.

Author contributions:

Russell, F.E. - Lead author, collected, processed and interpreted the data and wrote the manuscript.

Boyle, J.B. - Collected sediment cores, in-depth discussions and detailed manuscript review.

Chiverrell, R.C. - Collected sediment cores, in-depth discussions and detailed manuscript review.

Manuscript in revision,

AIM: Records of dissolved organic carbon (DOC) concentrations were derived from the sediments at four lakes in the UK Upland Waters Monitoring Network (UK-UWMN). Brownification and increasing concentrations of DOC characterise the last 30 years at these sites. To address a knowledge gap in that monitoring data programmes do not extend far enough back in time to evaluate many of the forcing hypotheses, we have developed a method to infer past aqueous DOC concentrations from lake sediments. Quantifying the sediment burial fluxes for humic and fulvic compounds using EMS-RS of NIR spectra and a simple process model, we calculated the aqueous DOC concentrations from the sediments (DOC_{NIRS}). The DOC_{NIRS} reconstruction agrees well with the monitoring record (1988-2016) for DOC in the water at these UK-UWMN sites ($r^2 = 0.78$), and the palaeorecords for the last 300 years show that the DOC rise predates both acidification and recovery at all four sites, and that values rise steadily through the industrial period. For this, the relationships with factors hypothesised as forcing DOC are explored, which suggested that enhanced terrestrial productivity may have played a central role in the increases.

CHAPTER 6 SEDIMENTARY EVIDENCE OF CHANGING DOC FLUXES DURING THE HOLOCENE FROM UK LAKES

Author contributions:

Russell, F.E. - Lead author, collected, processed and interpreted the data and wrote the manuscript.

Boyle, J.B. - Collected sediment cores, in-depth discussions and detailed manuscript review.

Chiverrell, R.C. - Collected sediment cores, in-depth discussions and detailed manuscript review.

Manuscript not submitted to date,

AIM: Holocene duration records of dissolved organic carbon (DOC) concentrations were derived from the sediments at Loch Grannoch and Llyn Cwm Mynach, comprising two lakes in the UK Upland Waters Monitoring Network (UK-UWMN) currently at either end of a dystrophy to oligotrophy gradient, with increasing concentrations of DOC characterising the last 30 years at both sites. The limited duration of short cores and monitored data sets potentially undermine critical evaluation of the causes of increasing DOC, and the analysis of longer palaeorecords preserved in lake sediment records provides the only means of rectifying this. Quantifying the sediment burial fluxes for humic and fulvic compounds using EMS-MR of NIR spectra and a simple process model, we calculate the aqueous DOC supply flux from the sediments (DOC_{NIRS}) for the whole Holocene period at both sites. Exploring how past episodes of climate and land use changes during the Holocene have impacted on our DOC_{NIRS} record tests how these two of the factors potentially contribute to the recent elevation of DOC levels in surface waters.

CHAPTER 7 SYNTHESIS AND FUTURE RESEARCH PRIORITIES

Author contributions:

Russell, F.E. - Lead author and wrote the manuscript.

2 LITERATURE REVIEW

2.1 WHY ARE LAKES IMPORTANT ON A LOCAL AND GLOBAL SCALE

Although lakes cover a relatively small proportion of the Earth's surface when compared with oceans, the 117 million lakes >0.002 km^2 equating to 3.7% of non-glaciated land surface (Verpoorter *et al.*, 2014) are highly valued as sources of water (drinking, agricultural, industrial and recreational) and habitat on every continent (Wetzel, 2001). Lakes and reservoirs have been identified as important components of the global carbon cycle, processing vast quantities of terrestrially derived organic matter leading to either sedimentation, transport or release of carbon to the atmosphere (Cole *et al.*, 2007; Downing *et al.*, 2008; Battin *et al.*, 2009).

Lake ecosystems are strongly influenced by their surrounding catchment areas, which are of course affected by local conditions (temperature, hydrological conditions, wind, geology, topography, and human activities). It is estimated that 30-80% of the carbon that enters a lake becomes incorporated into the sediment or is mineralized (Algesten *et al.*, 2003), the remainder being transported downstream to rivers and ultimately sea. Importantly, the amount of carbon sequestered in lake and reservoir sediments is believed to exceed that of oceans (Dean *et al.*, 1998; Battin *et al.*, 2009; Aufdenkampe *et al.*, 2011). Boreal lake sediments are estimated to store 0.6 Pg yr^{-1} of carbon (Drake *et al.*, 2018).

Recent estimates suggest that 25% of net earth to atmosphere CO_2 flux originates from lakes (Drake *et al.*, 2018) and based on projected increases in temperature, changes to hydrological conditions and vegetation cover (type and extent), supply of organic matter to surface waters is likely to increase (Hölzel *et al.*, 2016). Predicted climatic changes resulting in warming of Northern latitudes is expected to impact the supply and processing of carbon in water bodies resulting in a decline of between 0.9 and 6.4 TgC yr^{-1} in organic carbon burial to lakes annually (Gudasz *et al.*, 2010).

Concentrations of dissolved organic carbon (DOC) in rivers and lakes have increased over recent decades (Worrall *et al.*, 2003; Evans *et al.*, 2005) and various explanations including climatic changes and acid deposition have been suggested as the driver of this. Understanding how supply and processing of carbon will change as local and global conditions vary is vital in understanding the role that lakes will play in regulating the carbon cycle, and as a valuable resource and habitat. Lakes also, uniquely among aquatic ecosystems, have the potential to provide palaeoenvironmental records of changing DOC supply (Rosén, 2005).

2.2 CARBON IN LAKES

2.2.1 SOURCES AND QUALITY OF ORGANIC CARBON

The lacustrine carbon cycle includes interactions between atmosphere (gaseous), terrestrial and autochthonous forms of carbon (dissolved and solid), autochthonous carbon being produced in the lake by primary productivity (Dean *et al.*, 1998). Allochthonous dissolved organic carbon (DOC) is the dominant supply of organic matter from catchments to aquatic systems (Hinton *et al.*, 1997, 1998; Tipping *et al.*, 2010, 2016), transported via surface flows, atmospheric pathways and groundwater supply (Myrbo, 2012).

The terrestrial carbon supply is sensitive to climatic variations including precipitation, temperature and radiation (Hope et al., 1994; Sabine *et al.*, 2013). For example, warmer temperatures and changes to precipitation regime can impact erosion and transport regimes affecting the quantity and characteristics of sediment supply from terrestrial environments to water courses. Secondly, warmer temperatures can alter in-lake production of carbon since both CO_2 exchange driven by microbial activity and photosynthesis are temperature sensitive.

Several studies have shown that DOC quality varies according the source of the organic matter. In a study of six streams in Alabama, Shang *et al.*, (2018) found streams in agricultural catchments to have DOC with higher proportions of microbially derived humic compounds than forested catchment streams. In a study of 34 lakes in Estonia, Sepp *et al.*, (2019) found substantial variations in DOM quality with land cover type. Lakes with high catchment to lake area ratios and peaty soils were associated with high aromaticity and molecule size (humic rather than non-humic DOM), while autochthonous non-humic DOM was associated with lower catchment to lake area ratios, and calcareous bedrock.

A consequence of the influence of temperature, precipitation and vegetation type on DOC is that the allochthony of DOC increases with lake altitude (Rose *et al.*, 2015).

2.2.2 CONTROLS OVER SUPPLY OF ORGANIC CARBON

2.2.2.1 PRECIPITATION (RAINFALL, SNOW MELT)

Supply of carbon from the surrounding catchment is controlled by hydrological regime such as precipitation events including storms which dissolve (Hinton *et al.*, 1998; Rohlfs *et al.*, 2016) and transport of soil carbon via overland flow and stream networks to lake waters (Hinton *et al.*, 1998; Mitrovic *et al.*, 2016; Nielsen *et al.*, 2016; Robertson *et al.*, 2016). A study at the Experimental Lakes Area in Canada found evidence of decreased DOC input to lakes linked to lower stream flows (Schindler *et al.*, 1997). This study concluded that timing of rainfall events may also determine input of DOC, particularly when dry periods are followed by intense rainfall events. Conversely, high flow events have been linked to elevated DOC (Boyer *et al.*, 1997), and wet years also show higher DOC concentrations than drier years (Hope *et al.*, 1994; Erlandsson *et al.*, 2008; Köhler *et al.*, 2008). In particular, intense snowmelt events were correlated with high DOC concentrations in northern Sweden (Ågren *et al.*, 2010).

2.2.2.2 LAND USE

Land use is known to affect soil carbon stores and studies have shown that inputs of terrestrial DOC can vary in quantity and quality dependent on land cover and land management (Hope *et al.*, 1994). The strong association with wetlands and peat is widely reported (Hope *et al.*, 1994; Xenopoulos *et al.*, 2003; Kortelainen *et al.*, 2006; Creed *et al.*, 2008; Sepp *et al.*, 2019). Other associations are less universal, though an association with net primary production is predicted by Whittaker and Likens (1973). Land management effects are rather less studied than land cover and climate. Manninen *et al.*, (2018) report negligible impact of agriculture in Finland, with variation in DOC dominated by climatic factors. In contrast, for streams in Alabama Shang *et al.*, (2018) found DOC to be higher in streams from agricultural catchments than forested catchments. In moorland streams in Northern England, Yallop et al., (2010) show increased DOC concentrations in stream draining burned peatlands compared with unburned. In urban impacted catchments in Texas, substantial contributions from wastewater treatment works were observed (Aitkenhead-Peterson *et al.*, 2016). Flow regulation has been found to impact transport of DOC (Rohlfs *et al.*, 2016), most strikingly through weakening of the association between DOC and discharge for impounded rivers.

2.2.2.3 pH

Observing a negative correlation between DOC and sulphate concentration in US Experimental Lake Survey sites, Driscoll, Fuller and Schecher (1989) concluded that this was consistent with the hypothesis that acid rain had immobilised natural organic acids. Artificial acidification to a pH below 5 of lakes and catchments in the Experimental Lakes Area of Ontario was also associated with a reduction in DOC at most sites (Schindler *et al.*, 1992). Both studies offered support for a controversial suggestion by Krug and Frink (1983) that acid rain impacts had been mitigated by a complementary reduction in natural organic acids. Experimental studies on soil do confirm an impact of pH on DOC mineralisation (Curtin *et al.*, 1998). These ideas are central to the hypothesis that recovery from acidification may have led to increased stream and lake DOC (Erlandsson *et al.*, 2011).

2.3 FORMATION OF HUMIC SUBSTANCES

Humified organic materials are widely assumed to form by the microbial degradation of plants and organisms (Buffle, 1990). This process, referred to as humification, generates large molecules (atomic mass >700) enriched in aromatic functional groups that have been modified from the original plant compounds (Qualls *et al.*, 2002). The type and quantity of vegetation in a lake catchment will impact the quality and concentration of humic substances in soils (Rae *et al.*, 2001;

Fernández-Getino *et al.*, 2010), and consequently of DOC in surface waters. Generally speaking, temperate and boreal lakes have the highest observed concentrations of DOC, linked to their favourable climatic conditions and established vegetation (Hope *et al.*, 1994). Projected climatic changes are likely to result in changes to vegetation cover and type, for example shifting to a greater proportion of broad leaf trees compared with pine forest (Boisvert-Marsh *et al.*, 2014). Variation in vegetation types will be met with varying rates of decomposition of soil organic matter, which can lead to increased organic matter available for transport to the lake system (Qualls *et al.*, 2002; Tipping *et al.*, 2016)

Catchment characteristics such as geology and topography (Stallard, 1998) influence soil formation, which can be a limiting factor on quantity and quality of DOC. At the upper extreme are peatlands where the hydrological conditions favour preservation of humic substances (Clymo *et al.*, 1998). Furthermore, the lack of mineral matter which typically absorbs DOC in soils has the effect of enhancing the transport of DOC from peatland catchments (Urban *et al.*, 1989).

2.4 ALLOCHTHONOUS CARBON IN LAKES: IN-LAKE PROCESSING AND CATCHMENT ENVIRONMENT

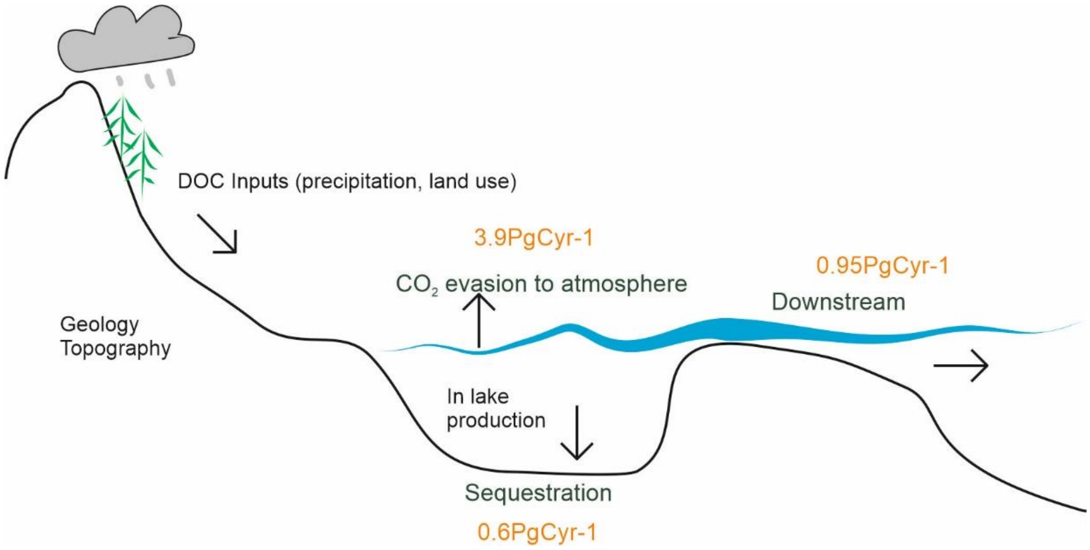


Figure 2.1 Summary of the global carbon cycle, showing pathways of carbon in surface waters. Values from (Drake *et al.*, 2018)

As lakes are slow moving water bodies, carbon entering their waters has the potential to:

a. settle to the lake bottom and become sediment, becoming permanently stored (0.6 PgC yr^{-1})
b. become mineralized resulting in a loss of carbon to the atmosphere (3.9 PgC yr^{-1})
c. to be transported downstream ultimately making its way to sea (0.95 PgC yr^{-1})

In typical boreal lake systems, dissolved organic carbon (DOC) constitutes 90-95% of total organic carbon (TOC) (Wetzel, 2001; Kortelainen *et al.*, 2006). The fate of carbon in lakes is important due to the potential for carbon to become incorporated within sediments where it can be stored permanently or alternatively vented to atmosphere where it will contribute increasing CO_2 concentration. Inland waters are usually supersaturated with CO_2 meaning that net influx of carbon from the atmosphere is uncommon (Cole *et al.*, 1994; Duarte *et al.*, 2005). The balance between storage and evasion to atmosphere is affected by external forcing such as climate and hydrology (Cole *et al.*, 2007). It is estimated that lakes sequester up to 15% and evade 48% of terrestrial carbon that would otherwise have reached oceans (Heathcote *et al.*, 2015).

2.4.1 MINERALIZATION, PHOTOLYSIS, RESPIRATION

The pool of carbon in the lake water column varies depending on the balance between the in-lake processes including: respiration (Del Giorgio *et al.*, 1994; Kritzberg *et al.*, 2006) that leads to evasion to the atmosphere; photosynthesis and UV degradation (Massicotte *et al.*, 2017) that leads to drawdown from atmosphere and sedimentation, and flocculation that leads to sedimentation (Wachenfeldt *et al.*, 2008).

Photomineralization (induced by sunlight) of DOC in freshwaters (Cole *et al.*, 2007; Tranvik *et al.*, 2009; Panneer Selvam *et al.*, 2019) leads DOC to be converted to CO_2, low molecular weight organic acids, partially oxidized recalcitrant DOC and small amounts of carbon monoxide (Cory *et al.*, 2014). Porcal et al. (2015) showed that DOC photomineralization can be particularly high when iron concentrations are high, especially in combination with extremely low pH. On the other hand, Panneer Selvam *et al.* (2019) find that low pH may limit photomineralization of terrestrial DOC. The impact of pH provides another pathway by which climate may impact lake DOC dynamics as lake acidity is influenced by climate (Boyle, 2008).

Studies have found that concentration of terrestrially derived DOC in surface water determines the sedimentation of organic carbon, implying that DOC presence and quantity underpins processes leading to settling organic matter (Wachenfeldt *et al.*, 2008; Tipping *et al.*, 2016). High concentrations of DOM and the associated yellow/brown colour will reduce light penetration and therefore reduce primary productivity (Karlsson *et al.*, 2009). Autochthonous DOC is preferentially respired, which when conditions are warmer may result in enhanced mineralization and reduced carbon burial (McCullough *et al.*, 2018). On the other hand, higher atmospheric CO_2 concentrations may promote primary productivity and offset negative impacts of increased light attenuation (Hessen *et al.*, 2017).

DOC is an important nutrient in waters, and in nutrient poor lakes allochthonous inputs may be a major source of phosphorus (Meili, 1992), nitrogen (Dillon, 2005) and iron (Kritzberg *et al.*, 2012). As a food source for bacteria and phytoplankton DOC impacts dynamics which control the microbial food web (Mitrovic *et al.*, 2016). The ratio of nutrients, in particular phosphorus and nitrogen, affect the rates of microbial activity (Brailsford *et al.*, 2019) with N limitation in particular having an impact on DOC metabolism.

The trophic status of lakes, and particularly eutrophication, is known to impact whether a lake functions as a source or sink of terrestrially derived organic matter (Evans *et al.*, 2017). In fact, as a result of eutrophication, which increases net primary productivity, lakes can become net sinks for CO_2 (Pacheco *et al.*, 2013).

2.4.2 HEAVY METALS AND MINERALS

It has long been known that DOC could form chemical complexes with dissolved metals altering their solubility and toxicity (Mantoura *et al.*, 1978; Tipping, 1998). In freshwaters, the impacts on reducing the toxicity of aluminium in acidic water (Trenfield *et al.*, 2012) and copper more generally (Gillis *et al.*, 2010) are particularly important. Mercury has a strong affinity to DOC (Lavoie *et al.*, 2019), particularly in environments undisturbed by human activities. Consequently, DOC is important in the transportation of heavy metals including mercury from catchments to streams and lakes (Rose *et al.*, 2012). In the presence of aluminium and iron oxides DOC is likely to be precipitated and incorporated into lake sediment (Pokrovsky *et al.*, 2002), a process which is used in water treatment (Bachand *et al.*, 2019).

2.4.3 FLOCCULATION, TURBULENCE AND COAGULATION

In-lake processes of flocculation and coagulation (which are affected by turbulence and metal presence) may cause DOC to form into particulate organic carbon (POC) which may ultimately promote the sequestration of carbon into the lake sediment (Dillon *et al.*, 1997; Wachenfeldt *et al.*, 2008). The underlying process is thought to be mediated by microbial activity (Von Wachenfeldt *et al.*, 2009), mediated in turn by factors such as temperature, nutrient availability, and pH (optimum at the *in situ* value of 5.2).

Sobek et al., (2011) found that the efficiency of organic carbon burial is linked to the type and source of organic material rather than oxygen availability in the water column and mineral characteristics. Results across Lake Kinneret show a variation of between 10-41% of OC buried in sediments linked to organic matter type.

2.4.4 LAKE CHARACTERISTICS

According to Verpoorter *et al.* (2014), based on analysis of high-resolution satellite imagery, there are globally an estimated 117 million lakes larger than 0.002 km^2. Of these, 90 million are classed as small (less than 1 ha), making up just 7% of the global lake surface area. Despite this low area proportion, smaller lakes tend to be more nutrient rich and susceptible to light penetration than larger lakes meaning smaller lakes are more integral to the carbon cycle (Verpoorter *et al.*, 2014). Since the pioneering work of Einar Naumann in the 1920s larger lakes have been known to have lower productivity, are often more dilute, deeper and light is limited to upper layers, resulting in slower in-lake processes (Wetzel, 2001).

Estimates from Messager *et al.* (2016) for lakes with surface area > 10ha suggest that water residence time ranges from 456 to 1834 days, and generally increases with lake surface area. Residence time is important for a range of processes including hydrological budgets and carbon exchange rates. Lake residence time controls the time DOC is subject to mineralization, flocculation and coagulation (Wachenfeldt *et al.*, 2008; Von Wachenfeldt *et al.*, 2009), such that the more rapid the lake water flushing is, the more likely DOC is to be transported downstream. Lakes with longer residence time usually have slower biotic production processes and therefore sedimentation is more likely to occur (Evans *et al.*, 2017).

2.4.5 CATCHMENT

When using lakes to understanding terrestrial ecosystem processes such as terrestrial DOC production it is essential to know the catchment area associated with a lake. While large data bases exist for lake areas, this is not the case for catchments. The large sample size precludes time-consuming map-based estimation, and some alternative estimation methods have been proposed. Most recently, Walter *et al.* (2020) have tested a power law scaling relationship and found a more or less linear association between lake surface area and catchment area. They demonstrate this to be an effective approximation in their study of DOC exports from forest catchments.

Clair et al., (1994) develop a model for DOC exports from Canadian forested catchments that clearly demonstrates a role for not just catchment area, but also specific properties such as slope. For such information there is no alternative but to have high quality DEM data and GIS tools to process the information.

2.4.6 TEMPERATURE AND PRECIPITATION (INCLUDING SNOW COVER)

Supply of carbon from surrounding terrestrial environments is increasing with global warming (Frey *et al.*, 2005, 2009). Increasing temperatures are associated with increased in-lake productivity and longer growing seasons, which have been found to correspond with a transition from burial to respiration dominated activities (McCullough *et al.*, 2018). Temperature within a lake is important to its ecosystem and to in-lake processing of carbon. Warmer temperatures are associated with greater rates of carbon mineralization by microbial activity, leading to evasion of carbon to the atmosphere (Von Wachenfeldt *et al.*, 2009).

In peat catchments, increased rainfall and storm events resulting in high overland or pipe flow can result in higher pH through dilution (Evans *et al.*, 2008). However, when groundwater dominates water supply, geological conditions have a stronger influence on water acidity, often resulting in more alkaline water conditions under base flow conditions. In sites where high flow events are associated with shallow acidic soils, then pH typically falls with flow magnitude (Christophersen *et al.*, 1982)

Low flows reduce the export of DOC from catchments (Hope *et al.*, 1994; Erlandsson *et al.*, 2008; Köhler *et al.*, 2008) partly because of loss in the transport medium, but also because of changed inflow pathways away from surface organic layers to deeper mineral-rich layers (Neff *et al.*, 2001). However, in some circumstances drought can prime soils for later export of DOC (Freeman *et al.*, 2001; Ritson *et al.*, 2017). A process associated with the so called "enzymatic latch" hypothesis where oxygen limitation restraining the activity of enzymes resulting in C storage in peatlands (Freeman *et al.*, 2001)

Freezing conditions have multiple effects on lake DOC concentration. Firstly, ice and snow cover limits the amount of light available for photosynthesis, thus reducing the amount of in-lake production of carbon (Garcia *et al.*, 2019). Secondly, it affects the input of carbon from the surrounding terrestrial environment (Ågren *et al.*, 2010).

Storm events can deliver major ions as a result of transport of sea salt to inland waters and is found to be linked to episodes of acidification (Evans *et al.*, 2006).

2.4.7 ANTHROPOGENIC ACTIVITIES

Human activities (forestry, agriculture, mining, etc.) and land management practices mobilise large quantities of catchment soils and minerals which are then transported to streams and lakes.

Land management practices including forestry and grazing have been adapted to limit their impacts on the environment. Catchments dominated by forest and wetlands are associated with high DOC loadings (Hope *et al.*, 1994; Gergel *et al.*, 1999). Forests are particularly effective at creating high DOC loading as they create large amounts of biomass and leachable litter layers (Hongve, 1999) which provide a DOC source (Stevens *et al.*, 1989; Kawasaki *et al.*, 2005)

Although many of the 'natural' processes described above may impact the acidity of a lake system, the most widely discussed driver of surface water pH change has been that of acid rain. Recovery from atmospheric acid deposition has been widely linked to the recent brownification of surface waters (Monteith *et al.*, 2007, 2014; Pagano *et al.*, 2014).

2.5 WHY IS DISSOLVED ORGANIC CARBON IN LAKES IMPORTANT?

Dissolved organic carbon has many varied and important roles in freshwater environments. Increased terrestrial input of organic carbon often can be derived from organic rich soils (Aitkenhead-Peterson *et al.*, 2003) leading to net heterotrophy, where respiration exceeds photosynthesis (Cole *et al.*, 2000). The balance between processing carbon by respiration and production by photosynthesis (Mitrovic *et al.*, 2016) within lakes determines whether a lake contributes to emission of CO_2 to the atmosphere (Moody *et al.*, 2013). Given the expected trends in climate there have been growing concerns about lakes switching from sinks of carbon to sources (Monteith *et al.*, 2007). Koehler et al. (2014) estimate that 10% of greenhouse gas emissions from lakes globally may be due to photo-mineralization of allochthonous DOC.

DOC is a vital resource impacting aquatic species by either providing a food source or by interactions influencing pH, metal and contaminate binding and transport (McDonald *et al.*, 2004). DOC behaves as a UV screen protecting life beneath the lake surface (Lean, 1998; Kaczmarska *et al.*, 2000; Nevalainen *et al.*, 2015), and regulating the lake thermal structure due to light limitation associated with brown colour of waters (Read *et al.*, 2013; Strock *et al.*, 2017). Therefore, the concentration of organic matter in surface waters is important as conditions such as light penetration affect the depth at which light is available and water temperature dynamics (Brown *et al.*, 2017).

Rising concentrations of DOC have been observed in many surface waters across the Northern Hemisphere (Worrall *et al.*, 2003; Evans *et al.*, 2005; Skjelkvåle *et al.*, 2005; Roulet *et al.*, 2006). Freshwater lakes and reservoirs are the main source of drinking water in many countries and rising DOC concentrations carry implications for water treatment processes (Ledesma *et al.*, 2012). DOC and POC are known to transport heavy metal and contaminants and if not treated correctly water containing DOC can produce carcinogens (Ledesma *et al.*, 2012). The common brown colouring of water is also associated with aesthetic concerns of colour, taste and odour which are considered negative by the public when relating to recreational and drinking waters (Volk *et al.*, 2002). Elevated concentrations of DOC in the ranges observed prior to anthropogenic influences can be regarded as positives in some situations. For example, there been suggestions that DOC can support river rehabilitation management strategies to improve water quality and support ecology (Stanley *et al.*, 2012; Mitrovic *et al.*, 2016).

2.5.1 DRIVERS OF RECENT TRENDS IN SURFACE WATER DOC CONCENTRATIONS

2.5.1.1 ACIDIFICATION

Discussion regarding the dominant driver of recent trends in surface water DOC concentrations is still ongoing. A convincing argument for the causes of recent declines in DOC concentration is the decline in atmospheric acid emissions (Monteith *et al.*, 2007), and particularly the decline in sulphur deposition (S). Acidification of catchment soils alters the ionic properties decreasing solubility of DOC (Evans *et al.*, 2005). DOC concentrations appear to be increasing in line with declines in atmospheric emissions, suggesting that organic carbon in surface waters is returning to pre-industrial levels (Monteith *et al.*, 2007).

2.5.1.2 LAND USE AND LAND MANAGEMENT

Anthropogenic factors can impact the supply of organic matter to surface waters. Activities such as animal herbivory and forestry can impact the soil stability and erode the landscape disturbing organic matter and causing changes to supply and pathways to lake systems. It is estimated that there has been an increase of 1.0 Pg C yr^{-1} transferred to inland waters from land since pre-industrial times as a result of human influences (Regnier *et al.*, 2013). Anderson et al., (2013) suggest that future land cover change and intensification of agriculture (linked to nutrient dynamics) along with continuing N deposition are driving increasing OC burial in lakes rather than climate change. Another explanation for acidification of soils is the effect of severe drought (Worrall *et al.*, 2008) which can also alter mechanisms controlling carbon turnover (Freeman *et al.*, 2001). Current climatic trends in the UK are observed to be towards more frequent and intense storm events and more frequent severe droughts.

2.5.1.3 CLIMATE

The potential impact of changing climate on trends in DOC is extremely complex. Both supply mechanisms and in lake processes are likely to be altered if hydrological and temperature changes occur, as detailed below:

- Greater uptake of CO_2 by lake waters as a result of increasing global atmospheric CO_2 (Freeman *et al.*, 2004).
- At the global scale, it appears that increased net primary productivity fuelled by rising atmospheric CO_2 levels is outweighed by increased soil respiration, leading to a net reduction in the soil carbon store (Yan *et al.*, 2019). However, increased soil carbon exports due to this process means there may be a larger flux of terrestrial carbon to lake systems.
- Increasing atmospheric CO_2 (Freeman *et al.*, 2004) leading to increased supersaturation of lake waters.
- Changes in precipitation and runoff (Tranvik *et al.*, 2002; Hongve *et al.*, 2004; Wen *et al.*, 2020) leading to increased erosion and transport from surrounding catchment.
- Increasing air temperature (Freeman *et al.*, 2001; Tranvik *et al.*, 2002) which encourages increased in lake productivity, respiration and photosynthesis.
- Eutrophication (Rosén, 2005) leading to increases in lake productivity.

Changes in precipitation regime and temperature, pH, nutrient supply, fire regime and light exposure also impact total organic carbon concentration observed in lake systems (Schindler *et al.*, 1997; C Freeman *et al.*, 2001; Tranvik *et al.*, 2002). In temperate systems, export of DOC and POC is enhanced during high energy events such as storms and seasonal snow melt (Raymond *et al.*, 2016).

2.5.2 PROJECTED CARBON TRENDS

Based on the expectation that average global temperatures are likely to increase and that precipitation events are likely to become more extreme, it is highly likely that there will be changes to terrestrial carbon stores and the fate of carbon reaching surface waters. Drake, Raymond and Spencer (2018) have estimated that lakes receive 5.1 PgC yr^{-1} and that over the past decade this amount has increased by 0.3 PgC yr^{-1}. Alterations in supply of DOC from surrounding catchments are likely to be the source of increases, suggesting that soils are losing carbon. Lakes are responsible for the processing of 2.7 PgC yr^{-1} eroded by chemical and physical weathering of soils (Battin *et al.*, 2008). Schindler et al. (1997) show for sites in the Experimental Lakes Area that declines in terrestrial inputs due to lower stream flow are linked to climatic warming, drought and increased forest fires which explained the declines in surface water DOC concentration between 1970-1990.

Between 1982 and 1999 satellite observations have shown an estimated increase in net primary productivity equating to an increase in carbon of 3.4 Pg (over 18 years), which appears to correlate with increased warming and possible CO_2 fertilization (Nemani *et al.*, 2003). Further increases of anthropogenic CO_2 and increasing temperatures are likely to increase NPP even further adding to the pool of carbon available.

From the papers discussed in this section it is apparent that monitoring records covering the last 30-40 years have observed increases in DOC correlating with atmospheric acid deposition declines, which would suggest that the two are linked. The trajectory and timing of DOC increase and acid deposition make a convincing case for this but are based on monitoring record data limited to relatively short monitoring periods. To date, palaeo-measurements of DOC or brownification are difficult to obtain and are few. In extending DOC records, it is possible to examine the relationship between recent atmospheric acid deposition, climate variations, land use and DOC variation. Lake sediments provide a record of how carbon characteristics and quantities have changed over longer time periods than monitoring programmes afford us and can also evidence potential drivers of changing flux including mineral supply, catchment vegetation and disturbance histories.

2.6 MEASURING CARBON: CONTEMPORANEOUS AND PALAEOMEASUREMENT TECHNIQUES

Dissolved organic matter (DOM) and dissolved organic carbon (DOC) are two widely used measures of the organic matter content of water. DOM refers to the total amount of dissolved organic matter comprising mainly C, O, N and H, while DOC refers only to the concentration of carbon. Typically, DOC is approximately half of DOM. An important difference between the two relates to the techniques and methods used in analysis. DOM is generally measured using chemical oxidation methods, while DOC is usually measured using combustion techniques, typically automated carbon analysers (McDonald *et al.*, 2004).

Measurement for both DOM and DOC, separation from particulate organic carbon (POC) and organic matter (POM) involves filtration. Since the 1990s the standardised definition for DOC is organic carbon which passes through a filter of <0.45µm (Thurman *et al.*, 1985). Prior to this other definitions were used making comparison of data sets sometimes difficult (Kalbitz *et al.*, 2000). POC is that retained on the 0.45µm porosity membrane and constitutes an estimated <10% of total organic carbon (Thurman *et al.*, 1985). Allochthonous organic matter is dominated by humic substances (humic acid and fulvic acid) comprising a complex mixture of aromatic and aliphatic hydrocarbon structures (Thurman *et al.*, 1985) including 30% hydrophilic acids and 20% carbohydrates and amino acids (Aitkenhead-Peterson *et al.*, 2003). DOC can be recalcitrant, persisting in aquatic environments without decomposition, and therefore can be preserved in sediments (McKnight *et al.*, 1998).

2.6.1 MEASUREMENT OF DOC CONCENTRATION IN WATER

To understand the changes in carbon of surface waters, measurement techniques have focused on quantifying the amount of DOC present. Methods divide into two classes: combustion and spectrophotometric. Combustion methods involve removal of inorganic carbon, where combustion is used to convert DOC to CO_2 followed by measurement of CO_2. Combustion may be chemical (Benner *et al.*, 1993) or, more usually today, thermal (e.g., Fukushima *et al.*, 1996). Newer analytical techniques include Total Carbon Analysers (TC) which use infra-red sources and thermal combustion of DOC to CO_2 to quantify concentrations of carbon present in water samples. Absorption spectroscopy, more rapid and lower cost, are commonly used by monitoring programmes. This spectrophotometric approach mainly uses absorption at 254 nm (Stevenson, 1975), though a range of longer UV wavelengths have been used (Lewis *et al.*, 1977; Edzwald *et al.*, 1985; Moore, 1987; Rostan *et al.*, 1995). Visible light has also been used in the case of Hazen scale measurements (Hongve *et al.*, 1996).

2.7 MEASUREMENT OF ORGANIC CARBON CONTENT OF SEDIMENTS

Monitoring programmes reporting the concentration of DOC (commonly in mg l^{-1}) are extremely useful at providing insight into short term (seasonal, drought) processes. However, due to the limited length (decadal) of reporting it is difficult to evaluate longer term changes and interactions, providing instead a snapshot covering a relatively short period. Crucially, such data sets do not extend back to the industrial revolution or beyond. Delays in response from in lake indicators could also be influencing results (Kernan *et al.*, 2010), particularly given the short term nature of many data sets. For confidence in the theories presented to explain DOC trends, more research must be conducted (Filella *et al.*, 2014).

One solution to this is to estimate historical carbon trends using sediment records, allowing comparison with modern records but also extending into the past (Campbell *et al.*, 2000). Lake sediments can provide records of local terrestrial change as well as changes in productivity (Diefendorf *et al.*, 2008). This is particularly important in relation to carbon budgets due to their sensitivity to climatic impacts. Although monitoring records of DOC are limited in terms of time scale and continuity of extraneous variables, they are the most extensively observed component of the terrestrial carbon cycle (Worrall *et al.*, 2018). And as such are a valuable source that we can use alongside improving sedimentary analysis techniques to understand DOC fluxes and drivers.

There is a general acceptance that spectroscopic methods (NIR, MIR, and IR) are suitable for characterising sediment components. In recent decades spectroscopy methods have been shown to successfully characterise organic and mineral content in samples (Rouillard *et al.*, 2011; Carsten Meyer-Jacob *et al.*, 2014; Pearson *et al.*, 2014; Russell *et al.*, 2019). These often use training sets, where samples of known environmental concentration can be used with chemometric methods to provide estimates of proxy information for unknown samples. This is the approach used by both Pearson et al. (2014) and Meyer-Jacob et al. (2014a). The limitations lie in the need for the training set, particularly in relation to obtaining a suitable DOC training set.

The studies described above all use FTIR to quantify a compositional component of the sediment (such as OM, mg/g), components that could have been measured using an alternative method. In other words, FTIR is being used in place of an existing method for reasons of cost, speed or convenience. However, there is another type of FTIR method where measured sediment spectra are used to infer the composition of the past lake water from which the sediment layer settled. This second approach differs radically from the former, for two reasons. First, the inference can only be based on chemometric training: the measured spectra of a sediment sample is blindly associated with the known lake water properties of the training set, there is no way of assessing spurious inference arising from covarying environmental variables. Second, there are no alternative methods that can achieve this, such that validation is problematic. This approach was applied by Rosén (2005), using NIRS data to infer past lake water TOC for eight Holocene lake sediment records in Northern Sweden. A subsequent study repeated this for one of the lakes using FTIR (Rosén *et al.*, 2006). Rouillard et al. (2011) used lake sediment surface samples to provide a training set for visible near-infrared spectroscopy (V-NIRS) to reconstruct DOC using chemometric methods which were then corroborated against previous multiproxy studies. A long record of DOC was presented, and although the data were not interpreted there was a clear trend of decreasing DOC towards to present day. Finally, Cunningham et al. (2011a) used NIRS to infer lake water TOC for sediment records across southern Sweden, with a view to understanding recent change in concentration. So, the focus of FTIR studies so far in reporting lake water DOC or TOC as inferred from sedimentary records has been on developing and testing analytic techniques.

Studies have shown that visual interpretation of lake colour can be a good proxy for estimating DOC concentration. Kritzberg (2017) utilised visual records of colour to reconstruct 80 years of brownification records for several Swedish Lakes. Whilst providing interesting findings regarding the brownness of water, these measurements cannot be assumed to represent DOC concentration, as not all colour can be attributed to organic matter, presence and concentration of iron can affect water colour.

2.8 THE UK UPLAND WATER MONITORING NETWORK (UK-UWMN)

In the 1980s the United Nations Economic Commission for Europe (UNECE) convention on Long Range Transboundary Air Pollution (LRTAP) was launched with the aim of reducing the impacts of acid deposition on soils, vegetation, and surface waters. In 1988 The United Kingdom Acid Waters Monitoring Network (UK-AWMN) was established by DEFRA (previously known as UK Department of Environment) to monitor chemical and ecological effects of this legislation. In 2013 funding streams changed and the network was re-named the UK Upland Waters Monitoring Network (UK-UWMN) and refocused its aims to monitor changes in surface water chemistry and biodiversity.

The overall aim of the network has been to provide a comprehensive data set quantifying the response of acid sensitive environments to changes in atmospheric acid deposition for use by researchers and policy makers. 14 streams and 12 lakes, where atmospheric acid deposition is the dominant source of pollution (on a gradient North to South), were selected in remote upland locations where limited land use, such as hill sheep farming and forestry take place (Figure 2.2).

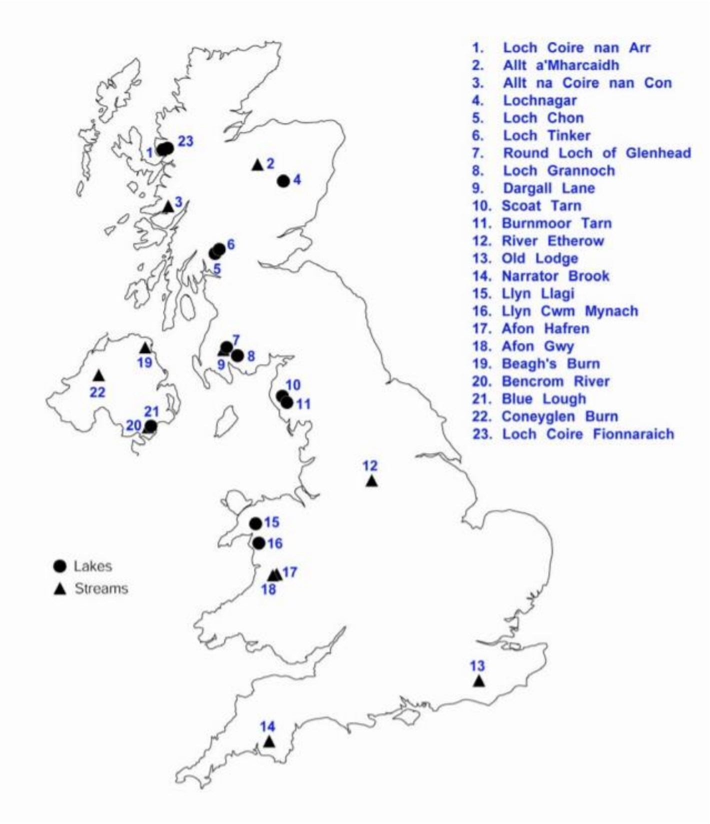
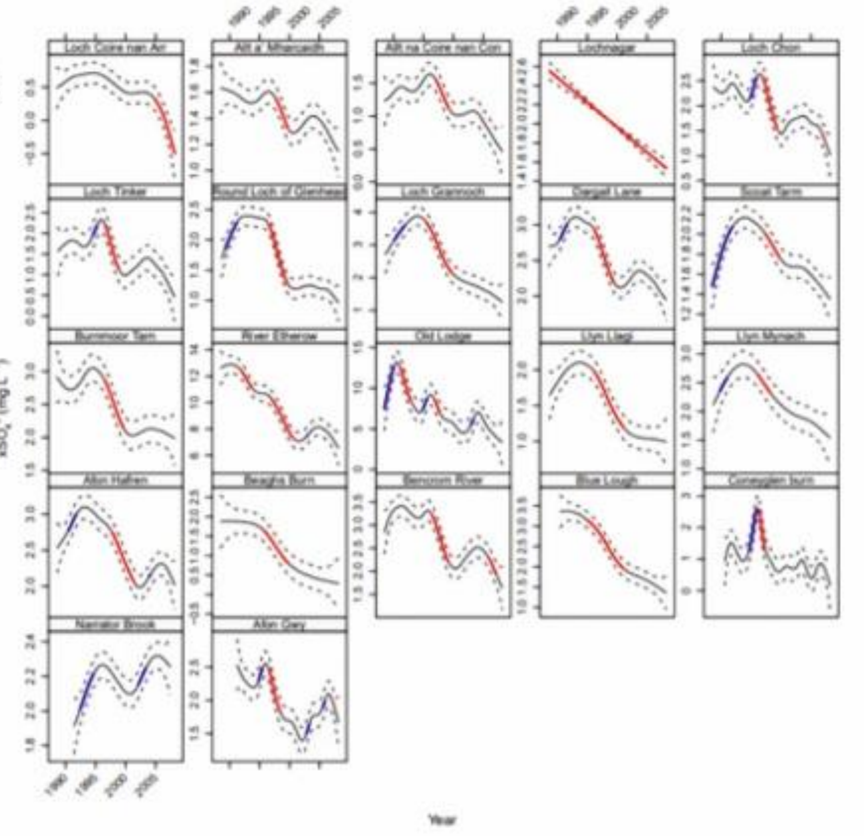


Figure 2.2 Map of UK-UWMN sites

Over time the monitoring network has evolved to improve and adapt to its overall aims and several additional parameters (such as total dissolved nitrogen and thermistors) have been added to the suite of chemical and biological measurements. Water samples collected quarterly at lake sites were measured for pH, conductivity, DOC and a standard selection of base cations, anions, and metals. Sediment traps are emptied annually with diatom species, trace metals and flux of carbonaceous particles measured.

2.8.1 FINDINGS

A



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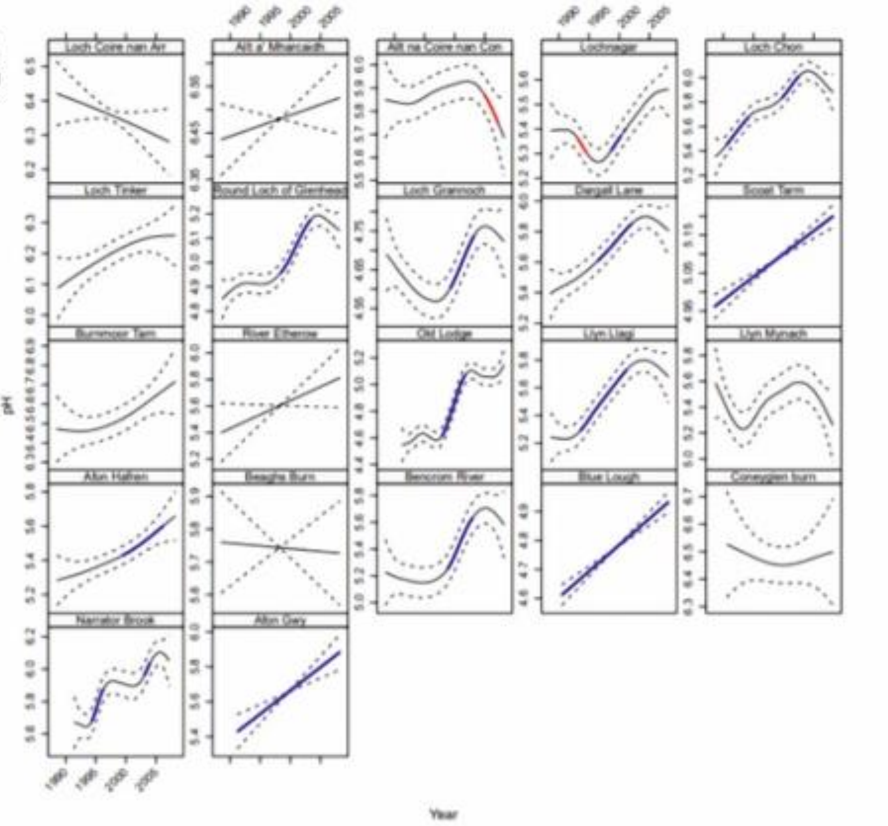


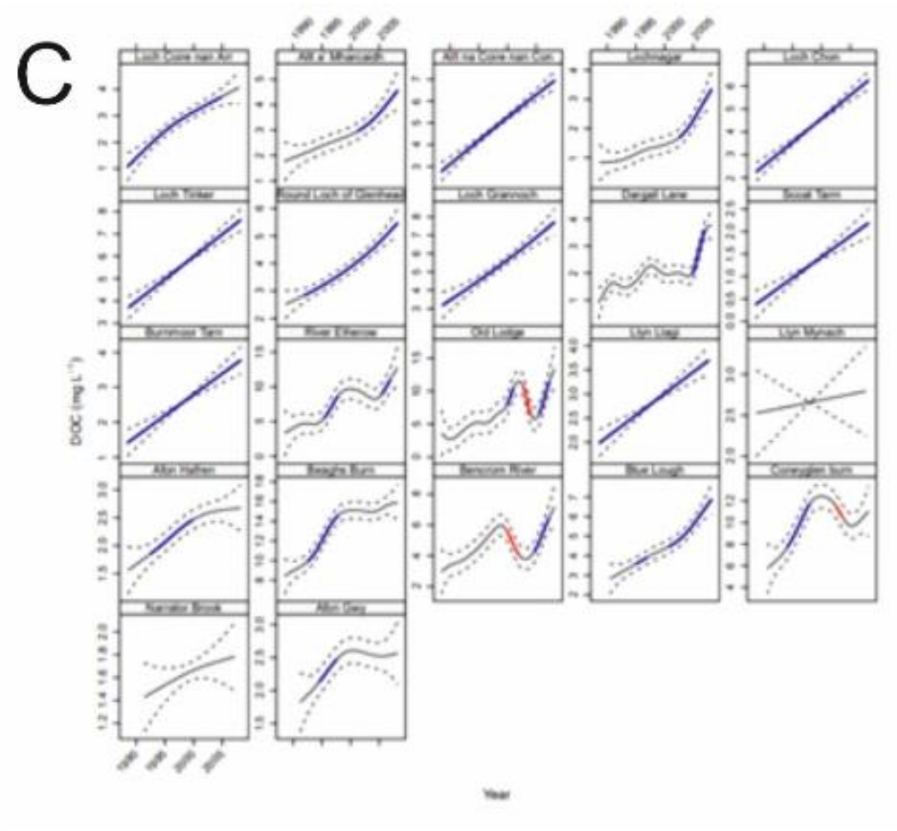


Figure 2.3 Fitted trends of surface water chemistry at all UK-UWMN sites, determined by derivative analysis. (Blue = increase, red= decrease) A) xSO_4^{2-} (mg l^{-1}) B) pH C) DOC (mg l^{-1}) (Kernan *et al.*, 2010)

The latest 10 year report by Kernan *et al.* (2010) provides the information and findings below. Findings from chemistry and biological indicators show improvements in water quality over the monitoring period. As expected, observations show that atmospheric acid deposition of sulphur reduced significantly until 2000, after which declines are limited (Figure 2.3A). The frequency and intensity of storm events (influx of sea salt) reduced over the monitoring programme which is likely to have contributed to reductions in chloride concentrations (Monteith *et al.*, 2007). In terms of biological recovery there have been observed differences between forested and moorland sites. This appears to be related to the greater acidity at the forested sites, promoting high concentrations of labile aluminium that is particularly harmful to aquatic fauna.

Appearing to coincide with the decreases in acid deposition, there have been increases in pH (decreases in acidity) at all sites (Figure 2.3B). Associated with increases in alkalinity are a change in diatom community and in some locations salmonid populations have re-established. At all sites DOC has increased in concentration (Figure 2.3C), which is generally assumed to be a result of falling sulphate. DOC trends are assumed to be recovery leading to a return to natural (pre-industrial) levels (Evans et al., 2005; Vuorenmaa et al ., 2006; Monteith et al., 2007; Sawicka et al., 2017 etc.). Acidified lakes and rivers in the network are recovering as measured by both chemical and biological parameters. However, it is also evident that recovery is only partial, and that additional drivers such as atmospheric N deposition and climate change environmental may interfere with any further recovery. In relation to levels of toxic metals (lead, mercury, zinc) (Kernan et al., 2010) continued elevated levels are seen, likely to be linked to remobilization of legacy contaminants in soils as opposed to current deposition (Rose et al., 2012; Yang et al., 2018).

The UK-UWMN was designed to encompass locations with limited catchment anthropogenic activity and variability in type and extent of forest cover. Forest cover is believed to affect acid deposition in catchments through the interception of pollutants by the rough forest canopy (Miller *et al.*, 1991). Interestingly, results from the network have shown that recovery is little impacted by the degree of catchment afforestation, evidenced by the convergence of sulphate concentration records at four forested/moorland site pairings. Whilst afforested sites initially had higher acid inputs, they have experienced the most rapid reduction and now present similar conditions to moorland sites.

2.8.2 HOW THE INFORMATION FROM THE NETWORK HAS BEEN USED

The UK-UWMN sites provide an excellent range of measurements at locations varying in land use, vegetation type and bedrock, allowing for comparison between natural characteristics and anthropogenic drivers of change. The data from the network provides an evidence base for policy decisions related to legislation on atmospheric acid deposition and the management of upland surface waters, informing decisions with implications for water quality and habitat management for many rare species. However, in addition to informing governmental policy, the network provides an invaluable scientific record of environmental change in the British uplands. Data collected by the network has contributed to several national and international research projects, in addition to forming an integral part of this research.

2.9 THE STATE OF KNOWLEDGE - A SYNTHESIS

This review spanning various scientific fields relevant to brownification reveals a number of observations pertinent to this research. It is estimated that lakes comprise 3.7% of non-glaciated land surface and have a disproportionately large impact on the terrestrial carbon budget. And, though generally heterotrophic, lakes are substantial sinks for allochthonous carbon, trapping 30-80% of the total supplied carbon. The 20-70% that is not stored is mainly returned to the atmosphere, a very substantial but poorly constrained fraction. This research addresses the question of what governs the rate of supply of allochthonous C delivered to lakes, essential information for understanding the ultimate fate of CO_2 in lake systems.

Supply of carbon to upland, acid sensitive lakes is primarily from their catchments, the rate varying with land cover (wetlands producing the most) and climate. The climate effect is broadly associated with net primary production, such that if water is not limiting, warmer climates produce more C than cooler climates. Aridity reduces long-term C supply, though short periods of drought can enhance C export. It is for this reason that the palaeoenvironmental approach of this thesis is particularly useful

Processes regulating DOC export at short timescale are expected to be different from those at long time scales. If we want to understand long-term change, then long-term data sets are essential.

DOC plays a fundamental role in lake ecosystem functioning. It reduces the photic zone thickness, shields biota from harmful UV radiation, and it strengthens the thermal stratification of lake by increasing the temperature of the uppermost water. While this research aims to test causal hypotheses for brownification, the DOC reconstructions derived are also relevant to understanding past ecosystem functioning.

The previous review of measurement approaches for organic carbon in water highlight and address the distinction between dissolved and particulate forms (DOC v. POC). This raises a question that is directly relevant here as lake sediment records collect carbon in both forms. It could be argued that the reconstruction methods applied here measure TOC rather than DOC. However, for two reasons the term DOC is used. First, in the cool temperate lakes of both this study and the remaining UK-UWMN sites DOC is the dominant form, typically 90% in boreal lakes (Wetzel, 2001), such that measuring TOC and DOC produces similar values. Second, TOC was not measured for the UK-UWMN sites, and thus the monitored test data for comparison with sediment records are DOC.

The review of the application of NIRS to understanding lake carbon supply illustrates an important methodological issue. Those studies that use NIRS to measure the dry mass concentration of organic matter in lake sediment rest on very different foundations to the studies that attempt to infer lake water DOC from sediment records. Both procedures use statistical chemometric methods, but in the case of dry mass concentrations the statistical model has a firm basis in terms of scientific understanding. The NIRS signal is expected to be proportional to the sediment composition. For lake water DOC reconstruction, however, no such assumption can be made; the chemometric method can be applied, but its results cannot take lake hydrology or sediment mass accumulation rate into account, both of which must impact the NIRS signal that the method relies on.

The UK-UWMN sites provide a unique opportunity to test a sediment inferred DOC record. Almost three decades of data for multiple sites covering range of DOC temporal trajectories provides a critical test. It also provides an opportunity to compare interpretations arising from monitored data with what may be inferred from longer records.

3 NIRS QUANTIFICATION OF LAKE SEDIMENT COMPOSTITION BY MULTIPLE REGRESSION USING END MEMBER SPECTRA

3.1 ABSTRACT

Here we develop a novel method for quantifying sediment components, e.g. biogenic silica, organic or mineral matter, from near infrared (NIR) spectra based on fitting by multiple regression of measured spectra for end-member materials. We show that with suitable end-members our new open-source multiple regression routine gives excellent simultaneous quantification of the major components of a sediment, the concentrations comparing well with independent methods of quantification. Widely-used partial least squares (PLS) regression approaches rely on large environmental training data sets; our method produces comparable results, but with the advantages of negating the need for a training dataset and with greater simplicity and theoretical robustness. We demonstrate that component NIR spectra are additive, a prerequisite for use of multiple regression to un-mix the compound spectra, and show that a number of environmental materials make suitable end-members for this analysis. We show that spectral mixing is not conservative with respect to mass proportion, but rather to the relative chromatic intensity of contributing sediment components. Concentrations can be calculated using the measured spectra by correction using a chromatic intensity factor (CIF), the value of which can be measured independently. We have applied our approach to a postglacial sediment sequence from Loch Grannoch (SW Scotland) and reveal a down-core pattern of varying dominance by biogenic silica, organic and mineral content from the late glacial to present. With isolation and measurement of appropriate end-members this multivariate regression approach to interrogating NIR spectra has utility across a wide range of sedimentary environments and potentially for other spectral analytical methods.

3.2 INTRODUCTION

Near infrared diffuse reflectance spectroscopy (NIRS) has proven to be a valuable tool for quantifying the components present in lake sediments, such as type and quantity of organic and mineral matters (Malley et al. 1999; Malley et al. 2014; Pearson et al. 2014). NIRS has the advantages of being quick, simple, and non-destructive and is consequently used in many different fields including environmental research, agriculture, and pharmaceutical industries. Applications of NIRS in palaeolimnology have focused on extracting key environmental parameters or proxies for inorganic/organic markers (e.g. % total organic carbon: Pearson et al. 2014). The overlapping absorption bands in near infrared (NIR) spectra make identification or quantification of signals attributed to individual materials or characteristics difficult (Brown et al. 2006; Zornoza et al. 2008; Korsman et al. 2001). Development in chemometric methods, particularly partial least squares (PLS) regression, during the 1980s (Workman *et al.*, 1996) improved and simplified the interpretation of spectra. Though highly successful applications have been made possible by these developments, the

PLS approach has two disadvantages. First, a substantial data training set is required for a component to be quantified from the IR or NIR spectra, which must be based either on large numbers of samples with independent measurement of that given component (for example, % total organic carbon studied by Pearson et al. 2014) or on artificial mixtures requiring large quantities of purified end-member materials (for example, biogenic silica studied by Meyer-Jacob et al. 2014, in this case by FTIRS). Second, because PLS methods cannot be applied simultaneously to a number of components, it is difficult to evaluate potential interference in the NIR spectra between components, which instead may remain hidden in the PLS numerical processing.

Here we propose and present an entirely novel approach to generating palaeoenvironmental data from NIRS, based on the assumption that the NIR spectra of mixtures comprise linear combinations of the spectra of sediment components. This allows each individual sample to be analysed by regressing its NIR spectrum on to the spectra of a chosen set of end-member materials, the regression coefficients quantifying the end-member mixing proportions. This is fundamentally different from traditional methods that use regression not to analyse samples, but to develop a statistical model using an extensive training data set. For example, in the widely applied weighted-average PLS methods a set of concentrations known independently are regressed onto entire or partial NIR spectra to evaluate coefficients that can then be applied to unknown samples. The training sets required for this process are based typically on either a range of modern environmental samples or on parallel independent measurements obtained for the same palaeorecord. Our method circumvents the need for such training sets, using instead regression to un-mix each sample spectrum from a library of end-member spectra. Consequently, our method provides simultaneous quantitative reconstruction for multiple components without requiring a training stage.

Here, we present and test our end-member regression methodology, address a number of key issues with applying multiple regression to un-mix spectra. Important among these are: the isolation and measurement of appropriate end-members; sensitivity testing of end-member choice; and comparison with the PLS approach. To have confidence in our multiple regression-based reconstructions some comparison is necessary with independently measured equivalent data, but critically the same issue applies to reconstructions by PLS. We report the results of an application of our approach tested on binary mixtures and on a full late-glacial to present lake sediment profile from Loch Grannoch, SW Scotland. We also test the generality of the procedure and end-member materials by applying them to the sediments of three additional lakes from differing regions (Wales, Norway and Sweden).

3.3 METHODS

3.3.1 SAMPLING AND THE END-MEMBER LIBRARY

To develop the end-member approach we collected and measured a library of organic and inorganic materials. Table 3.1 describes the locations and materials collected that form this end-member library. This includes materials that are homogeneous (e.g. individual minerals) and more heterogeneous materials (e.g. plant materials, rocks and sediments). To apply our end-member approach we obtained a postglacial sediment core from Loch Grannoch in the Galloway Hills (SW Scotland). Loch Grannoch is a small (1.14 km^2) upland (210 m O.D.) oligotrophic lake, with a granite bedrock (Cairnsmore of Fleet intrusion) (14 km^2) catchment area (Flower *et al.*, 1987). The Loch Grannoch core was sampled on 31 October 2016 from the central part of the lake (54.9954° N, 4.2832° W) from an anchored floating platform in ~16 m of water. The cores comprise 4 overlapping lengths sampled using a 0.075 x 1.5 m capacity hand-percussive Russian corer. Cores were wrapped and sealed in polythene and stored refrigerated until required for analysis. The sediments comprised 3.19 m of largely organic limnic muds and 0.6 m of inorganic muds that extend to deglaciation including the late glacial oscillations (Greenland Interstadial and Stadial 1), with regional deglaciation of the Galloway Hills dated to ~15 k years ago (Ballantyne *et al.*, 2013).

Table 3.1 Materials for which CIFM values have been measured

Sample code	Type	Material	Location	CIF_M	Latitude	Longitude
PeatMMoss	Organic	Peat	May Moss, N Yorkshire, UK	1.00	54.3559	-0.6532
Platanus	Organic	Platanus leaf	Liverpool, UK	2.70	53.4020	-2.9652
Sphag	Organic	Sphagnum sp.	May Moss, N Yorkshire, UK	0.77	54.3559	-0.6532
Erioph	Organic	Eriophylum	May Moss, N Yorkshire, UK	1.46	54.3559	-0.6532
Calluna	Organic	Calluna	May Moss, N Yorkshire, UK	1.55	54.3559	-0.6532
HAMMoss	Organic	Humic acid	May Moss, N Yorkshire, UK	4.51	54.3500	-0.6426
HARiv	Organic	Humic acid	Rivington Moor, Lancashire, UK	4.73	53.6204	-2.5380
FAMMoss	Organic	Fulvic acid	May Moss, N Yorkshire, UK	1.56	54.3500	-0.6426
DOCWhix	Organic	DOC	Whixhall Moss, Cheshire, UK	0.84	52.9175	-2.7596
DOCRiv	Organic	DOC	Rivington Moor, Lancashire, UK	0.78	53.6207	-2.5381
DOCMig	Organic	DOC	Migneint, N Wales, UK	0.87	52.9767	-3.8347
LGClayLOR	Sediment/soil	Late glacial silty clay	Lilla Öresjön, Sweden	1.26	57.5531	12.3170
LGClayMyn	Sediment/soil	Late glacial silty clay	Llyn Cwm Mynach,W Wales, UK	1.94	52.7960	-3.9609
LGClayGran	Sediment/soil	Late glacial silty clay	Loch Grannoch, Galloway, UK	2.26	54.9967	-4.2838
TillOgGrey	Sediment/soil	Till clay	Ogwen Valley, N Wales, UK	1.56	53.2301	-4.0789
TillOgBrown	Sediment/soil	Till clay	Ogwen Valley, N Wales, UK	1.79	53.2301	-4.0789
TillAfon	Sediment/soil	Till clay	Afon Gain, Gwynedd, W Wales, UK	2.82	52.8717	-3.8730
Rhyo	Rock	Rhyolite	Ogwen Valley, N Wales, UK	1.40	53.1289	-4.0316
RhyoWeath	Rock	Rhyolite, weathered	Ogwen Valley, N Wales, UK	2.60	53.1289	-4.0316
Gneiss	Rock	Gneiss	Vågsøy, Norway	3.03	62.0302	5.0034

MicrGabbr	Rock	Microgabbro	Ogwen Valley, N Wales, UK	3.09	53.1235	-4.0266
MicrGrani	Rock	Microgranite	Ogwen Valley, N Wales, UK	3.90	53.1221	-4.0095
Tuff	Rock	Tuff	Ogwen Valley, N Wales, UK	4.00	53.1246	-3.9961
LST	Rock	Limestone	Great Orm, N Wales, UK	6.73	53.3236	-3.8517
SiltST	Rock	Siltstone	Ogwen Valley, N Wales, UK	0.98	53.1405	-4.0371
SlatePurp	Rock	Slate, purple	Ogwen Valley, N Wales, UK	1.14	53.1730	-4.0572
SlateGrey	Rock	Slate, grey	Ogwen Valley, N Wales, UK	2.82	53.1730	-4.0572
SlateGreen	Rock	Slate, green	Ogwen Valley, N Wales, UK	5.22	53.1730	-4.0572
SST	Rock	Permotriassic Sst	Wirral, UK	1.35	53.3535	-3.1357
RockBWR0	Rock	Andesitic volcaniclastics	Dovedale, Cumbria, UK	3.74	54.4949	-2.9582
RockBWR5b	Rock	Andesitic volcaniclastics	Dovedale, Cumbria, UK	3.90	54.4971	-2.9505
RockBWR6	Rock	Andesitic volcaniclastics	Dovedale, Cumbria, UK	3.70	54.4967	-2.9569
RockBWR7	Rock	Andesitic volcaniclastics	Dovedale, Cumbria, UK	3.53	54.4950	-2.9584
DiatomMar	Biogenic silica	Marine diatom	California, USA	3.09		
DiatomEd	Biogenic silica	Diatom	Not known	3.79		
DiatomGM	Biogenic silica	Diatom	Grasmere, Cumbria, UK	2.50	54.4551	-3.0296

Specific end-member mineral samples were selected and ground to a fine powder using a pestle and mortar. The aim was to isolate single materials but in reality, some minor contaminant minerals potentially remain. Rocks were sampled from various catchments to reflect detrital sediment sources to lakes. These were cut to expose fresh surfaces, and fine powders were obtained using a diamond drill. In formerly glaciated environments the basal lacustrine muds lain down while ice was still affecting the lake could be regarded as a partially homogenised sample of catchment sediment sources, except where glacial ice external to the lake catchment was likely. Dried and powdered samples of these deglacial inorganic muds are used as end-members reflecting bedrock of the catchments.

Organic materials include specific plant samples (e.g. *Sphagnum, Calluna vulgaris* (L.) Hull), a sample of UK ombrotrophic peat (from May Moss, a site of varying composition in terms of plant remains and the degree of peat humification), natural dissolved organic matter from streams draining peatlands (Rivington Moor, Whixall Moss, and Migneint) isolated by freeze-drying, and separated humic and fulvic acid extracted from May Moss peat (collected March 2017). Humic acid was also collected from May Moss and Rivington Moor stream water by acidification to pH 2 and filtration.

Biogenic silica end-members were obtained using 1) the >90 µm fraction of diatom rich sediment taken from the edge of Grasmere (Cumbria), visually inspected to confirm the absence of mineral matter, 2) a cultured marine diatom (*Thalassiosira pseudonana*, supplied by Reed Mariculture, Campbell, California, USA), and 3) commercial food supplement diatomaceous earth (Ultra-fine freshwater diatomaceous earth, Diatom Retail Ltd, Leicester, UK). All three samples were treated with hot acidified hydrogen peroxide to remove organic matter.

Humic and fulvic acid were extracted from May Moss peat following the method of Hayes et al. (1975) but excluding the acid prewash (our samples lack carbonate). The extraction comprised (Stage 1): 10 g peat reacted with 100 ml of 1M NaOH, swirled for 16 hours at room temperature and then decanted following centrifugation. Stage 2 involved careful acidification of the NaOH extract with concentrated AnalR HCl, adjusting to pH 1. After 3 days at 4 °C, the humic acid precipitate was collected by centrifugation, and repeatedly washed in deionised water. Stage 3 involved neutralisation of the remaining solution with 1 M NaOH. The neutral solution was then freeze dried to recover a mixture of fulvic acid and NaCl. Stage 4 involved removal of the NaCl using dialysis tubing.

We also created artificial binary and ternary admixtures of materials to assess the impact of varying compositions on the quantitative information acquired from the NIRS analyses. All such mixtures were homogenised by grinding in a pestle and mortar. A ternary equal mass proportion admixture was created using the late glacial muds from Loch Grannoch, Llŷn Cwm-Mynach (N Wales) and Lilla Öresjön (S Sweden). May Moss peat and late glacial sediment (Loch Grannoch) were prepared in quantity for these synthetic admixtures. The raw materials were homogenised by repeated sieving (63 µm for the mineral matter, 125 µm for the peat). The binary admixtures were created on a mass proportional basis (0, 7, 20, 33, 47, 60, 73, 87, 93, 100%) of Loch Grannoch late glacial muds to May Moss peat to assess any deviation of fitting coefficients from a linear relationship with respect to mass proportions.

3.3.2 ANALYTICAL METHODOLOGY

NIR spectra for both Loch Grannoch sediment and the end-member materials, processed as outlined in this section, are available in the University of Liverpool Data Repository as tab delimited text files (http://dx.doi.org/10.17638/datacat.liverpool.ac.uk/550). These files are formatted for use in the R code, also provided.

NIR spectra were measured by diffuse reflectance using an integrating sphere on a Bruker MPA Fourier-Transform NIRS for both the end-member data set and for 65 discrete evenly spaced 5 mm thickness subsamples from the 3.19 m Loch Grannoch core. All samples measured were freeze-dried, homogenised by grinding in a mortar, and lightly hand pressed (Korsman et al. 2001), with the NIR spectra based on combining 64 scans collected at 8 cm^{-1} intervals across the range 3595-12500 cm^{-1}.

To compare partial least squares (PLS) regression methods applied conventionally to interrogate IR spectra (C. Meyer-Jacob *et al.*, 2014; Pearson *et al.*, 2014) with our new multiple regression end-member approach, PLS-WA analysis was undertaken using the Bruker OPUS software (Quant Package). A range of numerical processing procedures were used to systematically vary the numerical processing of the NIR spectra including various normalisation procedures and derivatives. We also used a Principal Components Analysis (PCA) on a correlation basis to examine the overall spectral structure. This approach has enabled assessment of the most appropriate numerical methods and wavelength range in the NIR spectra for determining organic and mineral components in the sediments. Similar to previous work (Burns *et al.*, 2001; Korsman *et al.*, 2001; Pearson *et al.*, 2014) we found using the 1st derivative of the NIR spectra was most appropriate. 1st derivatives for all NIR spectra were calculated using a centrally-weighted Savitzky-Golay smoothing (SGA) algorithm, and our analysis focuses on the wavelengths 8000-3800 cm^{-1}, minimising noise whilst containing the key spectral structure diagnostic of organic and mineral components.

Independently quantified sediment component concentrations in the Loch Grannoch core (Organic matter, biogenic silica, and mineral matter) were needed both to test the results of the multiple regression and as a training dataset for the PLS comparison. A subset of 22 samples from the Loch Grannoch core was used to train the PLS-WA regression. Organic matter concentrations were quantified by loss on ignition (LOI), with weight loss measured after 1 hour of ignition at 550°C on sediment previously dried at 105°C (Boyle, 2004). Element concentrations from which to calculate normative mineral matter and biogenic silica were measured using an Energy Dispersive X-ray Fluorescence Analyser (ED-XRF). Dried samples were hand-pressed in 20 mm pots, and measured under a He atmosphere using a Spectro XEPOS 3 ED-XRF that emits a combined binary Pd and Co excitation radiation and uses a high resolution, low spectral interference silicon drift detector. The XRF analyser undergoes a daily standardization procedure and has accuracy verified using 18 certified reference materials (Boyle *et al.*, 2015).

Garrels and Mackenzie (1971) demonstrated that mineral concentrations present in soil or sediment can be calculated using a method borrowed from igneous petrology. Idealised, or 'normative', mineral concentrations are calculated based on standard compositions for the constituent minerals, via application of a series of steps that allow for the elements in the soil or sediment to be fully accounted for. Details are provided in Boyle (2001). The following steps were applied:

Recalculate major elements as oxides (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, TiO_2, MnO_2, P_2O_5), and together with LOI normalise these to unity

Mineral matter is calculated as the sum of measured oxides excluding SiO_2; calculated SiO_2 associated with silicate minerals (chlorite, albite, orthoclase, anorthite); and quartz

Biogenic silica is calculated as measured SiO_2 minus quartz, and minus calculated SiO_2 associated with silicate minerals.

Silicate-associated SiO_2 is calculated by assuming it to be present only as chlorite, albite, orthoclase, and anorthite, considered to be the sole sources of MgO, Na_2O, K_2O and CaO, respectively. Silica/oxide ratios, from Deer et al. 1966, were taken to be 1.68, 6.13, 5.53, and 2.27, respectively.

Quartz is not measured directly, but is taken to be 30 times TiO_2. This value is the average ratio of "free" SiO_2 to TiO_2 for the late glacial sediment (assumed to contain negligible biogenic silica), where free SiO_2 is total measured SiO_2 minus silicate associated SiO_2. This approach is most reliable where mineral matter concentrations are low, and least reliable when they are high (where quartz uncertainty is maximal and biogenic silica is lowest).

3.3.3 DATA HANDLING AND STATISTICAL METHODS

The IR intensity arising from a mixture depends on the type and concentration of chromophores (the regions of a molecule that interact with photons) contributed by its component parts (Boroumand *et al.*, 1992) with intensity related to sample component mass concentration. The combined intensity is not expected to be linearly related to the mass proportions, as the chromophore density will vary among materials. However, the component IR intensities (mass proportion scaled by chromophore density) should be additive, such that their mixing proportions can be found by multiple regression (Equation 3.1).

Equation 3.1

$$I_{M,k} = b_0 + b_1 I_{C1,k} + \ b_2 I_{C2,k} + \cdots + \ b_n I_{Cn,k}$$

Where:

- I is the signal intensity at wavenumber k (cm^{-1}) for the mixture (M) and components (C_1 to C_n)
- b_0 to b_n are the regression coefficients

If chromophore density was equal for all materials, then the regression coefficient would yield the mass proportions (concentrations) of the components in a mixture. However, chromophore densities vary according to material, so the coefficients instead quantify what may be described as the chromatic proportions. To calculate mass proportions from this information we need to know something of the chromatic properties of the components. This need not be known in detail because we have measured spectra for the components, and are fitting these to the measured spectrum of mixtures. Instead, provided we assume (after Boroumand et al. 1992) that the component spectra are additive, then we simply need a coefficient that represents the average chromatic intensity of each component, which we term the Chromatic Intensity Factor (CIF). This allows mass proportions to be calculated (Equation 3.2).

Equation 3.2

$$w_x = \frac{b_1 CIF_1}{\sum_{x=1}^{n} b_x CIF_x}$$

Where, shown for component 1:

- w_x is mass fraction of component *x*
- CIF_x if the chromatic intensity factor of component *x*

The CIF value for each component may be found by parameterisation, if independent information is available for the composition of the mixture. However, it can also be measured using synthetic mixtures, if one component is chosen as a reference and assigned a value of 1, a 50:50 mixture of May Moss peat (our chosen reference) with component X yields a compound spectrum that can be regressed onto the spectra of its two components. The measured CIF value for component X relative to May Moss peat is given by Equation 3.3.

Equation 3.3

$$CIF_x = \frac{b_{MMPeat}}{b_X}$$

Multiple regression was used for each sample to fit end-member spectra to the sample spectrum. This is done using the linear regression model (LM) function in R (R Core Team, 2013), with regression model coefficients and confidence intervals returned using the COEF and CONFINT functions. Mass normalisation following correction for chromatic intensity was undertaken using Equation 3.2 and Equation 3.3. The R code reports and plots mixing proportions for each component included in the multiple regressions with 95% confidence intervals for each sample, and a measure (R^2) of the proportion of the variance in the sample NIR spectra explained by the selected component end-member NIR spectra. The R code is available in University of Liverpool Data Repository (http://dx.doi.org/10.17638/datacat.liverpool.ac.uk/550).

CIF values may also be found by optimisation if component concentrations are independently known. In such cases CIF values can be adjusted to minimise the mean squared difference between modelled and known component concentrations.

3.4 RESULTS

3.4.1 END-MEMBER NIR SPECTRA

A selection of raw unprocessed spectra for potential end-members (Figure 3.1) illustrates the high degree of similarity between widely different materials. Comparing the same materials, a greater distinction is achieved using 1st derivative NIR spectra, with clearer differences between organic and mineral end-members (Figure 3.1b and d).

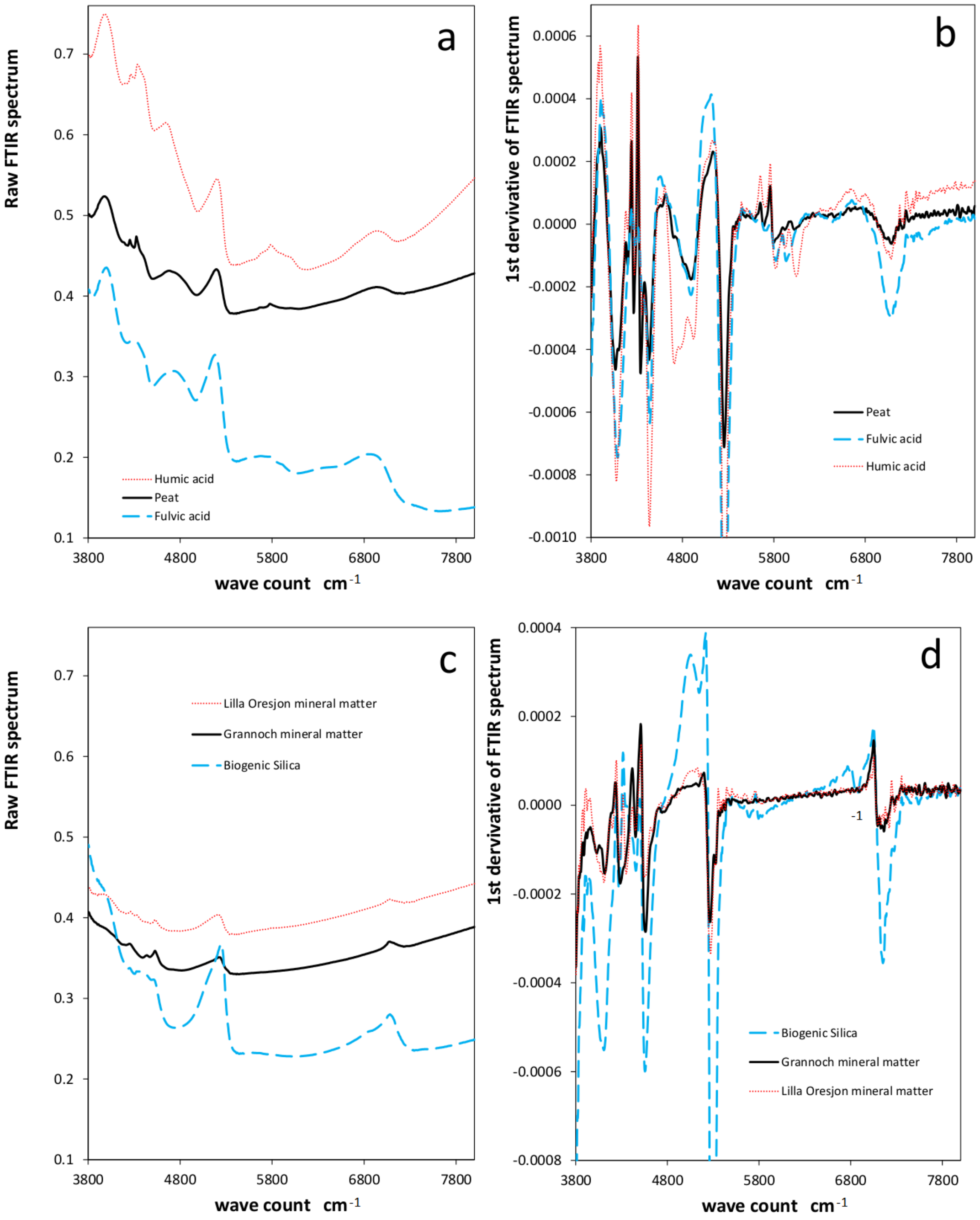


Figure 3.1 Exemplar NIR spectra showing raw NIR spectra for a) selected mineral and biogenic materials, b) selected organic matter end-members, and 1st derivative NIR spectra for c) mineral and d) organic end-members

Comparing the spectra of a 50:50 binary synthetic mixture (Red: Figure 3.2b) with May Moss Peat and Loch Grannoch mineral component end-member spectra (Grey: Figure 3.2a) shows that the 50:50 admixture spectrum lies between, but not midway between, its end-members at all wave counts. For an equal ternary admixture of Llyn Cwm-Mynach, Lilla Öresjön and Loch Grannoch mineral matter, the admixture spectrum is also bracketed by the end-members (Figure 3.2b), but the distinction between the original end-member 1st derivative spectra is less clear. In both cases (Figure 3.2), multiple regression has been applied to fit the component end-member spectra to the admixture spectrum, and a very high degree of fit is obtained for both the binary (adjusted R^2 = 0.991, F = 60723) and ternary mixtures (adjusted R^2 = 0.996, F = 93022). The regression coefficients, however, do not conform to the known mass mixing proportions of the end-member components (values shown in Figure 3.2).

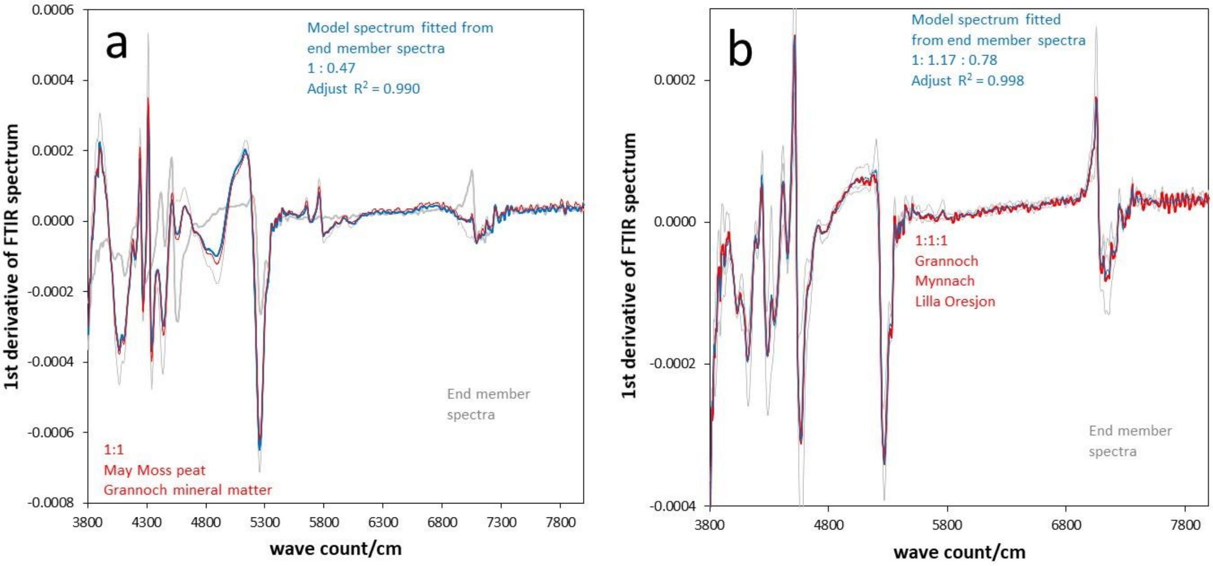


Figure 3.2 Mixing end-member components showing the 1at derivative NIR Spectra for a) a binary mixture of May Moss peat and Loch Grannoch mineral matter and b) an equal ternary mixture of Llyn Cwm Mynach, Lilla Oresjon and Loch Grannoch mineral matter. The NIR spectra shown include: the original raw end members (grey), the measured admixture (red) and the modelled fitted admixture spectra (blue) from the end-members derived from multiple regression

The non-linear NIR signal response to end-member concentration is further illustrated by a range of binary mixtures of Loch Grannoch mineral matter with May Moss peat(Figure 3.3).The raw multiple regression coefficients (Figure 3.3, filled symbols) do not lie on a mass-proportion mixing line, but do lie on a theoretically constrained line (form obeying Equation 3.2, with a fitted CIF value of 2.26 for Loch Grannoch mineral obtained by minimising the squared differences). If this CIF value is used to correct the regression coefficients using Equation 3.2(rearranged to yield chromatic proportions), then samples (Figure 3.3, open symbols) do lie close to the ideal 1:1 mixing line.

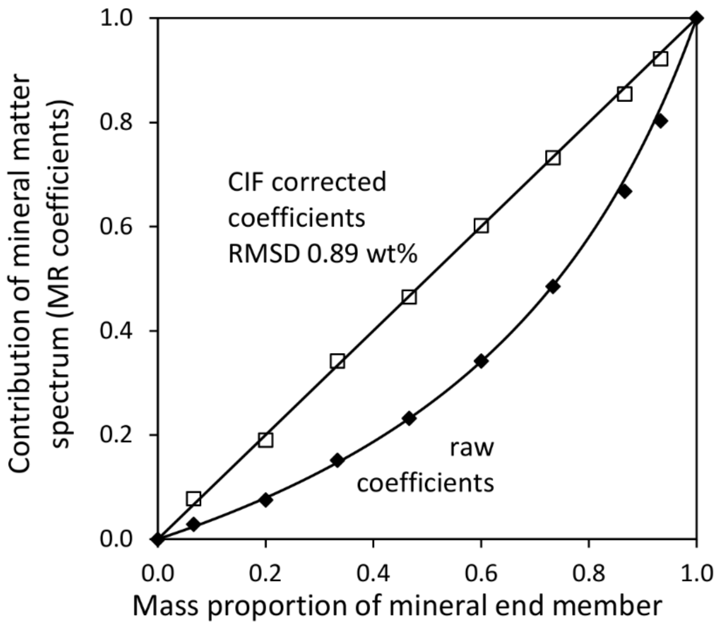


Figure 3.3 Known versus NIRS quantified mineral matter end-member proportions for synthetic binary mixtures (0, 7, 20, 33, 47, 60, 73, 87, 93, 100%) of May Moss peat and Loch Grannoch mineral matter. CIF corrected proportions were calculated from the MR coefficient using Equation 2 with CIF = 1 for the peat, and 2.26 for the mineral matter.

3.4.2 EVALUATING CHROMATIC INTENSITY FACTORS

The method used above to determine a CIF value for Loch Grannoch mineral matter could be applied to any other material. However, a logistically easier alternative is to calculate the value from a single point, for which we use the 50:50 mass admixture of each end-member (Table 3.1) with May Moss peat. This was done for all end-member materials (Table 3.1) to obtain measured CIF values, which range from 0.77 for Sphagnum and up to 6.73 for a limestone sample. For the materials we have measured to date, organic materials typically show lower values (except humic acids), biogenic silica are higher, and rock materials range widely (Figure 3.4).

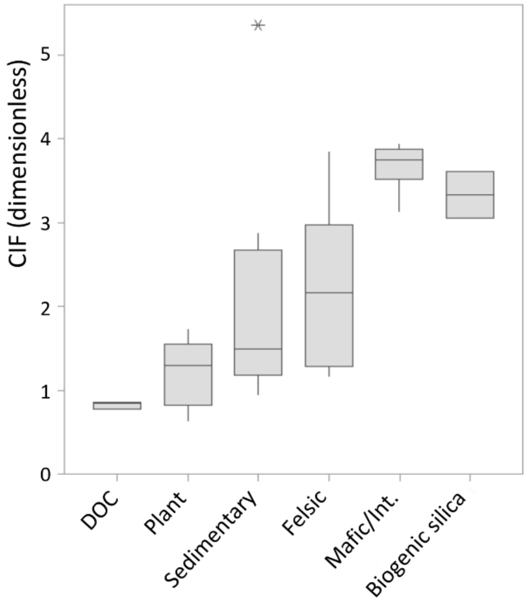


Figure 3.4 CIFM values plotted against broad categories of material type. Lowest CIFMs were encountered for organic matter, particularly DOC recovered from water. Measured rock types show considerable variation, with highest values in mafic and intermediate igneous rocks. The biogenic silica samples show high values. The asterisk indicates an isolated extreme value.

While testing the applicability of these measured CIF values, we observed some cases where mixtures were non-ideal. For example, where fine rock powder coated larger fibres of peat, low concentrations of the rock powder yielded exaggerated chromatic intensities, presumably because fibre surfaces were preferentially measured. Consequently, it is desirable to take an additional approach to CIF estimation, whereby values are found for natural admixtures (soil or sediment) by adjusting CIF values to optimise agreement with independently quantified component concentrations. We demonstrate this in the case of the Loch Grannoch sediment record (Figure 3.5 and Figure 3.6). We thus have two classes of CIF value, here distinguished as measured CIF_M and optimised CIF_O.

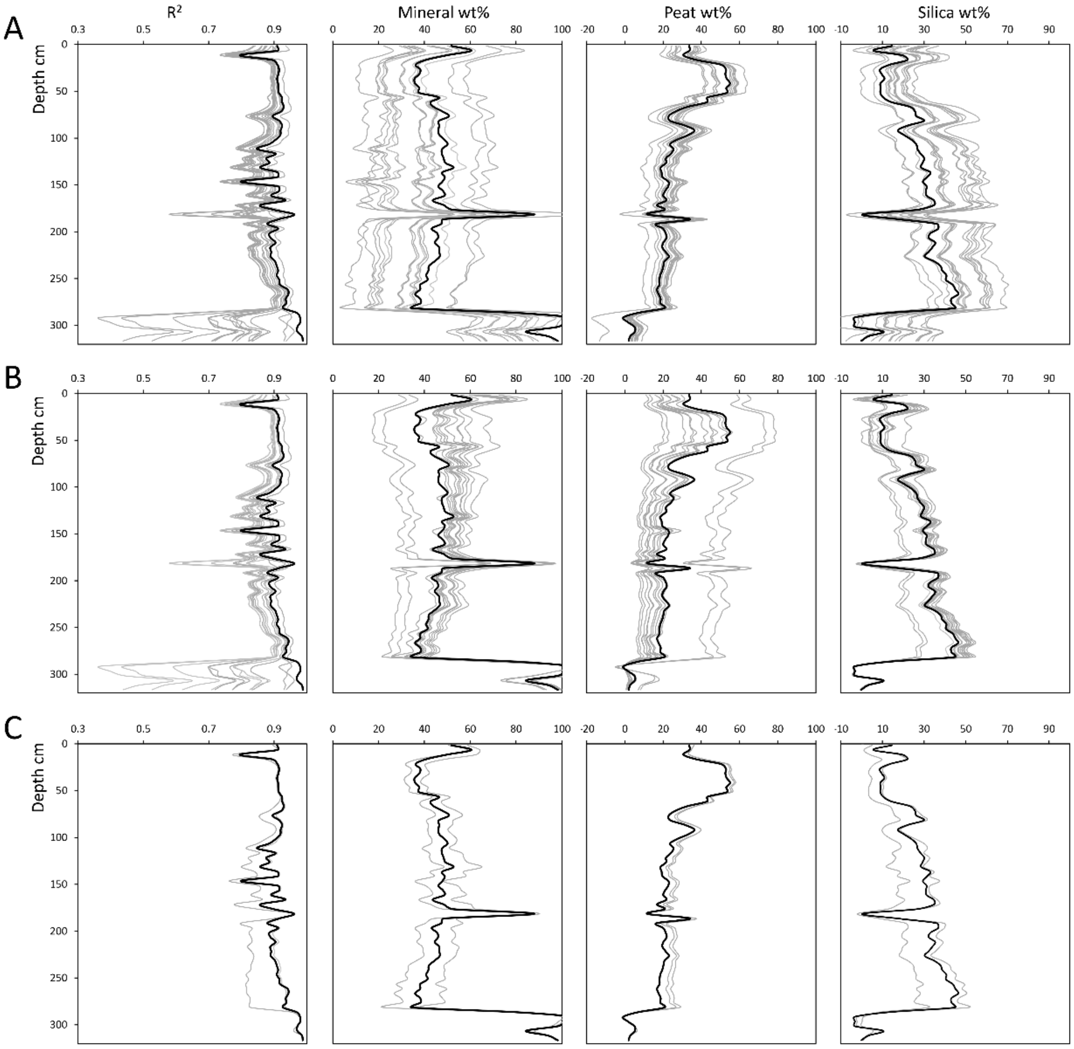


Figure 3.5 Example fitted concentrations for rocks, organic and biogenic silica end-members to sediment core from Loch Grannoch. A. Cycles through a range of differing minerogenic sediments and rock types, with May Moss peat and marine diatom as fixed end-members. B. Cycles through a range of differing organic matter types, with Loch Grannoch mineral matter and marine diatom as fixed end-members. C. Uses May Moss peat and Loch Grannoch mineral matter as fixed end-members, together with each of the three biogenic silica samples. The thick black line represent the preferred case with marine diatom, Loch Grannoch mineral matter, and May Moss peat

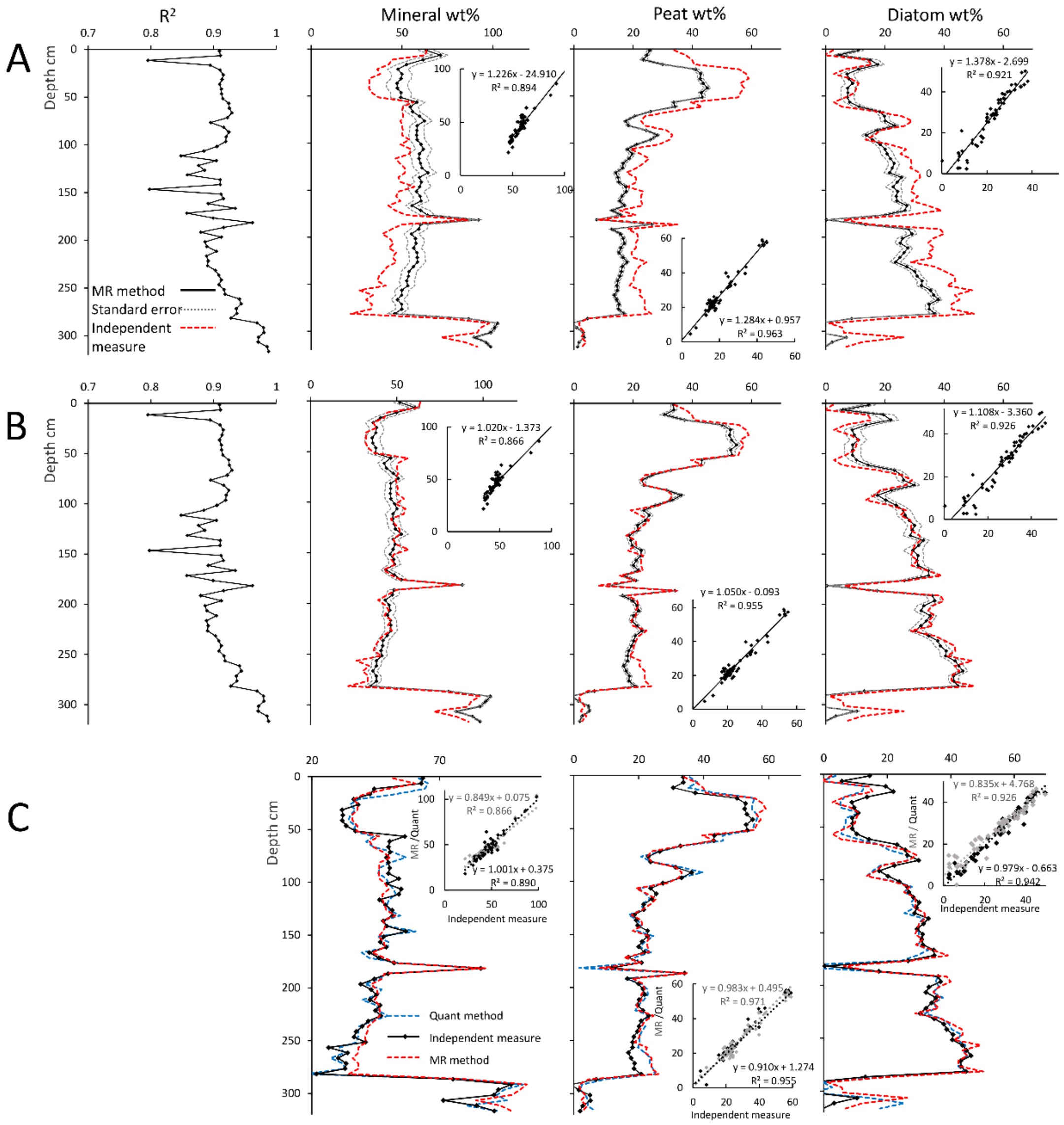


Figure 3.6 Fitted concentrations for Loch Grannoch using Loch Grannoch mineral matter, marine diatom, and May Moss peat end-members with (A) measured CIF$_m$ values (2.26, 3.09, 1 respectively) and (B)optimised CIF$_o$ values (1.4, 3.09, 1 respectively), and (C) values quantified by PLS. These are compared with independently quantified concentrations

3.4.3 SENSITIVITY TO THE CHOICE OF END-MEMBERS

To explore the sensitivity of our multiple regression approach to the choice of end-members, two further experiments were conducted holding two of the end-members constant and varying a third using a range of related materials (Table 3.1). The experiment uses the NIR spectra obtained for the Loch Grannoch sediment record (Figure 3.5). The primary end-member materials (the ones found to give the best overall fit) were May Moss peat (organic matter), marine diatom (biogenic silica) and Loch Grannoch late-glacial sediment (mineral matter). The first experiment (Figure 3.5a) uses May Moss peat and marine diatom as fixed end-members, and cycles through a range of differing minerogenic sediments and rock types in place of Loch Grannoch late-glacial sediment. The greatest impacts to fit are on the quantification of the mineral matter fraction with organic and biogenic silica content less affected by choice of mineral matter end-member. Whilst the principal down-core pattern of mineral variation is captured in all cases, the mineral component shows widely varying values. This variation shows some association with rock type. Thus, slates give low values, while quartz-rich rock types give high. However, there are exceptions, so predicting the outcome based on the known local rock type is not reliable. Instead, incorporating a local catchment specific mineral sediment end-member appears important in order to capture both the pattern and critically the magnitude of down-core variation in all end-members. Powdered local bedrock or glaciogenic lake sediments of late glacial age both appear to successfully account for catchment mineral matter. The second experiment (Figure 3.5b) holds the Loch Grannoch late-glacial mineral matter and marine diatom as fixed components, but cycles through various organic matter fractions. The impact of varying the organic component is substantial, affecting the fit for all three components. For example, humic acid yields low values for mineral matter and biogenic silica, and high values for organic matter. That said, the down core patterns remain broadly similar for all the end-members assessed. We currently have only three samples of biogenic silica in conducting the third experiment (Figure 3.5c). Very similar patterns are obtained with slightly varying magnitude.

3.4.4 APPLYING END-MEMBER MULTIPLE REGRESSION TO LAKE SEDIMENTS

To test the utility of the methods presented here in discerning evidence for environmental change from the NIRS analysis of lake sediments, three different approaches have been applied using NIR spectra obtained for the Loch Grannoch sediment record (Figure 3.6). The three approaches were:

1. End-member multiple regression using the NIR spectra for three materials with measured CIF values (CIF_M) (Figure 3.6a).
2. End-member multiple regression using the NIR spectra for three materials with optimised CIF values (CIF_O) (Figure 3.6b)
3. Using a PLS method relating the NIR spectra to independently quantified environmental parameters based on a training set that comprised a third of the samples from the Grannoch core (Figure 3.6c).

All three experiments attempt to reconstruct the concentrations of biogenic silica, organic and mineral matter for the sediment core. The results are compared with independently quantified measures of the three parameters. The end-member materials were May Moss peat representing natural organic matter; marine diatom representing biogenic silica; and Loch Grannoch late glacial sediment representing catchment mineral matter. When using the measured CIF_M values to estimate concentration of mineral matter, organic matter and biogenic silica in the Loch Grannoch sediment, we observe high correlations with the independently quantified concentrations, and good agreement in the depth of peaks and troughs (Figure 3.6a). However, the absolute values differ particularly for mineral and organic matter and the regression lines significantly deviate from the origin.

With optimised CIF_O values (Figure 3.3b), absolute magnitudes are constrained to be similar to those independently quantified. However, there is also a substantial improvement in that the regression lines now pass through the origin for all three components, and in the case of organic matter the R^2 value is substantially increased. The poor fit obtained for the biogenic silica in the basal samples need not indicate a failure of our method; a likely explanation is the poor independent quantification in these highly minerogenic sediments (Figure 3.1b).

The PLS method, trained using a third of the samples from the Loch Grannoch core with independently quantified concentrations, was successful in predicting the concentrations of these components. Correlation between independently quantified and PLS estimates should be and is strong (Red curve: Figure 3.6c). While the PLS approach is effective, equivalently good results are obtained using CIF corrected end-member multiple regression (Figure 3.6b), despite not using a training data set, or indeed being trained at all.

To further test the generality of our approach, and of our organic and biogenic silica end-member materials, we have measured NIRS spectra from three additional lake sediment cores from different regions and with differing climate and bedrock and applied our method (Figure 3.7). We fitted our two general end-members (May Moss peat and marine diatom) using the CIF_O values optimised for Loch Grannoch. Local mineral matter end-members were used to reflect the differing geology. No optimisation was undertaken. Site details are shown in Table 3.2, and the chosen mineral matter end-members are listed in the caption to Figure 3.7.

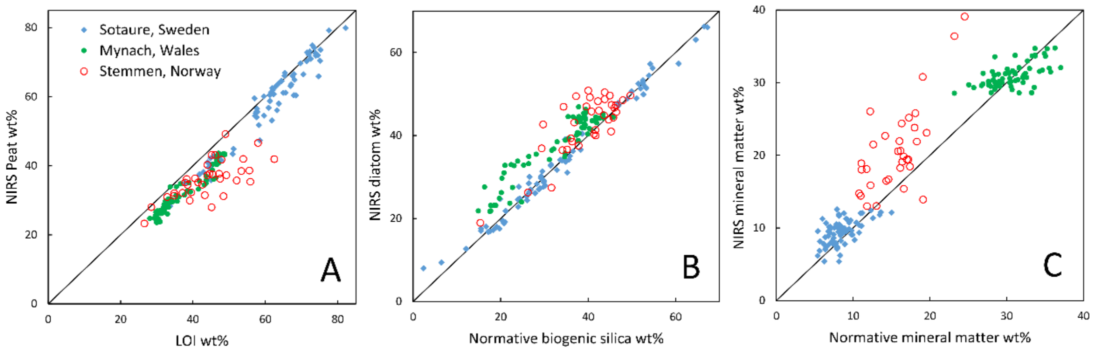


Figure 3.7 Fitted concentration of May Moss peat (A), marine diatom (B), and local mineral matter (C) for three additional sites. Site details in Table 3.2. Mineral matter end member used: schist for Sotaure, local late glacial sediment at Llyn Cwm-mynach, and orthoclase plus crushed anorthosite at Stemmen. 1:1 lines are plotted to emphasise any bias

Table 3.2 Site details for additional cores shown on Figure 3.7.

Site name	Sotaure	Tarn at Stemmen	Llyn cwm Mynach
Country	Sweden	Norway	Wales
Latitude °	66.7333	58.4534	52.7958
Longitude °	20.5734	6.0870	-3.9608
Rock type	Granitic gneiss and schist	Anorthosite	Ordovician metasediments
Core code	SO-2-1	N17-Lake1-GC1	MYN15-SC2
Date of coring	15/07/2012	21/08/2017	25/06/2015
Lake area km2	0.016	0.015	0.057
Catchment area km2	0.042	0.064	1.19
Coring depth m	6.2	9.5	11
Core length m	0.95	2.57	0.35
Core type	Russian	Russian	8 cm diameter, Gravity

The results reveal good fits with low bias and noise for May Moss peat and marine diatom for the sites in Wales and Sweden, with rather noisier results at Stemmen which has a rather unusual bedrock type. At all three sites mineral matter is the least well fitted. The results are therefore fully consistent with our experiments at Loch Grannoch; fitted organic matter is least impacted by choice of mineral matter end-member, and fitted mineral matter most so.

3.5 DISCUSSION

The approach demonstrated here affirms previous work showing that taking the 1st derivative of NIR spectra is the most effective way of reducing unwanted physical information, for example the effects of particle size (Rinnan *et al.*, 2009). Alternative normalisation procedures can also reduce or remove these signals, but have been shown not to enhance performance and are not recommended for pre-treatment (Dåbakk *et al.*, 1999). Here the 1st derivative is calculated using a centrally-weighted 9-point Savitzky-Golay smoothing algorithm combined to reduce unwanted noise, remove the baseline offset and amplify the spectral curvature; all of which contribute to it being regarded as the best mathematical pre-treatment choice for handling NIR spectra (Burns *et al.*, 2001; Korsman *et al.*, 2001; Pearson *et al.*, 2014).

The 1st derivative spectra exhibit well defined peaks, some of which may be attributed to specific chemical bonds (Terhoeven-Urselmans et al. 2006; Brown et al. 2006; Zornoza et al. 2008), with the intervals of the spectrum 4100-4500 cm^{-1} and 5100-5300 cm^{-1} dominated by organic chemical bonds (Korsman *et al.*, 2001). This observation appears to be in contradiction with empirical evidence (Pearson et al. 2014) that model prediction skill is not improved by restricting analysis to regions of the spectrum. Our results, however, offer a simple explanation. If component spectra are additive, then each influences all parts of the spectrum, and all parts of the spectrum would contain information about each component of the mixture.

The question of whether spectra are fully additive, in essence that the spectrum of a mixture comprises a linear combination of its component spectra, is fundamentally important to quantitative interpretation of NIR spectra. This behaviour is expected on the basis of theory (i.e., Boroumand et al. 1992), but our analysis of artificial mixtures demonstrates this to be the case in practice too. For the spectra of synthetic binary mixtures of mineral and organic matter (Figure 3.3) 99% of the variance can be explained by fitting the component spectra using multiple regression, which yields root mean squared differences between known and inferred concentrations in the order of 1% for both mineral and organic matter.

Success in component fitting is harder to assess for natural heterogeneous mixtures, because of the uncertainty in the nature of the end-member materials. Fitting three different materials (May Moss peat, Loch Grannoch late glacial mud, and marine diatom) to the Loch Grannoch core produced adjusted R^2 values that ranged 0.85-0.97. The best fits are unsurprisingly for the late glacial mineral matter, where our end-member has been specifically tailored to be suitable. The failure to explain the mineral matter more fully can be attributed to variability in its composition, with varying proportions of the constituent minerals (quartz, feldspars, micas and chlorite). Through the Holocene there are a number of events and intervals of higher or lower R^2, which may represent periods in which the component materials were slightly different, or periods during which additional materials different from the selected end-member materials were present. A crucial question is whether periods of poorer fit as measured by the R^2 of regression represent periods of poor quantification of the components or simply dilution by other materials. This cannot be fully answered, but the squared differences between the NIRS inferred and independently quantified values for the Loch Grannoch core do not co-vary with the R^2 value (Figure 3.6). Thus, although more work is needed, it appears that the fitted concentrations are relatively insensitive to the proportion of total variance (R^2) explained.

The additive nature of the 1st derivative NIR spectra (Figure 3.2; Boroumand et al. 1992) means that it is possible to separate end-members quantitatively using multiple regression. However, we have shown that the multiple regression coefficients are not linearly related to mass concentration (Figure 3.3). This result is consistent with the theoretical treatment of Boroumand et al. 1992, who show that varying chromophore density among materials means that conservative mixing by mass would be the exception rather than the rule. We demonstrate in the case of the binary mixture (Figure 3.3) that application of a simple chromatic intensity factor (CIF) corrects for this effect, such that we observe conservative mixing of what may be termed the chromatic proportions. This is fully quantifiable, such that mass concentration (mass/mass) may be calculated from the chromatic proportions provided the CIF values are known. However, we cannot extract end-members from natural mixtures, so our measured CIF values must be obtained instead using proxies, the appropriateness of which cannot be fully assessed. In the case of the Loch Grannoch core, we have used (Figure 3.6a) the measured CIF_M values for May Moss peat (definitively 1), Loch Grannoch mineral matter (2.26), and marine diatom (3.09). Yet, when we find CIF_O values by optimisation (minimising the squared differences from known values), a very different value is found for the mineral matter (1.4). The CIF_O for marine diatom is identical to the CIF_M value. The differing CIF values for mineral matter likely reflect the differences in the mineral matter mixture between the late glacial and the Holocene. This suggests that the issue of CIF magnitude is rather less important than the problem of being unable to choose end-members on a truly a priori basis. However, the sensitivity testing (Figure 3.5) shows that useful results are obtained even when an imperfect end-member material is used. When using optimal CIF values, it is apparent (Figure 3.6b) that multiple regression very successfully explains both magnitude and variation in the independently quantified components (biogenic silica, organic and mineral matter). Quantification of major sediment components in the Loch Grannoch core using multiple regression compares well with the independently quantified values despite not being trained in the manner that the PLS methods are. Indeed, this favourable comparison is still more encouraging given that the PLS method was trained using the independently quantified variable data set and would therefore be expected to predict it successfully, while our method did not include a training procedure.

Choice of organic materials can affect the fit for other major sediment components. In the case of the Loch Grannoch core, May Moss peat provides the best proxy for lake sediment organic matter. This is likely due to it comprising a mixture of organic materials which would be similar to those found in the lake sediment that are allochthonous in origin. It is possible that other combinations of organic materials would replicate this natural mixture. This has not been fully explored, but other examples of good fits for Loch Grannoch organic matter are combinations of humic acid, fulvic acid and *Sphagnum* spp. Generally, with the exception of May Moss peat, precision of fitting is improved when pairs or greater combinations of organic matter end-members, are used. Some combinations, owing to the similarity of spectra for some types of organic matter with consequent high multicollinearity, lead to excessively high (>>1) or low (<<0) regression coefficients. However, with favourable combinations, such as humic acid, fulvic acid and *Sphagnum*, coefficients generally lie between 0 and 1 even when both biogenic silica and mineral matter are also included as independent variables. This is highly promising, though further work is needed to test the validity of such results.

Due to a limited end-member library of biogenic silica materials, we cannot generalise with confidence. However, the similarity of results found using three widely differing sources of biogenic silica, and the good agreement with independently quantified biogenic silica for the Loch Grannoch core, are very promising.

The broader generality of our method is illustrated by its successful application, without optimisation, to sites with different characteristics and climate from Wales, Norway and Sweden. It is particularly encouraging that good results were obtained when applying May Moss peat and marine diatom, with only mineral matter choice adjusted for local conditions. On the other hand, based on the results from these three sites, and the experiments at Loch Grannoch, we can expect poorer results where the sediment mineral component is poorly represented by the selected end-member, so at new sites, particularly those with unknown or unusual bedrock types, some validation of the end-member fits is recommended.

3.6 CONCLUSIONS

With suitable end-member materials selected, our new open-source multiple regression procedure gives simultaneous quantification of the major components (biogenic silica, mineral and organic matter content) of lake sediments, with excellent performance compared with results obtained by independent methods. Poor choice of end-member can lead to bias in the quantification, thus tailoring the choice of mineral material, for example selecting a similar bedrock type to that of the sample environment, is the preferred option. An advantage of the multiple regression method is that it does not require a training data set of materials which have been independently quantified using alternative methods. A library of end-member materials has been created relatively simply with little time investment and is easily expanded. Fitting of end-member spectra by multiple regression is a valuable alternative to the various PLS methods (or other 'trained' methods), that do not transparently allow assessment of potential interfering factors. It has the further advantage of resting in theory rather than on chemometric statistical methods.

3.7 ACKNOWLEDGEMENTS

Thank you to Forestry Commission Scotland for providing us with access to the coring site at Loch Grannoch, and to Poonperm Vardhanabindu, Jenny Bradley and Maddy Moyle for assistance in the field. FER PhD is supported by the School of Environmental Sciences, University of Liverpool.

4 RECONSTRUCTING PEAT COMPOSITION FOR THE HOLCROFT MOSS OMBROTROPHIC PEATLAND USING NEAR INFRARED SPECTROSCOPY (NIRS)

4.1 ABSTRACT

Palaeoenvironmental techniques used routinely to analyse peat sequences (e.g. plant macrofossils, peat humification, calorific value) have been used to characterise the Holocene evolution of Holcroft Moss, an ombrotrophic peatland in northwest England. This paper explores the value of near infrared spectroscopy (NIRS) in rapid non-destructive characterisation of peat deposits. NIR spectra were collected throughout the sequence and a novel end-member multiple regression (EMS-MR) methodology was used to compare sample spectra with those obtained for known end member materials to estimate the proportions of plant matter, humin and humic acid. This approach negates the need for developing intensive NIRS training data sets necessary for chemometric methods. In part this was motivated by successes apparent in applying NIRS and EMS-MR to reconstruct dissolved organic carbon or humic acid proportions in lake sediments. For ombrotrophic peats, variations in the proportion of humic acid reflect the state of peat decomposition (humification) and dominate the Holcroft Moss stratigraphy. Thus, this environment and sequence provides an assessment of the robustness of NIRS-based quantification of humic acid concentrations. Data from more conventional methods of analysing peat were compared with these NIRS estimated proportions to test the value of the NIRS approach. Our end-member predictions for humic acid content, using a 50:50 mixture of humic and fulvic acids (Suwannee River standards), yielded down core variations in concentration that correlate with the light absorbance (%) of an alkaline extract of the peat and thermogravimetric mass loss (375-550 °C) both established measures of the degree of peat humification. The NIRS approach is limited in that the end-members include fresh plant matter, and the EMS-MR approach struggles to differentiate between individual plant species. This is in part due to the similarity of the end member spectra obtained for the plant samples and also the inherent sensitivity of the NIRS signal to the state of decay of plant matter e.g. loss of cellulose and chlorophyll. This hampers some of the comparisons between the plant macrofossil data and equivalent NIRS-based reconstructions, and so the EMS-MR NIRS method cannot as yet quantify proportions of plant species. Previous NIRS studies have claimed successful reconstruction of plant taxa and species using training sets and applying chemometric methods, but those studies would be limited by the similarity of NIR spectra across plant groups. In summary, the EMS-MR of NIR spectra demonstrates success in the rapid non-destructive and high resolution characterisation of the degree of humification and humic acid concentrations in peat, but further work is needed to develop applications to quantifying proportions of plant types, e.g. extending the end member library to include plant materials across a range of states of decay.

4.2 INTRODUCTION

4.2.1 AIMS OF CHAPTER

Here, we apply our end member spectra multivariate regression (EMS-MR) approach (Russell *et al.*, 2019) to characterise the organic matter components of an ombrotrophic peat sequence from Holcroft Moss, a remnant peatland in the former Chat Moss complex of south Lancashire (Birks, 1965; Leah *et al.*, 1997). Peats differ from lake sediments as they contain limited mineral and biogenic silica components. Given that the stratigraphy of peat sequences is often dominated by variations in humic acid concentrations, an ombrotrophic peat sequence could provide an ideal test of the practicality of the NIRS end member approach developed for reconstructing DOC from lake sediments (Chapter 3: (Russell *et al.*, 2019)). The principle underpinning this chapter is that the peat sequence can be used to generate multiple independent datasets for direct comparison with an NIRS-based quantification of humic acid or dissolved organic carbon. In addition, we explore further the testing of the utility of EMS-MR in analysing peat stratigraphy and contextualise earlier investigations of NIRS approaches at Moor House NNR (McTiernan *et al.*, 1998). The objectives are to:

- Compare the FT-NIR spectra for the Holcroft Moss peat sequence and a series of known end-member materials to assess their character and diagnostic properties.
- Use our EMS-MR method to reconstruct down core patterns in humic acid content for comparison to independent measures of peat humification.
- Compare the NIRS estimates of major peat components with equivalent data generated by plant macrofossil and humification analyses.
- Evaluate whether any DOC-related signal stands out from the EMS-MR reconstructions for peat and provides a support for NIRS quantification of humic acid in lacustrine environments.

4.2.2 THE UTILITY OF PEAT STRATIGRAPHY

Ombrotrophic or rain-fed peatlands are a wetland ecosystems that forms the largest terrestrial store of global carbon and approximately ~500 Pg of the global soil carbon pool (Yu *et al.*, 2010; Loisel *et al.*, 2014, 2017). These ecosystems also preserve sedimentary and palaeoecological records that have been invaluable in reconstructing Holocene climate and ecological changes for more than a century (Blytt, 1876; Sernander, 1908; von Post, 1909). In particular, the palaeoenvironmental techniques have collected evidence for changes in regional vegetation (e.g. pollen analysis) (Fyfe *et al.*, 2009), bog surface wetness (plant macrofossils, testate amoebae, peat humification) and by association hydroclimate (e.g. effective precipitation) (Barber, 1981; Charman *et al.*, 2006), fire and burning histories (e.g. charcoal) (Bradshaw *et al.*, 2010), atmospheric dust and pollutant deposition (Shotyk *et al.*, 1998), macronutrient stoichiometry (N and P) (Schillereff *et al.*, 2016), and carbon accumulation (Loisel *et al.*, 2014, 2017). The techniques underpinning these records vary in their laboriousness often affecting the stratigraphical resolution of analysis, though of late even time-consuming analysis of microfossils has been applied at fine <10mm resolutions (Amesbury *et al.*, 2011). Peat stratigraphical studies have also tended to employ multiple proxies to corroborate wetness histories and test linkages between proxy techniques, for example the influence of plant species on decomposition records (Payne *et al.*, 2008; Chambers *et al.*, 2011). Given the sensitivity of plants and microorganisms to wetness variations across the microtopography of pools and hummocks environments typical of peatlands the selection of core locations is important (Barber, 1981; Chiverrell, 2001; Payne *et al.*, 2008). Ideally multiple core sites across a bog would be taken and analysed (e.g. Chiverrell, 2001) in order to provide confidence in the reconstruction of the wider environmental conditions and external forcing (e.g. climate).

Methods for quantifying the bulk composition of ombrotrophic peat divide broadly into microscopy- and chemistry-based approaches. Plant macrofossil analyses routinely applied in reconstructing long-term changes in peat composition rely on a non-aggressive digest of peat (e.g. hot water) and sieving at (100-250 µm) to collection proportional data for the main plant components (e.g. bryophyte, monocotyledon and dicotyledon plants), often identifiable to species level (e.g. *Sphagnum species*). In terms of quantifying the mass proportions relying on quantified plant macrofossils neglects the fine-grained humic acid and organic materials. Chemistry-based approaches typically focus on quantifying organic compounds produced during the decay and decomposition of plant remains but vary markedly in their precision and scale from individual molecules (Artz *et al.*, 2008) to aggregated and complex compounds (e.g. humic acids) (Klavins *et al.*, 2013). With the focus of this thesis on developing long-term records of dissolved organic carbon fluxes for lakes, peat sequences represent a difficult to rival opportunity for the testing of methodology. Peat sequences contain marked variation in the state of decay or peat humification, represented as a series of changes in colour with darker brown more humified and lighter orange less humified peats. These changes in humification can be measured independently by multiple methods each with varying degrees of success.

4.2.3 PEATLAND STRUCTURE AND DECAY PROCESSES

Ombrotrophic peatlands grow, accumulate mass, and sequester C where the production of vegetation out-paces the decay of organic matter. Living plants take up C through photosynthesis from atmospheric carbon dioxide (CO2) for the most part, with a contribution via the fixation of ‘old’ CO2 from soil respiration (Kilian et al., 1995; Chambers et al., 2011) C is lost from peatland via decay processes both as gaseous loss to the atmosphere and aqueous loss to watercourses. Most of the vegetation decay takes place aerobically in the surface layers of peat above the water table. Peat sequences divide into two zones delimited on a basis of oxygenation and compaction, with a boundary transition typically at the minimum summer water table (Figure 4.1). Peat accumulates as surface vegetation additions to the surficial active zone called the acrotelm, with the cold and anaerobic catotelm below forming the remainder of the peat sequence (Belyea *et al.*, 2001). Above the acrotelm/catotelm boundary the aerobic breakdown and decomposition of plant matter into organic compounds (e.g. humic acid) is termed ‘humification’, but decay continues also under catotelmic anaerobic conditions at a much slower rate by release of primary minerals and CH_4. Humification is a process limited to the acrotelm and leads to build of brown to orange humic acids or dissolved organic carbon. Thus, the degree of humification of peat relates to the duration of acrotelmic decay, which is typically a function of the thickness of the acrotelm i.e. how long it takes for the addition of mass to the surface to be buried and incorporate into the catotelm.

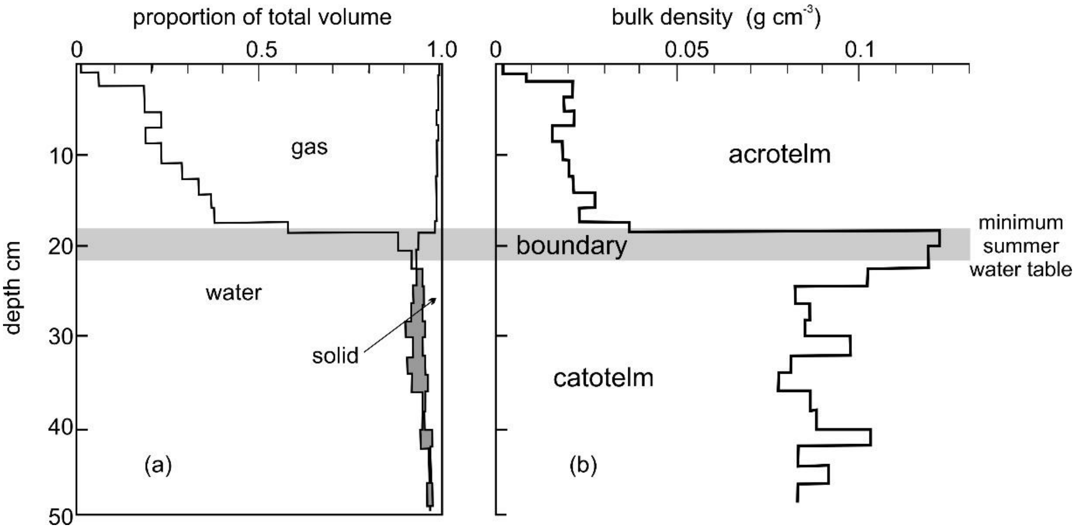


Figure 4.1 Schematic of a typical peat structure (adapted from Clymo, 1984) showing the locations of the acrotelm, catotelm, boundary zone and association with the minimum summer water table. The data in (Clymo, 1984) are (a) the proportion of volume occupied by water, gas and solid in a peat profile from Anghult, south Sweden. (b) Bulk density in the same profile. The hatched area in (a), where the sum of water and solids exceeds the total measured volume reflecting the inaccuracy in measurement (mostly in total volume).

The association of the acrotelm/catotelm boundary with the minimum summer water table and the ombrotrophic nature of many peat sequences has led to a proliferation of humification indices as a measures of bog surface wetness and palaeoclimate (Blytt, 1876; Sernander, 1908; von Post, 1922; Aaby *et al.*, 1975; Blackford *et al.*, 1993). Variations in bog surface wetness of intact ombrotrophic mires, whether assessed using humification or other proxy techniques (e.g. testate amoebae and plant macrofossils), broadly reflects a balance between precipitation and temperature (evapotranspiration). These stories are complicated by factors including differences in plant type affecting humification rates and subsequent drainage or water table variations perturbing the association between hydroclimate and peat humification.

Techniques used traditionally to measure the state of decay or humification of peat are based on either quantifying the degradation of plant remains or the accumulated decay by-products, e.g.

humic acid. Visual examination of the decay condition has a long history (von Post, 1922), but humification has also been measured using UV/Visual spectrometry of a filtered alkaline extraction (mass/volume extract 8% NaOH) of peat humic acids. High % light transmission (typically at 540 nm) indicated poorly humified materials and low light transmission indicating well humified (Blackford *et al.*, 1993). The N stratigraphy of peat sequences, typically measured on a CHN analysers, has also been used as an imperfect measure of peat decay with more N if more humified (Anderson, 2002). Numerous spectroscopic and calorific techniques have been used to address changes in peat humification over the past 2 decades (Biester *et al.*, 2014; Zaccone *et al.*, 2018).

Biester *et al.*, 2014 tested a variety of methods for accessing humification and decomposition profiles for two peat sequences concluding that a combination of C/N ratios, pyrolysis-GC-MS, and FTIR spectroscopy can provide a comprehensive picture of mass loss and changing abundances of OM components (e.g. carbohydrates versus aliphatics). Within their IR measurements Biester *et al.*, 2014 found that selected FTIR bands gave abundant information of major groups of organic components providing some qualitative and quantitative information in changes in OM structure during decomposition, and proposed a FTIR humification index as reflecting peat decomposition reliably.

Thermogravimetric methods have been used since the 1950s to characterise peat and coal in terms of calorific value as fuels. In the analysis of peat and plant remains Levesque *et al.* (1978) identified three zones of mass loss in thermogravimetric curves developed in an air atmosphere, these were: readily oxidizable compounds (e.g. sugars and cellulosic materials) in the range 275–325 °C, humic substances across 360–460 °C, and non-hydrolyzable residues (Schnitzer *et al.*, 1966) 500–560 °C. Exothermic peaks in thermogravimetric curves develop as a sample is gradually heated from 20 to >700 °C recording the mass loss, and are due to decomposition and combustion reactions of organic compounds and can provide information on the degree of humification (Zaccone *et al.*, 2018).

4.2.4 NIRS AS A TOOL FOR INVESTIGATING PEAT STRATIGRAPHY

Near infra-red spectroscopy (NIRS) is an analytical technique that uses the vibrational excitation that develops in the structures of inorganic minerals and the stretching/bending of atomic bonds in organic materials. Differences in the structure and composition of heterogenous materials like peat and lake sediments display characteristic vibrations that are reflected as absorption at NIR wavelength. Fourier transform NIRS measures all frequencies simultaneously providing rapid repeatable measurement using multiple scans per second and deriving higher signal/noise ratios. NIRS has been used to measure and characterise the organic content of lake sediment (e.g. (Pearson *et al.(*2014)). NIRS is routinely also used in characterising the chemical composition and digestibility of cereals and animal forages with changes related to the age and digested state of the materials (Park *et al.*, 1997; Decruyenaere *et al.*, 2009). These forage studies show subdued NIR spectra (flatter, less peaked) when organic materials are decayed or digested are compared with fresh examples.

For ombrotrophic peat this situation is like the analysis of plant samples, because there is little or no mineral matter or biogenic silica to complicate the material composition. By extension, the state of decay of the peat and differences in the plants making up the peat should dominate any differences in the NIR spectra. The conventional approaches to quantifying parameters from NIRS for both sediments and forage materials have used sets of training samples and developed partial least squares regression models to predict the key variables for a series of unknown samples (Stuth *et al.*, 2003). A limitation with this type of analysis is the reliance on these training sets, which can be time consuming to collect.

McTiernan *et al.* (1998) applied NIRS to a peat sequence from Moor House NNR (Teesdale) developing a training set of peat samples, with the independent data derived from plant macrofossil (% composition) and physical properties (bulk density, moisture content and humification by UV/Vis spectrometry of alkali extracts) measured for the sequence. The approach then used a series of specific NIRS wavelengths to build regression equations for multiple peat components, and then apply the regressions to predict peat components for a series of unknown samples. Russell et al. (2019) utilise NIRS spectra differently to training set methods, in quantifying specific end-member spectra fitted simultaneously to heterogeneous sample by multiple-regression of the NIR spectra. This approach does not reconstruct one or many ecological variables using individual bespoke training sets but reconstructs the relative proportions of major organic components simultaneously.

4.3 SITE AND METHODS

4.3.1 HOLCRFOFT MOSS

Holcroft Moss is part of a swath of lowland ombrotrophic mosslands that occupied the upper river terraces of the Mersey Valley lying to the west and north of Manchester (Figure 4.2) (Birks, 1965; Leah *et al.*, 1997). Chat Moss, the largest, is at 23 m (Ordnance Datum (O.D.)) and formerly occupied an area >42 km^2, with Holcroft Moss to the west >2.25 km^2 and Risley Moss further west >7km^2. The mires formed in small depressions in the former glacial diamictons, outwash sands and gravels that in turn are underlain by Triassic sandstones. These mosslands have been heavily denuded with drainage and conversion to agricultural lands and during the 20th century commercial extraction of the peat. Holcroft Moss Site of Special Scientific Interest (SSSI) and National Nature Reserve (NNR) is an intact remnant thought to be only known area of uncut lowland bog in Cheshire. Commercial peat extraction surrounding the SSSI has lowered the water table, but restoration work has been undertaken by Cheshire Wildlife Trust including plastic bunds to maintain the bog's ability to hold water. The dominant purple moor grass (*Molinia caerulae*) is being managed to encourage expansion of a more diverse flora including cross-leaved heath (*Erica tetralix*), cranberry (*Vaccinium* spp.), cottongrass (*Eriophorum* spp.) and *Sphagnum* species. Flanking the M62 motorway this remnant of the central dome has a peat stratigraphy that remains intact and untouched. Birks (1965) described the stratigraphy of Holcroft Moss recording 4-5 m sequence with basal <1m of *Phragmites* – *Equisetum* fen peats giving way to ~1.5 m of woody peat before 3m of *Sphagnum* dominated ombrotrophic peat was established across the site. The *Sphagnum* peat was recorded as showing variations in the degree of humification most likely reflecting changes in water table as the peat accumulated, supported by changes between wet- and dry-indicating testate amoebae communities (Birks, 1965). Though not ^{14}C dated, pollen data collected for the site (Birks, 1965) indicated peat inception occurred slightly before the mid-Holocene *Ulmus* decline 6350-5280 cal. yr BP.

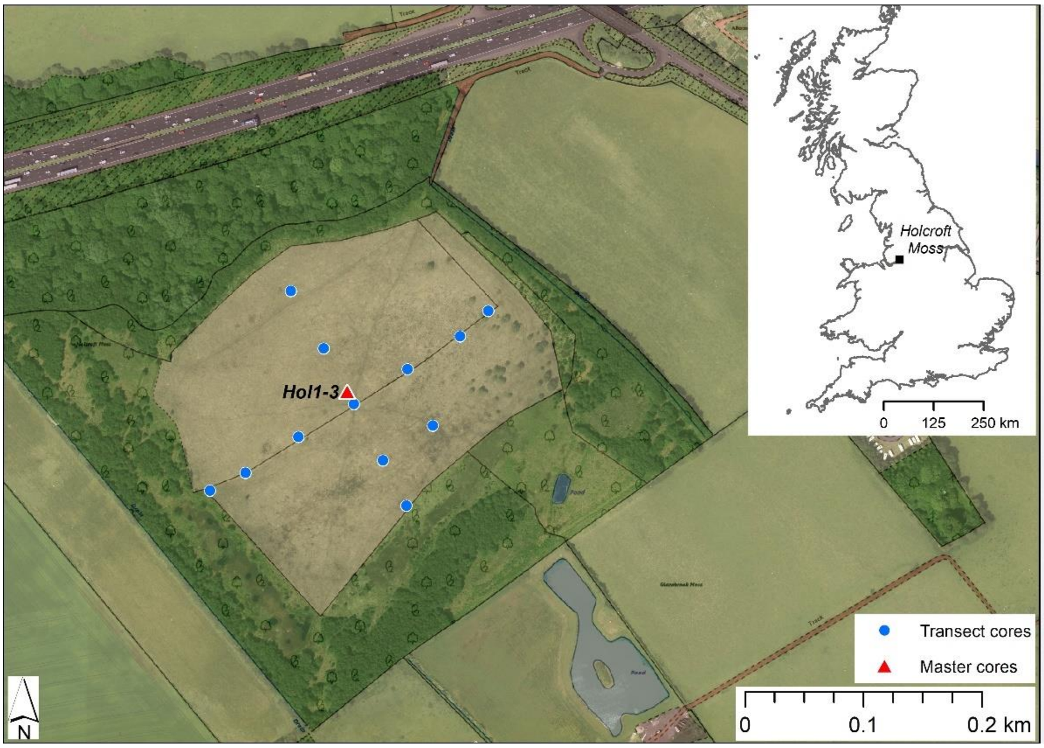


Figure 4.2 Holcroft Moss in NW England showing the core transects and core site. Aerial imagery © Getmapping Plc and contains OS data © Crown copyright and database right (2020).

4.3.2 SAMPLING AND AGE DEPTH MODELLING

In 2012 the stratigraphy of the site was revisited with two bisecting core transects and confirmed a sequence relatively unchanged since Birks., 1965. The stratigraphy is remarkably consistent across the site with comprising ~4 metres of peat overlying basal sands. Large volume duplicate overlapping cores were recovered from the middle of the site using a 0.5x0.1 m Russian-style peat corer. Traditional analytical methods (Plant Macrofossil analyses, degree of humification, thermogravimetric mass loss

Plant macrofossil analyses were undertaken at 40 mm intervals with preparation procedures following (Mauquoy *et al.*, 2010). Prepared samples were quantified for major components (Mauquoy *et al.*, 2002) under low power microscopy using a randomised 10x10 mm grid in square petri dishes. Scores (1-10) were given to each component, except for macroscopic charcoal fragments which were counted. The major components: total *Sphagnum,* Monocotyledon, Ericaceous, other Bryophytes and Unidentifiable Organic Matter (UOM) were totalled and converted to percentages. To subdivide the *Sphagnum* species 100 leaves were examined, identified (following Daniels and Eddy 1990) and counted using a (x400) Zeiss Axiovision microscope. The degree of humification was quantified by digesting 1g of dried ground peat in 8% Sodium hydroxide (NaOH), filtering (Whatman No.1), with percentage light transmission at 540 nm based on the average of three repeats on a Jenway 6305 UV/Vis spectrophotometer (Blackford *et al.*, 1993) (Blackford and Chambers, 1993). Mean light transmission values were corrected for loss-on-ignition (Payne *et al.*, 2008). Results are reported as absorbance% (absorbance = $\log_{10}$ (transmission)) because the Beer-Lambert law states that concentration is related linearly to absorbance.

The quantity and composition of organic carbon was analysed by pyrolysis, with differential scanning colorimetry and thermogravimetry recorded sequentially heated at 20 °C min^{-1} across the range 20–720 °C under a dynamic nitrogen air flow (10 L h^{-1}) on a PerkinElmer STA6000. Two high purity indium and silver standards (both 99.99%) were used to calibrate TG-DTA for both temperature (°C) and enthalpy (J g^{-1}). The thermal decomposition data (mass loss) were smoothed and expressed as 1st derivatives providing the rate of mass decomposition with temperature. The 1st derivatives of the thermogravimetric curve allows conversion of the trace into well-defined peaks and cluster analysis of these 1st derivative mass losses revealed breaks in thermal behaviour at 150, 375, 410, 490 and 550 °C (Figure 4.3). The major boundaries formed the basis for quantifying the mass loss totals across the ranges: 150-375 °C and 375-550 °C. These thermal bands affirm known thermal zones for decomposition of readily released compounds (e.g. sugars and cellulosic materials) from plant remains between 150–375 °C and more recalcitrant humic substances across 375–550 °C (Schnitzer *et al.*, 1966; Zaccone *et al.*, 2018).

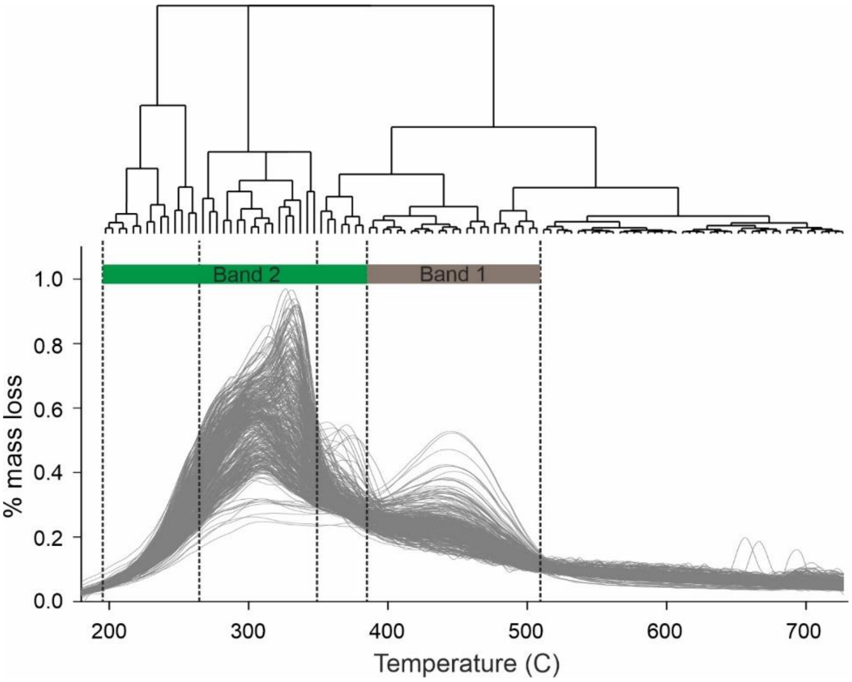


Figure 4.3 Cloud of Thermogravimetric mass loss and cluster analysis

4.3.3 NIRS MUILTIPLE REGRESSION USING END-MEMBER ANALYSIS

NIR spectra were measured by diffuse reflectance using an integrating sphere on a Bruker MPA Fourier-Transform NIRS for an assemblage of end-member materials reflective of the primary components that contribute to peat. In addition the entire Holcroft Moss peat profile was subsampled contiguously at 10 mm intervals The samples were freeze-dried, homogenised by grinding in a mortar and hand pressed (see Korsman *et al.* (2001). All NIR spectra were based on combining 24 scans collected at 4 cm^{-1} intervals across the range 3595-12500 cm^{-1}. NIR spectra were converted to 1st derivatives, calculated using a centrally-weighted Savitzky-Golay smoothing (SGA) algorithm minimising noise (Russell *et al.*, 2019). Our analysis focuses on the wavelengths 8000-3800 cm^{-1} as containing the key spectral structure diagnostic of peat organic and mineral components.

We interrogate the NIR spectra using a novel approach based on multiple regression of end-member spectra onto the spectra of the unknown samples (Russell et al. 2019). The principle is that the NIR spectra of the unknown samples comprise conservative mixtures of the spectra of their component materials. If appropriate end-member materials are available, then the multiple regression coefficient are the mixing proportions of the components, provided allowance is made for their differing chromatic intensities (Russell et al. (2019). The multiple regression analysis was undertaken in R using the (LM) function in R (R Core Team, 2013), with output concentrations reported in weight percent.

4.4 RESULTS

Here we present palaeoecological data including plant macrofossil reconstructions, macroscopic charcoal, peat humification measured as the light absorbance by a filtered alkali extraction, and thermogravimetric parameters for the Holcroft Moss sequence. These techniques quantify the bulk organic composition of the peat. The plant macrofossil analysis estimates the relative proportions of the dominant plant taxa and species present. The floral diversity and composition of ombrotrophic peatlands is heavily regulated by surface wetness, which given the strong coupling of wetness and a balance between precipitation inputs and evapotranspirative losses, provides information on past hydro-climate. The % light absorbance and thermal decomposition across 375-550 °C provide proxies for humification or decomposition of the organic materials. These humification data also reflect changes in bog surface wetness and hydroclimate given that the depth to the minimum summer water table governs the duration of acrotelmic decay and as a result peat humification. The humification data also provide independent measures of down-core patterns in the concentration of humic acid or dissolved organic carbon.

4.4.1 AGE DEPTH MODELLING

Age control for the peat sequence was secured by thirteen ^{14}C ages all obtained for handpicked *Sphagnum* remains to negate issues associated with the dating of peat bulk or organic fractions (Kilian *et al.*, 1995) and downward penetration of roots. The ages were incorporated in a Bayesian age-depth model (Table 1) using 'Bacon' (Christen *et al.*, 2009; Blaauw *et al.*, 2011) operating in the R environment (R Core Team, 2017). The MCMC repetitions were constrained by a gamma distribution with mean 10 yr cm^{-1} and shape 1.7 and a beta distribution with mean 0.26 and shape 25. These modelled chronologies (Figure 4.4) are used to constrain all data.

Table 4.1 Radiocarbon measurements and age-depth modelling.

Sample ID / Lab code	Age (cal. years BP)	Error (cal. years BP)	Depth (cm)	Chronological materials	Median (cal. years BP)	1 sigma range (cal. years BP) (min)	1 sigma range (cal. years BP) (max)
Top of profile	-62	1	0	Top of core = sample date	-62	-63	-61
SCP-peak	-27	5	8	Peak in SCPs (Valentine, data)	-28	-34	-23
Regional motorways	-10	5	15	Dust deposition	-6	-12	-0
SCP-rise	0	10	15	SCP rise (Valentine, unpublished)	-6	-12	-0
SCP-Base	100	10	25	SCP base (Valentine, unpublished)	83	74	92
Pb-rise	50	15	26	Sharp rise in Pb (regional marker)	88	79	97
Base-Pb	100	30	31	Airfall Pb onset (XRF data)	125	108	147
Beta-301556	680	30	50	14C age for *Sphagnum* spp. remains	575	563	592
SUERC-43137	894	38	76	14C age for *Sphagnum* spp. remains	756	749	848
SUERC-43138	1069	38	103	14C age for *Sphagnum* spp. remains	1028	971	1054
Beta-326587	1290	30	116	14C age for *Sphagnum* spp. remains	1165	1099	1204
SUERC-43139	1394	35	133	14C age for *Sphagnum* spp. remains	1290	1208	1312
SUERC-43140	1483	36	158	14C age for *Sphagnum* spp. remains	1398	1363	1465
Beta-326588	1810	30	204	14C age for *Sphagnum* spp. remains	1721	1691	1763
SUERC-43141	1892	38	217	14C age for *Sphagnum* spp. remains	1819	1777	1866
SUERC-43142	2179	38	250	14C age for *Sphagnum* spp. remains	2123	2067	2162
Beta-301555	2210	30	266	14C age for *Sphagnum* spp. remains	2237	2182	2284
SUERC-43143	2420	38	320	14C age for *Sphagnum* spp. remains	2664	269	2692
SUERC-43146	2808	38	352	14C age for *Eriophorum vaginatum* and *Sphagnum* remains	2992	2923	3100
Beta-301557	3890	30	404	14C age for Plant remains	4071	3709	4248

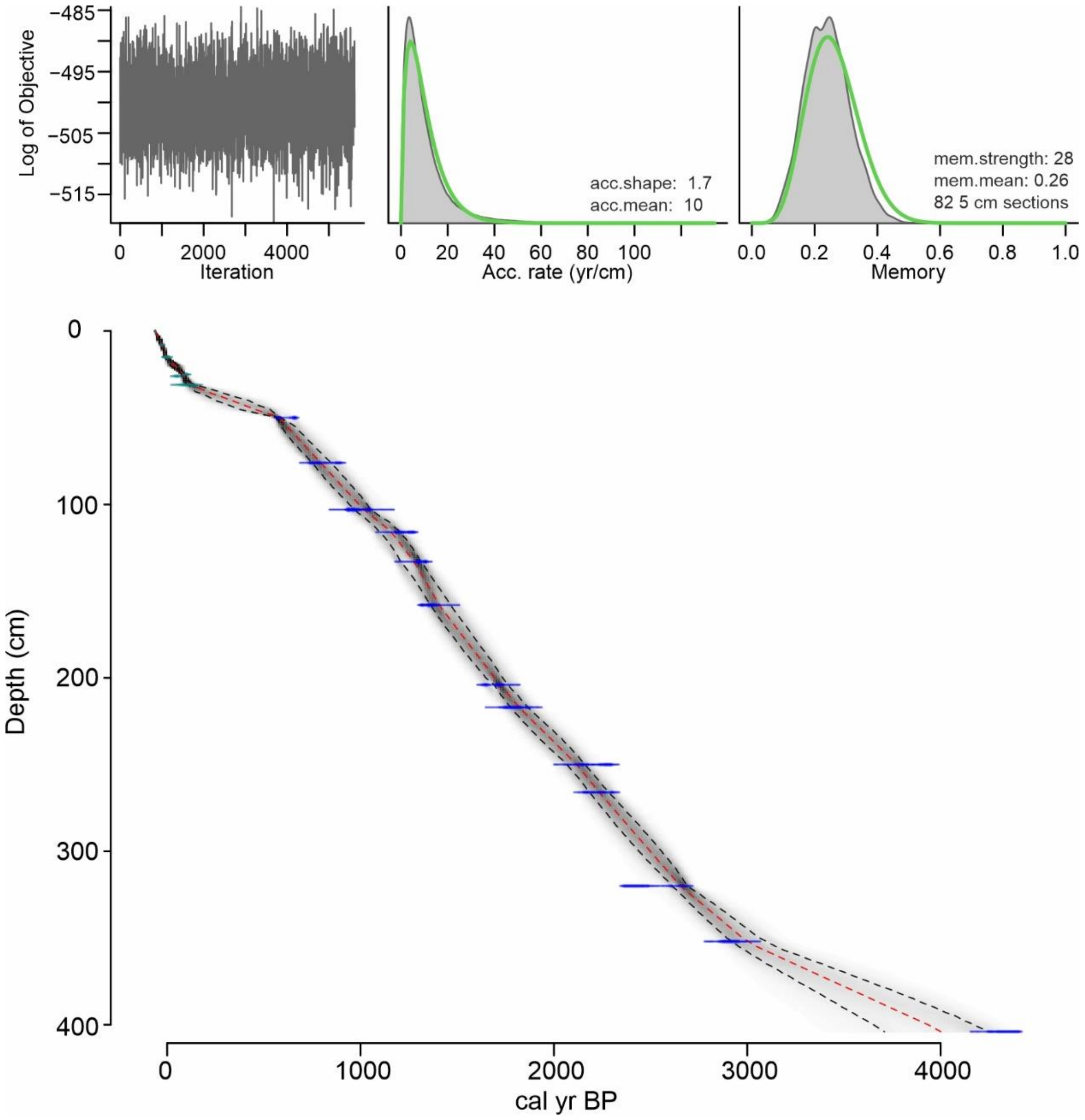


Figure 4.4 Age-depth model for Holcroft Moss using airborne pollution markers for Pb, Spheroidal Carbonaceous Particles and Motorway dust markers (green - near modern) and thirteen radiocarbon ages (green) modelled using the Bayesian routine 'BACON' in R (Blaauw and Christen, 2011). The grey area represents the 95th confidence intervals, and the red line delineates the mean probability.

4.4.2 PALAEOECOLOGY AND STRATIGRAPHY

The Holcroft Moss peat sequence has been divided into seven stratigraphical zones informed by a stratigraphically-constrained hierarchical cluster analysis of the plant macrofossil data using a variety of distance scalings implemented in PAST (Hammer *et al.*, 2001). The cluster analyses produced series of dendrograms (not shown) that identified the most significant changes in the plant macrofossil, which are shown alongside humification and thermal properties by TGA (Figure 4.5).

Zones I-III all contain well humified peat (high % light absorbance; Figure 4.5) and record the establishment of peat at Holcroft Moss, with the basal zone I (4.04-3.56 m) dominated by monocotyledonous (*Phragmites* sp.) peat containing large quantities of typically thermally mature, decayed unidentifiable organic matter (UOM). Zone II (3.56-3.18 m) is less thermally mature and contains less UOM and is dominated by Ericaceous and Monocotyledon plant remains. Zones I-II are also rich with macroscopic charcoal. Zone III (3.18-2.62 m) is dominated by woody Ericaceous remains with minor % monocotyledons and the first appearance of *Sphagnum* marking the probable onset of ombrotrophic conditions at Holcroft Moss.

Zone IV (2.62-1.14 m) is marked by the expansion of *Sphagnum* spp. to dominance, the most substantial change in the stratigraphical record (Figure 4.5). This shift to fully ombrotrophic conditions is accompanied by a shift to poorly humified peat (low % light absorbance; Figure 4.5) dominated by a less thermally mature component (TGA 175-375°C; Figure 4.5). Zone IV has been subdivided into eight subzones distinguished largely on changes in the dominant *Sphagnum* species. *Sphagnum imbricatum* tends to dominate, but in zone IVa *Sphagnum* sect. *Acutifolia* and sect. *Cuspidata* are also significant. Zone IVb contains declines in all *Sphagnum* spp. and abundant UOM and macro-charcoal. In zones IVc and IVe *Sphagnum imbricatum* recovers to dominate, but in zone IVd *Sphagnum* sect. *Acutifolia* and sect. *Cuspidata* are co-dominant. Zone IVf and IVg show increases in UOM and monocotyledons at the expense of *Sphagnum imbricatum*. Zone IVh sees expansion of *Sphagnum imbricatum* except for the uppermost 8 cm.

Zone IV peats are dominantly poorly humified and less thermally mature, with sub-zones containing less *Sphagnum imbricatum* and more well humified and thermally mature peat (peaks in TGA 420-490°C; Figure 4.5). Zone V (0.36-1.14 cm) is poorly humified and thermally less mature peat dominated by *Sphagnum imbricatum*. The zone is punctuated by two minor increases in *Sphagnum* sect. *Acutifolia* that are accompanied by shifts to well humified and more thermally mature peat. Zone VI (0.36-0.12 cm) is a more substantial expansion of *Sphagnum* sect. *Acutifolia*, though towards the top of the zone *Sphagnum imbricatum* and latterly *Sphagnum papillosum* recover. In zone VII *Sphagnum imbricatum* vanishes, and the peat is dominantly UOM and monocotyledons, mostly *Molinia caerulea*.

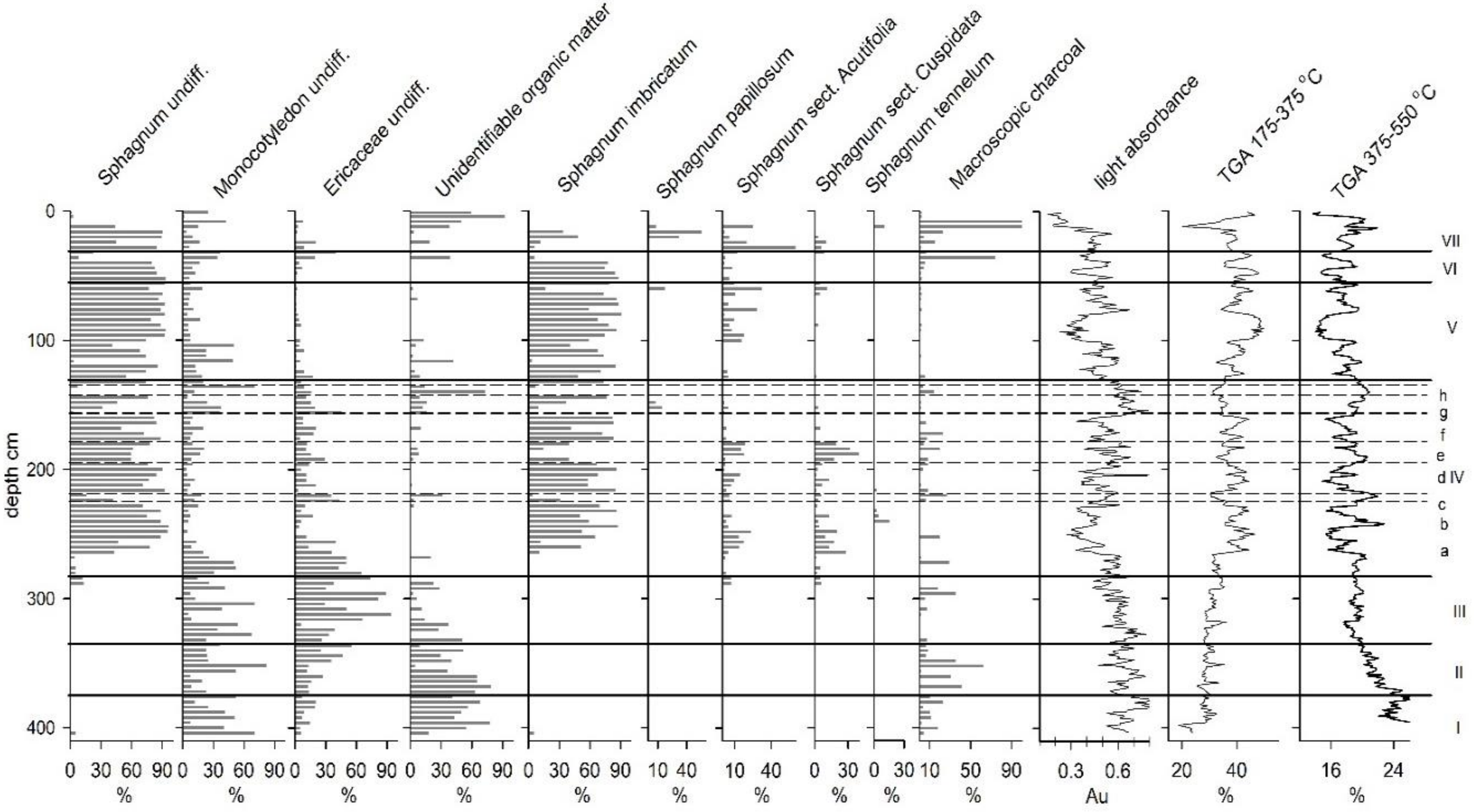


Figure 4.5 Holcroft Moss plant macrofossil and organic matter stratigraphy including the degree of humification and thermogravimetric mass loss bands.

Throughout the stratigraphy formed under ombrotrophic conditions (zones IV – VII) there is a strong negative correlation between the abundance of % *Sphagnum* and poorly humified peat (% light absorbance, r=-0.53, p<0.000001, n= 100) and strong positive correlation between % *Sphagnum* and the less mature thermal component (TGA 150-375°C, r=0.0.73, p<0.000001). Conversely, the proportions of Ericaceous and Monocotyledons are negatively correlated with indications of poorly humified and less thermally mature (p values all p<0.0004) peat. In summary, the changes in peat composition in zones I-III recorded the establishment of what was initially a fen wetland and then latterly ombrotrophic peat at Holcroft Moss, characterising a fen-bog hydrosere (*sensu* (Hughes, 2000)). The fluctuations in zones IV-VII are more typical of ombrotrophic peats (e.g. Barber 1981; Chiverrell 2001), with changes in bog surface wetness between wetter conditions producing poorly humified, less thermally mature *Sphagnum imbricatum* peat and drier conditions producing well humified, more thermally mature peat dominated by *Sphagnum* sect *Acutifolia*, Ericaceae and monocotyledon plant macrofossils. This compositional stratigraphy provides a structure for exploring the NIRS stratigraphy at Holcroft Moss.

4.4.3 NIRS MULTIPLE REGRESSION AND VALIDATIONS

NIRS has been used as a rapid non-destructive technique for quantifying organic materials present in sediment samples. Many studies utilise chemometric (partial least squares regression) methods for interrogating the NIR spectra based on developing training sets, typically a subset of samples where variables have been measured independently by other methods. It can be possible to use this PLS approach to then predict the concentration of almost any variable where a training data set exists. McTiernan et al. (1998) applied this approach to a blanket peat sequences from Moor House National Nature Reserve in the Pennines, showing some success in reconstructing the proportions of *Sphagnum* mosses, monocotyledonous and Ericaceae plant remains. However, when interrogating the spectra of an average of all samples from the Holcroft Moss core with end member spectra measured for these individual major peat components (*Sphagnum*, *Calluna vulgaris*, acid and alkali insoluble humin fraction, see Figure 4.5) we observe common spectral patterns. It is because of this similarity in spectra that NIRS methods based on training sets should be used with caution, and where our method using multiple regression of end-member spectra can improve the handling of NIRS data.

4.4.4 NIR END-MEMBER SPECTRA

Examination of the cloud of ~400 NIR spectra expressed as first derivative for the Holcroft Moss sequence (Figure 4.6A) shows broad similarity to the NIR spectra throughout the Holcroft Moss core, with the average sample sitting centrally to variations in amplitude. This contrasts with the end-member NIR spectra for the types of organic matter (Figure 4.6B) present in the plant macrofossil record and key peat decomposition components, which show greater variation. Visual comparison of the spectra highlights a number of key issues, foremost for some examples of plant matter, there is very little difference between spectra (e.g. *Sphagnum* and *Eriophorum*) which share both peaks and spectral amplitude. Comparing the cloud of peat samples with the end member spectra shows that most peaks in the core spectra can be attributed to one or more of the end-members. The similarity between spectra is the reason behind the doubts that exist around the claims that chemometric PLS methods are able to reconstruct individual plant species. Contrasting the 50:50 mixture of humic acid and fulvic acid selected to represent the dissolved organic carbon content of the peat (Figure 4.6B) it is interesting that many of the spectral features present in fresh plant matter spectra remain present but are heavily subdued in this humic/fulvic acid end-member, with only one clear example of a new unique peak. This suggests that the information held in the NIR spectra includes a very strong measure of the state of decay of organic materials.

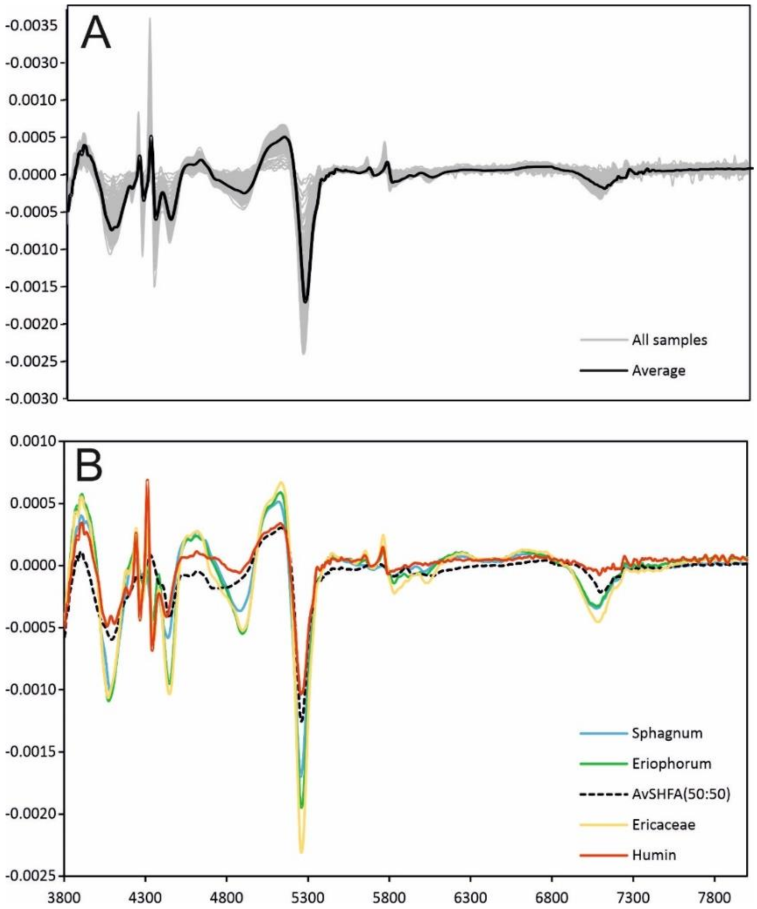


Figure 4.6 A) Cloud of the NIR spectra expressed as first derivatives for all Holcroft Moss samples (Grey) and an average (Black) B) Exemplar First Derivative NIR spectra for suitable end-members (colours)

4.4.5 DOWNCORE PATTERNS IN NIRS END-MEMBERS

To test the environmental significance of the NIR spectra obtained for the Holcroft Moss cores, our EMS-MR fitting procedure was used to calculate the mass proportion of a series of known composition peat components in the Liverpool End Member library. The EMS-MR fitting was conducted in an iterative manner exploring the fits for multiple combinations of end member materials. To assess the performance of these fits, a series of independent measures from the suite of data available for the Holcroft Moss core were used including plant macrofossils, thermogravimetric signals and peat humification measured as % light absorbance for validation. These independent data were recalculated as % mass proportion for these comparisons. The pyrolysis mass loss across 375-550°C by thermogravimetry is considered to represent humic compounds, based on previous analyses of humic compounds in coal (Rotaru *et al.*, 2008) and peat (Biester *et al.*, 2014; Zaccone *et al.*, 2018). The plant macrofossil proportions were estimated as % mass of the pyrolysis 150-375°C mass loss, regarded here as a measure of the low temperature release soft tissue plant remains (e.g. cellulose), with the more recalcitrant higher temperate mass loss measuring humic compounds.

A range of end-members (Table 4.2) can be chosen to represent the peat stratigraphy, informed by the current flora and particularly by the plant macrofossil data. The plant end members present similar spectra (Figure 4.6), in particular *Eriophorum vaginatum* and *Sphagnum*, whereas the Ericaceae (*Calluna vulgaris*) contains some unique structure reflecting presence of lignin. The analysis focuses on the upper 3 m and ombrotrophic tract of the peat sequence. This eliminates the need for incorporating mineral end-members by avoiding the fen and minerotrophic phase of the sequence. Above this depth, mineral inputs are limited to aerial fallout and our loss-on-ignition data typically >95% show this to be extremely limited with little to no influence over the NIRS spectra. The primary air fall impact occurs as recent pollution (e.g. Pb, Zn, Cu and spheroidal carbonaceous particles) in the top 15 cm of the core, which subdue the amplitude rather than change the structure of the NIR spectra.

Table 4.2 End-member materials used in the EMS-MR processing of the NIRS.

Peat characteristic/independently quantified variable	**End-member for NIRS fitting**	**End-member Details**
Unidentifiable Plant Matter (UOM) – from the plant macrofossil data	Humin	Acid and alkali insoluble fraction (HCl and NaOH) extracted from May Moss, which contains all degraded organic matter excluding large plant materials and alkali soluble humic/fulvic acids.
Humics - TGA mass loss in temperature range (375-550 °C)	50:50 mixture of Humic acid : Fulvic acid	International Humic Substances Society (IHSS): Suwannee River Humic Acid Standard III and Suwannee River Fulvic Acid Standard II with the spectra averaged to represent humic compounds
Plant matter – PLANT MACROFOSSIL data set	*Sphagnum*	Fresh plant matter
	Eriophorum vaginatum	Fresh plant matter
	Ericaceae *(Calluna vulgaris)*	Fresh plant matter

In Figure 4.7 we show the interactions of several possible combinations and numbers of end members to demonstrate the process behind the NIRS fitting, and our rationale for limiting the number of plant matter end-member components. The end members were chosen to represent the following major peat components; Unidentifiable Organic Matter (UOM) (humic/fulvic acid), *Sphagnum (bog-mosses)*, *Eriophorum vaginatum* (an abundant cotton-grass sedge) and a common member of the Ericaceae (*Calluna vulgaris)* (Table 4.2 for end-member detail).

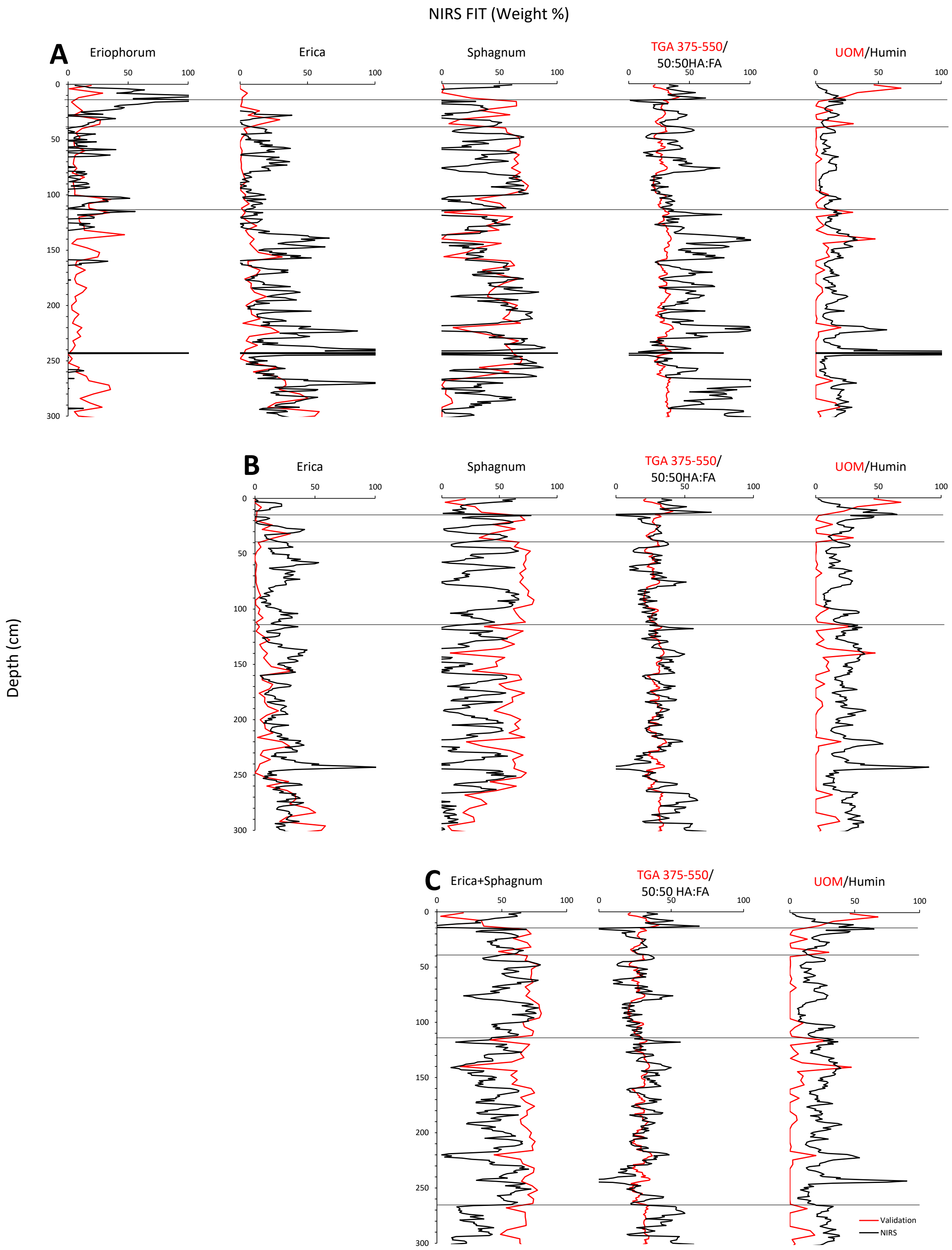


Figure 4.7 NIRS fitted mass proportions (black) for different combinations of plant matter type shown with the independently quantified % mass (red). A) EMS-MR fitted concentrations using three plant matter types, B) Fitted concentrations reducing the plant matter to *Sphagnum* and Ericaceae (lignin-rich) C) Fitted concentrations reducing to a single plant end member with summed % *Sphagnum* and Ericaceae. See Table 4.2 for details on the end members and associated independent verification.

Using three plant matter end members (Figure 1.5A), there is a clear failure to the plant matter fits when compared with the plant macrofossil validation and significant under prediction of the humic compounds. There is little tractable pattern to the mismatches, and this is probably a function of the similarity and overlap between the plant end member NIR spectra. This problem or challenge only emerges by applying the EMS-MR approach, conventional chemometric partial least squares regression of NIRS spectra may produce better fits but the apparent successes to the fits may be artificial and include significant covariance arising from the spectral similarities.

Reducing the number of plant matter end members in step B, there is an improvement in the overall fit of the end-members, and particularly for the fit of humic compounds (50:50 mixture of Humic acid : Fulvic acid). The NIR spectrum of *Eriophorum vaginatum* shares a great similarity with that of *Sphagnum* and for this reason EMS-MR is unable to produce simultaneous quantification of these end members. Despite the improvement to the EMS-MR fits when *Eriophorum vaginatum* is removed from the process as an end member, there remain shared NIR spectral features between Ericaceae and *Sphagnum* resulting in further misattributed quantification when compared to the plant macrofossil % masses.

In step C, the comparison between EMS-MR fit for plant matter and verification through comparison with independent measures improves further when those remaining plant matter fits are combined (*Ericaceae* and *Sphagnum*) (Figure 1.5C). This suggest that the EMS-MR method is successful at distinguishing between fresher less decayed plant matter and other more decayed peat components, but not at separating individual plant matter taxa or species *sensu* McTiernan et al. (1998). This balance between decayed organic bioproducts and well preserved plant remains chimes a chord with applications of NIRS to assessing animal fodder palatability and digestibility, where the decay/digest of plant tissue dominates the differences in NIRS spectra for plant species/taxa (Decruyenaere et al., 2009).

4.4.6 QUANTIFICATION OF ORGANIC COMPONENTS IN HOLCROFT MOSS PEAT USING NIRS MULTIPLE REGRESSION METHOD

An objective for this chapter was assessing the potential and utility of NIRS and EMS-MR in quantifying the humic compound proportion present in sediments by using an environment dominated by both organic matter and patterns of fresh versus decay organic matter. Figure 1.6 shows the NIRS EMS-MR fits for humic compounds (*50:50 Humic acid: Fulvic acid*) compared with two independent estimates of humic acid concentration or the humification of peat at Holcroft Moss. TGA mass loss in the temperature range of 375-550°C has been attributed to the thermal decomposition of humic substances (Rotaru *et al.*, 2008; Biester *et al.*, 2014; Zaccone *et al.*, 2018)) and % light absorbance of an alkali extraction from the peat has been associated with degree of humification (Payne *et al.*, 2008; Chambers *et al.*, 2011; Biester *et al.*, 2014; Zaccone *et al.*, 2018).

In summary, the NIRS fit for % mass humic compounds (50:50 HA: FA) follows closely the down core pattern of the two independent measures of peat humification, with NIRS HA: FA showing strong positive correlations with % absorbance (r=0.49 p<0.00001) and TGA 375-550°C (r=0.41, p<0.00001). The NIRS fitted humic compound curve varies more widely than either of the independent measurements in several places. Given the limitations imposed by the lack of unique NIRS spectra between end members and known limitations to the independent methods of quantifying peat humification (Payne *et al.*, 2008; Chambers *et al.*, 2011; Biester *et al.*, 2014; Zaccone *et al.*, 2018), a parsimonious conclusion is that the variations in NIRS fitted HA:FA reflect the humic compound concentrations in the peat. Peat humification measured by % light absorbance of an alkali peat extract is known to be sensitive to mineral content and plant types comprising the peat (Payne *et al.*, 2008; Chambers *et al.*, 2011).

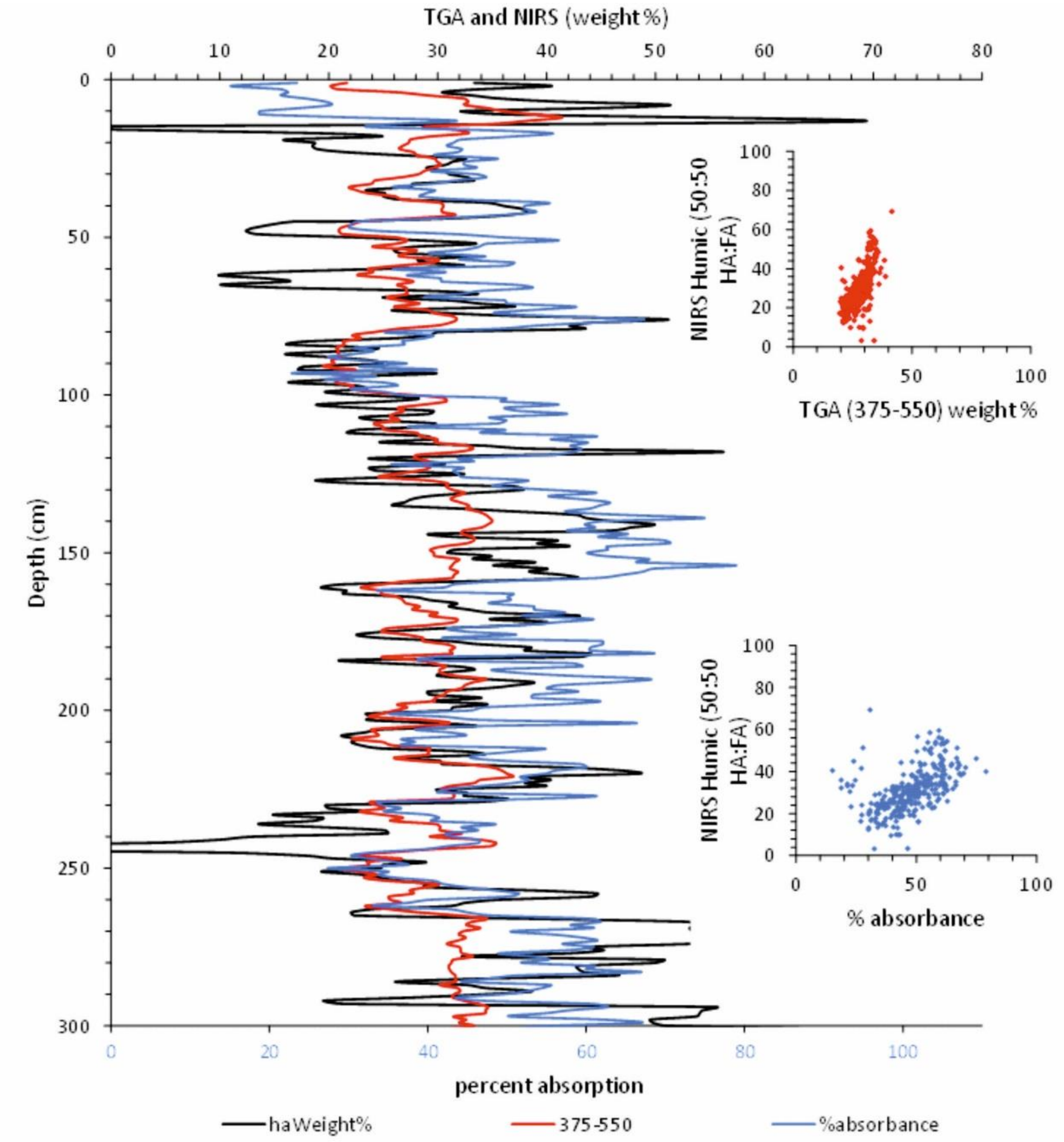


Figure 4.8 A) NIRS fitted humic compounds (*50:50 Humic acid : Fulvic acid*) against independent validation quantification A) weight% TGA (375-550°C) B) 1- mean% Absorbance and C) down core plot of NIRS fitted humics and independent quantifications.

Down core patterns in the humification stratigraphy of the Holcroft Moss peat are presented using the zonation devised from the plant macrofossil data, which comprises 5 distinct stratigraphical zones in the upper 3 m of peat (Figure 4.8).

Zone (III) shows initially high concentrations of humic compounds NIRS HA: FA, % absorbance and TGA 375-550°C, which then fall sharply ~ 2350 cal. a BP. The plant macrofossils show an environment dominated by Ericaceous plants and very low proportions of *Sphagnum*. The shift ~2350 cal. a BP to poorly humified peat across most of our proxies is associated with the shift to a *Sphagnum*-dominated peatland. This type of stratigraphical change typically reflects a shift to much wetter conditions on the peatland (Van Geel *et al.*, 1996; Chiverrell, 2001; Charman *et al.*, 2006, 2009). TGA

375-550°C is the one anomaly with a peak in thermally mature materials in the middle of this decline in humic compounds, but this corresponds with and probably reflects a peak in macroscopic charcoal. The declines in NIRS HA:FA at 2500 and 2350-2100 cal. a BP mirror shifts in % absorbance and increases in % *Sphagnum* reflect wetter conditions at Holcroft Moss, and correspond to well-known climate-driven shifts to wetter conditions recorded in peat sequences across Europe and in other climate archives around 2650 BP (van Geel et al., 1996; Charman et al., 2006; 2009).

Zone IV is dominated by abundant but fluctuating *Sphagnum* spp. as the most abundant plant species, and has been subdivided into a series of sub-zones that describe switches between poorly humified *Sphagnum* rich peat and *Sphagnum*-poor peat with a much higher humic compound content across all our proxies. In particular NIRS HA: FA appears to mirror the fluctuations in *Sphagnum* content. The humic compound record comprises a very noisy peak 1800-1600 cal. a BP, and this corresponds with a widely recorded drier phase in UK peat sequences and drier conditions during the Roman occupation of Britain (Chiverrell, 2001; Charman et al., 2006). The dips in *Sphagnum* 1500-1350 and 1250-1150 cal. a BP are accompanied by peaks in humic compounds. These phases with well humified peat are punctuated by pronounced shifts to wetter conditions and reduced humic acid content at 1550, 1350 and 1150 cal. a BP, all of which correspond with a shift to wetter conditions recorded in UK peat sequences (Charman et al., 2006).

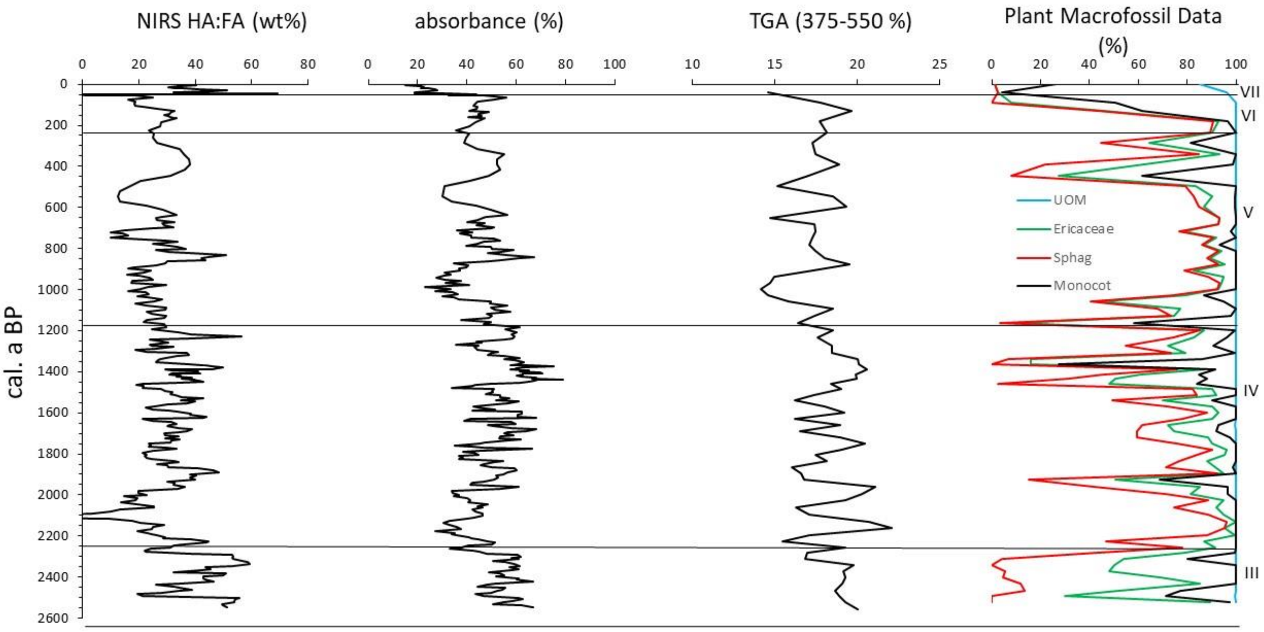


Figure 4.9 Changes in the humic compound stratigraphy of Holcroft Moss through the last 2500 years.

Zone V is dominated by a more extensive peak in *Sphagnum* and three distinct peaks in our proxies for humic compounds. The peaks in humic compounds and well humified peat occur 900-750, 700-

600 and 475-300 cal. a BP. These units in reflecting drier conditions show shifts from *Sphagnum imbricatum* to the drier indicator *Sphagnum* sect. *Acutifolia.* Shifts to lower concentrations of humic compounds suggesting both poorly humified peat and a wetter environment occur 900, 700 and 450 cal. a BP. These shifts all feature in the UK bog surface wetness palaeoclimate record, with the pronounced wetter shift ~450 cal. a BP synonymous with the onset of a broader 'Little Ice Age' (Charman et al., 2006).

Zone VI displays sharps falls from relatively well humified peat (%absorbance and NIRS HA: FA), becoming poorly humified and *Sphagnum* dominated throughout much of the zone. This pronounced wetter phase of bog surface conditions and palaeoclimate ~450-150 cal. a BP overlaps with wetter conditions evidenced in peat across the British Isles and with the 'Little Ice Age' (Grove, 1988; Charman *et al.*, 2006)

The uppermost zone VII is a little different to the remainder of the stratigraphy, with the humic compound indicators out of agreement. Thermal decomposition 375-550°C and % light absorbance shows a shift to poorly humified peat, whereas NIRS HA:FA shows a sharp increase in humic compounds. In the macrofossil record UOM is the most abundant component, which suggests that this zone is well humified with limited amounts of plant matter remains. Holcroft Moss, and the wider Chat Moss region, have experienced extensive drainage associated with peat extraction and development for agriculture, impacts that are reflected in the degraded condition of the bog flora. With this, there has been extensive deposition of pollutant (Pb, Zn, Cu), fly-ash (SCPs and Magnetic Susceptibility), and air-fall mineral dust from soils (Zr, Rb, K) (not shown). Both TGA 375-550°C and % light absorbance are known to be sensitive to elevated mineral content (Payne *et al.*, 2008; Chambers *et al.*, 2011). Equivalent impacts on the NIR spectra are limited to a dampening of the amplitude of peaks and trough, and so NIRS may be better at measuring degree of humification in these peats.

4.5 DISCUSSION

4.5.1 EMS-MR AS A TOOL FOR QUANTIFYING CONCENTRATIONS OF HUMIC COMPOUNDS

Our EMS-MR fits from the NIR spectra for HA/FA produces % mass concentrations that correlate with both Absorbance% and TGA (375-550°C). Both of the latter are recognised approaches to quantifying humification of peat (Zaccone *et al.*, 2018), while TGA (365-550°C) is also a recognised signature for humic compounds (Rotaru *et al.*, 2008). Assessing which of these is more accurate or precise at measuring humification is challenging as there is no universally accepted definition, leading to differences in the measured values obtained (Zaccone *et al.*, 2018). % light absorbance is an accepted measure for peat humification, the relationship of this to specific humic compounds is not well known (Biester *et al.*, 2014). Thus, the good correlation with Absorbance% shows a substantial shared signal, but discrepancies between them cannot be interpreted simply.

The TGA curve shows mass loss (Figure 4.3) across the entire temperature range, and zones of loss can be seen and associated with plant matter and humic substances (Zaccone *et al.*, 2018). However, not all organic material is lost in these temperature ranges, some is in fact altered and only lost during the air burn above 750 °C. Therefore, TGA may underestimate proportion of organic matter and humics. TGA must also be expected to not fully separate the two main components, as the peaks in rate of mass loss (Figure 4.3) are broad and overlapping. Consequently, we can expect the true range of values to be narrowed by TGA measurement. This is consistent with the observation (Figure 4.7) that % mass proportions of humic compounds measured by TGA vary far less than HA/FA measured by NIRS EMS-MR. This, and the comparison with Absorbance%, show that EMS-MR provides a useful measure of concentrations of humic compounds in peat. The NIRS EMS-MR approach also appears less affected by the influence of variations in mineral content and pollutant flux in surface peats. NIRS EMS-MR also avoids the need for a training set which would be required if a chemometric NIRS approaches were used.

4.5.2 INFERRING PALNT TISSUE CONCENTRATIONS BY END MEMBER SPECTRA

The EMS-MR procedure, using a dried fresh *Sphagnum* sample as an end-member, in this case *Sphagnum papillosum*, generates concentration values that correlate with total proportion of plant macrofossils. This is achieved with simultaneous quantification of total humic compounds. However, values generated when attempting to quantify the differing plant matter types present in peat do not correlate with the corresponding plant fossil data. Previous work using a chemometric approach with a training set of 14 of 36 measured plant macrofossil samples, McTiernan *et al.* (1998) obtained useful standard errors of prediction for three different *Sphagnum* species. To explain these differences in outcome, it is necessary to appreciate that the three approaches involved (MR-NIRS, chemometric NIRS, and plant macrofossil counting) measure different things.

Plant macrofossil counting generates a percentage value of fragments that are sufficiently identifiable to be distinguished. Here, this percentage was assumed to be proportional to actual abundance (mass) of the plant taxon. The chemometric method of McTiernan *et al.* (1998) statistically associates this count with the NIRS properties of the material to develop an empirical inference model which captures the highest proportion of variance in the training set. It does not, however, have any a priori basis, and a successful fit is as likely to arise from unknown confounding variables as from a direct causal association. The NIRS EMS-MR approach attempts to directly fit the NIR spectrum of a known end-member material with the spectral properties of the peat. This avoids the potential omitted variable bias of chemometric NIRS but depends on have a suitable end-member material.

The successful plant macrofossil prediction by McTiernan *et al.* (1998) provides some evidence that individual plant species can leave a distinctive signal in a peat NIR spectrum, though it cannot be ruled out that this fit is due to unmeasured confounding variables. Assuming the fit to arise from a causal signal, how then should the failure of the EMS-MR method to infer separate genera be interpreted? The likely explanation relates to the nature of the material in our Library of end-member spectra. The fresh plant materials we used as end-member may simply be too different from the decayed remains of the same species present in the peat. Applications of NIRS in assessing the quality of animal fodder, principally the palatability and digestibility, shows that the decay/digest condition of plant tissue can dominate the differences in NIRS spectra for organic materials e.g. individual plant species or taxa (Decruyenaere et al., 2009). By using a training set of total macrofossil counts McTiernan *et al.* (1998) the state of decay of the plant macrofossils therefore becomes irrelevant. Figure 1.5C shows that NIRS fitting tends to underestimate total plant matter, particularly where there are lower concentrations. This may be due to sensitivity of the NIRS in detecting decomposition of plant matter, which is not captured in the plant macrofossil counts and therefore we see higher estimates for humin or UOM.

Using our fresh end-member samples, the EMS MR method is likely to assign decayed plant matter to an end-member which represents humified material, hence the over estimation of UOM. The apparent success of McTiernan *et al.* (1998) raises the possibility that with additional end-member spectra of plant matter in varying stages of decay the EMS-MR method may be able to quantify plant matter more successfully. However, it remains possible that the similarity in spectra would occur between plant matter types of a similar stage of decay, and therefore the issue around difficulty in differentiating between materials would still exist. These similarities in NIRS spectra for differing plants may also limit the McTiernan *et al.* (1998) approach, with the signal a function in part of unmeasured confounding variables.

The EMS-MR method produces good fits for total plant matter, humic compounds and the humin fraction when compared with independent validation techniques. NIRS quantification of humics using the average of Suwannee River HA and FA standards successfully captures the trends observed in TGA mass loss associated with mature humic substances and %absorption. These findings provide confidence that the EMS-MR method is suitable for use in interrogating the humic composition of sediments in other depositional environments (e.g. lakes, soils, alluvial settings).

4.5.3 POTENTIAL APPLICATION IN PEAT PALAEOCOLOGY

Peat palaeoenvironmental techniques have been widely used to study changes in regional vegetation bog surface wetness (plant macrofossils, testate amoebae, peat humification) and by association hydroclimate (effective precipitation) (e.g. (Barber, 1981; Blackford *et al.*, 1993; Mauquoy *et al.*, 2002; Charman *et al.*, 2006; Payne *et al.*, 2008). The techniques underpinning these records can be very time consuming, affecting the stratigraphical resolution of analyses. Yet the benefits of high resolution measurements have been clearly demonstrated in the case of a microfossil analysis undertaken at <10mm resolutions (Amesbury *et al.*, 2011). While our new method cannot yet reliably reconstruct individual plant taxa, it can provide rapid, non-destructive high-resolution concentration data for total identifiable plant remains, and for humification. Profiles measured this way can be used either as data in their own right, or as supporting information. Payne and Blackford (2008) and Chambers *et al.* (2011), for example, used multiple proxies to corroborate wetness histories and test the influence of plant species on decomposition records. The method could also be used to aid core selection for subsequent more time-consuming analysis. A significant move towards analysing multiple cores and replicating bog surface wetness records could be assisted by the rapid non-destructive approach implicit in FT-NIRS. Determining wetness variations would greatly aid in the selection of decay-sensitive plants and microorganisms, as illustrated by (Barber, 1981; Chiverrell, 2001; Payne *et al.*, 2008). By providing supporting information to other palaeoecological proxies, our method has wider application in peat studies in fields as wide ranging as fire and burning histories using charcoal (Bradshaw *et al.*, 2010), atmospheric dust and pollutant deposition (Shotyk *et al.*, 1998), macronutrient stoichiometry (N and P) (Schillereff *et al.*, 2016), and carbon accumulation (Loisel *et al.*, 2014, 2017).

4.5.4 EMS-MR HA/FA AS PRECURSOR TO DOC?

The primary objective of this thesis is to assess the quantification of lake water DOC using an NIRS analysis of lake sediment records, and particularly to develop a method based on known physical processes rather than statistical inference models. Central to this is quantification of the humic fraction in lake sediments, such that the humic accumulation rate can be calculated. From this, and a simple lake model, the lake water content of humic compounds (DOC) can be calculated. This all relies on reliable quantification of humics in lake sediments, which can be proven most rigorously if the method works for a wider range of natural environments. In Chapter 3, we show that it is possible to fit total organic matter in a sedimentary environment influenced by mineral supply with R^2 of 0.955 when compared to independent estimate of total organic matter, tested at Loch Grannoch in southwest Scotland. We also successfully applied it to three additional sites in Scotland, Sweden and Norway. In Chapter 5 we successfully apply the method to quantify not just total organic matter but also concentrations of humic compounds at four UK lakes. Successful quantification of humics in these lake sediment shows that the method works in a medium that is rich in both terrigenous mineral matter and biogenic silica. Here, at Holcroft Moss, we show that HA: FA end-member can be fitted in a peat sequence that has negligible mineral matter and biogenic silica, and comprises instead by a mixture of various organics components. Again, our method quantifies humic compounds, yielding values that agree well with independent quantifications (TGA

375-550°C and %absorption). Consequently, we are confident that EMS-MR can successfully quantify the HA: FA content in sedimentary environments.

4.6 CONCLUSIONS

Plant macrofossil and humification indicators, here thermal decomposition across defined temperature ranges and % light absorption of an alkali peat extract for a peat core from Holcroft Moss, show distinct variations, including the establishment of an ombrotrophic peat sequence and also a series of stratigraphical changes related to bog surface wetness (Figure 4.5). This data set provides an ideal opportunity to test whether our NIRS analysis procedure, End Member Spectra Multiple Regression (EMS-MR), can quantify the major components in a dominantly organic setting, and for a location where a large data set has provided the means to independently validate the measurements. The results, revealing good agreement with both thermal decomposition 375-550°C and Absorbance%, show that EMS-MR provides a useful quantification of humic compounds in peat. Our methodology avoids the need for developing training sets which would be required if a chemometric NIRS approach was used.

The EMS-MR method produced good fits for total plant matter when compared with plant macrofossil count data. However, in using fresh plant samples as our end member library, the EMS MR method did not quantify successfully the proportions of individual plant taxa. Based on previous successful application of chemometric methods in quantifying *Sphagnum* species, we speculate that EMS-MR would be more successful with partially decayed plant end-member materials or it could affirm the similarity between the end member spectra undermining the approach whether applied by either EMS-MR or chemometric methods. The similarity of spectra leads to substantial covariance and reconstructions by chemometric methods could be more apparent than real.

While our new method cannot at present reconstruct individual plant taxa reliably, it does provide rapid, non-destructive high-resolution concentration data for total identifiable plant remains, and for peat humification based on the mass % of humic compounds. In providing supporting information to other palaeoecological proxies (e.g. analysis of plant macrofossils, testate amoebae), our method has wider application in peat studies and has potential roles in fields as wide ranging as fire and burning histories, (charcoal), atmospheric dust and pollutant deposition, macronutrient stoichiometry (N and P), and carbon accumulation. The successful quantification of humic compounds in peat, together with the successful application of the methods in lake sediments in the other chapters, confirms that EMS-MR provides a sound basis for models using sediment records to infer past changes in lake water DOC.

4.7 ACKNOWLEDGMENTS

We thank Cheshire Wildlife Trust for granting access permission to Holcroft Moss Site of Special Scientific Interest. The ^{14}C ages were funded by the Natural Environment Research Council through Radiocarbon Analysis Allocation Number 1619.0312. FER PhD is supported by the School of Environmental Sciences, University of Liverpool. The 2012 peat core was sampled and the stratigraphical analyses (peat humification and plant macrofossils) were undertaken by Julie Valentine (funded by a Liverpool John Moores University PhD Bursary) supervised by Jason Kirby (Liverpool John Moores University) and Richard Chiverrell (University of Liverpool).

5 DECIPHERING THE DRIVERS OF A 300-YEAR RECORD OF SEDIMENT INFERRED DOC CONCENTRATIONS AT FOUR TEMPERATE UPLAND LAKES FROM THE UK

5.1 ABSTRACT

Here we present records of dissolved organic carbon (DOC) concentrations inferred from the sediments at four temperate and upland lakes, selected from the UK Upland Waters Monitoring Network (UK-UWMN) of sites. Over the last 30 years concentrations of DOC in many British upland waters have increased. Commonly referred to as “brownification”, this is a concern not just for the impact on ecosystem function but also because of the increased cost of water treatment. Differing causal mechanisms have been proposed, including land-use or climate change, with the most widely quoted explanation interpreting the current DOC rise as a recovery from past DOC suppression caused by mid-twentieth century acid rain and sulphur deposition. Monitoring data programmes do not extend far enough back in time to evaluate these hypotheses, so we have developed a method to infer past aqueous DOC concentrations from lake sediments. This approach estimates the sediment burial fluxes for humic and fulvic compounds using a novel end member regression of Near Infrared Spectra (NIRS). The approach contrasts with methods that use inference models trained empirically to predict aqueous DOC from NIRS spectra. Our NIRS method quantifies sediment concentrations of humic/fulvic acid (HA/FA), alongside the concentrations of other organic matter types, mineral content and biogenic silica. Using a simple process model, we calculate the aqueous DOC concentration from the measured HA/FA sediment burial flux. The DOC concentration estimated this way agrees well with the monitoring record (1988-2016) for DOC in the water at these UK-UWMN sites ($r^2 = 0.78$). DOC concentrations reconstructed for the last 300 years show that the DOC rise predates both acidification and recovery at all four sites, and that values rise steadily through the industrial period. The record is thus not consistent with the acidification hypothesis. Likewise, the temporal patterns in DOC records are very different from variations in climate over the past 3 centuries. Instead, correlation of the sediment DOC record with proxies showing enhanced terrestrial productivity in the lake catchments suggests this may have played a central role in increased DOC. The timings are broadly consistent with fertilisation of upland catchment soils by enhanced atmospheric N deposition increasing the flux of soil derived DOC to the lakes, though other land use factors and recent climate warming are also likely to have contributed.

5.2 INTRODUCTION

In recent decades a trend of increasing dissolved organic carbon (DOC) concentration, 'brownification', has been identified in surface waters across the UK, North America and Northern Europe, occurring synchronously with rising alkalinity (Worrall *et al.*, 2003; Skjelkvåle *et al.*, 2005; Roulet *et al.*, 2006; Monteith *et al.*, 2007). It has been suggested that these parallel trends are linked causally, both being a response to recovery from surface water acidification in acid sensitive environments (Battarbee, Simpson, *et al.*, 2014). In the 1980s, legislation aimed at reducing atmospheric acid emissions was introduced. Research programmes including the UK Uplands Water Monitoring Network (UK-UWMN, known formerly as UK Acid Waters Monitoring Network), have collected data over several decades monitoring the responses of surface waters. The UK-UWMN sites show signs of recovery, with increasing pH, alkalinity and associated responses of biological and chemical indicators (Kernan *et al.*, 2010), but DOC has increased broadly in parallel with the de-acidification. A number of theoretical and experimental studies provide mechanisms that support such a link (Evans *et al.*, 2006), and more recent studies conclude that the dominant controls over DOC concentrations have yet to be resolved (Monteith *et al.*, 2014; Sawicka *et al.*, 2017). Thus, it is possible that other factors may be affecting surface water chemistry, such as changes in land use (e.g. afforestation) and climatic conditions. For example, shifts to wetter (Tranvik *et al.*, 2002; Hongve *et al.*, 2004; de Wit *et al.*, 2016), or to drier (Freeman *et al.*, 2001) and warmer conditions (Hedström *et al.*, 2017). The negative impacts associated with elevated concentrations of dissolved organic carbon (DOC) of inland waters are numerous. They include the release of terrestrial carbon stores to the atmosphere (CH_4 and CO_2) (Hanson *et al.*, 2004; Battin *et al.*, 2009), ecological repercussions such as loss of species diversity (Hedström *et al.*, 2017), potential increases of trophic status (Corman *et al.*, 2018), and higher treatment costs for the water industry (Köhler *et al.*, 2013). Consequently, uncertainty about the cause of recent DOC increases has important implications for approaches to mitigation, management and forecasting future trends.

A hindrance to critical evaluation of these competing hypothesis for the causes of recent DOC increases is the short duration of environmental monitoring programmes. Palaeoenvironmental approaches, for example those using lake sediment records provide potentially the only means for addressing this. For example, Cunningham *et al.* (2011) developed methods previously applied using chemometric analysis of sediment NIRS spectra (Nilsson *et al.*, 1996; Rosén, 2005) to reveal substantial apparent shifts in DOC inferred from the sediment records in southern Sweden through the 20th century. However, their approach (Cunningham *et al.*, 2011) is subject to uncertainty for two reasons. First, while NIRS spectra depend on the concentration of components in the lake sediment, mass balance considerations (Dillon *et al.*, 1997) suggest that it is the flux of organic compounds to the sediment that should reflect lake water DOC variation. Therefore, the DOC concentration inferred this way would be biased by changing sediment accumulation rates. Second, chemometric inference models based on training sets return a single parameter (e.g. TOC, pH), which hinders evaluation of potential compound interfering factors present in the NIR spectra. An alternative and potentially better approach would be to use NIRS to estimate the sediment organic components directly and then express these as fluxes. Here we develop and apply an approach to interrogating NIR spectra to estimate the quantities of major sediment components (Russell *et al.*, 2019). The approach uses a suite of recent sediments sampled from UK-UWMN lakes and then applies multiple regression of the NIR spectra for the lake sediments with an end member library of known materials including minerals, biogenic silica, and various organic matter (OM) types including humin and humic acid compounds. The UK-UWMN lake sites, Loch Chon, Loch Grannoch, Scoat Tarn and Llyn Cwm Mynach (Figure 5.1), provide an ideal test case for assessing the performance of this NIRS end member multiple regression (EMS-MR) approach in identifying and quantifying the organic fractions preserved in lake sediment. They are ideal because the sediment inferred DOC record can be compared directly at these sites with surface water DOC measurements taken 1988 to 2016 (Figure 5.2).

Figure 5.1 Field Photographs Top row L to R Loch Chon, B) Loch Grannoch, Bottom row L to R C) Scot Tarn, D) Llyn Cwm Mynach -

Temperate upland and boreal lakes derive their carbon from allochthonous sources predominantly in the surrounding catchment (Cole *et al.*, 1994; Kissman *et al.*, 2017) and in smaller quantities from autochthonous in-lake productivity (Schindler *et al.*, 1992) . In lakes, OM is incorporated into the lake sediment, transported via outflows to ocean or evades the system to the atmosphere by mineralisation in the form of CO_2 and CH_4 release (Mulholland *et al.*, 1982). Despite inland waters accounting only for <1% of the Earth surface (Battin *et al.*, 2009), a substantial proportion of terrestrial carbon exported fluvially is returned to the atmosphere via within lake processing (Molot *et al.*, 1997), contributing significantly to the global carbon cycle with implications for past and future climate change. Dissolved humic substances are found to accumulate in lakes due to flocculation (Molot *et al.*, 1997; Porcal *et al.*, 2015), and by co-sedimentation with iron-oxide particles (Tipping, 1986). Both processes are affected by DOC concentration, pH and UV light penetration which falls with increasing DOC concentrations (Porcal *et al.*, 2009). Although DOC retention efficiency is greatest in clear lakes (Gao *et al.*, 1998), the effect on the DOC burial is outweighed by concentration effects such that dystrophic lakes highly enriched in DOC have the highest flux of catchment derived DOC to the sediments despite lower retention efficiency. The relative importance of export, burial or evasion determines whether lakes are net sinks or net sources of atmospheric carbon and govern the rate of carbon accumulation in sediments. Consequently, factors influencing these pathways need to be quantified reliably if lake contributions to global carbon are to be understood. Process models of how lakes deal with carbon provide a means for achieving this.

The proportion of flocculated OC buried in lake sediments rather than evaded is less well known. Several studies report the proportions buried or evaded to be approximately equal (Wachenfeldt *et al.*, 2008), while Tranvik *et al.*, (2009) estimated that evasion exceeds burial by a factor of two. A modelling study by (Hanson *et al.*, 2004), considering only burial of autochthonous particulate matter, concluded that the ratio of burial to evasion increased with lake trophic status. It is not clear whether this applies to flocculated allochthonous organic carbon. There is, however, general agreement from both field observation (Dillon *et al.*, 1997; Wachenfeldt *et al.*, 2008) and modelling studies (Hanson *et al.*, 2004; Cole *et al.*, 2007; Tipping *et al.*, 2016) that most lakes are net heterotrophic, with OC burial plus sediment CO_2 evasion exceeding in-lake net primary productivity (NPP). This is certainly the case for the boreal and cool-temperate lakes subject to both acidification and brownification, such that lake sediment C burial reflects predominantly allochthonous rather than autochthonous supply (Wachenfeldt et al., 2008; Tipping et al., 2016). It follows that with development of appropriate methods, lake sediment profiles from lakes of this type should provide a record of allochthonous DOC supply.

The aim here is to quantify sediment burial fluxes and infer aqueous DOC concentration over the past 300 years at four UK Upland Water Monitoring Network lakes. Reconstruction of DOC trends over this length of time has the potential to provide new insight into the longer term variability of carbon dynamics in these acid vulnerable upland areas. The objectives are:

- To apply our EMS-MR method to FT-NIRS data for multiple sediment cores from four UKUWMN lakes, selected to encompass a variety of trends in monitored DOC, to reconstruct variations in concentration for a series of known organic and inorganic end-member materials.
- To develop age-depth models for the sediment profiles using stable airfall Pb and ^{210}Pb radiometric dating to calculate sediment burial fluxes for mineral matter, biogenic silica and organic components including humic compounds, our proxy for DOC in the sediment.
- To estimate past patterns in aqueous DOC concentrations using the sedimentary DOC fluxes using a simple process model that takes account of the main factors affecting DOC in boreal lake systems.
- To corroborate our approach and the records of past surface water DOC concentration derived from sediments by comparison with monitored DOC data collected for the UK-UWMN lakes 1988-2016.
- To explore the influence of the contended drivers of upland water brownification using our 300 year palaeo-records of aqueous DOC concentrations for these four upland temperate lakes.

5.3 METHODS

5.3.1 SITE DESCRIPTION AND FIELD SAMPLING

At Loch Chon, Loch Grannoch, Scoat Tarn and Llyn Cwm Mynach sediment cores were collected that extend from the sediment water interface back to CE 1700. Robust age-depth models have been generated using stable Pb pollution records that have chronologies secured using ^{210}Pb and ^{137}Cs radiometric dating. Measured total Pb concentrations in the sediments at each site are derived entirely from the air-fall deposition from regional Pb pollution (Renberg *et al.*, 2001; Yang *et al.*, 2018) and provide a basis for transfer of those radiometric age-depth models to undated cores. Parallel quantification of sediment components by NIRS, TCN analyses and XRF geochemistry is used to characterise down core patterns of changing sediment composition. This multi-method approach serves to corroborate signals between independent techniques and to provide additional palaeoenvironmental information on factors such as lake productivity and catchment erosion. Comparing the temporal patterns of sedimentary organic matter (OM) and monitored DOC with possible drivers provides an independent basis for exploring the factors driving fluctuations in the DOC flux from catchments to lake basins.

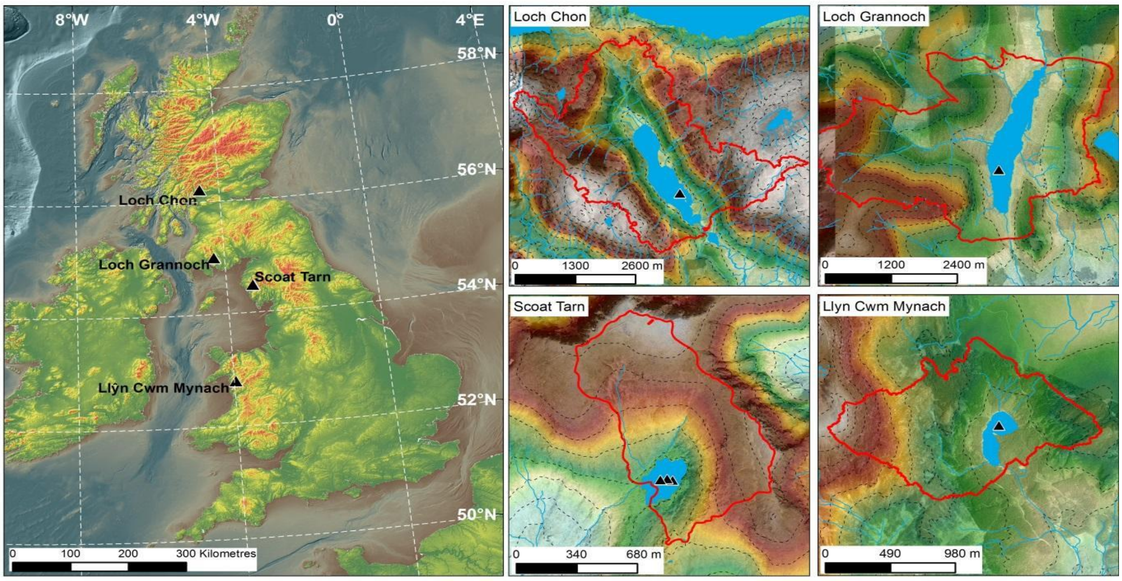


Figure 5.2 Location of the UK-UWMN lake sites, Loch Chon, Loch Grannoch, Scoat Tarn and Llyn Cwm Mynach

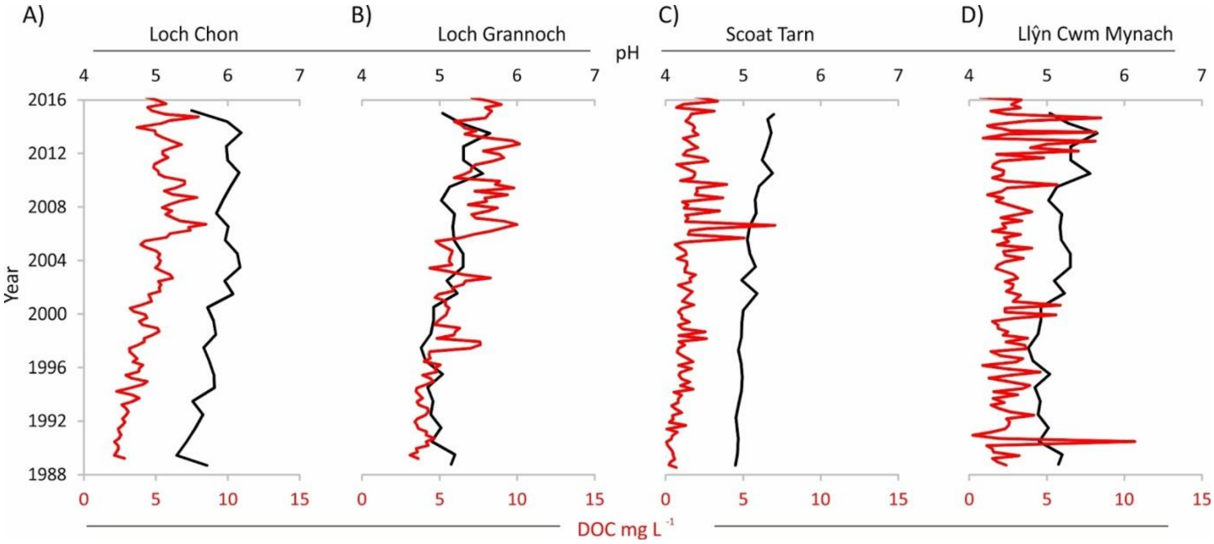


Figure 5.3 Monitored pH and DOC concentrations (mg l^{-1}) at A) Loch Chon B) Loch Grannoch C) Scoat Tarn D) Llyn Cwm Mynach.

The four study lakes are in acid sensitive locations on base poor soils and geology, and form a south-to-north gradient of declining acid deposition. The sites include both forested and not forested locations (see Table 5.1) that cover a range of DOC concentrations and fluxes. Between 1988 and 2016 chemical and biological measurements were taken at annual and quarterly intervals including DOC concentration, pH and diatom species. For the monitoring methods see Monteith and Evans

(2005). All four lakes have an oligotrophic macrophyte flora (e.g. *Subularia aquatica*, *Littorella uniflora*, *Isoetes lacustris*, *Nymphaea alba, Eleogiton fluitans* and *Nardia compressa*) with varying degrees of acid tolerance (Kernan *et al.*, 2010). Loch Grannoch represents oligotrophic-dystrophic sites with relatively high DOC and the highest total P of the four lakes, and where DOC increased steadily during the monitoring period. Loch Chon represents oligotrophic sites where DOC has been relatively high and increased steadily during the monitoring period. Scoat Tarn and Llyn Cwm Mynach represent oligotrophic sites with lower concentrations DOC, but with an increasing DOC trend observed at Scoat Tarn and no trend at Llyn Cwm Mynach (Figure 5.1 and Figure 5.2). DOC for the periods 1992-2011 and 2016-17 are 6.1 and 9.9 at Loch Grannoch, 4.9 and 5.1 at Loch Chon, 1.6 and 1.4 at Scoat Tarn, 2.6 and 4.3 at Llyn Cwm Mynach.

Combinations of multiple gravity (Boyle, 1995) and Russian-style sediment cores were taken from each of the four lakes providing materials spanning an intact water-sediment interface extending from the present to >300 years ago. At Loch Grannoch, Loch Chon and Llyn Cwm Mynach cores were taken from the deepest part of the lake. At Scoat Tarn the cores were taken along a lake-edge to centre transect. At Loch Grannoch and Loch Chon cores were sliced at 2.5 mm intervals for the upper 30 mm and at 5-10 mm for the remaining materials. At Llyn Cwm Mynach cores were sliced at 2.5 mm for the upper 20 mm, and 5 mm for the remainder. At Scoat Tarn cores were sliced at 5 mm intervals throughout. Samples were stored in sealed plastic bags, frozen and then freeze-dried collecting dry mass and water content data for the calculation of dry mass fluxes.

Table 5.1 Lake catchment characteristics (data from Kernan et al. 2010)

Site	Altitude Range	Geology	Soil	Catchment Area (ha)	Forest Area (%)	Lake Area (ha)	Max depth (m)	C:L
Loch Chon	100-600	Cambrian schist, grits	Podzol, gley	1470	56	100	25	15:1
Loch Grannoch	210-601	Granite	Gley, podzol, peat	1290	70	114	21	11:1
Scoat Tarn	602-841	Volcanic sediments	Peaty ranker	95		5	20	19:1
Llyn Cwm Mynach	285-680	Cambrian sedimentary	Rankers, peat	152	55	6	11	25:1

Table 5.2 Core location information

Site	Core ID	Locations	Water depths (m)	Sampled
Loch Chon	LC13GC1 LC13GC2 LC13GC3	All cores at 56.2106°N 4.5425°W	12.5	May 2013

Loch Grannoch	LG13GC1	All cores at 54.9969°N 4.2844°W	15.7	May 2013
	LG13GC1			
	LG13GC1			
	LG2016GC1	54.9967°N 4.2841°W	15.6	October 2016
Scoat Tarn	SCO14GC1	54.4816°N 3.2982°W	16	August 2014
	SCO14GC2	54.4817°N 3.2986°W	10.9	
	SCO14GC3	54.4816°N 3.2993°W	7	
Llyn Cwm Mynach	MYN15GC1	All cores at 52.7984°N 3.9609°W	6.15	July 2015
	MYN15GC2			
	MYN15GC2			

5.3.2 ELEMENT CHEMISTRY BY XRF

Major element and trace metal concentrations were determined for all samples on a dry mass specific basis by ED-XRF, using a Bruker S2 Ranger for Loch Chon and Loch Grannoch, and Spectro XEPOS 3 for Scoat Tarn and Llyn Cwm Mynach. The samples were hand pressed and measured under a He atmosphere under combined Pd and Co excitation radiation and using a high resolution, low spectral interference silicon drift detector. The XRF analysers both underwent a daily standardisation procedures and had accuracies verified using 18 certified reference materials (Boyle et al., 2015). The ‘normative’ concentrations were derived using standard element oxides measured by XRF and the composition of typical constituent minerals (Garrels *et al.*, 1971; Boyle, 2001). The major elements were recalculated as oxides (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, TiO_2, MnO_2, P_2O_5), and together with loss-on-ignition normalised to unity. SiO_2 measured by XRF is the sum of (i) biogenic silica, (ii) the SiO_2 in silicate minerals and (iii) Quartz. Normative biogenic silica (i) we calculate as XRF measured SiO_2 minus (ii) quartz and (iii) SiO_2 associated with silicate minerals. Quartz (ii) was not measured directly but calculated from TiO_2 using the average 30:1 ratio for “free” SiO_2 (total measured SiO_2 minus silicate associated SiO_2) to TiO_2 in deglacial sediments containing negligible biogenic silica. Chlorite, albite, orthoclase, and anorthite are considered to be the sole sources of MgO, Na_2O, K_2O and CaO, respectively, and so the silica/oxide ratios from Deer et al. (1966) can be used to estimate the (iii) SiO_2 associated with silicate minerals. Our calculated normative mineral matter is the sum of the oxides (Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, TiO_2, MnO_2, P_2O_5), silicate mineral SiO_2 (iii) and quartz (ii). Full details on these calculations are given in Boyle (2001) and Russell et al. (2019).

5.3.3 CHRONOLOGY

Radiometric dating was undertaken for Loch Chon (core LC13-SC2) using ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am records measured by direct gamma assay at University College London using a Canberra SAGe well-type coaxial low-background intrinsic germanium detector. Radiometric dating at Llyn Cwm Mynach had previously been measured at University College London using the same isotopes, instruments, and procedures. The ^{210}Pb was determined via its gamma emissions at 46.5 keV, and ^{226}Ra by the 295 keV and 352 keV γ -rays emitted by its daughter radionuclide ^{210}Pb following three weeks storage in sealed containers to allow radioactive equilibration. ^{137}Cs and ^{241}Am concentrations were estimated by their emissions at 662 keV and 59.5 keV, respectively. The absolute efficiencies of the detectors were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of within sample self-absorption of low-energy γ -rays. Supported ^{210}Pb activity was assumed to be equal to the measured ^{226}Ra activity, and unsupported ^{210}Pb activity calculated by subtracting supported ^{210}Pb from the measured total ^{210}Pb activity. In core LC13-SC2 ^{210}Pb activity reached equilibrium at 14 cm (Figure 5.4). A chronology was developed using the CRS (constant rate of supply) model (Appleby *et al.*, 1978), adjusted to place 5.5 cm peaks in ^{241}Am and ^{137}Cs at 1963. The deepest dated interval is 13-14 cm, with an age of 1834 (± 41 years). With a relatively constant CRS mass accumulation rate beneath this depth, ages were speculatively projected to 1700 for illustration purpose.

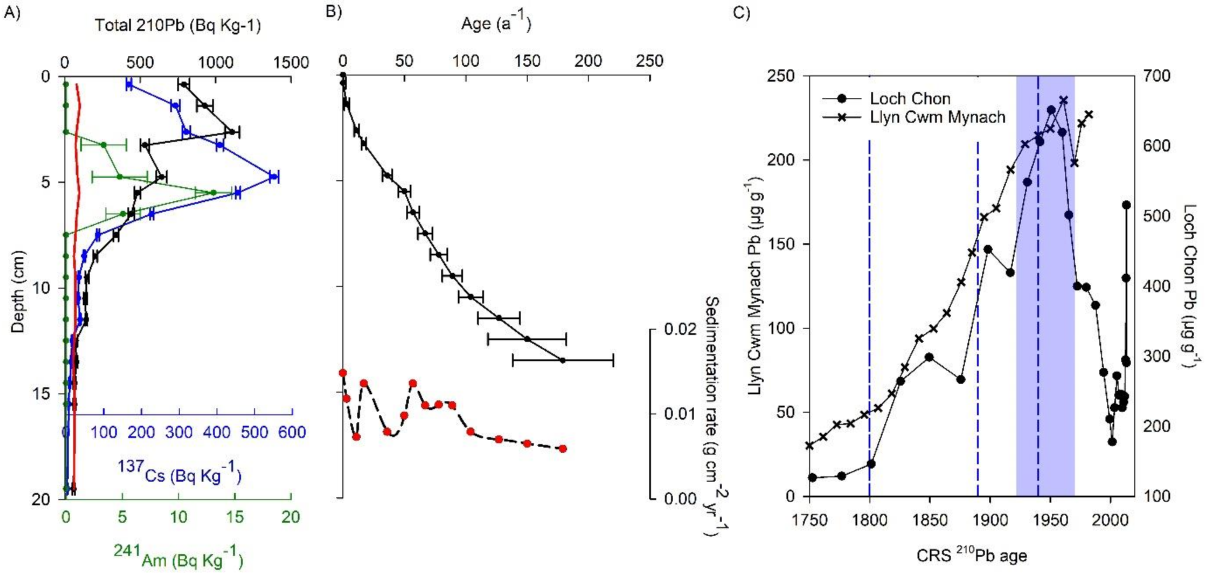


Figure 5.4 Radiometric chronology of core LC13-SC2 taken from Loch Chon. A) Fallout radionuclide concentrations in core LCSC2 taken from Loch Chon, showing total ^{210}Pb (black), unsupported ^{210}Pb (red), and ^{137}Cs (blue) and ^{241}Am (green) concentrations versus depth. B) the CRS model ^{210}Pb dates and sedimentation rates. C) Dated Pb profiles for LC13-SC2 and MYN1, (published data, Kreiser et al., 1987). The blue rectangle marks the central part of the Pb peak, centred on 1945. Two additional lines for the base of Pb peak (1800) and 50% of Pb increase (1880) are also shown.

Geochemistry provided a basis for the correlation between cores to derive sediment age-depth models. The total Pb concentration in the sediments has been measured by XRF for all the new cores to facilitate correlation of the ^{210}Pb geochronology to the new cores, with total Pb providing a record solely of atmospheric deposition at these sites (Yang *et al.*, 2018) making it suitable for core correlation. Three marker depths for Pb have been identified as sufficiently reproducible for this purpose (Figure 5.4C) which, together with an erosion event marker at Loch Grannoch (Figure 5.4), form the basis for a robust chronology. Depths in each core of the markers are shown in Table 5.3 with the chronological models illustrated using the stable Pb pollution record in the sediments (Figure 5.4). This shows the high degree of consistency in the airfall Pb profiles across cores at each site, and also between sites.

For sediment core intervals between age markers (defined by ^{210}Pb markers), the mean sediment dry density (determined from measured water contents) can be used to calculate sediment mass accumulation rates (Figure 5.4B). Smoothing via simple polynomials is applied to remove the steps in the accumulation rate signal, which are artefacts arising from the low temporal resolution of the chronology. Such smoothed profiles provide the best available estimate of temporal variation in mass accumulation rate.

The sediment accumulation rates were relatively constant at Scoat Tarn and Loch Chon, but fall in the late the 20th century at Llyn Cwm Mynach , and at Loch Grannoch show elevated rates in the mid-20th century (Figure 5.4B), with a particularly abrupt erosion event associated with catchment ploughing in preparation for forest planting between 1961 and 1976 (Battarbee *et al.*, 1985). Limited commercial planting of forest took place at Loch Chon (1950s) and Llyn Cwm Mynach (late 1950s), however, there does not appear to have been a significant response in the sediment record (Battarbee *et al.*, 1985).

Calculation of sediment yields would be based ideally on the averaging of many randomly located sediment cores. However, an alternative where relatively few cores are available is to apply a correction for local sediment focussing (Boyle et al., 2015) based on the conceptual lake sedimentation model of Håkanson, (2003). This uses a correction factor equal to mean lake water depth divided by depth at the coring site. This was performed using the core site depths shown in Table 2, and using mean lake water depths of 6m, 8.8m, 3.7m and 6.7m for Loch Grannoch, Loch Chon, Scoat Tarn and Llyn Cwm Mynach, respectively.

Table 5.3 Depth in centimetres for each core of markers in the Pb profile. In the case of the Loch Grannoch Russian core, two further Pb marker depth were used for the Medieval (1000 CE) and Roman (0 CE) Pb enrichment described by (Renberg *et al.*, 2001). Additional ages were used at Loch Grannoch based on an episode of erosion related to afforestation in the period 1961 to 1976 (depth in cm 12-18, 10-20, 9-15 for the three cores)

	Age of top	Centre of Pb peak	50% of Pb rise	Base of Pb peak
LG13-SC1	2013.4	26	38	-
LG13-SC2	2013.4	27	47	-
LG13-SC3	2013.4	23	36	-
LC13-SC1	2013.4	7.5	11	16.5
LC13-SC3	2013.4	7.5	10.5	15
SCO14-SC1	2014.5	7	12.5	21.5
SCO14-SC2	2014.5	3	6	9.5
SCO14-SC3	2014.5	3.5	5	9.5
MYN15-SC1	2015.5	6	12	17
MYN15-SC2	2015.5	7	14	25
MYN15-SC3	2015.5	8	18	-

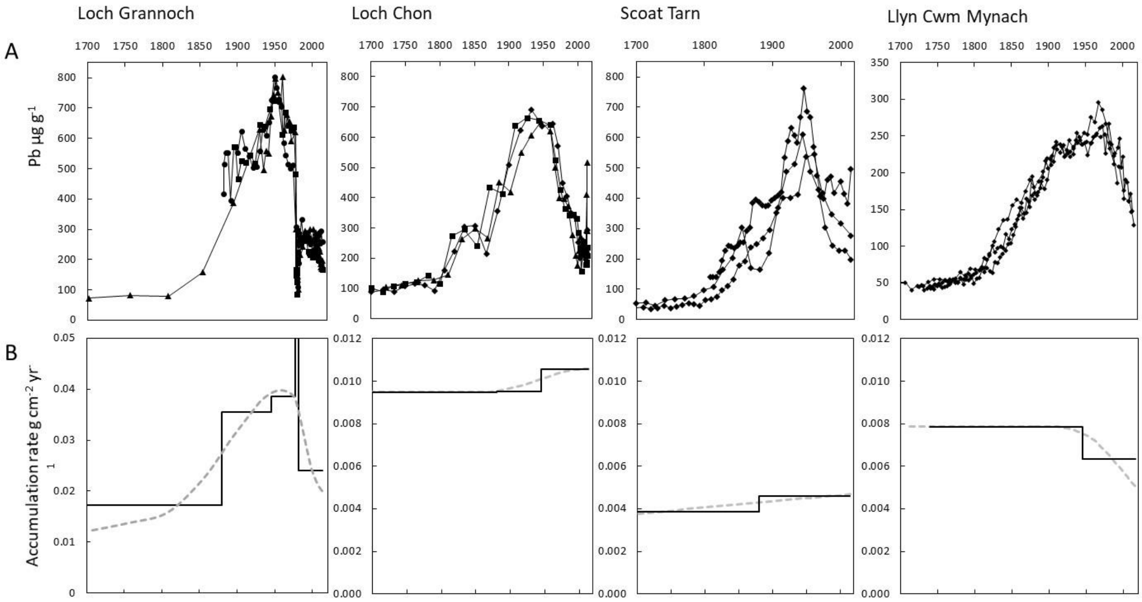


Figure 5.5 A) Age profiles for Pb concentrations, illustrating consistency within and between sites. B) Mass accumulation rates across dated interval, and smoothed values. The sharp spike in accumulation rate at Loch Grannoch is interpreted as an isolated erosion event and is disregarded in the general smoothed age-depth model

5.3.4 MODEL OF LAKE WATER DOC PROCESSING

A quantitative model for lake processing of DOC, allowing for both photolytic decomposition and settling to the lake bed, provides a means of calculating the lake water DOC concentration from the sediment burial flux. Here we apply a simple process model developed by Dillon and Molot (1997) for lakes in Canada, an approach utilising very well established principles for modelling of phosphorus retention by lakes (Vollenweider, 1975), whereby an apparent settling velocity of P within the lake competes with lake discharge for removal of P from the lake water body. Quantifying DOC input and output budgets for six small lakes in Ontario, Dillon and Molot (1997) modified the Vollenweider model to predict the amount of inflowing DOC that is retained in the lakes, representing lake capture of DOC due to burial and photolytic degradation as an apparent settling velocity. The model is in the form of a mass balance of DOC influx from the catchment with combined settling/degradation and discharge (Equation 5.2).

$$\mathrm{DOC_{in}} \times q_{\mathrm{S,in}} = \mathrm{DOC_{lake}} \times v + \mathrm{DOC_{lake}} \times q_{\mathrm{S,out}}$$

Equation 5.1

where, $\mathrm{DOC_{in}}$ and $\mathrm{DOC_{lake}}$ (g $\mathrm{m^{-3}}$) are concentrations of DOC, and $q_{\mathrm{S,in}}$ and $q_{\mathrm{S,out}}$ (m $\mathrm{yr^{-1}}$) are water loadings, for inflowing and lake water, respectively, and v is the apparent DOC settling velocity (m $\mathrm{yr^{-}}$

^{1}). The water loadings are normalised to lake area following the approach of Vollenweider 1975 (the unit of $m^3\ m^{-2}\ yr^{-1}$ simplifying to $m\ yr^{-1}$).

The apparent DOC settling velocity v ($m\ yr^{-1}$) includes both degradation and settling/burial of DOC, and there is no direct way to estimate the proportion of uptake by the lake that is actually buried in the sediment. Dillon and Molot (1997) concluded that on average half of the DOC supplied to their lakes is buried, with variable though similar proportions discussed by Tranvik et al. (2009) for a variety of lake types. Inserting this value into the second term of Equation 5.1 the average DOC burial rate ($gC\ m^{-2}\ yr^{-1}$) is given by ½ × v × DOC_{Lake}, where DOC_{Lake} is the concentration of DOC in the lake water ($g\ m^{-3}$). The lake water DOC concentration is therefore given by Equation 5.2.

$$DOC_{lake} = 2 \times OM_{MAR}/v$$

Equation 5.2

where OM_{MAR} is the lake wide average sedimentation rate of total organic matter, or some fraction of it (in $g\ m^{-2}\ yr^{-1}$).

The only adjustable parameter in this model is v. For the UK-UWMN lakes a value of 4 $m\ yr^{-1}$ for v gives good agreement between the long-term averages of sediment inferred and monitored aqueous DOC for all four lakes. The validity of this modelling approach is supported by the close similarity between our parameterised value for v and that found by Dillon and Molot (1997) for their lakes ($v = 3.2 \pm 0.7\ m\ yr^{-1}$), despite the rather different environmental setting in Ontario with lower effective precipitation and substantially higher net solar radiation intensity.

5.3.5 NEAR INFRARED SPECTROMETRY (NIRS) AND END MEMBER SPECTRA MULTIPLE REGRESSION (EMS-MR)

Fourier-Transform NIR spectra (FT-NIRS) were measured on a Bruker MPA FT-NIRS by diffuse reflectance using an integrating sphere on all the core samples and for our library of endmember materials (Table 5.4). All samples measured were homogenised by grinding in a mortar and lightly hand pressed. The NIR spectra are averaged from 64 scans collected at an 8 cm^{-1} interval across the range 3595-12500 cm^{-1}. The spectra generated are illustrated for the Loch Grannoch cores (Figure 5.6), where the cloud of sample 1st derivatives of the NIRS (Russell *et al.*, 2019) shows the compound nature of the NIR spectra for these sediments (Figure 5.6A). Contour plots of these NIRS 1st derivatives show the down-core patterns (LG1-3: (Figure 5.6B). Various peaks and troughs in part characterise the differing end member components (Figure 5.6C). For example, biogenic silica has a distinctive peak at 5250 cm^{-1} and within the signatures for organic materials there is some distinction between the humin (e.g. trough 4300 cm^{-1}) and the Suwannee River HA/FA (50:50 mix) (e.g. troughs at 4400 and 4900 cm^{-1}). However, such peaks have not proved useful for quantification (Russell *et* *al.*, 2019), and instead the whole spectrum contains information about all components that give rise to it. Rather than using the partial least squares (PLS) regression methods routinely applied conventionally to interrogate IR spectra, which require development of training set of samples accompanied by measured environmental parameters (Meyer-Jacob *et al.*, 2014; Pearson *et al.*, 2014), we have applied a new multiple regression end member approach (EMS-MR: Russell et al. 2019) to quantify sediment components. EMS-MR involves multiple regression of unknown sample NIR spectra (e.g., Figure 5.6A) onto NIR spectra for known end member materials (e.g., Figure 5.6C), a process that gives simultaneous quantification of major sediment components (Figure 5.6D). The advantages of the multiple regression method are that it uses a library of end member materials and NIR spectra, and it allows transparent assessment of the spectral interference between materials with similar NIR spectra. The EMS-MR approach has the further advantage of resting in theory rather than on chemometric statistical methods.

5.3.6 SELECTION OF NIRS END MEMBER MATERIALS

At the outset we had no expectation that a single combination of end member materials would fit and quantify the composition of sediment in these lakes, as the sites have differing bedrock, soils and vegetation cover, and silicate minerals have widely differing NIRS spectra (Russell *et al.*, 2019). Consequently, our approach involved critical testing of end member combinations, starting with a tailored choice of local bedrock minerals. Fitting performance, described in detail by Russell et al. (2019), is based on 1) high R^2 of multiple regression, 2) minimal negative coefficients, and 3) broad agreement of totals with independent measures. Geochemistry was used for the production of normative calculations to verify the NIRS quantifications of mineral and biogenic silica end members, with total organic matter calculated from loss-on-ignition data (LOI). Biogenic silica was fitted at all sites using a marine diatom NIR spectra for a sample that had been cleaned with a H_2O_2 digest to remove organic matter (Table 5.4). For Loch Grannoch and Llyn Cwm Mynach minerogenic late glacial sediments have been used to represent the mineral end member in the lake sediments. At Scoat Tarn and Loch Chon, where no late glacial sediments were recovered, either finely ground local bedrock, or materials similar to the catchment bedrock were used as the mineral end member (Table 5.4).

Selecting end member materials to represent the organic components used the same fitting performance criteria, and was also guided by a logical choice of materials. DOC is made up predominantly of humic and fulvic acids (HA and FA respectively), with minor contributions from carbohydrates and lignin We assume therefore, that HA and FA flocculated from the lake water comprise a measurable fraction of the lake sediment, that these dominate the HA and FA content of the sediment, and can be distinguished by NIRS from one or more additional organic matter end members also present that are not derived from DOC. To quantify these fractions, we use IHSS (International Humic Substances Society) Fulvic Acid standard III and Humic Acid standard III from

Suwannee River (https://ihss.humicsubstances.org/index.html) to represent HA and FA. To achieve analytical discrimination of HA and FA from other organic components of the sediment we tested a library of other plant tissues and decomposed plant–derived organic substances. This included a range of organic compounds including fulvic (alkali and acid soluble) and humic (alkali soluble acid insoluble) acid fractions extracted from various UK peatlands and from DOC rich waters from UK rivers, and humin (the acid and alkali insoluble material from peat samples)

Applying EMS-MR while using both FA and HA as end members yielded unstable results (with excessively high and low regression coefficients) owing to high degree of similarity between the NIR spectra for these two materials (Russell *et al.*, 2019). On the basis that the sediment fraction derived from lake water DOC comprises both HA and FA (Hope *et al.*, 1994), we created a composite HA/FA end member material (50:50 mixture, wt% of dry sediment) to represent this fraction, referred to as DOC_{NIRS}.

Experimentation with combinations of organic matter fractions found that significantly improved fits were obtained when an additional component was included. Best fitting performance (high R^2 of multiple regression) across the fitted end members, and comparison of the sum of fitted organic matter fraction with total organic matter (LOI), was used to find the best combination of organic materials. In general, fresh organic matter materials such as plant leaves and algae gave poor fits, while good fits were obtained with humin. The end member choices are detailed on a site-by-site basis in Table 5.4

After quantification of the sediment fractions, the HA/FA sediment concentration (wt%) was then used to calculate the lake water DOC concentration (DOC_{NIRS} mg l^{-1}) using Equation 5.2 and the sediment mass accumulation rate.

Table 5.4 End member selections for each lake for the target sediment components: mineral matter, biogenic silica, DOC and other organic matter.

End member - purpose	Loch Chon	Loch Grannoch	Scoat Tarn	Llyn Cwm Mynach
Biogenic silica – (algal silicates)	Marine diatom			
Mineral matter (total mineral content)	Norwegian Schist and chlorite	Loch Grannoch late glacial muds	Volcanic tuffs: Borrowdale series	Llyn Cwm Mynach late glacial muds

DOC (humic / fulvic acids)	IHSS Suwannee River Humic/Fulvic Acid Standards III (50:50 ratio) (referred to as $\mathrm{DOC_{NIRS}}$)			
Insoluble organic matter	OMMHumin (humin - May Moss)	Humin401 (humin - Holcroft Moss)	OMMHumin (humin - May Moss)	OMMHumin (humin - May Moss)

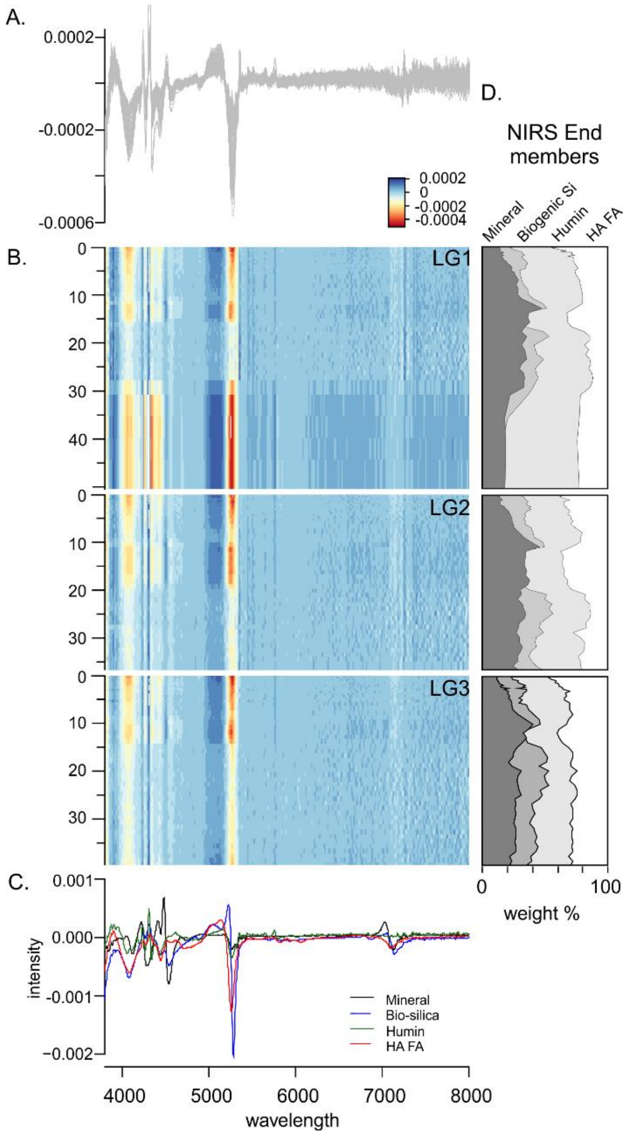


Figure 5.6 NIRS data for the Loch Grannoch cores. A) A cloud of 1st derivatives for all sample NIRS for the cores. B) Contour plots of NIRS 1st derivatives showing the down core stratigraphy. C) Best-fit end member NIRS 1st derivatives that were used to interrogate the Loch Grannoch sediments (Table 5.4). D) Relative proportions of the four end members (mineral, biogenic silica, humin and Ha/FA spectra) for the Loch Grannoch cores.

5.3.7 CARBON AND NITROGEN MEASUREMENT

Total carbon (TC) and total nitrogen (TN) contents were measured in duplicate (deviation in values was < 10% of the mean) using a Thermo Scientific Flash Smart Elemental Analyser. Total organic carbon (TOC) was determined after acid vapour (HCl) digestion of the carbonate fraction (Yamamuro *et al.*, 1995). The ratio of total organic carbon to total nitrogen (TOC= TN) is given as the molar ratio. C:N ratios provide information on the origin of the organic components, with algal and organic matter produced in the lake having lower C:N ratios than terrestrial vascular plants. The TOC sediment concentrations provide a basis for calculating an independent estimate of total organic matter (TOM), which should match the sum of the organic end members identified in the EMS-MR analysis of NIR spectra. The C:N ratio can also show shifts in sediment sources and rates of supply (Meyers, 1994).

5.4 RESULTS

5.4.1 TESTING OF THE END MEMBER RECONSTRUCTIONS

At each lake we selected a single master profile (LC13-SC3 at Chon, LG13-SC1 at Grannoch, Scoat14-GC3, and MYN14-GC-2) based on the optimum combination of resolution and record length. These profiles form the basis for testing the performance of the NIRS end member reconstructions against independent but equivalent palaeoenvironmental data (Figure 5.7). Biogenic silica and mineral matter end member proportions were compared with 'normative' concentrations derived independently from the XRF data. Parallel estimates of total organic matter based on both TCN analysis (OM-C %) and loss-on-ignition (OM-LOI %) provided the basis for testing the sum of our organic NIRS end members (HA/FA and humin fractions). For these sites the OM-C and OM-LOI measurements produced highly similar down core profiles, and they strongly resemble the sum of NIRS organic end members (Figure 5.7). At Loch Chon, Loch Grannoch and to a lesser extent at Scoat Tarn, there is some interference between the end member materials for silicate minerals and for biogenic silica. This can result in an under or overestimation of the mineral end member concentration, with the reverse occurring for biogenic silica. Russell et al. (2019) conducted sensitivity analyses to show that in varying the choice of mineral end member material the reconstruction of organic end members is largely unaffected and trends in mineral end members are captured regardless of end member choice. Similarity between concentrations quantified by NIRS and XRF based normative calculations improves when comparing the totals for mineral and biogenic silica, thus the NIRS performs particularly well in distinguishing OM from mineral materials. For the master core profiles selected at each lake the NIRS end member proportions display a strong match to the normative calculations for total mineral matter, biogenic and organic content (Figure 5.7).

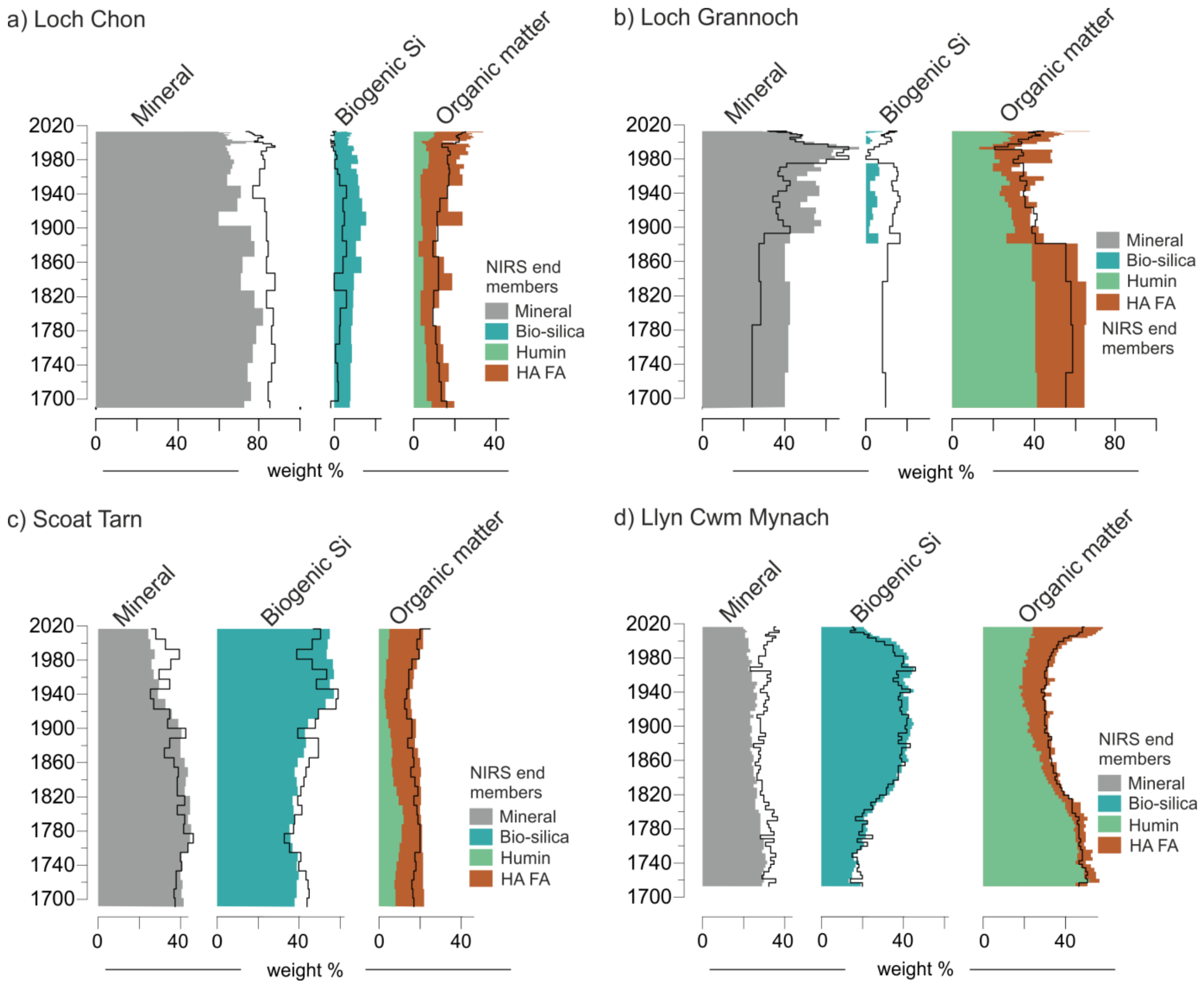


Figure 5.7 Sediment composition reconstructed using the NIRS EMS-MR (block colours) compared with independent estimates for Biogenic Silica and Mineral produced by normative calculations and using LOI (%) for organic matter (black line) for a) Loch Chon b) Loch Grannoch c) Scoat Tarn and d) Llyn Cwm Mynach.

5.4.2 REPEATABILITY OF END MEMBER RECONSTRUCTIONS

Sediment component concentrations measured by EMS-MR for all cores at all sites (Figure 5.8) show particularly good agreement for three sites where cores were collected in close proximity. Greater differences occur at Scoat Tarn where the cores progressed from littoral to profundal waters to assess within lake variability in the sediment record including the effects of sediment focusing in the lake. Here, the two shallower cores (Cores 2-3) have slower accumulation rates, and thus cover longer time periods. Scoat Tarn core 1 has a higher mineral content relative to biogenic silica, which probably reflects the focusing of allochthonous mineral matter towards the lake centre. However, the end member profiles for the organic components at Scoat Tarn are very similar in all three cores.

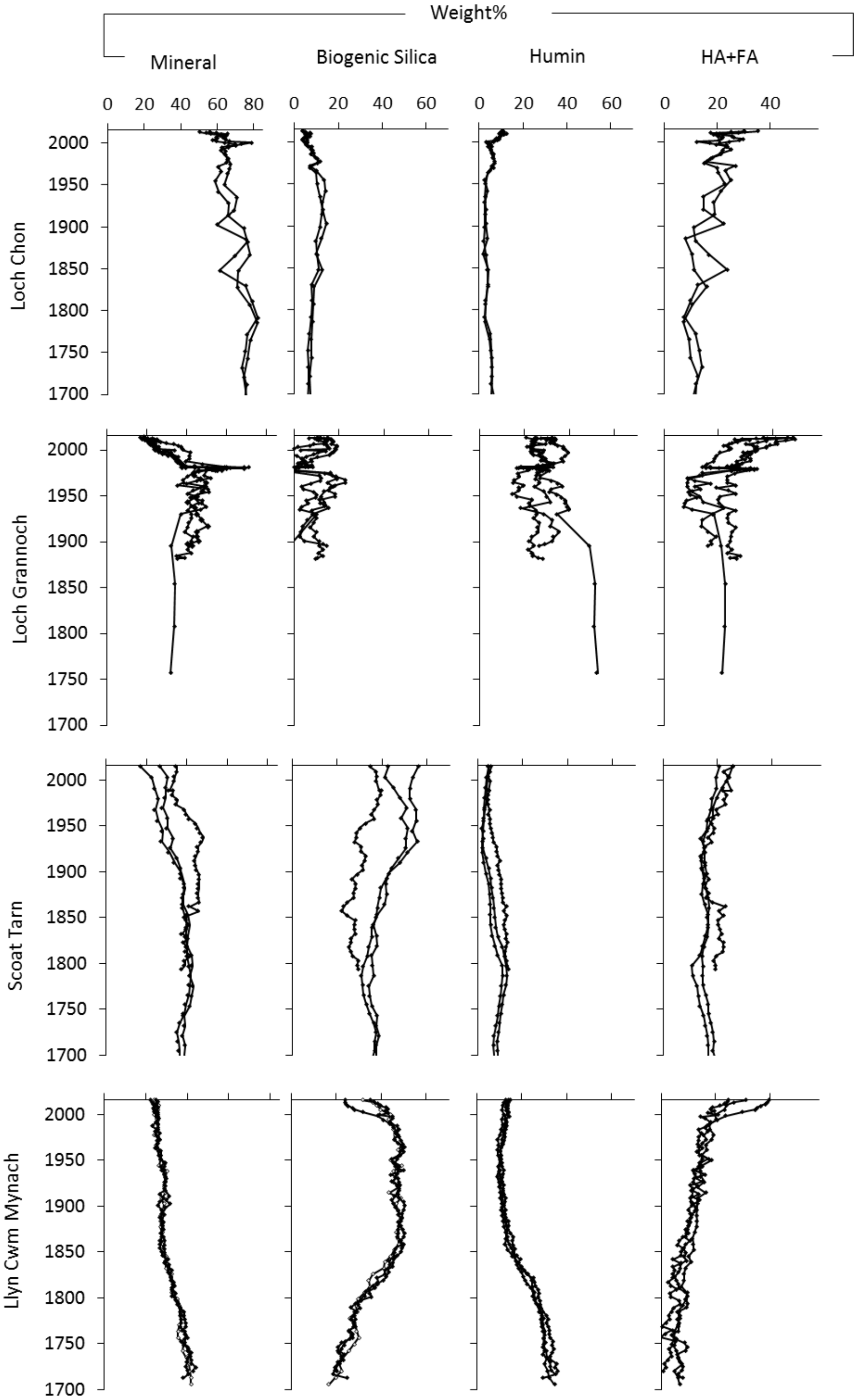

Weight%
Mineral
Biogenic Silica
Humin
HA+FA
0
20
40
60
80
0
20
40
60
0
20
40
60
0
20
40
2000
1950
1900
1850
1800
1750
1700
Loch Chon
Loch Grannoch
Scoat Tarn
Llyn Cwm Mynach

Figure 5.8 NIRS multiple regression fitted concentrations (wt%) for sediment components for all the cores recovered at the four lakes. See Table 5.4 for detail on specific end member combinations used at each site

All four sites show an increase in HA/FA (Figure 5.8) over the last century or two. Loch Chon is the most mineral rich of the lakes but shows increasing HA/FA since 1900s. At Loch Grannoch, the mineral matter concentration increases in the mid nineteenth century and sharply 1940-1980s associated with commercial forestation of the catchment. However, since the 1980s there has been declining mineral concentration and increasing organic matter including HA/FA. NIRS inferred biogenic silica is more abundant at Scoat Tarn and Llyn Cwm Mynach. At Scoat Tarn from the early twentieth century mineral matter declines relative to biogenic silica. At Llyn Cwm Mynach mineral matter declines from 1800s with a sharp increase in biogenic silica which persists to the 1990s after which biogenic silica declines in parallel with an increase in HA/FA. There is high organic matter concentration at Llyn Cwm Mynach, but this is predominantly humin with HA/FA increasing from 1850s initially gently and then sharply from 1990s. At Scoat Tarn organic matter concentration is relatively low throughout but dominated by HA/FA showing increases from 1800 and again from 1950 to present.

5.4.3 COMPARING SEDIMENT INFERRED AND MONITORED LAKE WATER DOC

Our sediment inferred lake water DOC concentration, DOC_{NIRS}, calculated using the procedure described in section 5.3.4 with a lake capture velocity of 4 m yr^{-1}, is plotted against interpolated smoothed UK-UWMN monitoring data (Figure 5.9). The value for the lake capture velocity was chosen to give DOC_{NIRS} values of comparable magnitude to the DOC_{monit} value, so the good average agreement shown in Figure 5.9 results from calibration. However, a single velocity value was applied to all four sites, so the good correlation (Figure 5.9: $r^2 = 0.78$) is not a result of data processing, instead reflecting the good agreement between the sediment records and the monitoring data. Furthermore, the optimised velocity lies within 1 standard deviation of the mean value observed by Dillon and Molot (1997).

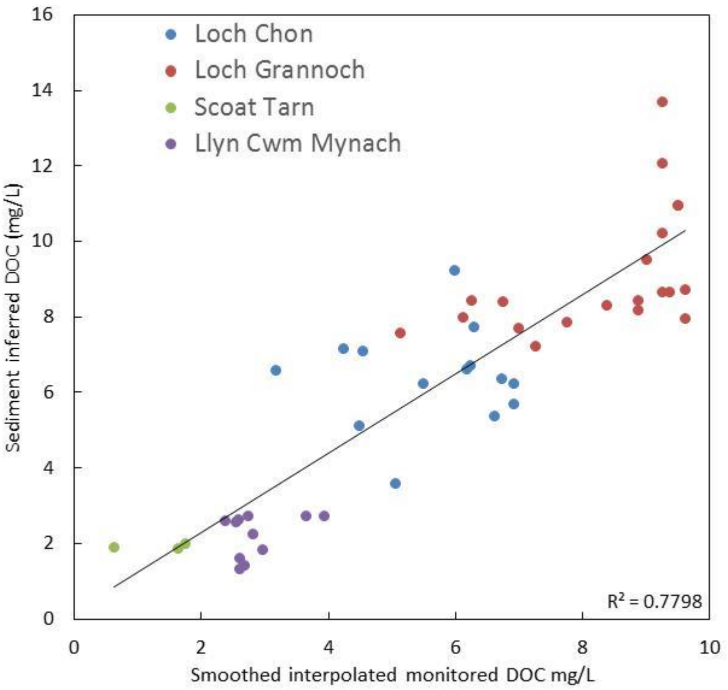


Figure 5.9 Sediment NIRS inferred lake water DOC concentrations (DOC_{NIRS}) compared to UK-UWMN monitored surface water monitored data (DOC_{Monit}). The linear regression line is shown.

5.4.4 ALLOCHTHONOUS AND AUTOCHTHONOUS FLUX OF DOC

To explore possible environmental controls over past changes in DOC_{NIRS} a number of quantitative environmental proxies were developed to reconstruct temporal patterns in catchment erosion, lake water acidity (Flower *et al.*, 1987; Kreiser *et al.*, 1987, 1990; Whitehead *et al.*, 1997), atmospheric sulphur deposition, and biological activity (Figure 5.10). At all four sites the sediment-inferred lake water DOC concentration (DOC_{NIRS}) shows fluctuations with an overall increasing trend from the nineteenth century that pre-dates the long-identified lake water acidification by 50 years (Evans *et al.*, 2005; Kernan *et al.*, 2010). So, although recent declines in DOC_{NIRS} since the mid-1990s follow the trend of decreasing acidity, the longer-term DOC_{NIRS} pattern shows no corresponding reduction associated with lake acidification. There is no consistent coupling between DOC_{NIRS} concentrations and lake acidification. There is a stronger association of DOC_{NIRS} and measures of atmospheric pollution (sediment Pb concentration and modelled S deposition), with the latter increased steadily from 1800 with a mid-20th century peak and DOC_{NIRS} climbing steadily throughout.

At Loch Chon and Loch Grannoch (Figure 5.10A and B) where DOC_{monit} and DOC_{NIRS} concentrations were highest there is good agreement between DOC_{NIRS} and C:N ratio, which consistent with an increasing autochthonous contribution to the organic matter. At Loch Grannoch (Figure 5.10B) increases in DOC_{NIRS} show no association with either the sharp increase in acidity in 1920s or to modelled atmospheric S deposition (which covary closely). However, rises in DOC_{NIRS} in the 1940s follow increases in Ti flux, suggesting greater terrestrial input to the lake including organic matter. This increase in erosion flux is probably associated with forestry activity in the catchment. The gently rising trends in DOC_{NIRS} at Scoat Tarn and Llyn Cwm Mynach (Figure 5.10C and D) show no similarity to lake water pH or to modelled atmospheric S deposition. Low Ti flux coupled with rising DOC_{NIRS} suggest that erosional terrestrial inputs are not a dominant source for the organic matter. This is supported by low C:N ratios which suggest increasing productivity at both sites. At Llyn Cwm Mynach (Figure 5.10D) broad similarities between biogenic silica and C:N are consistent and probably reflect changes in lake productivity.

In summary, across the four lakes there is no synchrony or correlation between patterns in surface water acidification and changes in the DOC_{NIRS} (Figure 5.10). The widely identified patterns in surface water acidification are closely related with known changes in sulphur dioxide deposition (Battarbee, Shilland, *et al.*, 2014), but this appears not to strongly associate, influence or be influenced by DOC_{NIRS}. None of the sites show increases in the delivery of fine-grained material from the catchment (low Zr/Rb) paralleling the increases in DOC_{NIRS}, however C:N ratios show a terrestrial catchment origin to the organic matter, particularly at Loch Chon and Loch Grannoch (Figure 5.10A and B) where measured DOC is highest. Sediment C:N ratios are often compared with trends in organic matter to help elucidate the origin of materials (Meyers, 1994). C:N ratios of 20 or above are held to indicate vascular plant material, while ratios lower than 10 or 6 are taken to represent aquatic plant or algal materials respectively (Meyers, 1994). All sites also show a recent sharp fall in C:N consistent with enrichment of the upper most sediment in plant tissues that have not yet degraded (Gälman *et al.*, 2008). However, this a short-lived diagenetic signal that is superimposed on longer underlying trends at all sites.

High C:N ratios occur at Loch Chon and Loch Grannoch, sites which have the highest DOC_{NIRS} concentrations (Figure 5.10A and B). In contrast, Scoat Tarn and Llyn Cwm Mynach (Figure 5.10C and D) manifest lower levels of DOC_{NIRS} in conjunction with lower C:N ratios. At Loch Chon and Loch Grannoch, the C:N ratios indicate predominantly terrestrial sourced materials. Declines in C:N ratio in the 1990s coupled with fluctuations in DOC_{NIRS} may indicate a reduction in amount of terrestrially derived materials. These changes occur in parallel with a falling Zr/Rb ratio indicative of fining, and likely reduction in catchment soil erosion. At both Scoat Tarn and Llyn Cwm Mynach, gradual increases in DOC_{NIRS} parallel declines in C:N ratio suggesting a change in source of organic material. In both cases there are similar patterns in the biogenic silica record (Figure 5.10 C and D), consistent with increasing aquatic productivity being the underlying cause of change. At Llyn Cwm Mynach, where the recent reduction in C:N ratio is strongest, a blanket of aquatic plants was observed across the lakebed at the time of coring. However, both sites also show falling grain size (as measured by the Zr/Rb ratio) in the most recent part of the record. Such fining can result in an increased proportion of inorganic N, which could affect the C:N ratio (Meyers, 1997). It is thus possible that the most recent changes in C:N relate to fining of the sediment rather than change organic matter source.

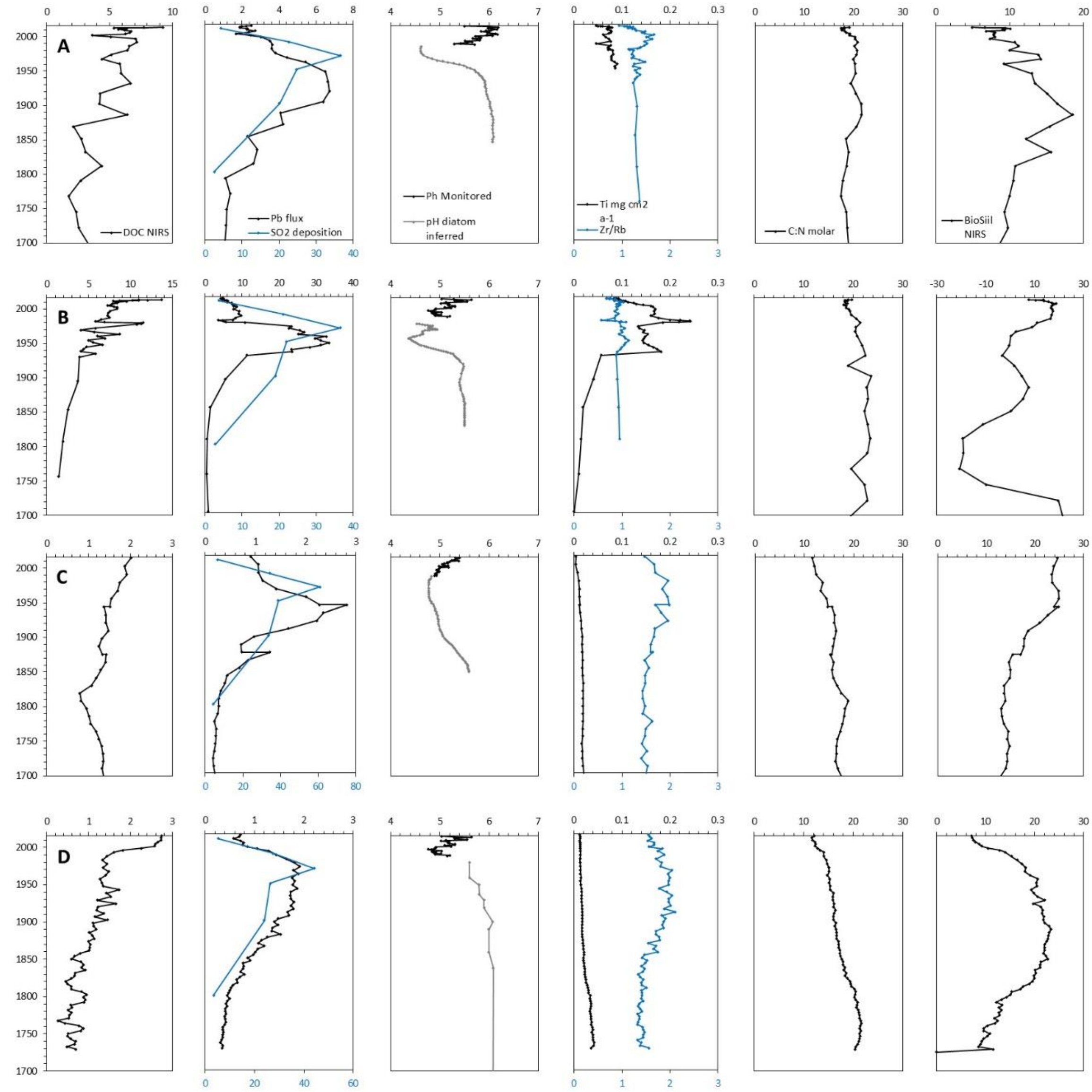


Figure 5.10 Sediment inferred DOC concentration (DOC_{NIRS}), modelled SO_2 deposition and Pb flux (Blue), pH (UK-UWMN monitored value in grey, and in black diatom inferred pH at A) Loch Grannoch ((Flower *et al.*, 1987), B) Loch Chon (Kreiser *et al.*, 1990), C) Scoat Tarn (Whitehead *et al.*, 1997) and D) Llyn Cwm Mynach (Kreiser et al. 1987), and sediment inferred biogenic silica.

5.5 DISCUSSION

NIRS and IRS using traditional partial least squares regression (Korsman *et al.*, 2001) methods have been shown to be capable of providing reconstructions of TOC and DOC (Cunningham *et al.*, 2011; Rouillard *et al.*, 2011). These empirical methods rely on data training sets, such that reconstructions are constrained by the type of lakes included the training sets and the environmental data available.

While satisfactory inference may be achieved, potential biases cannot be directly assessed, and it remains possible that collinear environmental variables will lead to spurious results (Juggins, 2013). For this reason, we adopted a wholly new approach, comprising three distinct steps. First, at each of the four sites in this study we applied a new method for quantifying the concentration of organic matter components in the sediment (Russell *et al.*, 2019). Using multiple regression of end member NIR spectra we determined the concentration (wt%) of humic and fulvic acids (HA/FA) using as spectral end member a 50:50 mix of IHSS Suwannee River fulvic and humic acid standards as representative of DOC. Second, we calculated the sediment burial flux record of HA/FA. Finally, we used the process model of Dillon and Molot (1997) to calculate the lake water DOC concentration consistent with the burial flux records. In this way we obtain an inferred sediment record of aqueous DOC (DOC_{NIRS}) that depends on mass balances rather than statistical inference models. Confidence in our inferred values is provided by comparison with the 1988-2016 UK-UWMN monitored values (DOC mg l^{-1}) smoothed appropriately to match the temporal resolution of our sediment record (r^2 =0.78). The four lakes can be arranged along a gradient in DOC concentration and supply flux, the highest DOC_{NIRS} being observed at the dystrophic site (Loch Grannoch) and lowest at the most oligotrophic lake (Scoat Tarn). This gradient in DOC concentration is reflected in the sediment composition at the sites, with Loch Grannoch receiving the highest amount of organic input derived terrestrially (interpreted from the C:N ratios), and Scoat Tarn and Llyn Cwm Mynach receiving the lowest amounts and also having lower concentrations of organic matter in the sediments.

Surface water brownification primarily reflects increased fluxes of OM, in particular the delivery of DOC alongside colloidal Fe, which enhances the brown colour of DOC (Köhler *et al.*, 2013; Weyhenmeyer *et al.*, 2014). A crucial question is whether the increases over recent decades can be expected to continue, and the answer depends on what processes are driving the changes. For example, it has been suggested that increases in precipitation as a result of climate change have been producing more terrestrially derived humic matter (Urrutia-Cordero *et al.*, 2017) and enhanced mobilisation of DOC from catchment soils (Sawicka *et al.*, 2016). If this is correct, then brownification of surface water can be projected to continue for the foreseeable future. On the other hand, there is a widely held view that surface water acidification from 1850 onwards was a precursor of brownification (Monteith *et al.*, 2007), with a period of reduced surface water DOC resulting from acidification, with current brownification being a response de-acidification following emissions reductions. UK-UWMN monitoring programme data are consistent with this theory, as measured DOC concentrations correlate with pH. At the four sites, diatom-inferred pH dating back to 1850 shows good correspondence with Pb fluxes and simulated SO_2 deposition data, showing that surface water acidity responds to atmospheric acid deposition. The pH of surface waters has recovered well with cleaner air and reductions in SO_2 deposition, and may have returned to pre-1850 levels (Battarbee, Shilland, *et al.*, 2014). If the correlation between pH and DOC observed in the monitored record holds for the longer record, then current DOC concentrations and fluxes should be like or at least approaching those experienced prior to acidification (1700-1850). Our DOC_{NIRS} records provide an estimate of DOC concentration pre-dating the onset of atmospheric acid deposition, allowing us to test this prediction. Our results show that DOC_{NIRS} has increased steadily through the period of historical acidification, and certainly has no interval of low concentration associated with peak acidity. Indeed, the onset of the DOC rise occurs before acidification at all sites and shows no response at all to the recent de-acidification. These findings are not consistent with a causal link between acidification and brownification, which require us to consider alternatives.

Comparison between C:N ratios and Ti flux reveals a significant positive correlation at three of the sites. Llyn Cwm Mynach and Scoat Tarn both show strong positive correlations of C:N with Ti flux (R^2 = 0.87 and 0.80 for the two sites, respectively). Loch Grannoch shows a significant positive correlation, once the erosion event associated with forestry is disregarded (R^2 = 0.33). At Loch Chon there is no correlation. A correlation of C:N with Ti flux is consistent with catchment soil erosion enhancing the supply of terrestrial organic matter. However, while the terrestrial organic matter signal increases with soil erosion, the DOC_{NIRS} does not. Thus, the decreasing Ti flux and C:N ratio in recent decades at each site occurs in parallel with increasing DOC_{NIRS}. Our interpretation is that enhancement of productivity whether in the catchment or lake, cannot be attributed to soil erosion and increases in productivity must be explained otherwise.

The close similarity between the DOC_{NIRS} and C:N profiles seen at Loch Chon and Loch Grannoch is consistent with a role for variations in terrestrial productivity within the lake catchment governing both. Thurman (1985) and Hood et al. (2005) both show that terrestrially derived aquatic humic and fulvic acids have widely varying C:N ratios depending upon the vegetation of the catchment. Increased terrestrial productivity leads to supply of humic substances with reduced C:N ratios (Heinz *et al.*, 2015). Thus, the falling C:N ratios seen at our sites are consistent with enhanced terrestrial productivity and increased terrestrial supply of aquatic DOC is also expected as a result of enhanced productivity. If NPP increases, whether in the soils or in the lake, are the primary control, and then other factors impacting primary production should also cause increases in lake water DOC concentration. This might include recent climatic warming, enhancing NPP at these upland environments which must be expected to show temperature limited productivity (Lieth, 1975). Additionally, enhanced P supply may play a role (Toberman *et al.*, 2015; Schillereff *et al.*, 2016) with both showing a significant role for atmospheric P in controlling enhanced NPP at ombrotrophic peatlands.

Upland management activities, including forestry and livestock and agricultural practices, may also contribute to surface water brownification. For example, enhanced terrestrial productivity causing increased DOC concentration is supported by (Kritzberg, 2017) who identified increased brownification of lakes in Sweden that pre-dates sulphur deposition, attributing this to alterations in land-use, in that case the transition to forestry. Other factors are harder to assess. For example, land use and burning regimes have been found to be the predominant forcing factors driving DOC flux from peat sites (Yallop *et al.*, 2010), something which is very difficult to evaluate at our lake sites. Likewise, climate is frequently cited as a driver of DOC flux yet is difficult to distinguish from other possible drivers such as land use change. Studies have suggested that increased precipitation may cause increased water levels and catchment soil hydration, in turn affecting run-off and water chemistry increasing delivery of humic substances (Hongve *et al.*, 2004; Erlandsson *et al.*, 2008; Lenard *et al.*, 2016). Given the trajectory of climate change and expected increases in both total precipitation and the frequency of extreme rainfall events, it is probable that DOC flux to surface waters will continue to increase over the coming decades. However, our DOC_{NIRS} records for temperate upland UK lakes display variations that are inconsistent with the longer-term patterns of climate change. There are no long-term trends in precipitation analogous to the steady rise we observe in DOC_{NIRS}, and while there are trends in temperature, these start far later than the initial rise in DOC_{NIRS}. On the other hand, given there is considerable covariation of environmental factors in the last two decades, and role for recent rapid climate change cannot be ruled out.

5.6 CONCLUSIONS

Integrating the use of novel end member multiple regression of NIR spectra to determine the sediment burial flux record with a process model (Dillon *et al.*, 1997), we have calculated time series of lake water DOC concentration from sediment that are consistent with the burial flux. For these four temperate upland lakes in the UK, the sediment inferred record of aqueous DOC (DOC_{NIRS}) shows a good agreement with monitored DOC (DOC_{monit}) across all sites ($r^2 = 0.78$) suggesting that our reconstructions are plausible. Thus, for these and equivalent other upland temperate and boreal oligotrophic lakes palaeo-records of this nature could contribute to our understanding the drivers of surface water brownification over timescales longer in duration than that available from environmental monitoring. In more eutrophic systems with greater in-lake productivity and autochthonous OC this approach will be less applicable and require further testing. While uncertainties inevitably remain, both the degree of rise in DOC_{NIRS}, and timing of the onset of increases in DOC_{NIRS} are inconsistent with the acidification hypothesis for brownification. Likewise, although recent increases in DOC_{NIRS} mirror trends towards a warmer climate, there are mismatches between the longer-term DOC_{NIRS} record and climate variations. Instead, the variations in DOC_{NIRS} are more consistent with enhanced terrestrial productivity altering the flux of DOC to lakes, and they show a magnitude and timing that is remarkably consistent with fertilisation related primarily to anthropogenically enhanced atmospheric N deposition. Thus, a key role for terrestrial productivity of catchments in governing the brownification and elevated DOC in surface waters appears very likely, though determining the relative contributions of land use change, climatic warming and atmospheric N deposition remain a challenge.

5.6.1 ACKNOWLEDGEMENTS

We thank Ulrike Dragosits Harding for providing model estimates for past sulphate deposition at the study sites; Rick Battarbee for providing ^{210}Pb dates for Loch Chon (core LC13GC2); Danielle Jameson for collection of cores from Loch Grannoch and Loch Chon and for handing over her MSc thesis data; Jenny Bradley, Jen Clear, Danielle Jameson, Amy Lennard, Agata Marzecova, Maddy Moyle, Dan Schillereff, Hugh Smith and Poonperm Ai Vardhanabindu for assistance with coring. Permission to core was kindly granted by Forestry Commission Scotland (Loch Grannoch and Loch Chon), Lake District National Park and Natural England (Scoat Tarn), and The Woodland Trust Wales (Llyn Cwm Mynach).

6 SEDIMENTARY EVIDENCE OF CHANGING DOC FLUXES DURING THE HOLOCENE FROM UK LAKES

6.1 ABSTRACT

Here we present sediment inferred records of lake water dissolved organic carbon (DOC) for two lakes in the UK Upland Waters Monitoring Network (UKUWMN). Using a novel end-member multiple regression NIRS method, Loss-on-Ignition, geochemistry (X-Ray Fluorescence) and sediment chronology we quantify sediment burial fluxes of mineral matter, biogenic silica, total organic matter (TOM) and dissolved organic carbon (DOC). From this data it is possible to identify trends in the controls and supply of terrestrial materials during the Holocene and identify whether recent increases in DOC captured by surface water monitoring programmes are unprecedented or commonly occurring over time. Our results show that DOC flux has varied over time and is predominantly controlled by vegetation and climate variations in the early Holocene. Human influences appear to drive supply or terrestrial materials from around 5000 YBP highlighting the importance of land management in limiting carbon loss from soils. Declines in DOC flux occur in line with cooler climate of the past 2000 YBP, however TOM does not fall suggesting either a change in supply or the controls over the processing of organic matter. We suggest that throughout the Holocene, climate and vegetation have been strong drivers of terrestrial organic matter supply to surface waters. In the future, further DOC flux increases are likely given expected future climate warming.

6.2 INTRODUCTION

During the 1970s the links between acidic rainwater and the industrial activities producing atmospheric emissions particularly SO_2 became apparent (Odén, 1968; Almer *et al.*, 1974; Wright *et al.*, 1980). Following a decade of research that proved environmental acidification was caused by this effect, legislation was drawn up and several environmental monitoring networks were established to record any recovery of water acidity in lakes and rivers with reductions in emissions (Battarbee, Simpson, *et al.*, 2014). The United kingdom Upland Water Monitoring Network (UK-UWMN) (Kernan *et al.*, 2010) recorded since 1988 recoveries in lake water acidity (Battarbee, Simpson, *et al.*, 2014). Parallel findings were identifying significant increases in the flux of dissolved organic carbon (DOC) at most sites. Increasing concentrations of dissolved organic carbon (DOC), the so-termed ‘brownification’ of surface waters, have been identified elsewhere across the UK, North America and Northern Europe (Worrall *et al.*, 2003; Skjelkvåle *et al.*, 2005; Roulet *et al.*, 2006; Monteith *et al.*, 2007). Similarities between the pattern and timing of declines in atmospheric acid emissions and increases in DOC led to suggestions of a causal link between the two (Evans *et al.*, 2006). A counter view is that the dominant controls over DOC concentrations in surface waters are not yet resolved (Monteith *et al.*, 2014; Sawicka *et al.*, 2017). A myriad of factors potentially affect surface water chemistry and DOC concentrations in lakes, including catchment land use (e.g. afforestation) and climatic change (Freeman *et al.*, 2001; Tranvik *et al.*, 2002; Hongve *et al.*, 2004; de Wit *et al.*, 2016; Hedström *et al.*, 2017).

The negative impacts associated with elevated DOC concentrations in surface waters are undisputed, and have been associated with numerous detrimental environmental impacts that include limiting light penetration into surface waters which impacts aquatic species (Hedström *et al.*, 2017) and increases water trophy (Corman *et al.*, 2018). Increased DOC can inhibit sedimentation of Fe due to suppression of flocculation, increasing aquatic Fe concentrations. DOC enriched lakes increase the release of carbon to the atmosphere resulting in increased greenhouse gases particular CO_2 and CH_4 (Hanson *et al.*, 2004; Battin *et al.*, 2009), furthermore elevated DOC levels are regarded as undesirable by water companies due to increases in the cost of water treatment (Köhler *et al.*, 2013). There are also complex interactions between DOC and lake acidity, with Schindler et al. (1997) showing that acidified lakes experienced increased rates of in-lake DOC removal caused potentially by enhanced flocculation of DOC with Al and Fe in turn leading to greater light penetration and more intense photochemical processing of DOC. This deeper light penetration can also increase water temperatures and microbial consumption of DOC. If falling soil acidity is the main cause of increasing DOC concentration, then the recoveries in acidity at UK-UWMN lakes (Battarbee, Simpson, *et al.*, 2014) would mean that reduced suppression of DOC would pose potential future problems as the DOC flux might then be expected to remain high.

The short duration of monitored data sets undermines critical evaluation of the causes of increasing DOC, and the analysis of palaeo-records preserved in lake sediment records provides the only means of rectifying this (Cunningham *et al.*, 2011). A barrier to the use of sedimentary records to address long-term patterns in aqueous DOC has been the availability and confidence in palaeoenvironmental methods that reconstruct DOC. The development of a novel end member multiple regression of Near Infrared (NIR) spectra (Chapter 2.8): (Russell *et al.*, 2019) has enabled determination of the sediment burial flux of humic and fulvic acid fractions (HA/FA) in sediments. Integration of these data with a process model (Dillon *et al.*, 1997) has provided time series of lake water DOC concentrations from lake sediment profiles (DOC_{NIRS}) based on the burial flux (Chapter 5). In applying this approach to four sites in the UK-UWMN, there was good agreement between the DOC monitored 1988-2016 (DOC_{monit}) and the records of aqueous DOC_{NIRS} inferred from the sediment record (Chapter 4). These palaeo-records extended our understanding of the drivers of surface water brownification to 300-year timescales. Examination of 300-year records of aqueous DOC_{NIRS} inferred from the sediment record and possible drivers support the view that increases in DOC_{NIRS} were inconsistent with the acidification hypothesis for brownification. There were also mismatches between the longer-term DOC_{NIRS} record and climate variations, even though recent increases in DOC_{NIRS} mirror trends towards a warmer climate. The variations in DOC_{NIRS} were more consistent with enhanced productivity in the terrestrial lake catchment, with patterns consistent with fertilisation related primarily to atmospheric N deposition. Thus, a key role for terrestrial productivity in governing elevated DOC in surface waters appears very likely, but the relative contributions from land use change, climatic warming and atmospheric N deposition remain a challenge to be resolved.

With the development of and increasing confidence in methods developed for quantifying aqueous DOC using the sediment record in lakes (Russell et al submitted) (Chapter 5), their application to Holocene sediment records has the potential to explore how land use and climate changes have impacted on the aqueous DOC. Consequently, uncertainly about the cause of recent DOC increases has important implications for approaches to mitigation and forecasting future trends. Definitions of what constitutes 'pristine' or pre-human disturbance conditions in UK lakes are varied. Palaeoenvironmental records from tree rings series, lake sediments and peat sequences show fluctuations in temperature and climatic wetness throughout the Holocene (Charman, 2010). People have been a significant agent of land use change since the Neolithic, but the scale of those impacts increases progressing through the late Holocene. Here, we use sediment profiles spanning the Holocene from two lakes in the UK-UWMN, Loch Grannoch (SW Scotland) and Llyn Cwm Mynach (NW Wales) to assess the longer-term patterns and controls over in the supply flux of reconstructed aqueous DOC. The objectives are to

- Quantify temporal patterns in the geochemical stratigraphy of both lakes, including large-scale changes in catchment erosion probably conditioned by anthropogenic land use.
- Use the heavy metal records, e.g. Pb, Zn and Cu, to discern the pattern of (pre)historical air fall pollutants to contribute to outline age-depth models for the sediment sequences alongside radiometric dating (e.g. using ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am profiles).
- Use Near Infrared Spectroscopy (NIRS), geochemical and the age-depth data to calculate fluxes for organic and mineral components in the sediments.
- Test the performance of NIRS-based reconstructions of aquatic DOC and Total organic matter (TOM), biogenic silica and mineral content by comparison with equivalent but independent data.
- Explore how past episodes with climate and land use changes during the Holocene have impacted on the DOC_{NIRS} flux record addressing competing hypotheses for the cause of elevated DOC levels in surface waters.

6.3 LONG TERM PALAEOLIMNOLOGICAL RECORDS OF ORGANIC MATTER

Surface water monitoring programmes have captured the increasing trend in DOC over the last three to four decades (Monteith *et al.*, 2005). Similarity in timescale of change in DOC and SO_2 (atmospheric acid deposition) have resulted in many studies associating the recovery of acid sensitive environments to reductions in acid deposition and in turn to increases in DOC concentrations. This assumption leads to the prediction that recent increases in DOC would be a return to the 'natural' state of DOC, as it would have been before the industrial era (Erlandsson *et al.*, 2011) an important factor when determining the status of lakes and the implications that follow from this.

One commonly used property of lake water for evaluation of DOC change is the intensity of the brown colouration, either through in-situ observations (Kritzberg 2017) or satellite monitoring (Kutser, 2010). Worrall et al. (2018) and Kritzberg (2017) utilised water colour (Hazen scale) as a proxy for DOC concentration to study potential drivers of change including climate and land-use over centennial time scales. Kritzberg (2017) found that DOC concentration increases occurred prior to the onset of atmospheric acid deposition. This 80-year data set extends further back in time than any monitoring data set. However, it still starts in a time period likely to be influenced by some form of anthropogenic activity, and thus fails to represent steady state pristine conditions.

NIRS has been identified as a tool for inferring past climatic changes from sediment records (Rosen et al. 2000; Korsman et al. 2005). Other studies have highlighted the successes and suitability of sediment NIRS as a tool for reconstructing various lake water parameters including pH, total phosphorus (TP) and TOC (Nilsson *et al.*, 1996; Rosén, 2005; Cunningham *et al.*, 2011). The approach of these studies relies on the development of data training sets and 'transfer functions', where NIR spectra of sediment samples with a paired lake water measured parameter (e.g. TOC, pH) are used to create a calibration function that can be applied to other sediment samples (those without a paired lake water measured parameter). Most studies focus on TOC; only a limited number of studies present DOC concentrations due to the difficulty in obtaining DOC training sets.

Studies using NIRS to measure TOC concentration using sediment records deposited over the past few hundred years, have successfully captured recent trends observed in the monitoring records and the years proceeding this to determine the drivers of change. Bragée et al. 2015 found that TOC concentrations were generally lower in the period 1930-1990, prior to the recent increases associated with recovery from atmospheric acid deposition and that TOC prior to 1900 exceeded recent concentrations. The general consensus appears to be that acid deposition has impacted the recent trends in DOC flux (Battarbee, Shilland, *et al.*, 2014; Meyer-Jacob *et al.*, 2015, 2020) and that environments are recovering to the point of 'natural' baseline conditions. Evidence from Cunningham et al. (2011) also supports this suggesting that TOC concentrations a century ago were double that of recent levels, indicating current increases may continue further as recovery continues.

Several reports have presented data for TOC spanning the Holocene and identified several changes in TOC flux linked to climatic and vegetation changes. For example Rosén (2005) and Rosén and Persson (2006) found TOC concentration varied more extensively in lakes with mires in their catchments (larger carbon pool available for transfer from catchment to lake), and varied with vegetation type. Their results from Holocene records in Northern Sweden indicate that warmer, wetter climate increases TOC concentration in lakes.

The Holocene record presented in Rouillard *et al.* (2011) is undated. However, trends in the core show that previous (mid Holocene) TOC concentrations exceed those of the most recent increased values. Trends also provide evidence that the mid-twentieth century declines in TOC concentration are lower than any that occurred since the period of catchment recovery after the last glacial period. Similar results have been published in Pearson and Juggins (2014), where an undated Holocene record from Japan shows the recent increases are preceded by low sediment organic carbon levels.

These observations confirm that DOC flux has varied during the Holocene and that climate and vegetation are likely drivers of DOC variations over time. Since the current DOC levels appear to be recovering, it may be assumed that climate, vegetation and land use are likely to be dominant control in the future (Meyer-Jacob *et al.*, 2020).

6.4 FIELD SAMPLING AND ANALYTICAL METHODS

6.4.1 STUDY SITES AND FIELD SAMPLING

Loch Grannoch in Galloway Hills (SW Scotland) and Llyn Cwm Mynach in Snowdonia (NW Wales) are two lakes in the UK-UWMN and situated currently at either end of a dystrophic to oligotrophic gradient respectively, though the water trophy of both lakes is likely to have varied through the Holocene. The lakes are in different upland areas, but both catchments sustain commercial forestry and are located on base poor soils and geology. Quarterly and annual UK-UWMN monitoring of chemical and biological characteristics spans the period 1988-2016 and collected data on DOC concentrations and pH (Monteith *et al.*, 2005).

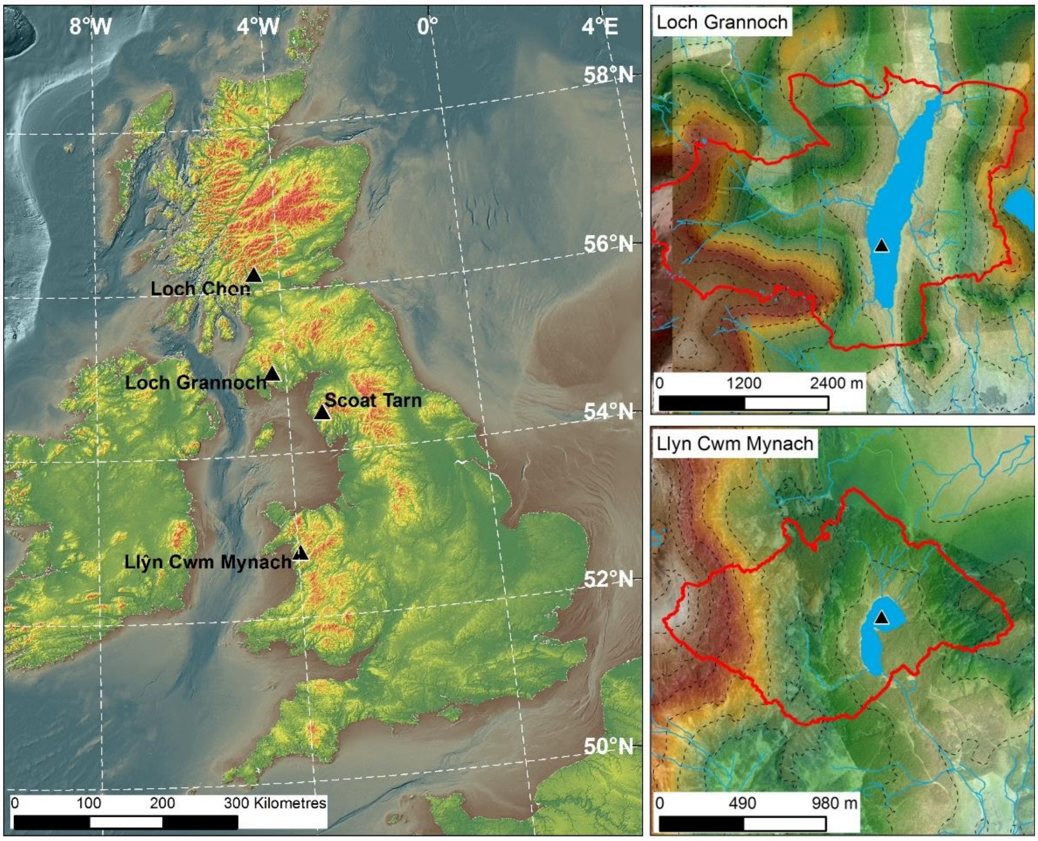


Figure 6.1 Location of the Loch Grannoch and Llyn Cwm Mynach.

Loch Grannoch is a large (1.14 km^2) upland lake (210 m O.D.) located in the Galloway Hills of southwest Scotland on the Cairnsmore of Fleet granite intrusion. The 14 km^2 upland catchment is small relative to lake area (C: L ratio 12.3:1) has a maximum elevation 391 m O.D. and is dominated (70%) by commercial forestry, mainly of *Picea sitchensis*, planted in two phases in 1962 and 1977-78. The catchment has a cool maritime climate receiving 2300 mm yr^{-1} rainfall (DEFRA, UKUWMN). Regional palaeovegetation reconstructions in the Galloway Hills from Round Loch of Glenhead (Jones *et al.*, 1989), ~6 km to the northwest, reveal a typical sequence of postglacial forest succession with *Betula* giving way to *Pinus* and *Corylus,* before *Ulmus, Quercus* and then *Alnus* dominated a mixed deciduous forest cover. From 4200 kyrs sharp declines in forest cover and expansions of upland blanket mire communities dominated by *Calluna vulgaris*, sedges and mosses reflect increasing anthropogenic disturbance of these uplands. Uninterrupted pollen records for cereals and various pastoral herbs point to greater agricultural activity from ~2000 kyrs onwards (Jones *et al.*, 1989)

Llyn Cwm Mynach is a small (0.06 km^2) upland lake (285 m O.D.) located south in the Snowdonia massif (NW Wales) and on lower Palaeozoic bedrock of siltstones, grits and greywackes. The 1.53 km^2 catchment is moderately large relative to lake area (C: L ratio 26:1) has a maximum elevation of 402 m O.D. and has commercial forestry covering 51% of the catchment. The catchment has a cool maritime climate receiving 2200 mm yr^{-1} rainfall (DEFRA, UKUWMN). The lake bathymetry is strongly asymmetric, with deep water located as an 11 m maximum depth northern basin but an average depth of 0.9 m. There are relatively few palaeoecological records from the southern Rhinog Hills of Snowdonia. Pollen data from Llyn Gwernan south of Cadir Idris (Lowe *et al.*, 1989) show an early Holocene forest succession with *Betula* and *Pinus,* with *Corylus* expanding after 10170-10370 kyrs followed shortly by early signs of increases in *Ulmus, Quercus* and then *Alnus*. Further north and east, ~40 km, pollen records at Bryn y Castell (Mighall *et al.*, 1995) affirm the establishment of the *Corylus, Ulmus, Quercus* and *Alnus* mixed deciduous forest cover. Anthropogenic impacts on the landscape are recorded from ~5000 kyrs as small scale temporary Neolithic and Bronze Age clearances and followed by more substantial regional Iron Age woodland clearances from 2700 kyrs (Mighall *et al.*, 1995). These reductions in woodland cover were accompanied by pollen evidence for expansions of heathland, acid wet grassland and pastoral grassland landscapes that persist to present.

Combination of gravity core (Boyle, 1995) and Russian style cores were collected from Loch Grannoch and Llyn Cwm Mynach, sampling the sediment water interface and extend from the present to the last deglaciation. Cores were sliced at 2.5mm intervals for the top 30mm and at 5mm for the remaining materials. Samples were stored in sealed plastic bags, frozen and freeze-dried, collecting dry mass and water content data to calculate dry mass fluxes.

Table 6.1 Core locational information

Site	Core ID	Core Location	Water Depth (m)	Core Date
Loch Grannoch	LG2016GC1 LG2016R	54.9967°N 4.2841°W	15.16	October 2016
Llyn Cwm Mynach	MYN15GC2 MYN15R	52.7984°N 3.9609°W	6.15	July 2015

6.4.2 ELEMENT CHEMISTRY AND ORGANIC CONTENT

Major element and trace metal concentrations were determined for both lakes on a dry mass specific basis using ED-XRF, using a Bruker S2 Ranger Energy Dispersive XRF for Loch Grannoch, and Spectro XEPOS 3 Energy Dispersive XRF for Llyn Cwm Mynach. The samples were hand pressed and measured under a He atmosphere under combined Pd and Co excitation radiation and using a high resolution, low spectral interference silicon drift detector. Daily standardisation procedures provide a system check on both XRF analysers and they have comparable accuracies verified using 18 certified reference materials (John F. Boyle *et al.*, 2015). The quantity of organic matter in the lake sediments was measured by loss-on-ignition (LOI) recording the weight loss measured after 1 h of ignition at 550 °C on sediment previously dried at 105 °C (Boyle, 2004). Objectives with the geochemistry and organic content were threefold, firstly to characterise the postglacial development of the lake and its catchment, to identify pollutant geochemical marker to provide a basis for age-depth models, and thirdly to undertake normative calculations to verify the NIRS quantifications of organic, mineral and biogenic silica end members.

The normative concentrations were calculated using standard element oxides measured by XRF and the composition of typical constituent minerals (Garrels *et al.*, 1971; Boyle, 2001). The objective with the normative calculations is providing independent values for corroboration of equivalent values derived by Near Infrared Spectrometry. The normative biogenic silica fraction was calculated as XRF measured SiO_2 minus the quartz and SiO_2 associated with silicate minerals. The normative mineral matter fraction is the sum of the oxides (Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, TiO_2, MnO_2, P_2O_5), silicate mineral SiO_2 (iii) and quartz (ii). Full details on these calculations are provided in Boyle (2001) and Russell et al., 2019.Near Infrared Spectrometry (NIRS)

NIRS were measured for all sediment samples and a set of end-member library samples using a Bruker MPA FT NIRS by diffuse reflectance using an integrating sphere. All samples were homogenised by grinding and were lightly hand pressed. NIR spectra are the product of 64 scans at an 8cm-1 interval across the range 3595-12500 cm^{-1}. Multiple regression of the NIR spectra for a selection known composition end-member materials (EMS-MR: Russell et al. 2019) with equivalent

NIR spectra for our unknown composition samples provides simultaneous quantification of major sediment components for both lakes. The limitations and advantages this EMS-MR approach over traditional chemometric statistical methods are discussed in Russell et al. 2019 (Chapters 2.8 and 4). We chose a tailored selection of end-members to reflect the major sediment components expected at each lake. This process included sensitivity analysis of the end member selections to obtain the overall best fitting performance, defined by high R^2 of multiple regression across the fitted end members. The end members were minerogenic late glacial muds from each lake, which we regard as representative of the catchment bedrock. Marine diatoms treated with H_2O_2 to remove any organic material to reflect the proportion of biogenic silica in lake sediments. Following Russell et al., (submitted; chapter5) the organic component of the lake sediment was rationalised to two end members, a composite 50:50 mixture of NIR spectra for IHSS (International Humic Substances Society) Fulvic Acid standard III and Humic Acid standard III from Suwannee River to represent DOC and humin, the acid and alkali insoluble material from peat, to represent less decomposed plant matter. End-member choices are outlined Table 6.2 and produced strong performance against equivalent normative calculations for biogenic silica, mineral and organic matter content giving confidence that NIRS reconstructions are capturing the changes in sediment composition.

As discussed in Chapter 5, the humic/fulvic acid (HA/FA) fraction is assumed to comprise the DOC component of organic matter, while the humin fraction is assumed to comprise the remaining organic matter, both terrestrial and aquatic in origin. A clear distinction must be made between the measured organic fractions and the assumed components. When referring to mass fractions in the sediment they are referred to as HA/FA_{NIRS} and $humin_{NIRS}$. However, when referring to the fluxes of supplied organic matter, the two terms DOC flux (= flux of HA/FA_{NIRS}) and TOM (total organic matter) flux (=flux of both HA/FA_{NIRS} and $humin_{NIRS}$) are used.

A decision was made not to calculate DOC_{NIRS}, as was done in Chapter 5 , but instead to consider the sediment burial flux. This is because terrestrial fluxes are the focus of this chapter. The fluxes are calculated as the product of mass accumulation and NIRS mass fraction.

Table 6.2 End-member selections for each lake representing major sediment components; mineral matter, algal silica, DOC (humic/fulvic acid) and other organic constituents (humin).

	Algal Silicates	Mineral	DOC (humic and fulvic components)	Other organic matter
Loch Grannoch	Marine Diatom (treated)	Loch Grannoch late glacial muds	Suwannee River Humic/Fulvic Acid Standards III (50:50 ratio)	OOMHumin
Llyn Cwm Mynach	Marine Diatom (treated)	Llyn Cwm Mynach late glacial muds	Suwannee River Humic/Fulvic Acid Standards III (50:50 ratio)	OMMHumin

6.5 SEDIMENT CHRONOLOGY AND AGE-DEPTH MODELS

In the absence, at present, of ^{14}C dating for these locations, outline chronologies and age-depth models were generated from a series of stratigraphical markers. The total Pb concentration measured by XRF provides a record solely of atmospheric deposition at these sites (Yang *et al.*, 2018) and was used for correlation with new or published ^{210}Pb, ^{241}AM and ^{137}Cs radiometric chronologies developed at each lake (see chapter 2.8). Three reproducible stratigraphical Pb markers were identified and provide the basis for the uppermost chronology. At depth further markers of atmospheric fallout Pb occur during the Medieval Period ~ CE 1000 and Roman Period ~ CE 2000. These regional markers have been dated tightly across Sweden (Renberg *et al.*, 2001), and more local to our sites in ombrotrophic peat bogs in southwest Scotland (Cloy *et al.*, 2008) and central Wales (Mighall *et al.*, 2002). At Llyn Cwm Mynach a further erosion and Pb marker occurs attributed to Bronze Age smelting in the region identified by (Mighall *et al.*, 2002). The late-glacial to Holocene transition is a very clear stratigraphical horizon to which an age from the Greenland ice core chronology has been applied. Confirmation of the appropriateness of using the Greenland chronology is provided by late-glacial to Holocene transitions radiocarbon dated near these lakes, with Llyn Gwernan (Lowe *et al.*, 1989) 8.2 km south of Llyn Cwm Mynach and Round Loch of Glenhead (Jones *et al.*, 1989) 6 km from Loch Grannoch. Depths in each core of all these markers are shown in Table 1.

Table 6.3 . Stratigraphical markers for Loch Grannoch and Llyn Cwm Mynach used to produce age-depth models. The markers relate to an air fall record of atmospheric Pb preserved in the sediments for the last 200 years dated independently by ^{210}Pb, ^{241}Am and ^{137}Cs radiometric dating at each site (see chapter 2.8). Two further Pb marker depth were used for the Medieval (1000 CE) and Roman (0 CE) Pb enrichment described by (Renberg *et al.*, 2001; Mighall *et al.*, 2002; Cloy *et al.*, 2008) and the base of the Holocene assigned an age from the Greenland ice core chronology informed by local chronologies from Llyn Gwernan (Lowe *et al.*, 1989) and Round Loch of Glenhead (Jones *et al.*, 1989)

a) Loch Grannoch			
Core depth	Age cal. BP	Uncertainty	Stratigraphical marker
0	-66	1	Sediment surface
16	10	10	Decline in Pb concentrations (secured by ^{210}Pb chronology - see chapter 3)
23.5	60	10	Peak Pb concentrations (secured by ^{210}Pb chronology - see chapter 3)
32	150	10	Major increase in Pb - industrial era (in part secured by 210Pb chronology - see chapter 3)
90	950	50	Increase in Pb - Medieval atmospheric fallout
138	2000	50	Pb increase - Roman Age atmospheric fallout (Renberg et al. 2001, Cloy et al., 2008)
297	11650	100	Transition from late glacial to Holocene organic muds
b) Llyn Cwm Mynach			
Core depth	Age cal. BP	Uncertainty	Stratigraphical marker
0	-65	1	Sediment surface
8	10	10	Decline in Pb concentrations (secured by ^{210}Pb chronology - see chapter 3)
16	60	10	Peak Pb concentrations (secured by ^{210}Pb chronology - see chapter 3)
25	150	10	Major increase in Pb - industrial era (in part secured by 210Pb chronology - see chapter 3)
77	950	50	Increase in Pb - Medieval atmospheric fallout
139	2000	50	Pb increase - Roman Age atmospheric fallout (Renberg et al. 2001, Mighall et al. 2002)
291	3470	50	Erosion markers and possible Bronze Age smelting (Mighall et al., 2002)
468	11650	100	Transition from late glacial to Holocene organic muds

The age models were produced independently for each lake, using all the geochronological control (Table 3) in the Bayesian package ‘rBacon’ (Blaauw and Christen, 2011; Blaauw and Andres Christen, 2018) operating in R (R CoreTeam, 2017). Markov Chain Monte Carlo repetitions in the age-depth modelling were constrained for Loch Grannoch by a gamma distribution with mean 50 yr mm^{-1} and shape 2 and a beta distribution with mean 0.57 and memory strength 8. Whereas Llyn Cwm Mynach was constrained by a gamma distribution with mean 20 yr mm^{-1} and shape 2 and a beta distribution with mean 0.5 and memory strength 8. The timing of events for the two lakes uses the probability weighted median and 95% uncertainties from the Bayesian age-depth models (Figure 6.2), with any fluxes calculated using smoothed sediment accumulation rates to correct for sharp changes in rate around age markers which are an artefact of the age-depth modelling.

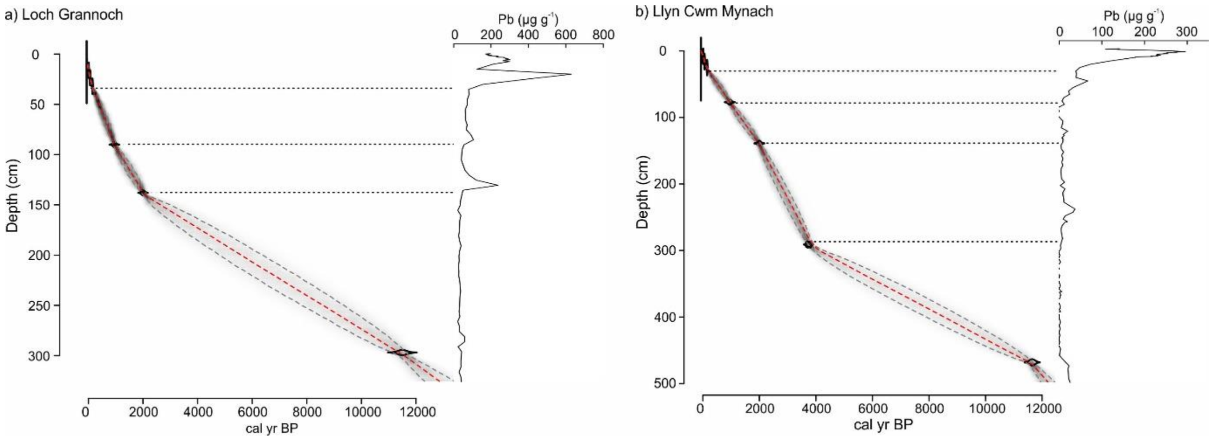


Figure 6.2 Age-depth information for Loch Grannoch and Llyn Cwm Mynach, showing the Bayesian age-depth model including the markers, the modelled weighted mean age (red pecked line), the 2 σ age probability (greyscale), and 2 σ uncertainty age range (grey pecked lines). These are plotted alongside the Pb stratigraphy.

6.6 RESULTS

6.6.1 RELATIONSHIPS IN THE SEDIMENT COMPOSITION – GEOCHEMISTRY AND ZONING

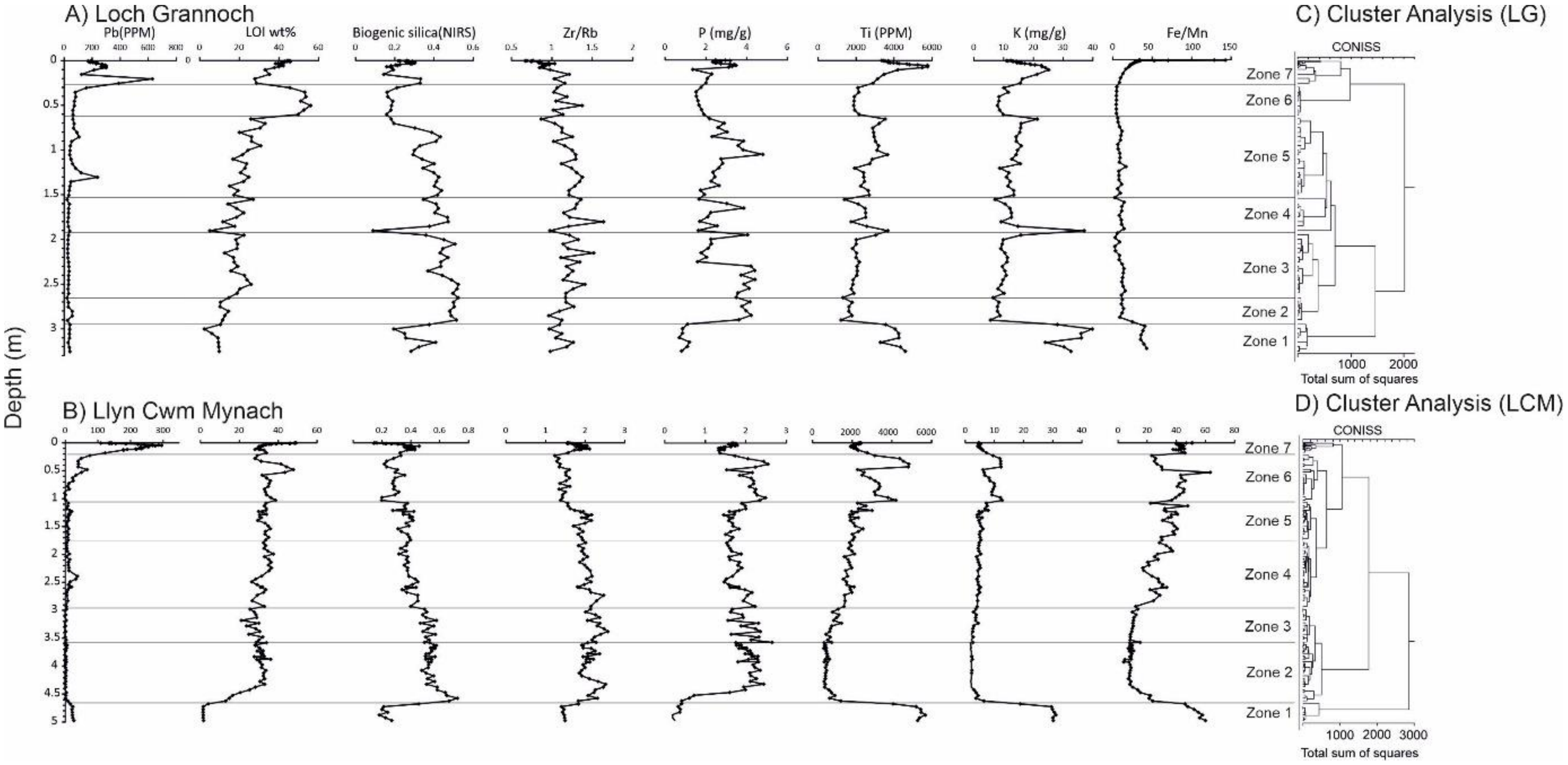


Figure 6.3 Geochemistry against depth at A) Loch Grannoch and B) Llyn Cwm Mynach and C) D) cluster analysis at Loch Grannoch and Llyn Cwm Mynach respectively.

Geochemical zones were selected for sediment cores from Loch Grannoch and Llyn Cwm Mynach using a stratigraphically constrained cluster analysis based on cord distance (Figure 6.3) and are described below.

6.6.1.1 LOCH GRANNOCH

LG Zone1, 2.93-3.23m (11,255-12,855YBP)

The basal samples are dominated by high concentrations of minerogenic elements Ti and K, and a low organic content (LOI %). This sediment composition is consistent with the cold temperatures of the late glacial and Greenland Stadial 1. Zone 1 contains oscillations between mineral and biogenic silica rich sediment with an early mineral rich phase giving way to increased algal productivity (high biogenic silica), before declining with increasing mineral matter. These oscillations resemble the structure of the GS2-GI1-GS1 climate variations (Rasmussen *et al.*, 2014) with warmer phases associated with increased algal productivity and consistently low organic matter supply. The upper zone boundary is marked by a clear increase in organic content and decline in mineral supply that reflects the onset of the Holocene, warmer temperatures and increasing catchment stability.

LG Zone 2, 2.64-2.93m (9,590-11,255YBP)

From the zone base concentrations of K and Ti are low, algal productivity has increased and remains high. Organic matter (LOI %) shows an increasing trend and the Fe/Mn ratio suggests oxygenated conditions. These results suggest that that vegetation cover is establishing and the catchment has stabilized during the early Holocene with more oxygen available and increased in lake productivity.

LG Zone 3, 1.92-2.64m (5,187-9,590 YBP)

Organic matter has increased to above 20%, then declines slightly whilst remaining relatively high. Ti and K remain at low concentrations but increase slightly towards the upper zone boundary at which there is a sharp increase in mineral concentration. In terms of lake productivity there is a punctuated decline in biogenic silica and this parallels a shift to more oxygenated conditions moving through the zone.

LG Zone 4, 1.52-1.92m (2,760-5,187 YBP)

The base of zone 4 is marked by a sharp spike in Ti and K that is mirrored by a sharp decline in biogenic silica. There are also less severe dips in organic content and the Zr/Rb ratio suggests that the mineral input is relatively fine grained. The mineral layer is accompanied by a shift to slightly more reducing conditions that persists throughout zone 4. Above the mineral layer Ti and K revert to lower concentrations and biogenic silica (algal productivity) returns to 40% and there is an increase in organic matter up to 20%.

LG Zone 5, 0.62-1.52m (632-2,760 YBP)

Organic matter increases steadily throughout the zone, punctuated by gradual stepped increases. Concentrations of Ti and K initially increase at the base of the zone, decline before increasingly sharply at around 1600YBP. The increases in mineral matter seem to be reflected in reducing conditions (Fe/Mn) and by dips in biogenic silica (algal productivity).

LG Zone 6, 0.27-0.62m (158-632 YBP)

Fe/Mn remains stable and low across this zone whilst there is a clear shift from mineral to organic dominance. LOI% increases sharply at the base of the zone reaching approximately 55%, whilst minerogenic elements, Ti, K and P decline. Biogenic silica is low and steady initially, increasing rapidly alongside the decrease in OM and increases in minerogenic elements towards the upper zone.

LG Zone 7, 0-0.27m (0-158 YBP)

Zone 7 sees a rapid increase in minerogenic elements likely as a result of catchment activity, Zr/Rb ratio suggesting that materials are fine grained. Low biogenic silica suggests that these inputs of mineral materials are reducing the in-lake productivity. The Fe/Mn may indicate reduced oxygenation, but might instead reflect reduced retention of Mn due to lake acidification. Towards the upper zone mineral supply declines sharply, whilst biogenic silica recovers suggesting recovery of in lake production. LOI % increases throughout this zone, in part due to catchment activities.

6.6.1.2 LLYN CWM MYNACH

Zone 1, 4.65-5m (11504-12238 YBP)

These basal sediments are dominated by fine grained (low Zr/Rb) mineral input. Organic matter LOI %) and in-lake productivity (biogenic silica) are low, likely associated with the cold conditions and high mineral matter supply rate. The high Fe/Mn likely reflects the mineral species rather than lake oxygenation.

Zone 2, 3.58-4.65m (6,700-11,504 YBP)

At the onset of zone 2 there is a sharp decline in minerogenic elements (Ti and K) and decline in Fe/Mn which may be a result of either catchment weathering increasing input of biotite or increased oxygenation in the water column. In contrast to the declines in mineral trends, LOI%, P and biogenic silica increase sharply suggesting warmer conditions. At approximately 4.35m there is a stabilisation in organic and mineral content. Zr/Rb and P fluctuate suggesting that catchment vegetation is establishing

Zone 3, 2.98- 3.58m (4,000-6,700 YBP)

In zone 3 there is a slight decline in oxygenation which occurs in line with increases in Ti. In lake production (biogenic silica) declines slightly as does organic matter (LOI %)

Zone 4, 1.69-2.98m (2,400-4000 YBP)

Here we see a steady increase in minerogenic elements Ti and K which appear to become finer (decline in Zr/Rb) towards the upper zone. In lake productivity (biogenic silica) continues to decline in line with increases in reducing conditions (increase in Fe/Mn). Organic matter (LOI %) and P show similarity in fluctuations across the zone, both gradually increasing suggesting a productive lake catchment.

Zone 5, 1.08-1.69m (1,500-2,400 YBP)

Mineral supply increases gradually, the grain size indicator suggesting that the rapid increase in mineral in the upper section of zone 5 (Ti, K) is dominated by fine grained materials. Biogenic Silica appears to be subdued by mineral supply potentially linked to oxygen supply (Fe/Mn).

Zone 6, 0.33-1.08m (300-1,500 YBP)

Initially, Zone 6 suggests a stable state as organic supply is steady and mineral supply (Ti, K) is declining. However, an event towards the top of the zone shows a sharp rise in organic (LOI %) and mineral matter. Supply of P increases in parallel, suggesting land disturbance could be the cause of these increases. Mineral matter increases appear to suppress in lake production (biogenic silica), which recovers with the sharp decline in catchment derived materials (organic and mineral) towards the upper zone.

Zone 7, 0-0.33m (0-300 YBP)

In this zone mineral supply initially falls sharply recovering towards the present day. Zr/Rb ratio indicates that the most recent supply of mineral (Ti, K) is coarser grained. In contrast, organic matter (LOI %) increases from around 30% up to 50%. P rises with mineral supply, again suggesting that activities within the catchment may be driving changes in sediment supply to the lake.

6.6.2 RELATIONSHIPS IN THE SEDIMENT COMPOSITION – PCA

The postglacial evolution of the dystrophic (Loch Grannoch) and oligotrophic (Llyn Cwm Mynach) end member lakes is reflected in the down core patterns of a series of major geochemical elements measured by XRF and normative calculations for total biogenic silica, mineral and organic matter derived from the XRF. Geochemical ratios for Fe/Mn and Zr/Rb provide indications of reducing conditions in the lake and the presence of coarser grain sizes respectively (Davies *et al.*, 2015). Interrogation of the NIR spectra has provided independent estimates of the sediment proportions of mineral, biogenic silica (diatom), HA/FA$_{NIRS}$ (representing DOC) and humin$_{NIRS}$ fraction (representing less degraded organic matter). Total organic matter is calculated independently from the loss-on-ignition measurements and from NIR spectra by summing the HA/FA$_{NIRS}$ and humin$_{NIRS}$ components. Principal components analysis (PCA), based on a correlation matrix, was used to explore the relationships between these components and the down-core patterns for each lake (Figure 6.4). A stratigraphically constrained cluster analysis for the parameters that were all standardised to ± one standard deviation unit length and produced dendrograms that identify the major changes in the sequence and a series of zone boundaries (Figure 6.5).

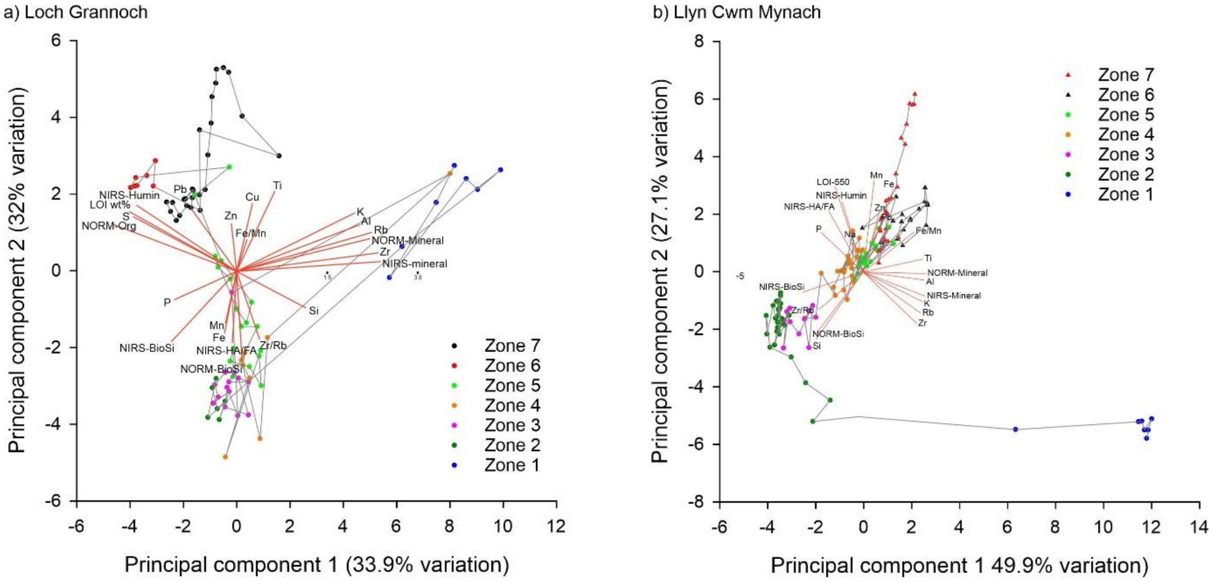
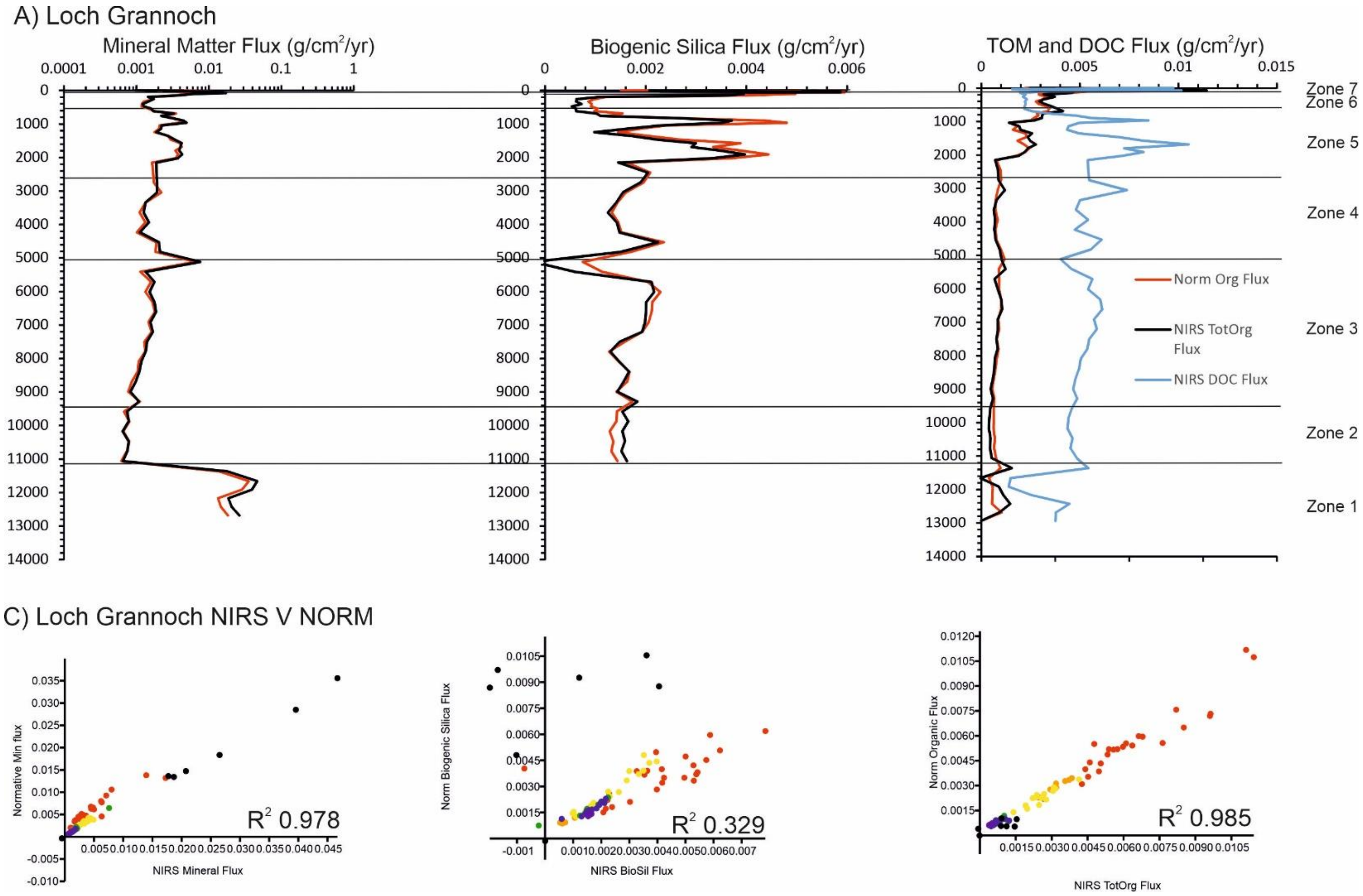


Figure 6.4 Principal Component's plots for PCA1 and PCA2 at a) Loch Grannoch and b) Llyn Cwm Mynach

For Loch Grannoch 68% of the variation in the PCA is summarised by the first two components, and a bi-plot of the measured parameters shows three distinct clusters (Figure 6.4). There is a strong stratigraphical order to the distribution of the zones on principal components. Zone 1, the most mineral rich section associated with late glacial sediments, shows samples clustered with minerogenic indicators (Zr, NIRS and NORM mineral). Zones 2, 3, 4 and 5 have samples clustered in the centre of the plot, along with in lake productivity indicators and HA/FA$_{NIRS}$. In the upper left-hand section zones 6 and 7 have samples clustered together with organic matter indicators. In zone 7, the upper most sediments also grouped with Pb suggesting sediments are impacted by pollution. These three distinct clusters suggest that organic supply, mineral supply and in lake productivity have varied in being the predominant feature of the lake sediments.

For Llyn Cwm Mynach 77% of the variation in the PCA is summarised by the first two components. Although clusters are less distinct at this site, there are still four identifiable groups. Again zone 1, which is characterised by late glacial sediments, has samples clustered together with mineral indicators and mineral-associated elements. Zones 2 and 3 have samples clustered towards the left of the plot together with in-lake productivity indicators (biogenic silica and Si). Zones 4 and 5 show similarity with organic matter indicators (HA/FA$_{NIRS}$, P). Finally, zones 6 and 7 samples also cluster with organic matter indicators, but additionally with Fe and Pb suggesting the sediments are contaminated by atmospheric deposition.

6.6.3 NIRS ORGANIC FLUX RECONSTRUCTION



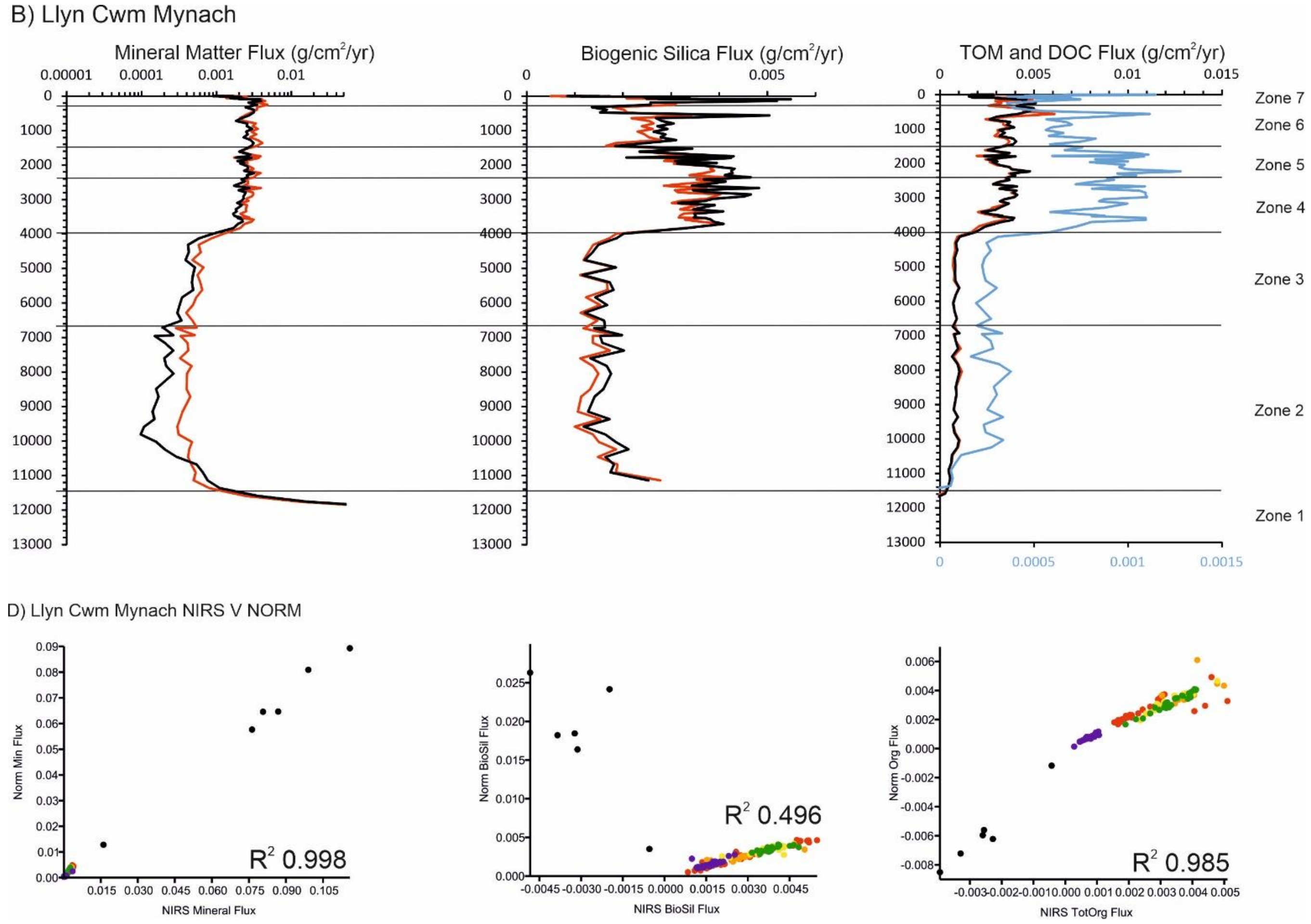


Figure 6.5 Major sediment component fluxes estimated by NIRS (black) and independent normative fluxes based on XRF (for mineral and biogenic silica) and LOI% for organic matter at a) Loch Grannoch and b) Llyn Cwm Mynach. Note that the late glacial sediment data for Biogenic Silica has been removed due to limitation in NIRS ability to differentiate between biogenic silica and quartz resulting in over estimation of biogenic silica in this mineral rich phase. Normative V NIRS flux calculations (colour coded by zone for C) Loch Grannoch and D) Llyn Cwm Mynach

Below are descriptions of NIRS quantified fluxes of major sediment components, including biogenic silica, mineral matter, Total organic matter (TOM) and DOC, against age (Figure 6.5), and divided into zones as identified from concentration values (5.7.1).

In chapter 5 we show that NIRS inferred DOC_{NIRS} is a successful measurement for estimating surface water DOC concentrations at the time of sedimentation; that validation also applies to the fluxes presented here. For the other three NIRS measured components, validation is by compassion with independent methods. TOM is compared with LOI, while normative mineral concentrations have been calculated from the XRF element concentrations to estimate mineral matter and biogenic silica.

6.6.3.1 LOCH GRANNOCH

R^2 values of 0.74 0.95 and 0.97 show strong positive correlation between NIRS flux and normative flux for biogenic silica, mineral content and total organic fluxes, respectively. Late glacial sediment flux values (zone 1) were removed from statistical analysis for Loch Grannoch due to clear disparity in mineral and biogenic silica estimates likely due to presence of quartz in these sediments affecting the NIRS method (see Chapter 2.8 for further discussion).

LG Zone1, 2.93-3.23m (11,255-12,855YBP)

Here we observe high flux of mineral associated with late Holocene glacial retreat and establishment of warmer conditions. High mineral flux correlates with low biogenic silica flux, likely due to mineral content impacting in lake productivity. Rise in TOM is less pronounced, with declines during mineral flux peaks and recovery as mineral supply declines. This may suggest that in-lake production is contributing to TOM content and that the catchment vegetation is limited at this stage as mineral flux is not associated with increased TOM inputs. DOC_{NIRS} flux remains low in this zone, rising as organic flux rises.

LG Zone 2, 2.64-2.93m (9,590-11,255YBP)

In this zone DOC flux (estimated by NIRS) rises strongly at the onset of the zone before declining slightly. TOM flux follows a similar trend but with larger flux and initial decline. Similar patterns are observed in biogenic silica and mineral matter flux. These trends likely reflect a more stable catchment with increased vegetation cover and lower rates of terrestrial supply of eroded materials than zone 1.

LG Zone 3, 1.92-2.64m (5,187-9,590 YBP)

In Zone 3 we observe a very gradual increase in mineral flux until a sharp increase at approximately 5300YBP when there is a sharp increase towards the zone boundary. Flux of biogenic silica fluctuates throughout this zone and falls rapidly at approximately 5700 YBP, preceding the timing of increase in mineral flux. Flux of organic material broadly follows mineral matter including the increase towards the upper zone. Biogenic Silica flux dips towards the zone boundary. DOC flux again follows a similar trend as mineral matter, consistent with terrestrial supply controlling DOC flux. However, DOC declines slightly towards the upper zone boundary. The combination of decline in biogenic silica and DOC fluxes in this upper section of zone 3 may indicate that in-lake productivity had been the dominant source of organic carbon.

LG Zone 4, 1.52-1.92m (2,760-5,187 YBP)

At the base of this zone biogenic silica is at its lowest observed value during the Holocene indicating low in lake productivity. The period of low in lake productivity occurs in time with a high flux of mineral matter. As mineral flux declines at approximately 5050YBP we observe recovery in the biogenic silica flux. This suggests the catchment has stabilised and increases in algal productivity occur. The period of increased mineral flux at the onset of this zone appears to have limited impact on TOM flux. However, after the mineral flux stabilises there is similarity in TOM and DOC flux including a slight peak at approximately 3000YBP.

LG Zone 5, 0.62-1.52m (632-2,760 YBP)

At approximately 2100YBP we can observe increases in all of the fluxes. This suggests that there is a change in the catchment altering the supply of terrestrial materials. DOC flux differs from that of TOM in the upper half of this zone, appearing to parallel mineral flux instead. This suggests that DOC flux is dominated by allochthonous material and TOM flux a combination of both allochthonous and autochthonous materials. Biogenic silica flux peaks twice, at 2000YBP and 950YBP. A decline at approximately 1200YBP in biogenic silica occurs earlier than mineral and organic flux, and is therefore unlikely to be driven by variation in terrestrial supply dynamics.

LG Zone 6, 0.27-0.62m (158-632 YBP)

In this section DOC flux is negligible while TOM flux continues to be high. Fluctuations in TOM flux do not seem to be similar to biogenic silica or mineral flux, however the overall trend of starting higher, dipping, and then rising again occurs in all.

LG Zone 7, 0-0.27m (0-158 YBP)

In this zone, which reflects a period of forestry management and planting phases, we see clear responses in all fluxes. We initially see a sharp increase in fluxes of mineral matter, biogenic silica, TOM and DOC. Mineral matter flux rises to peak at around 75YBP, after which it declines towards the present day with slight fluctuations. Similar trends appear in TOM flux suggesting that catchment supply dominated TOM content of sediments. At approximately 100 YBP there is a decline in biogenic silica flux which recovers at around 50 YBP, likely driven by mineral inputs limiting productivity. Recent trends in the DOC flux appear to follow TOM flux in the lower part of this zone, however when TOM flux declines towards the present, we see an increase in the DOC flux suggesting that different mechanisms are driving these organic constituent fluxes.

6.6.3.2 LLYN CWM MYNACH

R^2 values of 0.99, 0.96 and 0.98 show strong positive correlation between NIRS-inferred and normative-inferred fluxes for biogenic silica, mineral content and total organic content respectively.

Zone 1, 4.65-5m (11504-12238 YBP)

Characterised by the onset of warming conditions associated with the end of the glaciation, we see a sharp decline in the mineral matter flux. Towards the more recent we see this flux fall, reflecting the stabilisation of the surrounding catchment. There is also an increase in the biogenic silica flux indicating increases in lake productivity, likely as the climate warms.

Zone 2, 3.58-4.65m (6,700-11,504 YBP)

The mineral flux is low after the initial high value. The opposite trend can be seen in the organic flux which climbs initially and then stabilises after about 10000 YBP. Flux of biogenic silica rises at the onset of this zone to a peak at 11000YBP, and then declines to a steady value after about 10000 YBP.

Zone 3, 2.98- 3.58m (4,000-6,700 YBP)

This zone initially shows flux values that continue from the previous zone. However, from about 6500 YBP the mineral matter flux increases slightly.

Zone 4, 1.69-2.98m (2,400-4000 YBP)

In this zone we begin to see major fluctuations in all of the variables and higher flux values than in previous zones. At the base of this zone we see sharp increases in fluxes of mineral, biogenic silica, TOM and DOC. The magnitude of flux values for this peak are not seen elsewhere in this sediment record and the DOC flux covaries closely with the TOM flux in this zone. Peaks in all flux parameters occurs at approximately 3600 and 2700 YBP.

Zone 5, 1.08-1.69m (1,500-2,400 YBP)

At the onset of zone 5 we continue to observe high flux values in all parameters. From around 1800 YBP there is a decline in the fluxes of DOC and biogenic silica, but little trend of change in TOM or mineral matter flux, consistent with a decline in lake productivity.

Zone 6, 0.33-1.08m (300-1,500 YBP)

At the base of the zone the trend from zone 5 continues, with low fluxes of DOC and biogenic silica, but unchanged fluxes for mineral matter and TOM. The fluxes of biogenic silica, TOM and DOC show a sharp peak at 550 YBP, before strong declines in DOC and biogenic silica flux towards the upper zone at approximately 400YBP. The mineral flux tends to rise through the period, while TOM flux varies little.

Zone 7, 0-0.33m (0-300 YBP)

As per Loch Grannoch, we see an increase in all variables in the most recent zone. At Llyn Cwm Mynach the increases seen in this zone are less extreme than have occurred earlier in the Holocene. At the onset of zone 7 strong increases occur in the fluxes of biogenic silica and DOC, peaking at approximately 100-150 YBP, while TOM and mineral maintain the high values seen in the previous zone. At 100 YBP sharp fall are seen in all variables. Both organic matter fluxes are at a minimum between 50 and 80 YBP, before increasing to the present day, strongly in the case of the DOC flux. In contrast, the biogenic silica and mineral fluxes after briefly stabilising in the mid-20th century then fall to the present day.

6.6.4 DOC AND TOTAL ORGANIC CARBON FLUX

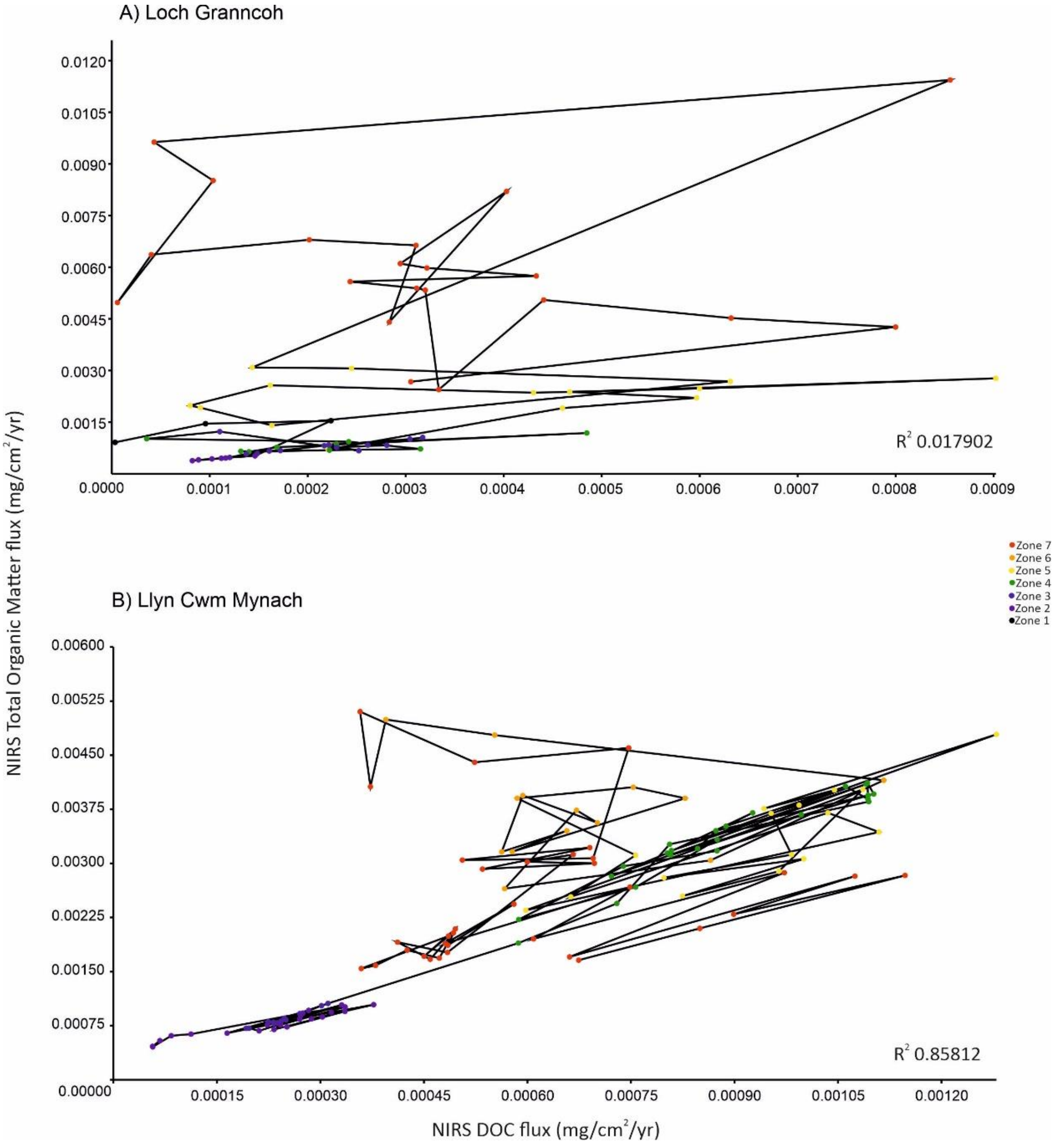


Figure 6.7 Relationship between TOM flux and DOC flux at A) Loch Grannoch and B) Llyn Cwm Mynach. Note that zone 3 appears missing from Loch Grannoch as NIRS flux measured zero

The results from the down core plot (Figure 6.5) highlight a difference in the relationship between DOC flux and TOM flux at both sites after 2000 YBP, a pattern that is emphasised by Figure 6.. At both sites, there is a close correlation of TOM flux with DOC flux for zones 1 to 5, but zones 6 (orange) 7 (in red) have TOM fluxes that are high relative to the DOC flux. These results show that the fluxes of DOC and TOM do vary, at times shifting to more humic inputs relative to TOM. At both Llyn Cwm Mynach and Loch Grannoch the DOC flux mimics the TOM flux through most of the record, but they deviate in the upper zones, showing a strong decline.

At both sites it is evident that the DOC flux is high until the last 500-1000 years, prior to abrupt falls relative to the TOM flux. It is also evident that the DOC flux closely follows the biogenic silica flux throughout the record, including the prolonged spell of lower DOC flux. This association with in-lake productivity is consistent with control via primary production, whether in the lake or catchment.

6.7 DISCUSSION

6.7.1 THE DOC AND TOM FLUX HISTORY

During the Holocene we see a broadly similar trend in DOC flux at Loch Grannoch and at Llyn Cwm Mynach. DOC flux increases are seen in the early and mid-Holocene, then lower flux in the centuries preceding the recent increases, occurring around the time of the industrial revolution.

Subsequent to an initial rapid increase at the start of the Holocene, DOC flux stabilises with a rather higher rate at Loch Grannoch than at Llyn Cwm Mynach. This increase in flux is consistent with increased supply of allochthonous organic matter following warming, and followed by only gradual environmental change. Indeed, the shape of the flux profiles are broadly consistent with the early Holocene rise in global mean temperature (Liu *et al.*, 2014; Kaufman *et al.*, 2020). The flux profiles are also paralleled by successional changes in vegetation cover, as evidenced by the pollen records at neighbouring sites. These show rapid transition from open to forested landscapes (Jones *et al.*, 1989; Mighall *et al.*, 1989, 1995), and then only gradual changes in land cover until after 5000 YBP. The sites differ in one principle way; at Loch Grannoch, the DOC flux shows a gradual rise, paralleling the slow replacement of *Quercus*, *Ulmus* and *Alnus* forest by blanket bog (Jones *et al.*, 1989). Modern observations (Hope *et al.*, 1994; Xenopoulos *et al.*, 2003; Kortelainen *et al.*, 2006; Creed *et al.*, 2008; Sepp *et al.*, 2019) strongly a suggest that the increasing DOC flux has resulted from this blanket bog expansion. At Llyn Cwm Mynach there is no such development, and just a slow shift in forest composition with falling *Alnus* abundance, and increasing *Corylus* (Mighall *et al.*, 1989). After 7000 YBP, both sites show slight signs of human disturbance of the forest, in the form increasing abundance of light demanding taxa including *Calluna* and *Plantago*. These land cover changes are not associated with any clear change in the DOC flux. At Loch Grannoch DOC flux briefly deviates from TOM flux at approximately 5800 YBP, though retaining its association with the flux in biogenic silica. It is not clear what explains this event.

A change occurs after the mid Holocene, weakly at ca. 5000 YBP at Loch Grannoch, and strongly and abruptly at ca. 4000 YBP at Llyn Cwm Mynach, in the form of increased supply of soil mineral matter, and increased and fluctuating DOC flux. At Loch Grannoch, this change coincides with final replacement of forest by blanket bog, with some indication of human land disturbance in the form of grazing indicator species (Jones *et al.*, 1989). A similar change in land cover is observed at Bryn y Castell (Mighall *et al.*, 1989), dated at 2600 YBP, much later then the increase in soil erosion at Llyn Cwm Mynach. It is likely, however, this difference in timing is due to the locations, which are 21 km apart, and that the introduction of early farming plays a role at both lakes. At both sites, the parallel increases in soil erosion, and fluxes of both DOC and biogenic silica, point to a role for erosion in altering allochthonous supply of mineral and organic materials and increasing in lake productivity. These increases are approximately coincident with the onset of mid Holocene climatic deterioration (Liu *et al.*, 2014), which may suggest a causal link. However, they also coincide with the first evidence for substantial human disturbance of the landscape, consistent with enhanced catchment productivity due to agriculture leading to enhanced DOC flux and in lake productivity.

At around 2000 YBP at both sites the fluxes of DOC and biogenic silica peak briefly (strongly at Loch Grannoch), before declining strongly, though with fluctuations. Importantly, this is the first time that DOC flux separates from OM flux (Figure 6.5, zone 6). In older sediment the fluxes of DOC and TOM correlate and have similar ratios. But after 2000 YBP, the flux of DOC but not TOM falls strongly. At Loch Grannoch this drop in the flux of DOC and biogenic silica is accompanied by a decrease in mineral matter flux, while the TOM supply rises. At Llyn Cwm Mynach, the mineral matter and TOM fluxes hold steady, despite the reduction in DOC and biogenic silica flux. This substantial change coincides with a marked climatic cooling both in the global mean temperature (Liu et al., 2014), and in July mean temperature as recorded at Talkin Tarn in Northern England (Langdon *et al.*, 2004). At Loch Grannoch there is also pollen evidence for coincident land cover change, as flora of the blanket bog changes from *Calluna* dominance to Poaceae dominance, attributed to changed land management, including burning (Jones et al., 1989). At Llyn Cwm Mynach we have no land-use evidence as the sediment record cannot be confidently matched to the Bryn y Castell pollen record. On the other hand, the patterns are consistent with enhanced erosion at both sites; erosion of organic soils at Loch Grannoch, with its blanket peat catchment, and mineral soils at Llyn Cwm Mynach. This process may explain the change in ratio between the DOC and OM fluxes but not why the fluxes of DOC and biogenic silica falls so strongly. Cooling could explain reduced terrestrial productivity, and cooling over this time period is broadly supported (Liu *et al.*, 2014; Kaufman *et al.*, 2020). However, soil erosion is also occurring at this, which might conceivably have contributed to reduced productivity. It is known that severe soil erosion, which substantially depletes topsoil, reduces NPP (Lal, 2005), so erosion might contribute to this effect.

Within the last 1000 years, at both sites, there is a prolonged minimum in the flux of DOC and biogenic silica, lasting until a little over a century ago. At Loch Grannoch this is paralleled by increases in soil mineral supply, but this is not the case at Llyn Cwm Mynach, suggesting the erosion is not casually linked to the change in DOC supply. Broad coincidence of minimum DOC and biogenic silica flux with the Little Ice Age is consistent with temperature control over the effect. Importantly, the DOC flux increases relative to the total OM flux, though not returning to values seen before 2000 YPB.

At both sites the very recent increases in DOC, which feature in monitoring data sets, is paralleled in the TOM flux and biogenic silica flux. The DOC flux continues to increase relative to the total OM flux, beginning to approach values seen before 2000 YPB.

6.7.2 COMPARISON WITH OTHER PALAEO-RECONSTRUCTIONS

The DOC records at the two British sites are expressed in term of DOC flux, therefore differing from the other studies that reconstruct aquatic TOC concentrations. While there are scaling differences, these records are less different than they appear. First, TOC and DOC are closely correlated (Hope *et al.*, 1994), and in the case of a single palaeoecologically reconstruction of both (Rouillard *et al.*, 2011), yield very similar records. Second, as is shown in Chapter 3, sediment DOC burial flux and lake water DOC concentration are correlated. In the following discussion, therefore, TOC and DOC flux are assumed to be measuring the same properties of the lakes, and are essentially interchangeable.

Holocene TOC reconstructions have been reported from northern Sweden (Rosén, 2005; Rosén *et al.*, 2006; Rouillard *et al.*, 2011), and a single late Holocene reconstruction is reported from the North West Territories of Canada (Rouillard *et al.*, 2011). These show two general similarities to Loch Grannoch and Llyn Cwm Mynach. First, those studies extending to the start of the Holocene show an initial rise in TOC concentration that lasts from 1000 to 1500 years (Rosén, 2005; Rosén *et al.*, 2006), similar in timing. Second, towards the end of the Holocene, the concentrations fall at all but one of the lakes (Rosén, 2005; Rosén *et al.*, 2006; Rouillard *et al.*, 2011). At the only lake for which total organic matter was measured, Seukokjaure in northern Sweden, the ratio of inferred TOC to total organic matter falls at the same time, a further striking similarity to the British sites. The timing of the fall, however, differs. At the Swedish sites, and the single Canadian site, the recent fall starts at about 1000 YBP, thus approximately 1000 years later than at the two British sites. A greater difference, however, is seen in relation to the mid Holocene increase in DOC flux at the two British lakes. Only one of the 8 Swedish lakes shows a mid-Holocene increase (Seukokjaure). The others sites show some fluctuations through the mid Holocene, but with no consistent increases. Rather, 6 of the Swedish lakes show declines through the Holocene, starting 7000 year ago in the Alpine lakes, and 3000 years ago in the boreal forest lakes. This suggests that different processes controlled DOC flux during the mid-Holocene in Britain.

During the last 1000 years there are also similarities between British lakes and those in Sweden. The two lakes reported by Bragée et al. (2015) show systematic variations in both TOC concentration, and the ratio of this to total sediment organic matter. After approximately 500 YBP, thus consistent in timing with the Little Ice Age and the DOC flux minimum at the British lakes, the inferred lake water TOC concentrations fall, and the ratio of this to total organic matter falls more strongly. Like the British lakes, both of these lakes then show a strong 20th TOC concentration minimum. At one the lakes, Lindhultsgöl, the TOC concentration and ratio fall steady to about 1900 AD, and then fall more strongly to a minimum during the 1940s. At the other lake (Abodasjön), the concentration and ratio fall until approximately 1800, before recovering until the concentration falls again from about 1900. A 1980s minimum is followed by recovery. The recent part of this record is similar to what is reported for 4 southern Swedish lakes by Cunningham et al. (2011). Dated less precisely, these show TOC concentrations falling from the 19th century, and reaching a minimum during the 20th century. An association of increased DOC flux with a recovery from acid deposition is not apparent in the records at Loch Grannoch and Llyn Cwm Mynach

Both the similarities and differences to the British lakes are striking. The absence of a mid-Holocene increase in TOC concentration in Sweden, contrasted with the strong increase in DOC flux at the British sites, is fully consistent with the difference in their land-use histories and the absence of farming at the high latitude locations. Such an effect might be expected at the southern Swedish lakes, but none have records long enough to test this. The onset of late Holocene reduced DOC flux, about 2000 years ago in the British lakes, contrasts with the rather later declines in TOC concentration at the high latitude sites, including in Sweden and Canada, which might conceivably reflect the cooler climates. Again, it would have been interesting to see whether earlier declines occurred in southern Sweden had this been tested. However, once we are into the last 1000 years, greater similarity is confirmed.

6.7.3 EVALUATION OF COMPETING HYPOTHESES

Since it was first recognised in the early 2000s (Monteith *et al.*, 2000; Driscoll *et al.*, 2003; Hejzlar *et al.*, 2003) increases in surface water DOC concentration from the 1980s in Europe and North America have been interpreted primarily in terms of rising temperature and falling sulphate deposition (Evans *et al.*, 2006). As the trends in DOC, temperature and sulphate occur in parallel for the duration of the monitored records, distinguishing between these has proved difficult.

Temperature change has been widely proposed as a cause of changing DOC export, based both on empirical analysis of stream and lake monitoring data (Evans *et al.*, 2006) and experimental studies on peat (Freeman *et al.*, 2001; Freeman *et al.*, 2004; Clark *et al.*, 2005). This position is supported by both Cunningham et al. (2011) and Bragée et al. (2015) who developed proxy records long enough to show that TOC concentrations had fallen from past higher values at a date prior to acidification. Thus, while the recent browning trend could conceivably be attributed to recovery from acidification, prior decreases in TOC could not be attributed solely to the onset of acidification (as evidenced in Chapter 5). That climate could impact TOC fluxes is well-known from a theoretical perspective, being related to NPP (Whittaker and Likens, 1973; Davies *et al.*, 2016), such that in landscapes where temperature limitation of NPP occurs, increasing temperature can be expected to cause an increase in TOC export. And, this effect is also apparent in the Holocene TOC concentration records of (Rosén, 2005), in both the close correlation of TOC concentration with Holocene temperature trends at the Alpine sites, and also in particularly strong falls in TOC concentration 1000 year ago due to cooling at treeline sites. Loch Grannoch and Llyn Cwm Mynach reinforce this view, and show still more strongly that each known drop in palaeotemperature of the last 3000 years is reflected in reduced DOC exports (Chapter 5).This association with temperature is broken only for the mid-20th century, where there are falls in TOC/DOC in both Sweden and Britain, but temperatures have risen not fallen.

Vegetation change has also been invoked to explain changes in TOC concentration prior to the 20th century (Rosén *et al.*, 2007; Bragée *et al.*, 2015). However, it is not clear that this effect can be separated from climate change or land use change. The two British lakes both show that mid Holocene disturbance related to early farming coincides with increases in DOC flux. No other studies in landscapes impacted by early farming have yet been tested, so the generality of this finding cannot be judged. But this does not mean that land use is an important factor in later Holocene changes in DOC. Indeed, the coincident lows of DOC flux at the British sites and TOC concentrations in Sweden during the last millennium, and coinciding with the Little Ice Age cooling, argues strongly for synchronous climate impacts rather than land use across these very different landscapes. The earlier abrupt falls in DOC flux, and altered balance between DOC flux and OM flux at approximately 2000 YBP in Britain, but rather later in Northern Sweden and the Northwest Territories of Canada, cannot reasonably be attributed to land-use change, cooling providing a more plausible explanation.

The recent 20th Century DOC increases occur in parallel with falling atmospheric acid inputs, but these fluctuations are small when compared with the fluctuations evident at Loch Grannoch since approximately 2000 YBP, and at Mynach over the last 4000 years. In Chapter 5 it is concluded that there is no association of recovery from acidification and DOC flux. This reinforces the view that future trajectories of increased DOC are likely to be impacted by climatic warming.

6.8 CONCLUSIONS

In the early Holocene record, DOC flux appears to be driven by the onset of warming conditions and associated vegetation expansion. From approximately 5000 years ago findings suggest that pressures exerted by human activities resulted in increased rates of catchment erosion and of TOM and DOC supply to both lakes. Interestingly, DOC and OM flux are synchronous until approximately 2000 years ago, suggesting that there had been similar source material and supply of organics. After 2000 YBP DOC flux deviates from TOM flux which may be linked to cooling climate resulting in decreasing terrestrial productivity and soil erosion. A similar finding has been observed in NIRS studies of lake sediments from Sweden and Canada, although the declines occur approximately 1000 YBP which may be due to differing regional climatic regimes. Here we show that the late 20th century DOC rises captured in surface water monitoring programmes are likely to be primarily controlled by strong climate and vegetation controls (enhanced primary productivity), just as throughout the Holocene. Therefore, future DOC flux increase is expected, driven by projected climatic warming.

6.9 ACKNOWLEDGMENTS

Thank you to Forestry Commission Scotland and The Woodland Trust Wales for providing us with access to the coring site at Loch Grannoch and Llyn Cwm Mynach respectively, and to Poonperm Vardhanabindu, Jenny Bradley, Maddy Moyle and Daniel Schillereff for assistance in the field.

7 SYNTHESIS

The aim of this research was to develop methodologies and which could be applied to reconstruct and quantify the palaeo DOC record preserved in Holocene lake and peat sequences. The principal focus was to develop and then apply these techniques to take the longer-term perspective afforded by the palaeorecord to explore and critically evaluate the various drivers and forcing mechanisms proposed to explain recent increases in the DOC concentration of surface waters (e.g. rivers and lakes). To achieve this, the approach was to:

- Develop a method for Near Infrared Spectra (NIRS) analysis of sediment records that avoided the widely applied chemometric statistical method that are underpinned by empirical associations, but instead to develop an approach that was founded in sound physical principles. The approach (EMS-MR) used multiple regression (MR) to fit a selection of end member (EMS) spectra to the spectra measured for heterogenous materials (e.g. lake sediments) and thereby quantify proportions of those end members in the sediment.
- Create an extensive NIR spectra end-member library with a suite of mineral, organic and biogenic silica materials representative of all likely individual sedimentary components of both peat and lake sediments.
- Apply and evaluate the performance of this EMS-MR interpretation of NIR spectra as a method for reconstructing concentrations of dissolved organic carbon (DOC_{NIRS}) using the Holocene lake sediment from Loch Grannoch.
- Apply EMS-MR of NIRS to an ombrotrophic peat with a stratigraphy dominated by variation in humic acid content. This application demonstrated success in the rapid non-destructive characterisation of the degree of humification and humic acid concentrations in peat, but quantifying proportions of plant types was constrained by the influence of plant tissue decay on the NIRS signal.
- Use NIRS EMS-MR quantification of humic compounds in lake sediments to generate short (300 year) and long (whole Holocene) lake sediment DOC fluxes and then infer palaeorecords for aqueous DOC to characterise the longer-term patterns of DOC concentration in surface waters. From these new palaeorecords of DOC, the array of possible environmental drivers of surface water ‘brownification’ are critically evaluated.

Previous approaches to reconstruction of lake water DOC, or more commonly TOC, from sediment records have used chemometric models. For the chemometric methods, training sets are necessary, whereby a statistical model is trained to associate measured lake water or sedimentary characteristics with properties in the corresponding NIR spectra. This is achieved using approaches such as partial least squares regression, and depends on the assumption that the underlying biogeochemistry has led to a direct proportionality between sediment and surface water composition that is preserved in the properties of the NIR spectra. Such an assumption cannot easily be tested, but it is not consistent with any conceptual model of how flocculated DOC/TOC is incorporated the sediment. Such models suggest that the rate of settling of flocculated DOC/TOC should be proportional to the lake water aqueous concentration, but that the concentration of this in the sediment would vary inversely with the sediment mass accumulation rate (MAR). Chemometric methods therefore must give biased results both at sites where MAR is higher or lower than average, and where MAR changes through the record.

Consequently, a more direct approach was taken, based on multiple regression NIRS quantification of the concentrations of organic matter in the sediment, and then applying a simple mass balance model to calculate the lake water DOC that is consistent with the DOC burial rate. The procedure is built primarily from a novel method for NIR analysis of sediment records. The new NIRS method differs fundamentally from previous approaches. The existing partial least squares (PLS) regression approaches rely on the collection or availability large environmental training data sets and use statistical models to explain lake water DOC (or TOC) from measured sediment NIR properties. These environmental trainings sets typically comprise either a large number of sites where environmental parameters have been monitored and the surface sediments have been measured by NIRS (Rosén, 2005; Pearson *et al.*, 2014), or the sediment records has been measured for NIRS and independent measures for the same sediments provide the training data (McTiernan *et al.*, 1998). Instead this new method (Russell *et al.*, 2019) uses a direct multiple regression, underpinned by a library of end-member NIR spectra for known materials and a sample dataset of NIR spectra for the heterogenous materials that comprise peat and lake sediments. The multiple regression approach has the advantages of theoretical robustness, greater simplicity, and negating the need for acquiring training dataset.

To develop and prove the usefulness of this alternative approach a number of steps were completed, showing that component NIR spectra for heterogenous materials are additive, and that available environmental materials would make suitable end-members for this analysis. Additivity was confirmed, though spectral mixing was found not to be conservative with respect to mass proportion. Instead, mixing was found to be conservative in relation to chromatic intensity of contributing sediment components. Fortunately, mass concentrations can be calculated using the measured spectra by correction using a chromatic intensity factor (CIF), the value of which can be measured independently (Chapter 3). End member suitability was assessed by assembling and testing a library of materials. It was found that poor choice of end-member can lead to bias in the quantification, thus tailoring the choice of mineral material, for example selecting a similar bedrock type to that of the sample environment, is the preferred option. On the other hand, organic matter and biogenic silica materials were found that fitted successfully for a diverse set of test sediments (e.g. differing lake and peat deposits), and appeared to provide useful proxies for important sediment components. With suitable end-member materials selected, and processed using a dedicated open-source multiple regression procedure developed in R (R Core Team, 2013), simultaneous quantification of the major components (biogenic silica, mineral and organic matter content) of lake sediments is achieved, with excellent performance compared with results obtained by independent methods (Chapter 3). Indeed, the method has proved so successful that with isolation and measurement of appropriate end-members this multivariate regression approach to interrogating NIR spectra has potential utility across a wide range of sedimentary environments (Kuosmanen et al., 2020) and potentially for other spectral analytical methods (Stoichev *et al.*, 2020).

In chapter 4, the EMS-MR method is applied to quantify compositional components in a setting where organic materials are predominant, as a further test of the robustness of the technique. The Holcroft Moss is an ombrotrophic peat bog, where the stratigraphical sequence provides a unique opportunity for this purpose. For Holcroft Moss there were existing plant macrofossil, humification and thermal gravimetric mass loss data, which provided the possibility of independent validation of the NIRS end-member fits. Findings show short-coming in the approach regarding quantification of individual plant species. There are two thoughts on this. Firstly, that with additional examples of plant matter across a variety of states of decay in the end member library, as is observed in peat sequences, improved fits might be possible. Alternatively, the failure to fit individual plant matters may be due to an inherent similarity between the spectra measured for similar plant materials. Despite these issues, the EMS-MR approach to NIRS analysis has provided useful measures of the concentration of humic compounds in peat and has estimated well the downcore pattern of changes in peat humification producing results similar to independent measures of humification by thermo-gravimetry and UV-Visual light spectroscopy of alkali extracts from the peat.

The palaeorecords of lake water DOC concentrations and fluxes derived from sediments provide a difficult to rival opportunity for assessing the competing hypotheses mooted regarding the causes of surface water ‘brownification’. Increasing DOC concentrations across the last three decades, rising in parallel with falling acidity, has inevitably led to speculation about a direct causal link. Indeed, such a link had been predicted before ‘brownification’ had been observed, there being some laboratory experimental support for such an effect. This hypothesis has important consequences for management of the phenomenon, a matter of great concern to water supply companies for whom the cost of water treatment is increasing due to enhanced DOC fluxes. Couched in terms of recovery, based on the idea that environmental acidification had suppressed these naturally higher DOC concentrations, current policy encouraging reduced acid emissions to the atmosphere would then have played a part in driving up DOC concentrations (Evans *et al.*, 2005; Kernan *et al.*, 2010). This is an interpretation that has received support from previous palaeoecological investigations of past DOC concentrations (Cunningham et al. 2011; Bragée et al. 2015). These studies show that DOC was substantially higher prior to 20th century environmental acidification. However, the one study Bragée et al. (2015) with sufficiently long records (extending back 800 years), shows the 19th century to be a period of particularly enhanced DOC concentration. Speculatively attributing earlier change to land-use practices, this adds to the uncertainty about future trajectories of DOC fluxes, which might be driven either by changing land use or climate.

In Chapter 5, the EMS-MR has been applied to four lakes chosen from the UK Upland Waters Monitoring network (UK-UWMN). Aqueous DOC concentration records were quantified based on the principle that lake water DOC becomes incorporated into the lake sediment by flocculation and settling, at a rate that is a function of the concentration of DOC in the lake water. The concentration of this DOC component in the sediment depends on not only on the supply rate, but also the mass accumulation rate of other sedimentary components. Consequently, the sediment DOC-component concentration is only weakly related to the aqueous DOC concentrations. Their fluxes, however, are directly related, such that a burial flux record of the sediment DOC-component is an excellent proxy for the settling flux of aqueous DOC from the lake water column. Furthermore, if hydrological flushing of DOC from the lake via its outflow is taken into account, the lake water aqueous DOC concentration can be calculated from the DOC burial flux, which itself can be readily calculated from the sediment mass accumulation rate and the concentration in the sediment of the settled DOC. At the four UK Upland Waters Monitoring Network lake sites the resulting sedimentary record of past lake water DOC compares well with corresponding monitored values from the UK-UWMN data set. These show very good agreement with a good correlation across all sites ($r^2 = 0.78$) suggesting that the reconstructed record is plausible. This lends support to the approach more generally, suggesting that the palaeorecords can be used to test hypothesised causes for lake brownification.

But are such interpretations constrained, as the monitored data were, by their limited temporal extent? A 300-year duration represents a great improvement over 30 years of monitoring data, but still leaves more than 96% of the Holocene available for analysis at two of these lakes, Loch Grannoch and Llyn Cwm Mynach. Chapter 6 develops Holocene scale DOC reconstructions for Loch Grannoch and Llyn Cwm Mynach revealing a substantial mid Holocene variation in DOC supply and that the DOC maximum occurred much earlier than 19th century. In the early Holocene record, increases in DOC flux appears to be driven by the onset of warming conditions and associated expansion of vegetation and soil cover. From approximately 5000 years ago increased rates of catchment erosion and of TOM and DOC supply to both lakes reflect a response to the pressures exerted by human activities. Interestingly, DOC and TOM flux appear correlated and show synchronous patterns until approximately 2000 years ago, suggesting that there had been both similar sources and supply history for organic matter to the lake. After 2000 a BP the flux of DOC deviates from TOM flux which may be linked to cooling climate resulting in decreasing terrestrial productivity (reducing the DOC flux) and increasing soil erosion (increased the TOM flux). A similar finding has been observed in NIRS studies of lake sediments from Sweden and Canada, although the declines occur approximately 1000 a BP which may be due to differing regional climatic regimes. Here I show that the late 20th century DOC rise, captured in surface water monitoring programmes, is likely not impacted by changing patterns in acid deposition, but by a strong influence from the climate and vegetation cover, as has applied throughout the Holocene. Therefore, in the future increases in DOC flux are expected, driven by projected climatic warming affecting the terrestrial productivity of catchment landscape.

7.1 LIMITATIONS AND FURTHER POSSIBLE RESEARCH

One of the immediate challenges to improve this project is expanding the end-member library of NIRS. Firstly, this would allow for the EMS-MR application to be used in more environments where there are specific bedrock or differing vegetation types, and secondly it would provide an opportunity to investigate the potential for NIRS to quantify the degree of decay of organic matter. Decay has been shown an important influence over NIRS in applications to quantifying the quality of animal fodder (Decruyenaere *et al.*, 2009) and plant biomass (Marrs *et al.*, 2020). Measuring NIRS for decayed plant components could potentially provide significant improvement in reconstructing organic matter in peat environments (e.g. quantifying plant taxa). Results from chemometric studies certainly provide evidence that NIRS has the capability to deliver this information in a non-destructive rapid manner. With either plant matter decayed in a lab setting (after collection of fresh material matter) or the extraction of decayed materials from sediment samples this area of end-member library can be created with relative ease and limited investment. That said, the spectral similarity of NIRS across plant types may remain a barrier too far for the methodology.

During experimental data handling several anomalies were observed in the NIR spectra of sediment samples, often in the upper most sediments and peat layers. These anomalies tended to be a subdued spectral signal which correlated strongly with pollutant signals, evidenced in the core geochemistry (e.g. Pb concentrations). Given the focus here primarily on the reconstruction of natural organic matter, and that the suppression did not result in biased component fits, these signals were investigated but not reported. Several potential end-members were isolated and measured, such as coal ash from a domestic fire. They showed similar subdued signal to those sediments observed to be impacted by atmospheric pollution, suggesting that fine ash particles had coated coarser natural materials in the peat and lake sediment, weakening the natural signal. It was observed that signal resolution improved slightly with longer NIRS measurement time, however, not significantly enough to merit altering the method. This blanketing effect of 20th century atmospheric pollution affecting NIRS signal has not been reported elsewhere, possibly due to other PLS methods negating the effect of this feature during spectral peak picking. The impacts of this atmospheric pollution on ecology and biogeochemistry of terrestrial and aquatic ecosystems is unknown, but changes in the flora of ombrotrophic mire have been associated with atmospheric pollutants. Perhaps, the widely recorded damage to UK upland ecosystems, particularly *Sphagnum* mires and typically attributed to gaseous sulphur dioxide, has been misinterpreted.

A relatively simple but time consuming improvement to the research would be to expand the number and variability of lake sites included in the study. For example, to include all eleven lakes in the UKUWMN programme. This would help improve confidence in the method and enhance and consolidate the findings of this research. And with continued expansion of the end-member library more varied sites and materials could be studies for additional analytical purposes. That said, this approach would retain the focus on upland British largely oligotrophic acid affected lakes. Other potential applications of the NIRS method using multiple regression to provide rapid insight into sedimentary variations (particularly when used in multiproxy paleoenvironmental investigations). In the Department of Geography at Liverpool studies utilising the EMS-MR method for both teaching and research currently include:

- Rapid quantification of total organic matter and carbon content by NIRS in place of destructive loss-on-ignition and more expensive total carbon analysis.
- Rapid quantification of major sediment components for flood reconstruction and catchment erosion studies using lake sediments.
- Rapid quantification of major sediment components, including biogenic silica, marl precipitates, and growing number of silicate mineral species.

7.2 CONCLUDING REMARKS

The novel method developed using multiple regression of Near Infrared Spectra to quantify major sediment components has proven to be a useful tool to extend the current understanding of surface water brownification and the DOC flux from catchment to lake responsible, providing data that extends beyond the measurement period of monitoring regimes. Although extremely valuable, it is difficult to isolate the individual drivers from an assemblage that occur concurrently (such as climatic variations, storm events, atmospheric pollution) during the 30-40 year monitoring periods and compare these to DOC flux in order to fully understand the trajectory of DOC.

The findings presented here are particularly important to the understanding of underlying controls over DOC flux from catchment to lakes that data from these monitoring networks cannot provide. In reconstructing DOC variations using the sediment records, the application of EMS-MR NIRS at four upland temperate and oligotrophic lakes when compared to contemporaneous aqueous DOC measurements, the findings show that it is possible to reconstruct DOC fluxes over both 300-year and Holocene timescales.

Holocene DOC flux variations appear to occur due to climatic changes and associated changes in vegetation and catchment soils. The recent DOC increases that are commonly associated with ‘brownification’ are as expected given 20th century warming, but we reject the theory that the phenomenon is enhanced by declining acid deposition with cleaner air policies of the late 20th century. Given the trajectory for future warming, the datasets developed here suggest that landscape DOC fluxes and surface water ‘brownification’ can be expected to continue increasing.

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