

University of Stirling

Faculty of Biological and Environmental Sciences

School of Natural Sciences

**Source-to-Sea: The Transport and Storage of
Organic Carbon and Iron from Forested
Environments to (Fjord) Sediments**

by

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Abstract

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Fjords are globally important carbon stores due to their ability to store carbon long-term. However, the source of organic carbon and the influence of catchment processes and land cover on sedimentary carbon storage is poorly understood. This impacts our ability to effectively protect and manage dynamic coastal environments. Globally, ~ 20 % of organic carbon (OC) stored in sediment is directly bound to reactive iron (FeR). In this study, I explore the role of OC-FeR associations on the preservation and storage of OC in catchment and sediments of a mid-latitude Scottish fjord, Loch Creran. On average 37 % of OC was bound to FeR in forested catchment soils, 41 % in freshwater sediments, and ~16 % in fjord sediments. Ferrihydrite was found to be the dominant species of iron throughout the catchment and sediments, indicating that some OC-FeR complexes may travel from source (upstream and surrounding terrestrial environments) to fjord sediments without extensive reworking. On average, 47 – 67 % of OC in fjord sediments originated from terrestrial sources, identified from Bayesian modelling, and this was further explored using n-alkanes, specific $\delta^{13}\text{C}$ isotopic signatures and pine resins. Methyl dehydroabietate (pine resin) was able to capture the presence of coniferous material where n-alkane abundance and isotopes could not. Furthermore, biomarkers were stored effectively in fjord sediments over long time periods, showing little degradation of either proxy downcore. Through conducting a source to sea study and utilising biogeochemical information across vegetation, soils, rivers and sediments, I was able to create a better understanding of the mechanisms that promote lateral carbon movement and the chemical changes that carbon complexes can withstand. I demonstrate that in mid-latitude fjords OC-FeR complexes play an important role in biogeochemical cycling, OC storage in forest soils, and OC transport and storage from source towards sea.

Research Thesis: Declaration of Authorship

I, Celeste Cecilia Indidi Kellock, declare that this thesis and work presented in it are my own.
I have generated this work as the result of my own original research.

Signed: Celeste Kellock

April 2024

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Time is our most precious asset, and I am happy knowing that I have dedicated this time to the pursuit of a greater scientific understanding of the environment. The journey of carbon is fascinating, and brilliant, and complex and something that will continue to capture my curiosity. I finish this PhD feeling even more enthused about land-sea connections and holistic management than when I started, so I think we can call that a success.

Every year is another adventure, but so is every single day. This adventure lasted 1662 days, and now it is complete. I'm excited to see what comes next.

Chapter 1 Introduction

1.1 Overview

Scottish fjords are very efficient carbon stores (e.g., Smeaton et al., 2021; Smeaton and Austin, 2019, 2017) but the mechanisms controlling carbon storage in these regions are largely unexplored. Globally, it is estimated that ~20 % of organic carbon (OC) is bound to reactive iron (FeR) as a mechanism for carbon preservation. In this study we aim to better understand how OC and FeR interact in a mid-latitude fjord setting and to what extent OC storage may be influenced by catchment forest cover and terrestrial inputs.

1.1.1 Carbon cycle

Carbon is present throughout all environmental systems and is a major component of life on earth and biogeochemical cycling. Carbon is stored across the lithosphere (Gislason and Oelkers, 2014), biosphere (Cannell et al., 1999; Keenan and Williams, 2018; Krankina and Harmon, 1994), atmosphere and oceans (e.g., Khatiwala et al., 2013), all of which serve as important carbon stores. It can be transported between these different reservoirs and stored for different periods of time depending on biological, chemical and physical conditions. The cycling of carbon throughout the biosphere helps to regulate atmospheric carbon dioxide (CO₂) concentrations through photosynthesis and respiration from plants (Hopkins et al., 2014), the oceanic biological pump (biologically mediated carbon sequestration) and solubility pump (physical and chemically mediated carbon sequestration) (Rose and Waite, 2003). The marine environment is the largest of the carbon reservoirs storing ~2322 Pg C in the top 1m of sediments alone (Atwood et al., 2020) and longest-term carbon sink on earth (Burdige, 2007). Briefly, carbon can be removed from the atmosphere by photosynthesis of plants, some of this may be released back into the atmosphere through respiration, but a portion of it contributes to soils through transport from roots and dead plant material which can provide relatively long-term carbon storage. Carbon buried in coastal and marine sediments can be stored for much longer periods of time due to their isolation from the atmosphere and exposure to oxygenated conditions. Terrestrial deposits can contribute to sedimentary carbon stores through lateral transport, as can all plants and organisms in the oceans. Over millions of years, this can form coal, oil and gas, that we have utilised for centuries for fuel and energy, releasing this long-buried carbon back into the atmosphere as CO₂.

The imbalance in Earth's natural carbon cycle has largely been caused by anthropogenic emissions (Figure 1.1), primarily through the burning of coal, oil and gas and additionally through large scale land use change and deforestation (Friedlingstein et al., 2023). As such, industries with the highest emissions continue to be energy, transport, construction and agriculture (Ritchie et al., 2020). Marine and terrestrial environments continue to uptake increasing amounts of CO₂ from the atmosphere, but the constantly increasing CO₂ emission

and changes in land use and land cover (i.e. vegetation change and ice melt) make this unsustainable.

The global carbon cycle

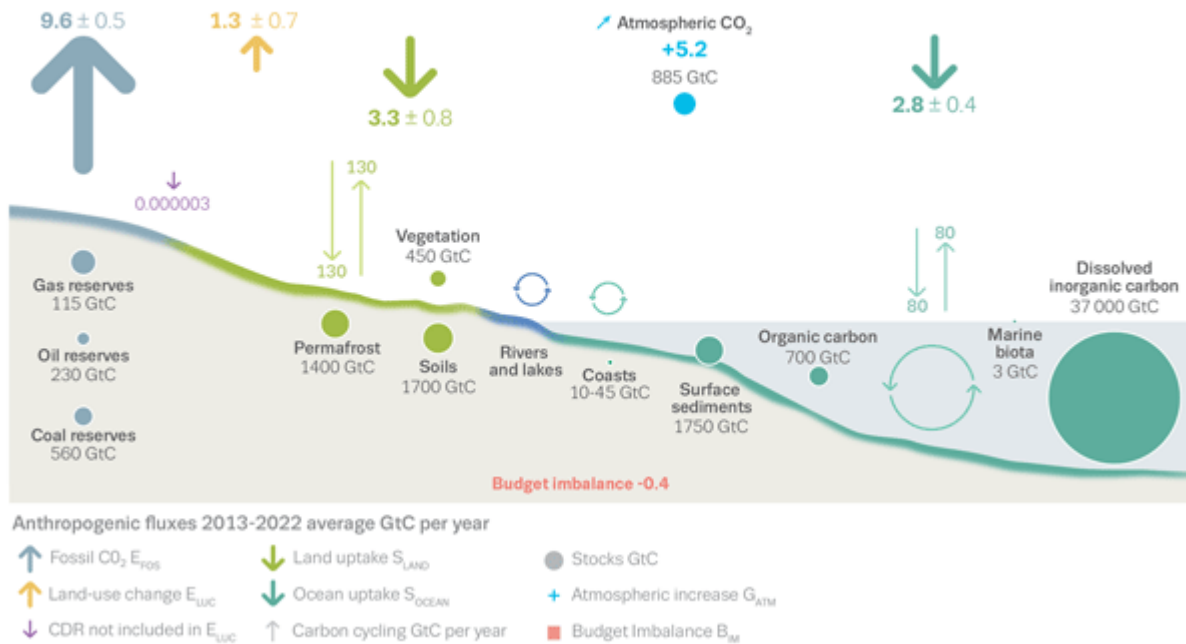


Figure 1.1: A schematic of the global carbon cycle highlighting the main fluxes of carbon across different environmental systems (Friedlingstein et al., 2023).

1.1.2 The importance of coastal systems

Recently, the global importance of sedimentary coastal carbon stores has been recognised (Atwood et al., 2020; Smeaton et al., 2016) (e.g., “blue carbon” in mangrove forests, seagrass beds, saltmarshes; (Duarte et al., 2005). In particular, fjords have been highlighted as highly effective carbon stores (Bauer et al., 2013a; Bianchi et al., 2020; Cui et al., 2016; Smeaton et al., 2017; Smith et al., 2015) which is influenced by their physical characteristics. Fjords are U-shaped valleys carved by glaciers that are elongated and relatively narrow in shape and are often encapsulated by steep topography. Most fjords have terminated moraine at their mouth (opening towards the sea) that forms a sill (Dürr et al., 2011) and in addition this can result in formation of different basins within a fjord. Sills help to create a semi-enclosed environment in which terrestrial sediments can accumulate (Smith et al., 2015). This accumulation can result in high resolution records of climate (Howe et al., 2015) and land use change (Macklin et al., 2000) and aid OC accumulation.

Fjords account for 75 % of the coastline above 70° North (Dürr et al., 2011) and are responsible for ~11 % of global oceanic OC burial (Smith et al., 2015). They are globally important features, located across North-west Europe (Norway, Sweden, and Scotland), Greenland (Eastern and Western), Svalbard, Western and Eastern Canada (British Columbia, sub-Arctic and Arctic), Alaska, Chile, New Zealand and Antarctica (Dürr et al., 2011; Smith et al., 2015) (Figure 1.2).

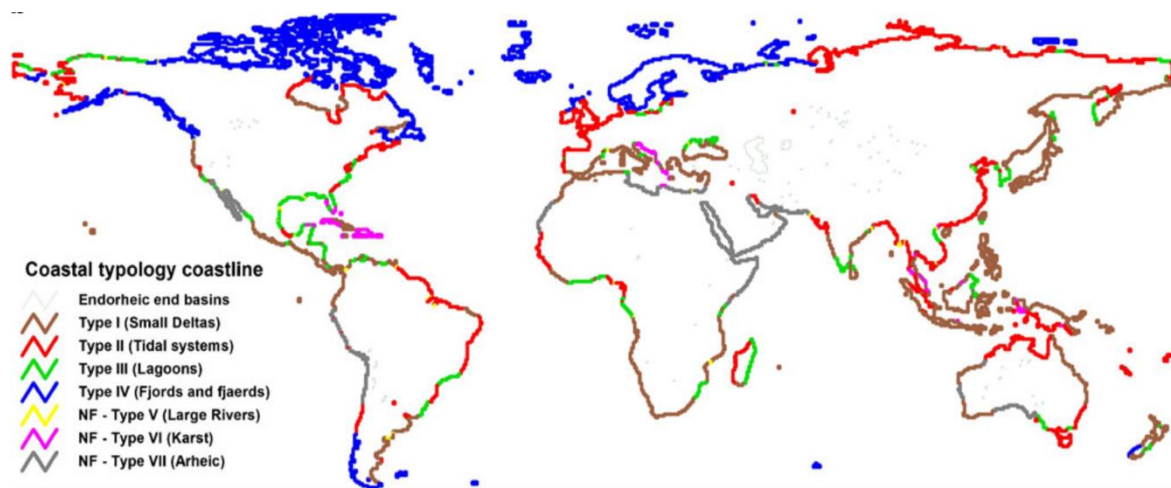


Figure 1.2: Global coastal environments highlighting deltaic and tidal systems, lagoons, fjords, large rivers, endorheic basins, karst and arheic systems (Durr et al., 2011).

1.2 Vertical and lateral fluxes of Carbon

Carbon can be exchanged vertically and transported laterally throughout Earth's systems. Vertical fluxes of carbon between the atmosphere and terrestrial / marine environments have been the focus of research and policy (e.g. Friedlingstein et al., 2019; IPCC, 2013) for a considerable amount of time, while the lateral transport of carbon and the importance of coastal systems have been largely dismissed in global carbon budgets and cycles until recently (IPCC., 2021, Regnier et al., 2022). While terrestrial and marine environments, and soils and sediments, represent distinct systems, studies often do not consider or address the inherent links between them. Terrestrial and marine ecosystems are connected through rivers and coastal systems. Rivers are important sources of (both dissolved and particulate) carbon and nutrients to coastal systems (Gao et al., 2022; Stutter et al., 2008; Wang et al., 2004) and river catchments are the primary source of material to fjords (Smith et al., 2015). Rivers, inland waters, and coastal regions can be strongly influenced by terrestrial flows and land use (Battin et al., 2023). Water flows freely (unless anthropogenically disturbed) from source to sea and provides the opportunity for the transport and transformation of carbon (Cole et al., 2007) between different storage reservoirs (soils, sediments, atmosphere).

Understanding what controls the lateral fluxes of carbon is key to fully understanding the global carbon cycle, terrestrial and marine carbon budgets, and how these might be influenced by a changing climate. The amount of carbon transported globally through lateral transport is thought to be comparable to the net carbon stored in global terrestrial systems ($\sim 2.3 \text{ PgC yr}^{-1}$) (Regnier et al., 2022), and the lateral contribution of carbon to rivers ($\sim 113 \text{ Tg}^1$) is comparable to the amount of carbon stored in European forests (Ciais et al., 2008). Therefore, lateral carbon fluxes account for a sizeable and important portion of carbon in the global cycle.

This lateral carbon transport is generally driven by erosion, run off, and riverine transport (Olson et al., 2016; Regnier et al., 2022; Zhang et al., 2022). Lateral flows are sensitive to land-use change, erosion, anthropogenic flows and climate (Bauer et al., 2013a; Cummins et al., 2011; Jobbagy and Jackson, 2000; Olson et al., 2016). Soils are the largest terrestrial carbon store (Scharlemann et al., 2014) and losses of soil OC were previously considered to be mostly through respiration to the atmosphere. However, while terrestrial OC can be lost to the atmosphere while being transported from land to the ocean (Blattmann et al., 2019; Campeau et al., 2019; Hope et al., 1994) it is thought that 25-50% of terrestrially derived OC that is transported through rivers is exported to coastal sediments (Cai, 2011). The non-respired carbon is buried en-route in riverine and coastal sediments, but this proportion is not well constrained largely due to a lack of observational data (Zhang et al., 2022).

Recent work has begun to assess riverine inputs to coastal systems (Araujo et al., 2014; Gao et al., 2022) with models incorporating lateral carbon fluxes across the land-sea interface into carbon budgets (Fendrich et al., 2024; Zhang et al., 2022). While the lateral movement of carbon (dissolved and particulate) across the land-sea interface has been examined (Amon et al., 2012; Cole et al., 2007; Regnier et al., 2022; Tank et al., 2018) we do not yet have a comprehensive understanding of the sources and mechanisms of carbon transport across systems due to limited research on the physical and chemical mechanisms supporting OC transport.

1.3 The iron and carbon cycle

Iron (Fe) cycling plays an important role in global marine biogeochemical cycling (Rose and Waite, 2003) and is an essential element in many biological processes and for almost all living organisms, both in the oceans and on land (Melton et al., 2014). Fe plays a vital role in the biological pump (Muller, 2018) influencing the cycling of both carbon and nutrients (Tagliabue et al., 2017) while playing an essential role in the removal of CO_2 from the atmosphere (Muller, 2018). The main sources of Fe are from atmospheric dust, coastal and shallow sediments,

sea ice, oceanic upwelling, hydrothermal fluids, and chemical weathering of rocks (Boyd and Ellwood, 2010; Hawkings et al., 2014; Rafter et al., 2017; Tagliabue et al., 2017). Fe mainly exists in two states on land and in water: Fe(II) and Fe(III), the former being soluble and the latter being thermodynamically stable but insoluble (Laglera et al., 2011). The speciation of Fe is dictated by environmental factors that can vary between seasons and locations (Öztürk and Bizzel, 2003) but changes in redox and salinity are the largest governing factors.

Organic carbon and Fe bind in organo-mineral complexes (explained below) which means that the lateral and vertical distribution of Fe is important in biogeochemical cycling and carbon storage. Therefore, understanding how Fe reacts across the land-sea interface is critical to understanding one of the controls on OC transport and storage. Studies suggest that >90% of Fe may be stored or removed in the zone of transition between rivers and coastal environments (Öztürk et al., 2002) but this is not well constrained. OC-Fe complexes can be transported across changes in salinity (Herzog et al., 2020; Muller, 2018) but it is unclear why some complexes remain intact while others do not. Furthermore, riverine flows of Fe to coastal waters are often underestimated as only the largest rivers have been taken into consideration (Schröder et al., 2016).

1.3.1 OC-Reactive Fe associations

Carbon can be sequestered biologically, physically and chemically. Physical mechanisms include associations with silts and clays (Solomon et al., 2005), formation of aggregates (Fritzsche et al., 2015), or mineral association of OC in soils (Han et al., 2016; Kaiser and Guggenberger, 2000; Kopittke et al., 2020; Wagai and Mayer, 2007; Ye et al., 2022; Zhao et al., 2016), and freshwater, estuarine and marine sediments (Barber et al., 2017; Faust et al., 2021; Hemingway et al., 2019; Keil and Mayer, 2013; Lalonde et al., 2012; Shields et al., 2016; Wang et al., 2018). Reactive Fe (FeR) phases (e.g. iron oxides) and species (e.g. ferrihydrite, hematite, akageneite) exist as nanoparticles, colloids or amorphous materials (Schröder et al., 2016) and OC can bind on the surface of Fe oxides (sorption) or within aggregates (co-precipitation) (Barber et al., 2017). Different functional groups are involved in the binding of FeR and OC, principally; carboxylic, phenolic and catechol (Muller, 2018). The presence of highly reactive binding sites on organic matter is also crucial to mineral associations (Muller, 2018). Dominant FeR phases can vary depending on environmental conditions such as temperature, light (Öztürk et al., 2002), redox and pH (Morrissey and Guerinot, 2009) and therefore can differ in systems across the land-sea interface. Carbon can bind to different mineral surfaces such as clay and aluminium minerals. However, Fe has a higher sorption capacity to carbon than other metal oxides (Zhao et al., 2016).

OC-FeR associations are termed the 'Rusty Carbon Sink' (Lalonde et al., 2012) because the complexes prevent OC from decaying into CO₂. This complexation may enhance the transport of particulate Fe and OC to coastal waters but it decreases the amount of bioavailable iron and carbon (Schröder et al., 2016). Iron minerals stabilise and preserve OC in sediments over geological timescales (Faust et al., 2021; Lalonde et al., 2012). OC also stabilises Fe minerals (Schröder et al., 2016), particularly when they form nano-sized aggregates in sediments (Muller, 2018). Free Fe oxides are not thermodynamically stable under anoxic conditions therefore, complexation with OC inhibits their dissolution and stabilises the Fe in return for protection (Muller, 2018). This mutual stabilisation enables FeR and OC to avoid degradation (Barber et al., 2017). Both dissolved and particulate carbon can adsorb to minerals increasing protection against mineralisation of OC and dissolved OC (Kaiser et al., 1996; Kaiser and Guggenberger, 2000; Kindler et al., 2011).

Examples of types of bonds that can occur between OC and FeR include: binding between FeR and functional carboxyl groups (Barber et al., 2017), single and multi-layer sorption (Wagai and Mayer, 2007), co-precipitation (particularly at redox boundaries) (Lalonde et al., 2012; Riedel et al., 2013), and sorption of OC to pre-established OC-mineral aggregates (Kopittke et al., 2020). OC-FeR associations can occur pre- and post-deposition in sediments (Shields et al., 2016). To determine the type of binding between OC-FeR complexes, the molar ratio of OC:FeR is used. OC:FeR values <1 indicate sorption is the dominant binding mechanism, while values >1 (particularly between 6-10) indicate co-precipitation is the dominant binding mechanism (Wagai and Mayer, 2007). All OC released from extraction experiments is likely to be bound to FeR, but not all FeR is necessarily bound to OC, therefore there can be slight discrepancies in the OC:FeR ratios tending to lower values (Fisher et al., 2020).

Iron minerals play an important role in OC storage, an average of 20% of marine sedimentary OC is thought to be bound to FeR (Lalonde et al., 2012) and variable amounts of soil OC is bound to Fe minerals (Ye et al., 2022; Zhao et al., 2016). On average, it is thought that ~63% of OC may be bound to Fe (and potentially aluminium) minerals in soils (Kramer and Chadwick, 2018). OC-FeR binding in terrestrial environments can be influenced by latitude (Zhao et al., 2016), soil and sediment properties (Ye et al., 2022) and land use and land-use change (Basile-doelsch et al., 2009; Bond et al., 2021; Giannetta et al., 2022; Longman et al., 2022). OC-FeR relationships have been well-studied in terrestrial systems (Han et al., 2016; Kaiser and Guggenberger, 2000; Kopittke et al., 2020; Wagai and Mayer, 2007; Ye et al., 2022; Zhao et al., 2016) and marine sediments (Lalonde et al., 2012; Shields et al., 2016), but few studies have made connections between soil OC-FeR and OC-FeR stored in coastal and marine sediments.

Our understanding of OC-FeR relationships has progressed across land-sea interface to varying extents, e.g., coastal systems (Bianchi et al., 2020; Zhao et al., 2023), riverine to coastal waters (Batchelli and Lee, 2010; Herzog et al., 2020; Krachler et al., 2016, 2010; Kritzberg et al., 2014), river-estuary sediment transects and the transport of particulate matter (Jilbert et al., 2018). Jilbert et al., (2018) provide the closest OC-FeR source-to-sea study that I know of at present, but despite this research being conducted several years ago, there still lacks a collective discussion and rise in research that evaluates source materials (vegetation, soils) and transport (rivers, inland waters) of OC-FeR complexes through to coastal sediments to obtain a full source-to-sea view of carbon transport in different catchment systems.

1.3.2 Methods of extraction

A variety of analytical techniques can be used to characterise OC-FeR interactions in water, soil and sediments. To characterise Fe speciation, conventional analytical techniques such as XRD (Hepburn et al., 2020), SEM and BET (Von Der Heyden et al., 2019) are not sufficient. To establish the presence, concentration and speciation of Fe in samples, elemental analysis and chemical iron extraction methods are necessary (e.g. Hepburn et al., 2020; Poulton and Canfield, 2005) and Mössbauer spectroscopy can enable different Fe species to be identified (Schröder et al., 2016; Zhao et al., 2018).

Extraction techniques vary depending on the desired Fe species and carbon dissolution. Poulton and Canfield (2005) have a well-established sequential extraction technique that enables the division of FeR into several pools; carbonate iron, oxyhydrides, magnetite, pyrite and silicates, but it relies on firm dissolution boundaries between different minerals, and this does not hold true across all samples, meaning that not all FeR pools are dissolved with each chemical extraction (Hepburn et al., 2020). Modified versions of this method have been used to determine Fe speciation and the total FeR pool in samples (Burdige and Christensen, 2022; Wang and Zhu, 2018).

The dithionite-citrate-bicarbonate (dithionite extraction) method is one of the most common methods used, particularly for sediment extractions, which was first introduced by Mehra and Jackson, (1958) and later adapted by Lalonde et al., (2012). Due to its popularity, this method and variations of it, can be utilised for a wide-ranging comparison of studies (e.g. Kaiser and Guggenberger, 2000; Lalonde et al., 2012; Zhao et al., 2023) but these are not always well calibrated to methodological variations and inconsistencies in the amount of the total FeR the method is able to dissolve (Fisher et al., 2020). Therefore, while this method is well used, there are several studies that show that the dithionite extraction method has difficulty dissolving all

FeR phases (Adhikari and Yang, 2015; Fisher et al., 2020; Hepburn et al., 2020) potentially leading to an underestimation of the OC and FeR pools across different environments.

1.4 Carbon storage in Scotland's Fjords

A national assessment of carbon stocks in Scotland's mid-latitude fjords provides estimates of their carbon storage capacity (~641 Mt C) and carbon burial rates (up to ~40615 T yr⁻¹) (Smeaton et al., 2017) while a variety of other studies have progressed our understanding of the sediment type (Hunt et al., 2020; Smeaton and Austin, 2019) and sources (Loh et al., 2008b; Smeaton and Austin, 2017, 2022). However, there remains a lack of studies investigating the land-to-sea journey of OC, and the mechanisms that may support this terrestrial and marine OC transport and burial. Projects such as LOCATE (Land-Ocean carbon transfer e.g. (García-Martín et al., 2023; Tye et al., 2022)) have progressed understanding of the movement of carbon across the land-sea interface in the UK but did not sample fjord catchments on the west coast of Scotland, of which there are 111 (Edwards and Sharples, 1986) so do not provide information on the transport and associated mechanisms controlling OC storage in these regions. There's a growing range of research in OC-FeR associations in fjords in northern and southern latitudes (Bianchi et al., 2020; Burdige and Christensen, 2022; Cui et al., 2022; Lalonde et al., 2012; Longman et al., 2022), but little to no information on OC-FeR associations in Scottish fjords and coastal environments.

Recent studies have highlighted that significant amounts of terrestrial OC are buried in Scottish fjords (Loh et al., 2008b; Smeaton and Austin, 2022). Fjords can be surrounded by many different types of land cover and land uses, but there is little research showing the links between terrestrial and coastal carbon stores in Scotland. In particular, changes in forest cover are of interest as increasing global tree cover is one mechanism being used to increase CO₂ sequestration and mitigate climate change globally and there are ambitious targets for afforestation in Scotland (The Scottish Government, 2019). Current climate and available area can support an additional 0.9 billion hectares of forest which could sequester over 200 gigatonnes of carbon globally (Bastin et al., 2019). Estimates of historical land cover suggest that Scotland may have had 50-60% forest cover thousands of years ago (Heitzman, 2003; Mather, 2004) but a range of factors led to extensive forest decline, and by 1900, only ~5% forest cover remained (Heitzman, 2003). Over the last ~100 years Scotland has undergone a significant period of afforestation from 5 % to ~19% (The Scottish Government, 2019) Scottish forest cover remains below the EU average of 38%. Despite this change in land use there are few studies that show the impact this deforestation and afforestation has had across the land-sea interface, in particular on OC transport and storage. Felling events are capable of causing

large increases in lateral dissolved OC transport (Laudon et al., 2009; Nisbet, 2001; Schelker et al., 2012), therefore significant deforestation in Scotland and smaller continuous felling events may be visible in coastal sediments.

During the 20th century, a desire to afforest areas of the UK resulted in mono-culture planting in an attempt to help reduce atmospheric CO₂. For example, in Scotland, Sitka spruce accounts for up to 33 % of the woodland cover, some of which was planted across peat bogs (Sloan et al., 2018). The current desire to increase forest cover within Scotland has previously led to trees being planted in largely uninhabited spaces, such as peatlands. It is estimated that Scottish peatland occupies 1727 kha and stores 1620 Mt of carbon (Chapman et al., 2009). A lack of understanding regarding the valuable carbon storage capacity of peatlands resulted in the drying of many peatland areas for planting (Sloan et al., 2018) that caused a release of CO₂ into the atmosphere (Hargreaves et al., 2003). Peatlands store more carbon when in a healthy condition, therefore the drying of peatlands for tree planting caused a release of CO₂ from an efficient and relatively long-term carbon store due to a lack of understanding regarding the valuable carbon storage capacity of the land (Hargreaves et al., 2003; Sloan et al., 2018). As forests approach harvesting age, peatland restoration is being considered (Sloan et al., 2018). However, this can change redox conditions (Riedel et al., 2013) which can result in the release of nutrients, dissolved OC and iron from soils (Zak and Gelbrecht, 2007). This provides an apt example for the need to understand environmental systems before conducting large scale changes in land use (such as tree planting), to ensure that valuable carbon resources can be fully understood and utilised. The desire to afforest Scotland continues, with an increasing interest in diversification and biodiversity benefits (The Scottish Government, 2022, 2020) therefore, understanding the impact of changes in forest cover across different environmental systems is beneficial.

1.5 Thesis objectives and structure

The importance of terrestrial carbon stores (soils, forests) is well known, as is the central role that oceans play in the global carbon cycle (e.g. Friedlingstein et al., 2023; Khatiwala et al., 2013; Scharlemann et al., 2014). Recent research has highlighted the importance of a range of coastal and intertidal environments to the global carbon cycle, such as saltmarsh (Miller et al., 2023; Smeaton et al., 2023), seagrass (Potouroglou et al., 2021), mangrove environments (Alongi, 2020, 2012; Huxham et al., 2018), and coastal sediments (Deb and Mandal, 2021; Luisetti et al., 2019; Craig Smeaton et al., 2021). Mineral associations with OC act as a mechanism for OC burial globally in marine environments (Barber et al., 2017; Cui et al., 2022; Faust et al., 2020; Lalonde et al., 2012; Longman et al., 2022; Zhao et al., 2023) and terrestrial

environments (e.g. Borggaard, 1982; Gabriel et al., 2018; Keil and Mayer, 2013; Kögel-Knabner et al., 2008; Zhao et al., 2016). However, there remains a limited studies that assess the spatial and temporal associations of OC and FeR across the land-sea interface and this thesis aims to address this.

The aim of this study was to evaluate and develop understanding of organo-mineral binding in a mid-latitude fjord. This was done through the following objectives:

1. Determine how much organic carbon in Loch Creran is bound to reactive iron and the broad origin of this material.
 - a. Estimate whether OC-FeR align with measurements from other studies.
 - b. Explore spatial and temporal variation in binding mechanisms.
 - c. Better constrain estimates of terrestrial OC throughout the fjord.
 - d. Determine whether this dataset indicate the main drivers of OC-FeR complexation.
2. Explore the role of catchment forest cover on the origin, transport and storage of OC in freshwater and fjord sediments.
 - a. Investigate how effective bulk geochemical and biomarker data are at identifying specific sources of OC in soils and sediments. In particular, tree species.
 - b. Establish whether n-alkane data and indices can be used for tree species identification in soils and sediments.
 - c. Improve understanding of the composition and transport of terrestrial OC in this fjord.
3. Investigate OC-FeR associations in catchment soils and contribute to a better understanding of where sedimentary complexes come from along a soil-freshwater sediment-fjord sediment transect.
 - a. Evaluate the differences in OC-FeR complexation in soils in comparison to fjord sediments.
 - b. Investigate whether OC-FeR binding mechanisms and iron speciation the same in soils and sediments.
 - c. Understand the dissolved and particulate loads of carbon and iron in river and lochan waters.
 - d. Establish whether the freshwater lochan acts as a sediment trap for terrestrial OC.

This forms three scientific chapters:

1.5.1 Chapter 2 – The influence of reactive iron on C storage in a mid-latitude fjord

A range of geochemical techniques were employed to assess the amount of OC bound to FeR in a mid-latitude fjord and establish the main binding mechanism for this association and primary species of Fe involved. Data from this study suggest that an average of 16% OC is bound to FeR in Loch Creran, providing an example for mid-latitude fjords which is comparable to the 20% average for marine sediments. Mössbauer Spectroscopy identified ferrihydrite as the dominant species of FeR in the fjord. This chapter found FeR exerts a significant influence on OC storage spatially and with depth, and that OC is capable of preserving less stable species of iron in this fjord and likely many other locations.

1.5.2 Chapter 3 – Exploring the use of n-alkanes for investigating the distribution and origin of organic C from forested catchment to fjord sediments

This chapter focused upstream to provide insight into the terrestrial carbon stored in fjord sediments. I utilise bulk sediment measurements from Chapter 2 and build upon them with biomarker analysis of n-alkanes and pine resins (methyl dehydroabietate) to establish the composition of catchment vegetation and soils. N-alkanes and biomarker specific carbon isotopes were able to distinguish differences in vegetation signatures and to some extent soil and freshwater sediment inputs, particularly for deciduous vegetation, but were ineffective at determining coniferous inputs in any sediments.

1.5.3 Chapter 4 – Iron and carbon associations from source-towards-sea

This chapter introduces soil and freshwater sediment OC-FeR data to provide a transect of mineral bound OC from land-towards-sea. I find soil in this mixed catchment to be consistent with other forested catchments at ~37% OC-FeR and higher than other land cover / uses (grasslands, peatlands). The primary binding mechanism in soils and freshwater sediments is sorption, akin to fjord sediments. Ferrihydrite appear to dominate soils, freshwater and fjord sediments within this catchment. I suggest that a portion of the OC-FeR in fjord sediments may be directly transported from catchment soils through rivers and run-off as binding mechanisms and iron speciation remain consistent and there are relatively high particulate Fe concentrations transported downstream, supporting the notion that Fe may be complexed to OM in the rivers in this catchment.

Chapter 2 The Influence of Reactive Iron on Carbon Storage in a Mid-Latitude Fjord

2.1 Abstract

Fjords are recognised as globally important carbon stores due to their efficiency for long-term carbon storage. Despite this, there is a lack of knowledge regarding the mechanisms by which carbon is stored, which impacts our ability to understand, protect and improve these environments. Mineral associations are one mechanism that can facilitate carbon storage. We assess the influence of reactive iron associations on the preservation and storage of organic carbon in the sediments of a mid-latitude fjord. A suite of samples from the head towards the mouth of Loch Creran were analysed using various geochemical techniques to determine the abundance of organic carbon and iron in this fjord, dominant influences, origins, binding mechanisms, and abundance of organic carbon-iron associations with space and depth. On average we find ~16 % of organic carbon in Loch Creran is bound to reactive iron and this varies from ~3-39 % spatially and with depth, which is comparable to that of marine estimates. We estimate that 47–67 % of organic carbon in the fjord comes from terrestrial sources and suggest that a proportion of the organic carbon-reactive iron compounds are transported from upstream terrestrial environments. The efficiency and longevity of these complexes are investigated in surface sediments and downcore, and our results show that iron minerals play an important role in the storage of organic carbon, and that organic carbon effectively stabilises reactive iron phases at different depths in fjord sediments. This research is important for understanding the mechanisms of sedimentary carbon stores in mid-latitude fjords.

2.2 Introduction

Fjords are key components of the global carbon cycle (Bianchi et al., 2020). Situated at the interface between terrestrial and marine systems, they can be influenced by both environments. Globally, it is estimated that fjord sediments capture approximately 11 % of the OC buried in the marine environment each year (Smith et al., 2015) and between 55-62 % of OC held within fjord sediments originate from the terrestrial environment (Cui et al., 2016). Until recently fjord sediments have been missing from global sedimentary organic carbon (OC) estimates. However, it is now recognised that fjord sediments play an important role in the burial (Smith et al., 2015) and storage (Smeaton et al., 2016, 2017) of OC. Despite this, there remains a limited understanding of the mechanisms that facilitate the transport and storage of OC over time in fjord sediments, in particular the role of mineral associations. This lack of understanding can hinder our ability to effectively manage and protect these environments and the services that they provide.

It is well known that OC-mineral binding can play a vital role storing OC in marine sediments (Lalonde et al., 2012) with several studies highlighting the importance of OC-Fe associations in marine sediments and coastal shelves (e.g. Lalonde et al., 2012; Shields et al., 2016; Zhao et al., 2023, 2018) with few focussed specifically on carbon storage mechanisms in fjords (e.g. Cui et al., 2022). In particular, iron (Fe) plays an important role in global marine biogeochemical cycling (Rose and Waite, 2003) and mineral preservation of OC in marine sediments (e.g. Hemingway et al., 2019; Lalonde et al., 2012; Schröder et al., 2016). While OC can bind to different mineral surfaces and metal oxides, reactive iron (FeR) is found to have a relatively high sorption capacity to OC (e.g. Kaiser and Guggenberger, 2000; Tipping, 1981; Zhao et al., 2016) and is the focus of this work. Global estimates suggest that ~20% of OC is preserved by FeR in marine sediments and these complexes are termed the 'Rusty Carbon Sink' (Lalonde et al., 2012) as they prevent OC degrading into carbon dioxide (Schröder et al., 2016). Here we consider FeR to be forms of Fe (III) that can, or should, be reduced by sodium dithionite extractions, including but not limited to ferrihydrite, lepidocrocite, goethite (Hepburn et al., 2020; Lalonde et al., 2012; Zhao et al., 2018). The speciation of Fe is dictated by environmental factors that can vary between seasons, locations (Dang et al., 2015; Öztürk and Bizsel, 2003) and changes in salinity gradients (Herzog et al., 2019; Herzog and Kritzberg, 2017; Ussher et al., 2007). The timing of OC-mineral binding remains unclear, with recent research suggesting that binding may occur before the sediment-water interface (Faust et al., 2023), indicating that binding may occur in the water column or in riverine and terrestrial environments. While we know that OC-FeR associations are present in soils, whether these associations remain intact from terrestrial environments to coastal sediments is not well understood. The land-sea interface is therefore an interesting study site for carbon-mineral binding to establish the role that FeR plays in carbon storage in fjord sediments.

The sediments of Scotland's mid-latitude fjords store 252 ± 62 Mt and annually bury 84,000 tonnes of OC with an estimated 52 ± 10 % of the OC originating from the terrestrial environment (Smeaton and Austin, 2019, 2022). In coastal environments, OC can be derived from natural, anthropogenic, marine and terrestrial sources (Thornton and McManus, 1994). Progress has been made to quantify the amount of OC stored (e.g. Cui et al., 2016; Smeaton et al., 2021a; Smeaton et al., 2017; Smith et al., 2015, Faust et al., 2014, 2017, 2019) and to determine the terrestrial and marine contributions to mid-latitude fjords sediments (Smeaton et al., 2021b; Smeaton and Austin, 2022). The sediments of Scotland's fjords have been shown to be hotspots for OC with roughly half of the annual OC burial originating from the terrestrial environment (Smeaton et al., 2017; Smeaton and Austin, 2019, 2022). Though clearly an important component of the coastal C cycle we know little about the role of Fe in these fjord systems. Research in sedimentary OC-FeR complexes has generally concentrated

on 'surface sediments' with minimal analysis focussed on mineral binding with depth and across different redox dynamics (e.g. Faust et al., 2021). Through this work we aim to further understand the spatial and temporal role of OC-FeR associations in a mid-latitude fjord. We investigate the main Fe species present, whether these change over time in the sediments, and the main drivers of OC-FeR binding. Furthermore, we are able to test the effectiveness of the dithionite extraction technique in dissolving FeR.

2.3 Study Area

2.3.1 A descriptive heading about methods

Loch Creran is one of the 111 large fjords (over 2km long with a fjord length that is at least twice the fjord width) located on the West Coast of Scotland (Figure 2.1). Loch Creran is 12.8 km in length, occupies an area of 13.3 km² and is relatively shallow with a maximum depth of 49 m. A catchment of ~164 km² drains into the relatively well mixed and ventilated waters, which maintain mostly oxic conditions (Smeaton et al., 2017). There is one main inflow from the River Creran and one outflow into Loch Linnhe, making it a relatively enclosed system. Within Loch Creran, there is a sill at Creagan that separates a smaller upper basin from the larger lower basins (Figure 2.1). UB1 and UB2 are the cores taken within the upper basin, and LB1 and LB2 are the cores taken within the lower basins (Figure 2.1). The lower basins are separated by two further sills (Loh et al., 2010). In this study, the 'upper basin' will refer to the basin closest to the riverine/terrestrial input, and the 'lower basins' will refer to the basins after Creagan narrows (encompassing the lower two basins separated by sills into one term). The deepest point of the upper basin is 37 m while the lower basins reach a maximum depth of 49 m (Loh et al., 2010). The fjord is flushed every ~3 days, where 60 % of the water volume is exchanged with coastal water (Edwards and Sharples, 1986) and mixing is sufficient to ensure ventilation of bottom water (Gage, 1972). The salinity of the water in the fjord near the mouth of Loch Creran had <1 ‰ difference to water outside the fjord and there was a difference of ~8‰ between surface and deeper waters (ranging from ~25-33 ‰). The upper basin, above the Creagan narrows is thought to be the source of low salinity fresh water (Gage, 1972). Strong winds and high tidal currents enable mixing of fresh and saline water within the fjord (Almroth-Rosell et al., 2012). The cores in this study have not been dated but it is estimated that sediment accumulation rates do not drastically differ between the upper and lower basins based on previously dated cores in Loch Creran (Smeaton et al., 2021). A twin sediment core for UB2 dates 27.5cm depth with the year 1904 (sedimentation rates vary between 0.12 – 1.10 cm yr⁻¹) and comparatively, a sediment core taken from the lower basins below LB2, dates 27.5 cm at the year 1892, and sedimentation rates varied between 0.12 – 3 cm yr⁻¹.

Loch Creran Overview

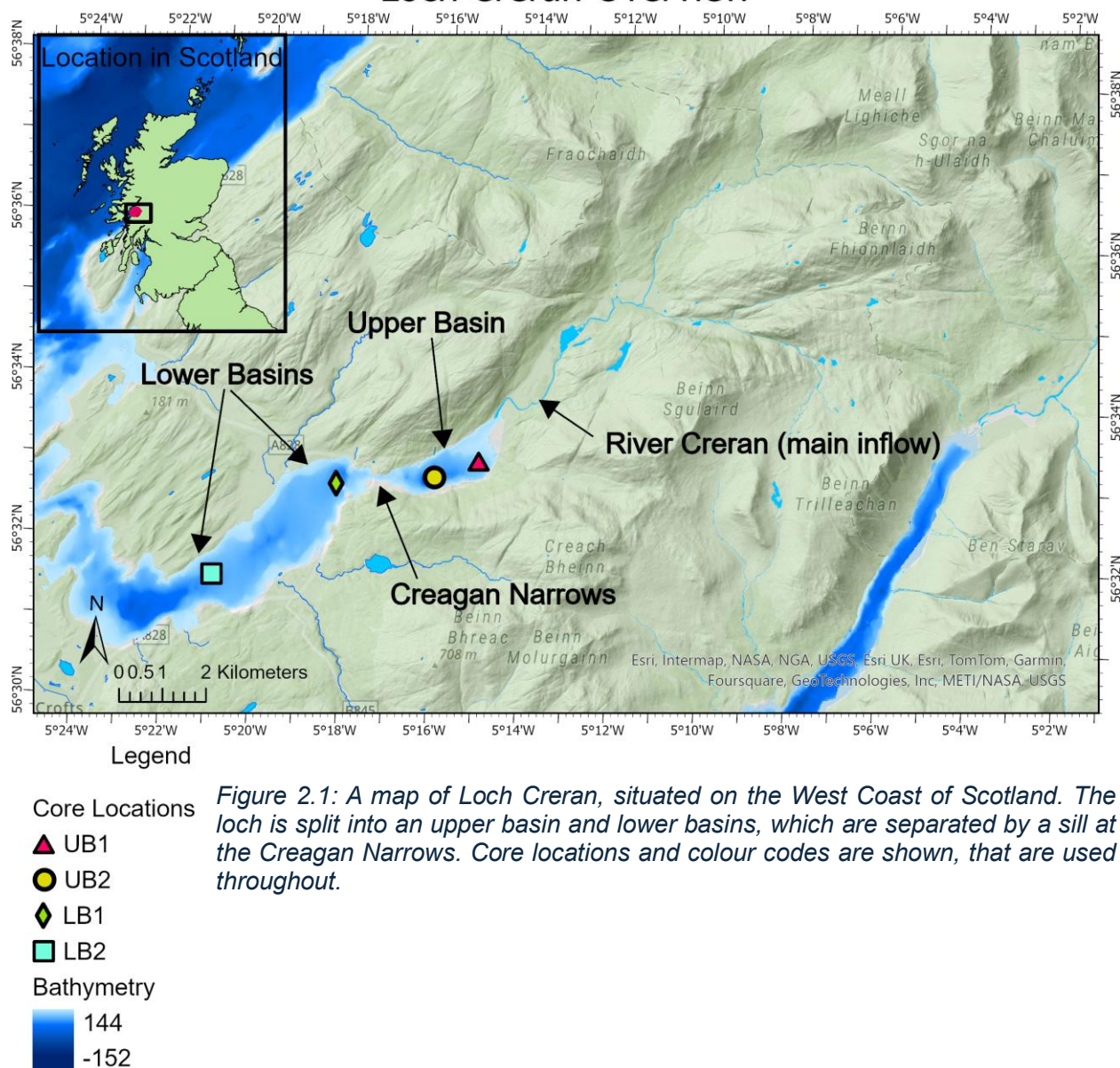


Figure 2.1: A map of Loch Creran, situated on the West Coast of Scotland. The loch is split into an upper basin and lower basins, which are separated by a sill at the Creagan Narrows. Core locations and colour codes are shown, that are used throughout.

There has been a variety of research in Loch Creran trialling carbon mapping techniques (Hunt et al., 2020) quantifying OC stocks (Loh et al., 2010; Smeaton et al., 2017) and OC burial rates (Smeaton and Austin 2019). The postglacial sediments of Loch Creran are estimated to hold 2.6 Mt of OC (Smeaton et al., 2017) and accumulate on average $42.3 \pm 18.4 \text{ gC m}^{-2} \text{ yr}^{-1}$, which results in the fjord sediments gaining a further 205 ± 89 tonnes of OC annually (Smeaton and Austin, 2019) with $66 \pm 13 \%$ of that OC originating from the terrestrial environment (Smeaton and Austin, 2022). In comparison, accumulation rates across Scottish fjord sediments are estimated to be higher (averaging $\sim 57.1 \text{ gC m}^{-2} \text{ yr}^{-1}$), and the global average is slightly lower at $\sim 24\text{-}35 \text{ gC m}^{-2} \text{ yr}^{-1}$ (Smeaton et al., 2021 and references therein).

2.4 Methods

2.4.1 Sample collection and storage

Sediment cores were collected in 2016, using a Sholkovitch corer (~50cm long) from onboard the research vessel, RV Seòl Mara, in Loch Creran. Sediment cores were sliced using plastic implements at 1cm intervals and freeze dried. Full description of sample collection can be found in (Smeaton and Austin, 2019). Four cores are analysed in this study, two in the upper basin (UB1, UB2) and two across the lower basins (LB1 and LB2), positions of which are shown (Figure 2.1). These cores were selected to provide a transect from the head towards the mouth of the fjord, while avoiding aquaculture sites (Figure 2.1). Samples were sliced in oxic conditions, freeze dried and then stored in sealed, labelled bags at a constant temperature until analysis.

2.4.2 Bulk Elemental and Isotopic analysis

Freeze-dried samples were ball milled into a fine powder before all analysis.

2.4.2.1 XRF

Elemental analysis was carried out on all sediment core samples using X-Ray Fluorescence using a Thermo-Scientific Niton XL3t portable XRF mounted on a Thermo Scientific Smart-stand at the University of Stirling. Samples were pressed into individual pellets and analysed in Mining Cu/Zn mode, with no Helium, at a spot size of 8mm. Total time to run through all elements was 60 seconds split to accommodate elements of differing atomic weights. Samples were analysed on both sides, a total of 5 times to gain average values.

2.4.2.2 ICP-OES

Microwave digestions were carried out on sediment samples to enable the elemental composition to be determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (iCap 6000 series ICP-OES from Thermo Scientific). The microwave digestion was carried out in a MarsXpress Microwave Digestion System from CEM, using program 'Soils 3C', based on the Mars 6 Method (CEM, 2023).

Briefly, 125 mg of sediment was weighed into a Teflon microwave tube, 1.5 ml concentrated HCl was added to each tube using a graduated glass pipette and allowed to settle in a fume cupboard for 15 minutes. 3.5 ml of concentrated HNO₃ was then added to each tube using a

graduated glass pipette, swirled and left for a further 10 minutes until frothing had subsided. The lid was placed on the tube and the screw cap closed. A minimum of two blanks were ran per batch. Tubes were placed in the microwave carousel and into the MarsXpress Microwave Digestion System. The program used was 'Soils 3C', based on the Mars 6 Method (CEM, 2023) which ramps up from room temperature to 210 °C over a period of 22 minutes at 75 % of 1600W, and then maintains at a constant temperature of 210 °C for 20 minutes before cooling down. The digested material was then filtered (150 mm, Whatman No2) into 100 ml glass volumetric flasks. Samples were labelled and stored in acid cleaned plastic bottles before being ran on the ICP-OES. Acid blanks were used in every run as were estuarine sediment CRMs (Standard reference material 1646a, Estuarine Sediment, NIST).

2.4.2.3 *Isotopic analysis and Bulk C, OC, N*

Freeze-dried samples were weighed into tin and silver capsules, for total and organic concentrations respectively. ~12 mg of milled sample was placed in tin and silver capsules. Tin capsules were sealed after weighing, while silver samples underwent acidification using 1M HCl to remove inorganic carbon. Acid was carefully added to each of the silver capsules which were then dried at 40 degrees for up to 24 hours before being tested (additional HCl added and then re-dried for up to 24 hours), and then sealed and sent for analysis at the James Hutton Ltd.

$\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}$, Total N, Total OC were measured at James Hutton Ltd. Values were determined using a Flash EA 1112 Series Elemental Analyser connected via a ConFlo III to a DeltaPlus XP isotope ratio mass spectrometer (all Thermo Finnigan, Bremen, Germany). The $\delta^{13}\text{C}$ VPDB and $\delta^{15}\text{N}$ Air-N₂ values were normalized to their respective scales using international reference materials USGS40 and USGS41a (both L-glutamic acid obtained from International Atomic Energy Agency, Vienna, Austria and Reston Stable Isotope Laboratory, Virginia, USA). Additionally, the USGS40 was used as a reference material for both C and N concentrations, measured using the area output of the mass spectrometer. Running organic and total fractions independently prevents $\delta^{15}\text{N}$ and Total N values being altered by the acidification required for the OC analysis (Kennedy et al., 2005).

2.4.3 Bayesian mixing models

To estimate the fraction of terrestrial and marine contributions to the sediments we used the elemental ratios and stable isotope values in a Bayesian isotope mixing model (FRUITS) as per Smeaton et al. (2021). The FRUITS model can use several tracers, in this instance; N/OC,

$\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ values, to estimate proportional contributions of marine and terrestrial derived OC. The N/OC ratio was chosen over the more commonly used C/N ratio, as the N/OC ratio represents changes in OC rather than N (Moossen et al., 2013; Perdue and Koprivnjak, 2007). The terrestrial and marine values for this model were obtained from a variety of catchments and fjords along the West Coast of Scotland as detailed in Smeaton and Austin (2017), Smeaton et al. (2021b), and Smeaton et al. (2022) (Table 2.1), which are representative for this area. Caution should be applied when using downcore data for these models as degradation of OC can alter isotopic signatures and cause a bias towards an increase in the relative abundance of Terrestrial OC (OC_{Terr}) in relation to Marine OC (OC_{Mar}) (Smeaton and Austin, 2017). This is because OC_{Mar} can be more labile and readily degraded than OC_{Terr} (Lamb et al., 2006). When downcore values are compared to surface sediments using the FRUITS model, there is no indication of preferential degradation of OC_{Mar} therefore we are confident that our model estimates are robust (A.1.0 FRUITS model outputs). It has also been calculated that there is <0.1 % petrogenic / fossil OC input in sediments in this region, which is a result of the metamorphic and igneous geological setting and will therefore not impact the determination of OC sources (Smeaton et al., 2021c).

Table 2.1: Isotopic endmember values used for terrestrial and marine OC sources, errors are displayed as 1 standard deviation (Smeaton and Austin, 2017; Smeaton et al. 2021b)

Source	$\delta^{13}\text{C}_{\text{org}}$ (‰)	$\delta^{15}\text{N}$ (‰)	N/OC molar
Marine	-18.99 ± 2.13	7.56 ± 3.3	0.16 ± 0.04
Terrestrial vegetation	-28.86 ± 1.64	2.53 ± 3.45	0.03 ± 0.01
Terrestrial soil	-28.25 ± 0.77	2.23 ± 2.41	0.05 ± 0.02

2.4.4 Dithionite Extractions

Three samples were selected from each of the four sediment cores for dithionite extractions. Sample selection was based on concentrations of, and changes in, Fe (as measured with the XRF) with depth, which allowed the cores to be split in to three sections (A.1.1 Iron and sulphur XRF profiles), the sample with highest Fe concentration was selected from each of the three sections from each core. Elemental analysis and Mössbauer measurements throughout the core highlighted that Fe concentrations were not especially high and that Fe species were not pronounced (A.1.2 Mössbauer data). Selecting the samples with the highest Fe concentrations ensured the clearest results were obtained for pre and post extraction

comparison with Mössbauer spectroscopy and allowed us to capture measurements from different redox conditions downcore.

The concentrations of Fe-bound OC were determined by an established method of dithionite extractions as used by LaLonde et al. (2012). This extraction is designed to extract a majority of Fe oxides (goethite, hematite, ferrihydrite and others) while not affecting the Fe in clay minerals (LaLonde et al., 2012; Zhao et al., 2016). Like LaLonde et al. (2012), duplicates and controls were ran for every sample.

Briefly, 250 mg of sediment was combined with 15 ml solution of 0.27 M trisodium citrate and 0.11 M sodium bicarbonate in a 30 ml centrifuge tube and mixed in a heated bath (80 degrees), 0.1 M sodium dithionite solution was added, and the solution was shaken at the constant heat for 15 minutes. All chemicals used were analytical grade. All samples were run in duplicate with the triplicate sample acting as a control to quantify OC loss unrelated to the dissolution of Fe oxides, this enabled us to measure the amount of OC lost without the addition of dithionite to the solution. This control solution was buffered with sodium chloride to ensure the ionic strength mirrored that of the dithionite solution. Samples were then centrifuged at 6000 rpm for 10 minutes, initial supernatant was removed, then 5 ml of deionised water was added to the sample tube, vortexed and centrifuged at 6000 rpm for ten minutes. This rinsing was repeated three times for every sample. The elemental composition of pre and post extraction samples was measured using the ICP-OES analysis mentioned above on the supernatant (including rinses) and digestions were carried out on the solids only, the $\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}$, Total N, Total OC measured using methods above (section 3.2.3). We use the post-extraction iron measured in the supernatant to make calculations in this study. The pre and post extraction speciation of solid samples was measured using Mössbauer spectroscopy, as below (section 3.5).

2.4.5 Mössbauer Spectroscopy

A selection of samples from each of the four cores were analysed using a standard transmission Mössbauer Spectrometer (Wissel, Germany) with a ^{57}Co in Rh matrix radiation source in constant acceleration mode at the University of Stirling. Samples were weighed into acrylic glass discs (between 0.07-0.12 g) and sealed. Samples were measured at room temperature (295K) and 4.2K to establish the magnetic ordering of the Fe species present. Samples were cooled in a DRY ICE 4K Mössbauer Cryostat (ICEoxford, UK). Mössbauer spectra were produced after a period of analysis (2-4 days) and these were fitted using Recoil software using the Voigt-based fitting routine (Rancourt and Ping, 1991). Mössbauer

spectroscopy allows for comparison between the relative contributions of Fe^{2+} and Fe^{3+} and facilitates the identification of specific Fe species (Gütlich and Schröder, 2012). Samples were analysed pre and post extraction to demonstrate the amount of reactive Fe dissolved/remaining and to determine which Fe species were preferentially dissolved by dithionite. The spectra were calibrated against a measurement of α -Fe foil (25 μm thickness) at room temperature.

2.4.6 XRD

Mineral composition was determined via X-Ray Diffraction (XRD) using a Panalytical X'Pert PRO PW3040/60 fitted with a PW 3050/60 goniometer in theta-theta configuration at the National Museums Scotland. 'Zero background' sample holders were used made from a single silicon crystal.

2.4.7 Statistical analysis

The Pearson Correlation Coefficient tests were performed in Microsoft Excel to determine correlations between different variables within this study.

2.5 Results and Discussion

Downcore elemental variation

Despite sills separating the upper basin cores, UB1 and UB2, from LB1, there is little variation in downcore Fe/Al between these sites with concentrations ranging from ~0.42 % to 0.6 % (Figure 2.2). Closest to the mouth of the fjord, across an additional sill, LB2 concentrations are lower ranging from 0.36 – 0.4 %. Differences observed in Fe concentrations could be due to differences in sedimentation rates between basins and core sites.

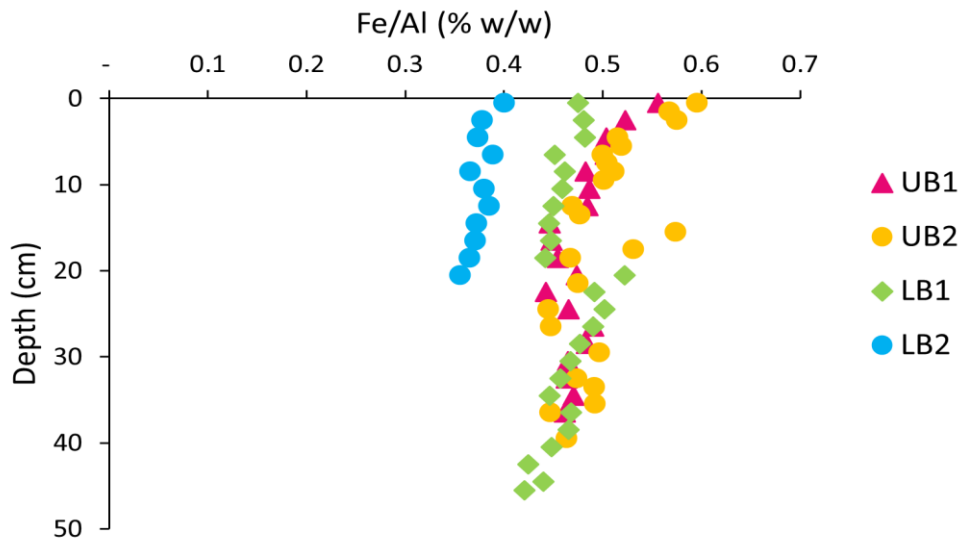


Figure 2.2: Downcore profile of Fe/Al for all sediment cores. Average error of 0.15 for all cores.

There are many global sources of Fe (Boyd and Ellwood, 2010); volcanism, seasonal ice-retreat, hydrothermal activity, resuspension of sediments, dust, bathymetric and current interactions. In this fjord, sediments are subjected to regular physical forcings as a result of tidal flushing every ~3 days (Edwards and Sharples, 1986). This is likely to play a role in sediment resuspension and remineralisation at the sediment-water interface and increase exposure of sediments to changes in salinity and oxygenation. Riverine Fe has previously been viewed as a negligible input to marine waters as it can be removed relatively quickly by flocculation and estuarine mixing. However, recent research in boreal regions suggests that OC-Fe complexes are relatively resistant to salinity-induced aggregation (Herzog et al., 2019). While we do not observe a gradient in Fe concentrations between UB1-LB1, we do observe an increase in Fe concentrations in the basin closest to the marine environment (core LB2, Figure 2.2) in comparison to all upstream cores. This may indicate that there are multiple sources of Fe from riverine and sedimentary (terrestrial and marine) because the basins closer to land have higher Fe concentrations. This may also be influenced by the sediment type, transport times and changes in water chemistry from the head towards the mouth of the fjord. The salinity is likely to be elevated in LB2 as it is the basin closest to the sea, that will be flushed more consistently than basins closer to land.

2.5.1 Organic carbon burial and origin

The OC concentrations observed from the head towards the mouth of the fjord are higher than surface samples measurements by Loh et al. (2008) but the concentration gradient is consistent with surface TOC samples by Loh et al. (2008) that measured higher concentrations (4.0 – 4.8 % TOC) in the upper basin in comparison to the lower basins (3.1 % TOC in lower basin 1, 1.8 % in lower basin 2). OC concentrations are low and relatively consistent downcore in LB2 (1.6 – 1.9 % TOC), but as we move upstream there is increasing variation with depth, with surface sediments (top 10 cm) exhibiting the highest OC concentrations (5 – 5.8 % TOC). The amount of OC stored in sediments appears to coincide with variations in sediment type between the basins of Loch Creran from a mud, muddy sand and mixed sediment in the upper basin to coarser material towards the mouth of the fjord (Hunt et al., 2020; Smeaton and Austin, 2019). The downcore $\delta^{13}\text{C}_{\text{org}}$ profiles (Figure 2.3b) suggest that the basins have varying efficiency for storing terrestrially derived OC (OC_{Terr}) and marine derived OC (OC_{Mar}) (when compared to values by Smeaton and Austin (2017), Smeaton et al. (2021b)): $\delta^{13}\text{C}_{\text{org}}$ in surface sediments ranges from $\sim -25\text{‰}$ to $\sim -23\text{‰}$ from UB1 to LB2 respectively (Figure 2.3c). UB1 sediments display the most terrestrial (more depleted) $\delta^{13}\text{C}_{\text{org}}$ signals throughout the core and we observe mirror images in OC % (Figure 2.3a) and $\delta^{13}\text{C}_{\text{org}}$ (Figure 2.3c), which indicates that increases in OC may have been driven by changes in terrestrial input. UB2 $\delta^{13}\text{C}_{\text{org}}$ is relatively stable ($\sim -24\text{‰}$ to -23.5‰), LB1 shows larger variability, with values of -23.2‰ in surface sediments and -24.5‰ at depth ($>30\text{ cm}$), while LB2 varies from -23.5‰ to -22‰ . Down core variations in the isotopic signatures of $\delta^{13}\text{C}_{\text{org}}$ could be due to a change in abundance of terrestrial and marine inputs and preservation with depth, and / or could be influenced by preferential decay of labile terrestrial / marine OC at depth by increased microbial activity and respiration. Overall, OC profiles measured across UB1, UB2, LB1, and LB2 (Figure 2.3a) suggest that proximity to terrestrial inputs has an influence on OC concentrations as they are highest in the inner basin, and lowest close to the mouth of the fjord (where the fjord opens towards the sea).

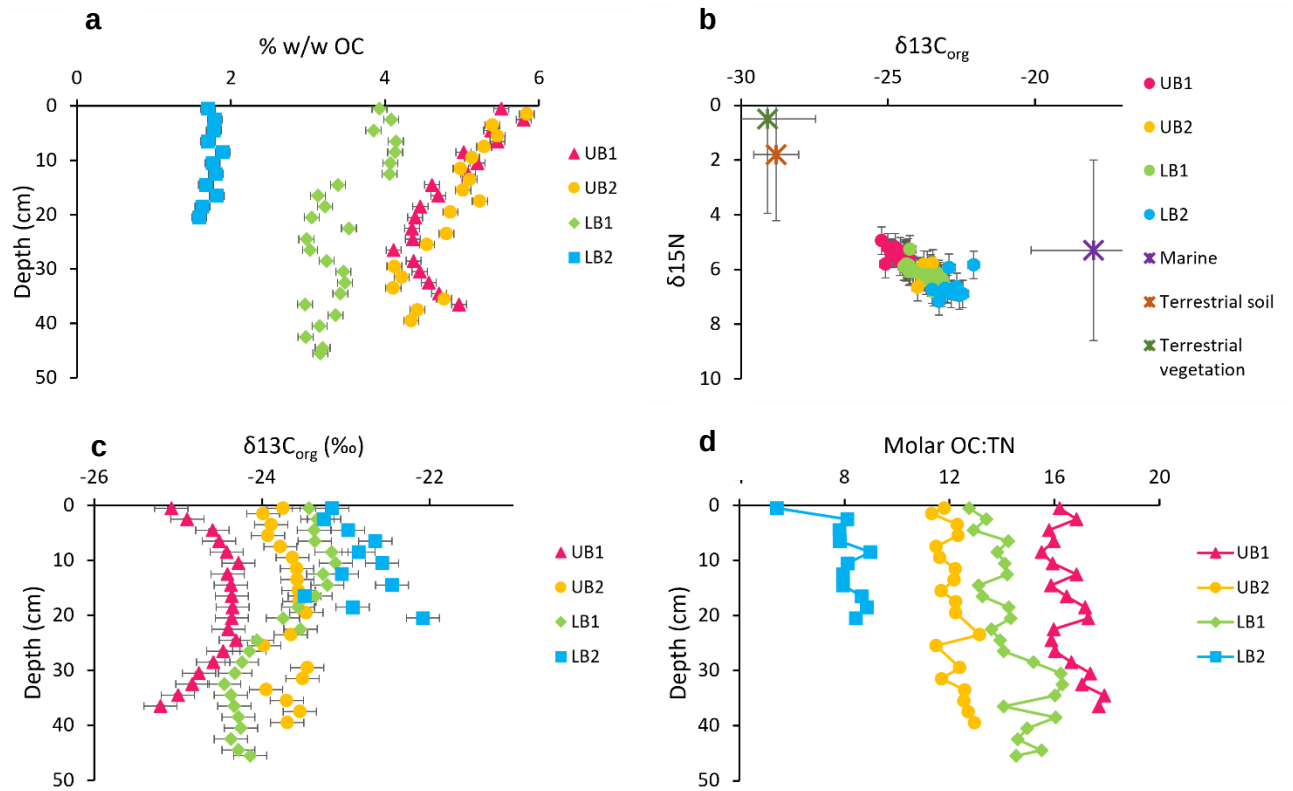


Figure 2.3: Bulk OC and Isotopic data across all cores of the Loch Creran basins a) Downcore organic carbon profiles, a percentage of total carbon, b) The relationship between $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$. Error based on standard deviation of duplicate and triplicate samples (a and b) c) Downcore profiles of $\delta^{13}\text{C}_{\text{org}}$, Error calculated from standard deviation of samples $n=6$. d) Downcore OC:TN profile. Error averaged from OC and N % data (0.0488) and added to graph, though not visible due to size of sample points. Marine and terrestrial (soil and vegetation) values are from Smeaton and Austin (2017), Smeaton et al. (2021b).

There is a gradient from UB1 to LB2, closer to the mouth of the fjord the $\delta^{13}\text{C}_{\text{org}}$ values become more enriched (Figure 2.3c) and OC:TN values decrease (Figure 2.3d) to <10 are which is indicative of marine input (Bauer et al., 2013). This is supported by Bayesian model data that shows OC_{Terr} dominating the upper basin cores and a decreasing OC_{Terr} signature as a function of distance to head of fjord (Table 2.2). We use TN/OC, opposed to OC/TN as above, as it is better suited to showing changes in OC.

Table 2.2: Terrestrial organic carbon FRUITS model outputs in full core and surface sediments

Core	Terrestrial OC Mean Downcore Value (% of Total OC)	Surface sediment OC _{Terr} Mean (% of Total OC)
UB1	66.82 ± 9.62	67.35 ± 3.99
UB2	56.81 ± 4.44	57.82 ± 2.90
LB1	57.64 ± 14.40	51.62 ± 1.08
LB2	47.78 ± 9.11	47.90 ± 3.29

We observe little variation in the distribution of OC_{Terr} between surface sediments and the downcore average (Table 2.2) suggesting that there may not be a strong bias to degradation of more labile OC_{Mar} (Smeaton and Austin, 2017). Some difference is observed in core LB1 (Table 2.2) but there is a relatively large downcore range within this core that still encompasses surface values. Running the FRUITS model with whole-core and separated surface sediment profiles also confirms that surface sediment OC_{Terr} calculations are not influenced or altered by the inclusion of downcore measurements (Table 2.2). Our estimations of OC_{Terr} content are higher than the average 33% observed in marine sediments (Burdige, 2005) and are lower than those measured by Smeaton and Austin (2022) in Loch Creran, where they estimated 66 +/- 13 % of OC to be of terrestrial origin. This highlights the variation present in OC (bulk and isotopic) concentrations and signatures within fjords and beyond the surface sediments.

2.5.2 OC-FeR associations in fjord sediments

Between 5-15 % of total Fe (based on ICP analysis) was dissolved as a result of the extractions throughout the different sediment cores (Figure 2.4a), this is therefore thought to be FeR as defined by (Lalonde et al., 2012). All OC-FeR and FeR values have been calculated based on control values (A.1.3 OC-FeR dataset). UB1, UB2 and LB1 have pronounced decreases in FeR with depth, while LB2 displays a relatively low and stable concentration of FeR dissolved by the extractions (Figure 2.4a). The average OC% bound to FeR (as extracted through this method) in Loch Creran is ~16 % but there is much variation across cores ranging from ~3-39% (Figure 2.4b). For core UB2 15.5 cm, the sample repeatedly displayed a higher OC value relative to the control, hence it's omission from this graph and some subsequent

figures. Comparatively, the amount of FeR in the sediments (as a percentage of total Fe determined by ICP) ranges from ~5 - 15 % across cores (Figure 2.4a). The difference in post extraction trends for %FeR, and %OC bound to FeR, indicates that abundance of FeR in the sediments is not the primary control on OC association (Faust et al., 2021, 2020; Sirois et al., 2018). For example, UB1 has an inverse relationship between the %OC extracted and the %FeR dissolved (Figure 2.4c), which is also the case, on a different scale, for LB1 and LB2. One UB2 value shows a negative OC% value due to a measured increase in OC post extraction, so this value has been discounted. While we do not observe a terrestrial – marine gradient in Fe from UB1-LB2 (Figure 2.2a) as is observed with OC (Figure 2.3a), we do observe a decreasing terrestrial-marine gradient in FeR concentrations (Figure 2.4a) (Table 2.2) which could be due to variable success in the transport of OC-FeR from terrestrial soils to the lower basins, which may be influenced by changes in salinity (surface sediments) and redox conditions (below the surface layer).

In previous research, some have focused on surface sample measurements to explore the role of Fe in mineral preservation of OC (e.g. Ma et al., 2018; Wang and Zhu, 2018; Zhao et al., 2018) but examining only surface sediments is likely to be biased towards oxic conditions. Fe chemistry can change with depth when there is a change in redox conditions. We observe that surface samples have the highest FeR concentrations across cores; UB1 and LB1 ~15%, UB2 ~11 % and LB2 ~7 %. Despite relatively high FeR there are variable OC-FeR associations in surface sediments (Figure 2.4a and b): ranging from 17-20 % in the upper basin, ~3 % in LB1 and ~28 % in LB2. We find a negative correlation between the abundance of FeR and OC-FeR in surface sediments (Figure 2.4c) ($R = -0.06$, $P = 0.85$) which highlights that OC-FeR associations are greater where there is a lower abundance of FeR in the sediments. We also examine the consistency of OC-FeR associations below the surface sediments (>10cm depth, which is likely below the oxygenated section of the sediment) to establish how effective these OC-FeR relationships are downcore and to determine whether surface sample measurements may be representative of longer-term carbon storage in a mid-latitude fjord. More FeR is found in surface sediments than at depth across a majority of cores (UB1, UB2, LB1) (Figure 2.4a) and the decrease in FeR downcore is likely influenced by changes in redox conditions and porewater chemistry, causing a change in Fe speciation and stabilisation (i.e. reduction of Fe (III) to Fe (II)). Unlike surface sediments, there was no correlation (Figure 2.4d) between the OC-FeR % and FeR % in sediment samples ($R = -0.06$, $P = 0.85$). This is in agreement with Faust et al., (2020, 2021) because we do not consider FeR availability to be the primary control on OC-FeR associations with depth. Therefore, other biological, chemical and physical processes must influence this relationship. When we examined the OC-FeR downcore relationships for each core we observed an increase in the relative abundance of

OC bound to FeR with depth (in all cores except UB2) (Figure 2.4b), despite lower FeR concentrations (Figure 2.4a). This confirms that within this setting, OC-FeR associations preserve OC and effectively stabilise FeR with depth.

Cores in the lower basins, LB1 and LB2, exhibit different patterns in FeR core content in comparison to UB1 and UB2 in the upper basin (Figure 2.4a). In LB2, FeR concentrations are consistently lower with low variability (6.7 % - 7.3 %) but despite this, OC-FeR associations are relatively high (14.3 % – 36.8 %) (Figure 2.4b) and LB2 maintains the highest OC_{Mar} content (average $\sim 52.8\% \pm 2.9\%$). LB2 data suggests that proximity to the marine environment may influence the abundance and stability of OC-FeR associations. OC-FeR associations in LB2 are the highest of any site in the fjord (averaging $\sim 26\%$ OC associated with FeR in LB2). This is despite lower concentrations of Fe in LB2 in comparison to others (Figure 2.2) and consistently lower FeR (based on %Fe dissolved in dithionite extraction measured by ICP-OES) (Figure 2.4a). This may be influenced by the presence of fine-grained sediments that have large surface areas for carbon association in the lower basins, and the higher FeR values observed from Mössbauer analysis (A.1.2 Mössbauer data, Table A.1). It may also indicate that FeR is very effective at maintaining bonds with both young and old OC_{Mar}, it is worth noting that we found a positive and significant correlation between abundance of OC-FeR associations and the origin (marine/terrestrial) of OC ($R = 0.70$, $P = 0.01$) (Figure 2.5a) but this is likely influenced by the location of the core. Presuming that depth and OC age are correlated, our data provides no evidence to suggest that younger marine material is preferentially bound over pre-aged material, as observed in Arctic sediments (Faust et al., 2023), nor that there is preferential preservation of pre-aged OC_{Terr}, as observed by Zhao et al., (2023). However, without ^{14}C dating, we do not know the age of the terrestrial, or marine, material entering this system, nor do we know the age of the OC that is lost at depth, relative to that which remains bound. This may also be indicative that different environments and input sources can result in differences in preferential binding. Other influences on the OC-FeR binding capacity that are tested and discussed hereafter include; abundance of OC in sediment, the type of binding (sorption/co-precipitation may have greater longevity in tidally flushed waters and sediments), depth, species of FeR.

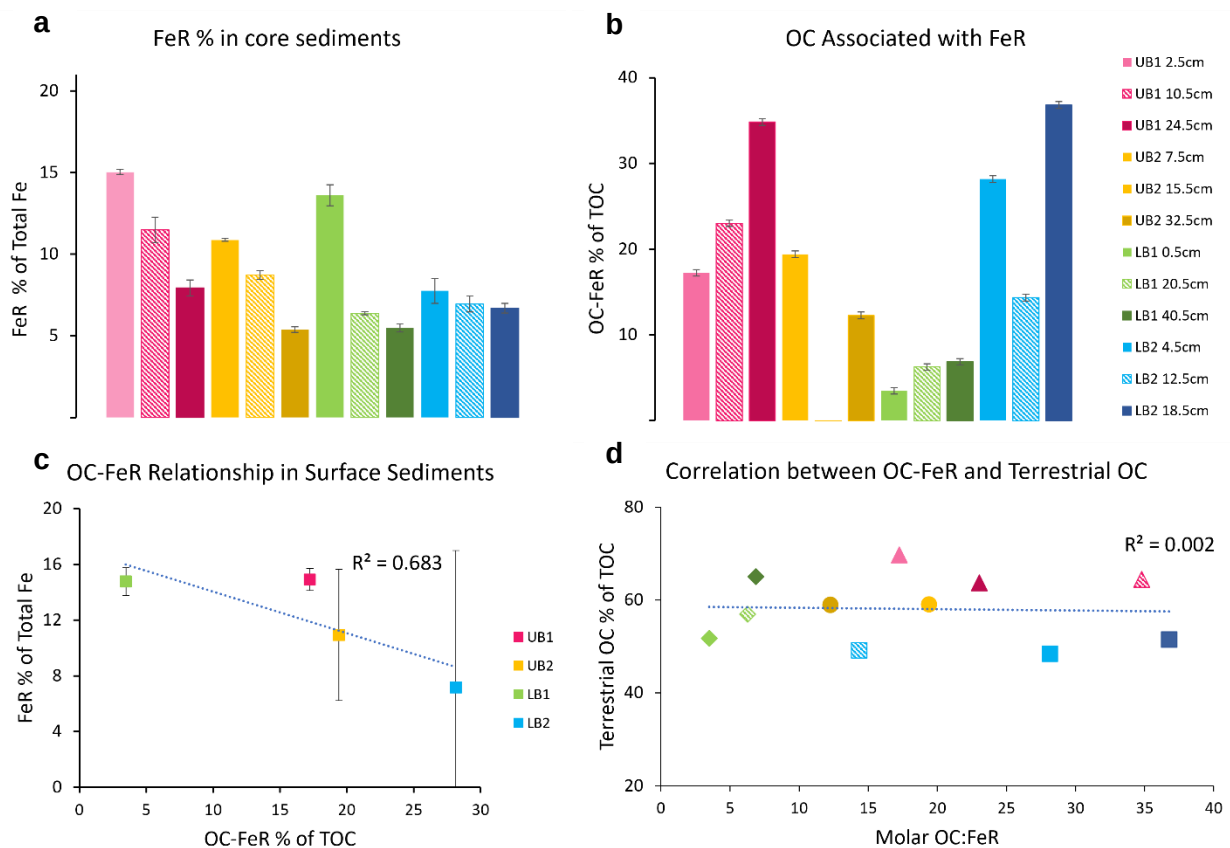


Figure 2.4: FeR-OC associations: a) Percentage of reactive iron within core sediments at three depths within each core. (UB1 - 2.5cm, 10.5cm, 24.5cm. UB2 - 7.5cm, 15.5cm, 32.5cm. LB1 - 0.5cm, 20.5cm, 40.5cm. LB2 - 4.5cm, 12.5cm, 18.5cm.) Total Fe determined by ICP and the error calculated from the standard deviation of duplicate samples b) Percentage of organic carbon (of total organic carbon) bound to reactive iron within sediment across three depths (as above) within all cores. Error calculated from the standard deviation of duplicate samples . c) Percentage of reactive iron and organic carbon in surface sediments <10cm depth (based on Fe³⁺ lost during dithionite extractions, measured by ICP). Error is the standard deviation between 3 samples per core across different depths d) organic carbon and reactive iron associations across sediment core samples (based on total OC % lost during dithionite extractions). FTerr calculated using FRUITS isotope model. Errors plotted but partially obscured by marker. The same legend applies to a, b, d.

Abundance of TOC in sediments shows a positive and significant correlation with abundance of OC-FeR, ($R = 0.68$, $P = 0.02$) (Figure 2.5a). This means that OC input may play a greater role, in comparison to elevated FeR presence (as previously discussed), on OC-FeR associations (within this setting and within these parameters).

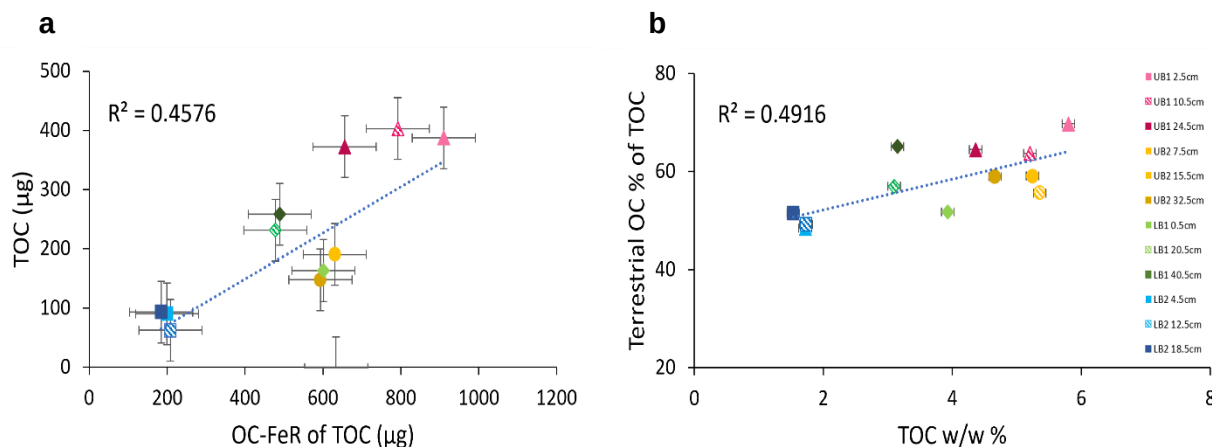


Figure 2.5: Relationships between a) OC-FeR and Total OC. The OC associated with FeR is a percentage of the total OC. Pink triangles represent UB1, yellow circles UB2, green diamonds LB1, blue squares LB2. Error based on average standard deviation (μg) from samples $n= 12$. b) Terrestrial OC and Total OC w/w %. Terrestrial OC is a percentage of the total OC calculated by the FRUITS isotope model. Pink triangles represent UB1, yellow circles UB2, green diamonds LB1, blue squares LB2. Error based on the average standard deviation (%) of samples $n= 6$. The legend applies to both a) and b).

We find subtle indications that a greater amount of marine or terrestrially derived OC was bound to FeR in sediment cores as observed in the pre and post extraction isotopic signatures of $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ (A.1.3 OC-FeR dataset), but caution should be taken when assessing the significance of these changes as the isotopic signature observed in control samples is variable, highlighting some degree of chemical alteration during the extraction process. When looking at surface sediments in individual cores, in UB1 we observe enrichment in $\delta^{13}\text{C}_{\text{org}}$ post extraction, suggesting preferential binding between FeR-OC_{Terr}, but this trend does not continue downcore. In LB2 surface sediments there is a depletion of $\delta^{13}\text{C}_{\text{org}}$ post extraction, suggesting preferential binding between FeR-OC_{Mar}. Neither pattern is observed in cores UB2 or LB1, suggesting that proximity to terrestrial and marine environments, and therefore the abundance of terrestrial and marine OC in the sediments, may have an influence on OC-FeR binding and mineral preservation in surface sediments. This could be influenced by an input of fresh terrestrial / marine organic material at either end of the fjord. To support this, OC_{Terr} is ~69 % in UB1, and ~48 % in LB2 at equivalent surface depths to extracted surface sediment (2.5cm and 4.5cm respectively) (Figure 2.5b). This pattern is not consistent downcore in UB1, and for a majority of the cores (UB2, LB1, LB2) we observe that below the surface sediment (top 10 cm) there is a slight enrichment in $\delta^{13}\text{C}_{\text{org}}$ in post extraction core samples (enrichment ranging from 0.2 - 0.9 ‰, or from control 0.2 - 0.43 ‰) (A.1.3 OC-FeR dataset), which suggests that OC_{Terr} may have been preferentially preserved by FeR in these locations and released

during extractions. $\delta^{13}\text{C}_{\text{org}}$ values remain relatively terrestrial in UB1 pre and post extraction, but post extraction values do decrease below surface sediments, this may be due to some marine OC being released during the extraction, or that some isotopically lighter OC_{Terr} was released, as terrestrial source signatures will vary.

Overall, we observe distinct differences in preferential binding in surface sediments of UB1 and LB2, where terrestrial and marine material (respectively) were preferentially bound. At depth (>18 cm) in UB2, LB1 and LB2, we observe preferential binding of OC_{Terr} , while the opposite is observed in UB1. This provides some agreement with Zhao et al., (2023); there is preferential preservation of OC_{Terr} in sediments, in our study we find that this can occur in surface sediments and at depth, indicating that OC_{Terr} of different ages may be preserved depending on the proximity to the terrestrial source and the environment. Marine OC is thought to be more labile, allowing easier decomposition (Lamb et al., 2006) which could result in weaker preservation in comparison to OC_{Terr} . This data shows that OC-FeR associations play an important role in OC preservation and burial. Figure 2.4a,b highlight that these complexes do not decrease with depth indicating that they are a long-term carbon storage mechanism and that there is a mutual stability of OC and FeR downcore.

2.5.3 Adsorption vs co-precipitation

OC binds to FeR through two main mechanisms: sorption and co-precipitation (Lalonde et al., 2012; Shields et al., 2016). An OC:FeR molar ratio <1 is indicative of sorption of organic matter onto FeR surfaces while a OC:FeR molar ratio of 6-10 is indicative of co-precipitation (Wagai and Mayer, 2007). The OC:FeR molar ratio is <1 for all cores indicating that sorption is the dominant binding mechanism spatially and with depth in this fjord. There is a correlation observed between OC:FeR molar ratios (binding mechanisms) and OC-FeR ($R = 0.931$, $P = <0.01$)(Figure 2.6b) where we observe greater concentrations of OC-FeR correlating with a lower OC:FeR ratio. However, no correlation was found between the FeR% and OC:FeR molar ratio ($R = -0.07$, $P = 0.81$)(Figure 2.6c). Overall, we observe that there is more OC bound to FeR via sorption than co-precipitation and that the sorption OC:FeR molar signature are consistent with depth, suggesting that sorption is a stable bond over time. As co-precipitation can result in particles, i.e. carbon, being enclosed within an aggregate opposed to being bound to the Fe itself, these bonds may be more vulnerable to chemical change, and OC may be released more easily than if it were bound through sorption. We observe no correlation between binding mechanism and proximity to, or inputs from, terrestrial / marine environments ($R = 0.28$, $P = 0.38$) (Figure 2.6d).

OC can have a strong affinity for Fe^{3+} phases, such as ferrihydrite, that are precipitated in upper surface sediments, and it has previously been proposed that this may be the primary control on co-precipitation / adsorption of OC-FeR (e.g. Riedel et al., 2013). However, our data suggests that availability of FeR is not the primary control on OC association as cores display a negative and non-significant correlation between FeR concentrations and OC-FeR ($R = -0.062$, $P = 0.85$). In UB1 there is an inverse relationship between the amount of FeR and OC lost from the extractions (where there is less OC-FeR there is more FeR in the sediment). Increases in OC-FeR in UB2 have no influence on %FeR bound. Data agrees with that of Sirois et al., 2018, Faust et al. (2023, 2021) and Zhao et al., (2023): FeR availability is not the primary control on OC association and a portion of OC-FeR binding is likely to have occurred before reaching the sediments and may come from terrestrial sources. This pattern is therefore consistent across a range of environments (Arctic fjords, mid-latitude fjords and temperate and subterranean estuaries).

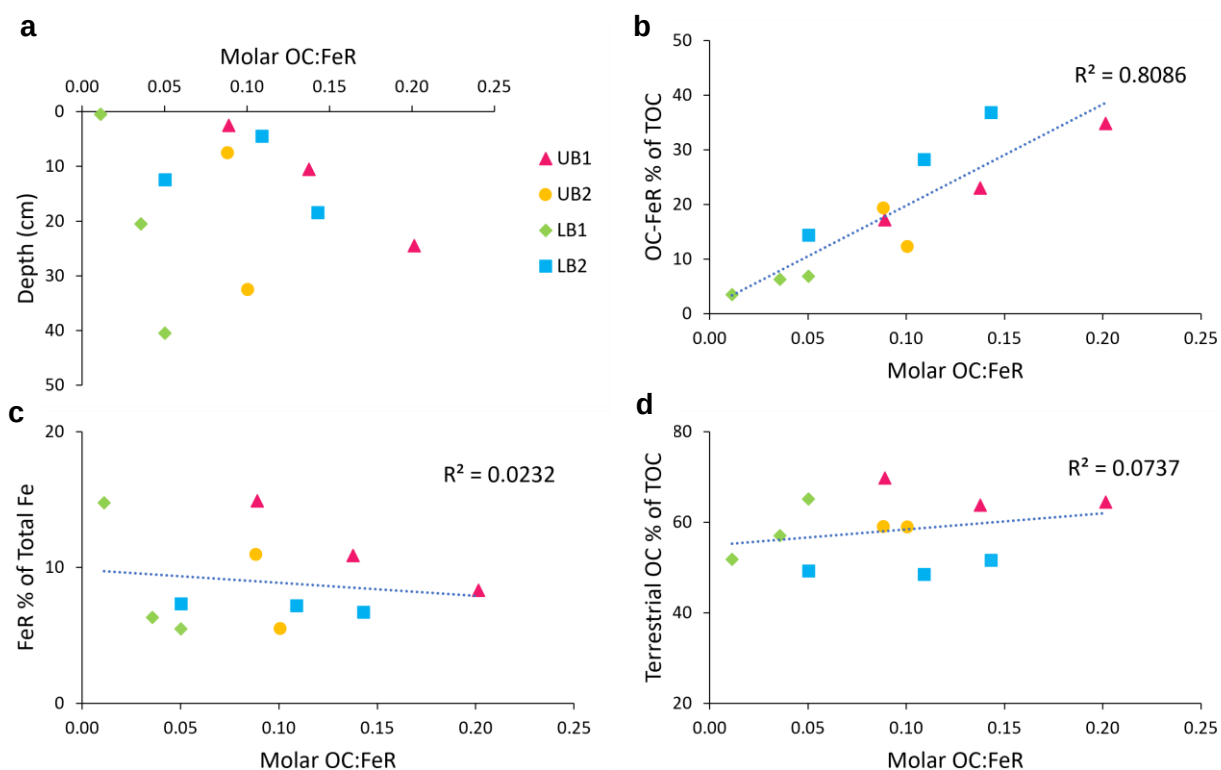


Figure 2.6: Determining the type and pattern of OC-FeR binding by assessing the relationships between a) OC-FeR with depth, error is a calculated average per core using bulk OC% and ICP Fe standard deviations. b) OC-FeR with OC% bound (which is a percentage of total OC) OC% error is calculated from $n=6$ duplicate bulk OC post extraction measurements. c) OC:FeR and FeR%. Total Fe determined by ICP and error calculated from duplicate ICP measurements. d) OC:FeR and Terrestrial OC% (which is a percentage of the total OC), error calculated from FRUITS model standard deviations from terrestrial soils and vegetation. All figures use the same legend as seen in a). Error of OC:FeR values: UB1 = average 2.55, UB2 = average 1.36, LB1 average = 1.94, LB2 average = 3.72.

2.5.4 Determining FeR patterns and species

Mössbauer spectroscopy was used to determine the species of Fe present across all sediment cores. By extending the post extraction measurements to include Mössbauer spectroscopy at room temperature (295 K), and in some cases low temperature (4.2 K), we gain a greater understanding of the accuracy and efficiency of the dithionite extractions in removing FeR from sediment samples (Figure 2.7). Previous work (e.g. Figure S3 in Zhao et al., 2023) has shown that in room temperature Mössbauer spectra, FeR generally correlates with the Fe^{3+} phase (grey lines in Figure 2.7a-b) and not with well-crystalline hematite (yellow line in Figure 2.7a-b). The Fe^{3+} phase at room temperature incorporates Fe^{3+} in clay minerals (the Fe^{2+} phase likely represents clay minerals) as well as (super)paramagnetic iron (oxyhydr)oxides. Because only the latter are associated with FeR, this explains why a significant amount of the Fe^{3+} phase remains after extraction, which is corroborated with the low temperature Mössbauer spectra. Measurements at 4.2 K (Figure 2.7c-d) are below the superparamagnetic blocking temperature and/or the magnetic ordering temperatures of iron (oxyhydr)oxides, which manifests in Mössbauer spectra as a transition from a two-line to a six-line sub-spectrum. The Fe^{3+} phase (grey line) has diminished because it now represents the fraction of Fe^{3+} in clay minerals only, while some of the ferric iron is now incorporated in the oxide mix (yellow line) and some in the background feature (green line), which represents amorphous iron oxide. The parameters for the iron oxide mix allow us to identify specific iron (oxyhydr)oxide minerals. While hematite is the present Fe phase at room temperature, other phases such as ferrihydrite or lepidocrocite dominate at low temperature (see full Mössbauer results in A.1.2 Mössbauer data). It has previously been observed that the dithionite extraction method (Lalonde et al., 2012) does not dissolve all FeR within samples (Hepburn et al., 2020, Fisher et al., 2020). This is further confirmed through this work, where only a portion of FeR is dissolved within the samples. Figure 2.7d shows that after extraction, some of the iron oxide mix and the background phase remains. The low temperature measurements presented here suggest that the results from the dithionite extraction may underestimate the amount of OC-FeR in sediments (Figure 2.4a-b) as a portion of the FeR remains, and that the isotopic signatures of OC-FeR (A.1.3 OC-FeR dataset) and source data (Figure 2.4c-d) may not be representative of the whole OC-FeR pool.

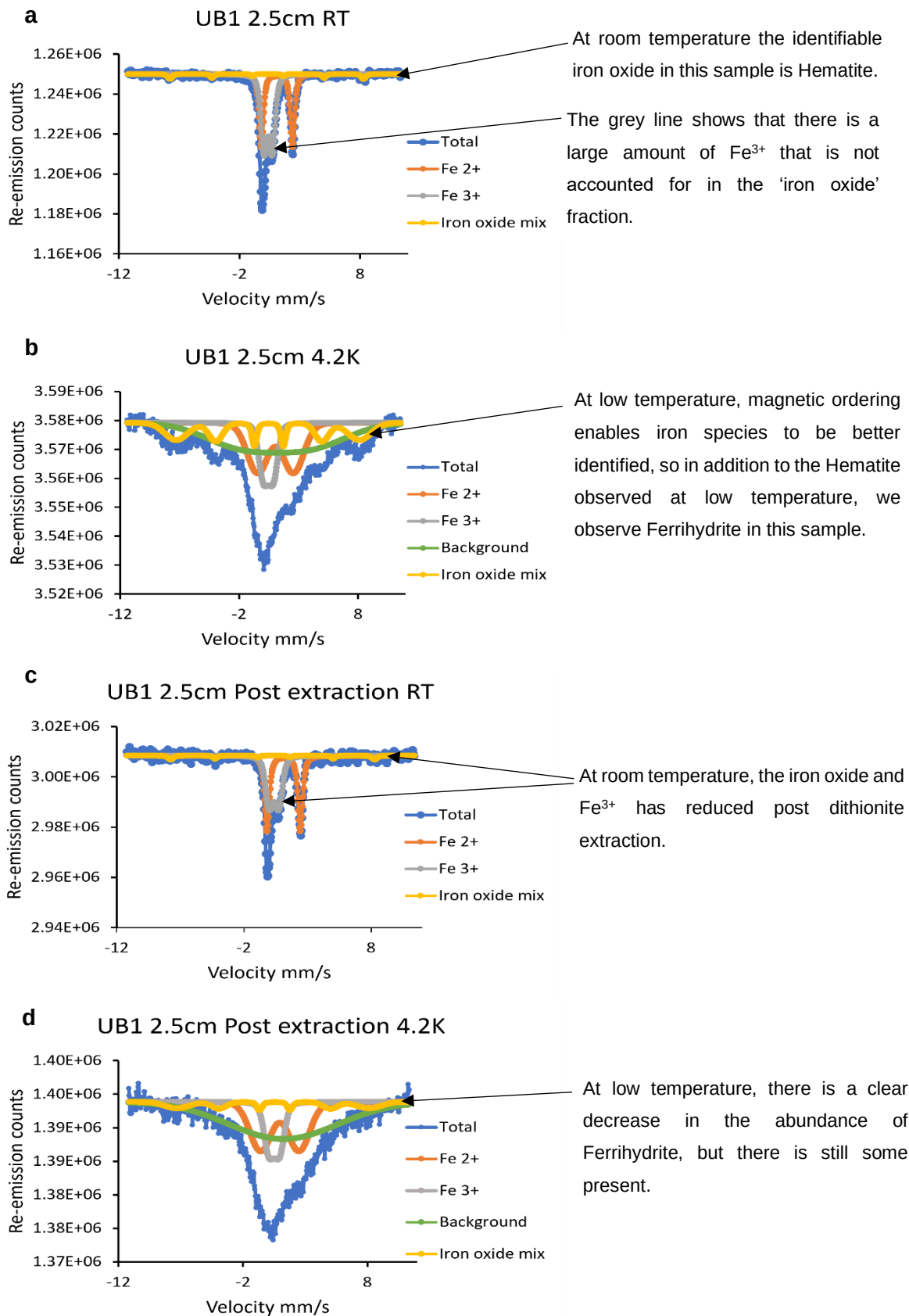


Figure 2.7: Mössbauer measurements from core UB1, sample 2.5cm depth highlighting how Mössbauer was used across two temperatures to determine the presence of reactive iron a) Core UB1 Mössbauer spectra at 2.5cm depth at room temperature b) Core UB1 Mössbauer spectra at 2.5cm depth at 4.2K c) Core UB1 Mössbauer spectra at 2.5cm depth post dithionite extraction at room temperature d) Core UB1, sample 2.5cm Mössbauer spectra post-extraction at 4.2K.

OC-FeR values were calculated from post extraction sediments using ICP-OES and room temperature Mössbauer spectroscopy and normalised to μg Fe lost from original sediment (Figure 2.8a). For FeR content of sediment cores, there is a positive and significant correlation between ICP-OES and Mössbauer measurements ($R = 0.948$, $P < 0.01$) (Figure 2.8) showing that there is reasonable agreement between ICP and Mössbauer estimates. The difference between these estimates may lessen some of the underestimation of OC-FeR by ICP-OES, but in all surface sediments Mössbauer measurements were higher than ICP-OES and have larger deviations. ICP-OES values were only higher than those of Mössbauer at depth.

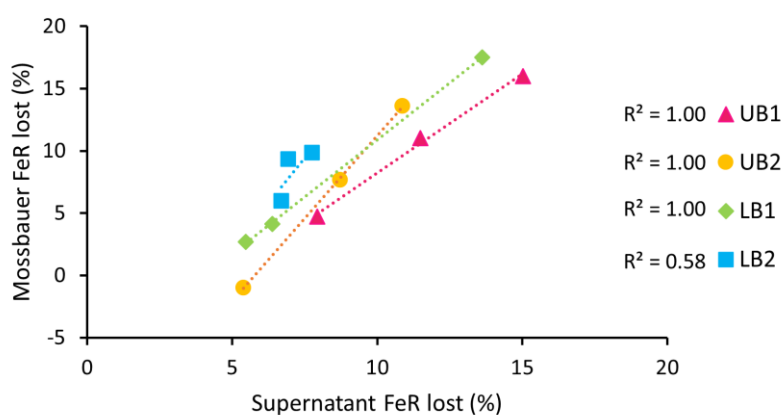


Figure 2.8: a) Correlation between iron lost from Mössbauer results and ICP-OES results across individual cores. Error was calculated from duplicate measurements from ICP Fe (UB1 = 4.7 %, UB2 = 2.33 %, LB1 = 3.49 %, LB2 = 7.05 %) and Mössbauer standard error is 2 % on the y-axis.

Low temperature Mössbauer measurements were conducted at 4.2 K and provide a qualitative understanding of sediment properties. These measurements suggest that in surface sediments the (super)paramagnetic Fe^{3+} fraction includes the Fe oxyhydroxides in the form of ferrihydrite, lepidocrocite and goethite (as determined by values from Cornell and Schwertmann, (2003)) (A.1.2 Mössbauer data). Below surface sediments, ferrihydrite is the dominant species of Fe^{3+} within the sediments (A.1.2 Mössbauer data). We do not observe any transformations to more stable Fe oxide phases with depth, which may explain the relatively high OC-FeR associations with depth as ferrihydrite has a large surface area allowing ample opportunity for OC attachment, and transformations to different species can result in decreased surface area and the liberation of bound particles (Postma et al., 2010). There are also no patterns in Fe speciation changes with depth, with a majority of the variation observed being in surface sediments. This variation in surface sediments may be linked to differences in surface sediment type and origin. The presence of ferrihydrite with depth provides strong evidence that OC effectively stabilises FeR when associated in fjord

sediments and prevents the transformation of ferrihydrite into more thermodynamically stable mineral phases (Schröder et al., 2016).

Many samples had high background readings when measured at low temperature (4.2 K) (A.1.2 Mössbauer data) which may be indicative of the presence of poorly crystalline fine particles in the sediments, that likely make up a portion of the Fe^{3+} fraction.

2.5.5 Wider context for organic carbon burial in fjord sediments

Our datasets show that FeR is integral to the preservation of ~16 % of OC in this fjord, with values ranging from 3-39 % OC-FeR. This is below the global OC-FeR average of 20 % (Lalonde et al., 2012) but higher than values observed in some estuarine and deltaic sediments (<10 %) (Zhao et al., 2023) and 15 % (Shields et al., 2016). While differing supply (terrestrial/marine) can influence OC-FeR associations, it is also likely that differences in OC-FeR associations can occur across environments (fjords, deltas, shelf sediments). Sediment resuspension and tidal currents can transport Fe rich material across shelves (Vosteen et al., 2022) but there is likely to be varied transport times of material in different locations. Our results indicate that a portion of the OC-FeR associations may be transported from terrestrial upstream sources in this fjord (therefore we suggest a portion of the FeR originates on land), so it would be expected that environments that are not in close proximity to terrestrial inputs would display different OC-FeR association patterns and behaviour. There may also be latitudinal differences expected in OC-FeR associations as Fe is often a limiting nutrient in some marine environments and could be biologically utilised before OC binding occurs.

Regarding the binding mechanisms of OC-FeR, it is thought that oxic conditions are linked with sorption of OC-FeR opposed to co-precipitation, which is observed in anoxic sediments (Lalonde et al., 2012). Our data supports that, in the recent past, it is likely that Loch Creran was well-mixed and did not experience periods of low oxygen conditions or severe stratification as sorption is proportionally high. We also find that even in anoxic conditions within sediments, bonds formed through sorption for OC-FeR remain intact, highlighting an effective rusty carbon sink.

We do not observe the same preferential binding between FeR and marine OC as observed by Faust et al. (2023) but something closer to the OC_{Terr} preferential binding signature observed by (Wang and Zhu, 2018; Zhao et al., 2023, 2018). Our data suggests that sediments in mid-latitude fjords have less variability / distinct signatures in preferential binding of OC-FeR to marine / terrestrial derived OC in comparison to other depositional environments in global datasets (Lalonde et al., 2012). OC-FeR binding is now uniform throughout this fjord

and displays a greater spatial and temporal mix of OC-FeR binding preferences. To better understand the influences on OC-FeR binding, an investigation of upstream OC and OC-FeR sources would be beneficial.

2.6 Conclusions

An average of 16 % of OC was bound to FeR throughout the fjord which is lower than, but comparable to, the global marine average of 20 % (Lalonde et al., 2012). FeR accounted for 0-34 % of OC stored in the upper basin, 3-7 % of OC stored in the second basin and 14-36 % of OC stored in the lower basin nearest the mouth of the fjord. We find that mineral binding can be variable throughout space and depth in a fjord, so global and regional averages should not solely be based upon surface samples from limited spatial points. Surface measurements of OC-FeR associations were not representative of the amount of OC-FeR with depth, and often under-represented the role of mineral binding in OC preservation in this fjord. Isotopic signatures and model data show that a large portion of the OC stored within these sediments (43-73 %) is of terrestrial origin, indicating that the surrounding land has a large influence on OC input, and that some of the OC-FeR associations may have occurred before the sediment-water interface having been transported from upstream terrestrial environments. Cores with the highest and lowest terrestrial signature were found to have the greatest OC-FeR associations. This study has provided an insight into the spatial heterogeneity of sediments in fjords and the mechanisms behind the storage and mineral preservation of OC in mid-latitude fjord sediments. The mapping of Hunt et al., (2020) may be used in future studies to determine how the distribution of different material can provide insight into where different processes (sorption / co-precipitation) occur with respect to varying sediment types.

Sorption is found to be the preferential binding mechanism in this environment, perhaps due to its ability to withstand greater changes in chemistry. OC-FeR associations in Loch Creran vary with depth / time and proximity from land. There is a distinct decrease in FeR with depth which is likely controlled by changing redox conditions in porewaters with depth. In a majority of cases, this decrease in FeR correlated with an increase in OC-FeR associations highlighting that these OC-FeR associations are preserved over unbound FeR and act as an important mechanism for carbon storage and FeR preservation. Through using Mössbauer Spectroscopy we find ferrihydrite is the dominant species of FeR in the fjord, even with depth, highlighting the stabilising effect of the OC-FeR associations on Fe. Results confirmed that dithionite extractions do not exclusively or completely dissolve all FeR within the sediments and it is therefore likely that we are underestimating the role of FeR in OC preservation when using this method. The heterogeneity of OC-FeR relationships downcore means that

measurements from surface sediments are not necessarily representative of OC-FeR relationships with depth, which could also result in underestimations. We lose some FeR downcore through redox, but OC associated with FeR is not lost in the same pattern, it tends to increase with depth, perhaps because a majority of the FeR that remains at depth is associated with OC, highlighting the mutual preservation that occurs within these sediments. We therefore find that FeR exerts a significant influence on OC storage spatially and with depth, and that OC is capable of preserving less stable species of iron in this fjord and likely many other locations.

**Chapter 3 Exploring the use of n-alkanes for
investigating the distribution and origin of organic
carbon from forested catchment to fjord
sediments**

3.1 Abstract

Fjords sediments are known to be globally important long-term carbon stores. However, there remains a limited understanding regarding origin of organic carbon in fjord sediments, and how sedimentary carbon storage might be influenced by catchment processes and land cover. Large-scale changes in land cover (e.g. afforestation and deforestation) can influence the type and quantity of material delivered to coastal sediments so it is important to fully understand these interactions at the land-sea interface to effectively utilise valuable carbon stores. We use n-alkanes, specific $\delta^{13}\text{C}$ isotopic signatures and pine resins, alongside bulk data to establish whether this combination of techniques can enable us to characterise source material and provide a greater insight into the sources of carbon to fjord sediments and the role of forestry within this catchment. To do so the abundance, distribution and $\delta^{13}\text{C}$ composition of n-alkanes and methyl dehydroabietate are reported across the source-to-fjord continuum in Loch Creran, Scotland.

Specific $\delta^{13}\text{C}$ signatures provided some differentiation of plant groups and insight into the burial of deciduous material, while methyl dehydroabietate was able to capture the presence of coniferous material where n-alkane abundance and isotopes could not. We demonstrate that a combined biological and geochemical approach to sample analysis can provide greater detail on the origin of organic carbon to fjord sediments, and that catchment vegetation can contribute to organic carbon stored in the fjord sediments through riverine inflow and catchment run off, which is significantly correlated with slope of the surrounding land. Bulk, isotopic and n-alkane data may exclude some vegetation signals, i.e. coniferous forestry, and this highlights the need for specific resinous markers to be included in organic carbon source analysis. This research contributes to understanding the origins of organic carbon stored in sediments, and the techniques that may be used to assess the influence of catchment vegetation (forestry) in fjord sediments.

3.2 Introduction

Fjords are naturally efficient sediment traps due to their submarine geomorphology. They can store large quantities of organic carbon in their sediments. Globally, it is estimated that fjord sediments capture approximately 11% of the organic carbon (OC) buried in the marine environment each year (Smith et al., 2015) and between 55-62% of OC held within fjord sediments originate from the terrestrial environment (Cui et al., 2016). Terrestrial environments are globally important sources of OC to coastal and marine systems (Bianchi, 2011), and in mid-latitudes (Smeaton and Austin, 2017). The sediments of Scotland's mid-

latitude fjords store 252 ± 62 Mt (Smeaton et al., 2017) and bury 84,000 tonnes of OC annually. It is estimated that $52 \pm 10\%$ of the OC buried originates from the terrestrial environment (Smeaton and Austin, 2022). Comparatively, the proportion of the OC held in other temperate vegetated systems ranges, with 42% and 76% of the OC in Chilean and NW European fjords originating from the terrestrial environment (Cui et al., 2016).

Quantitative tools are necessary to try and identify the complex sources of OC within sediments. Several techniques are established and widely used to determine organic matter sources in sediments: OC and nitrogen (N) data, isotopic measurements (primarily $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) (Meyers, 1994; Thornton and McManus, 1994), and biomarkers (such as lignin, n-alkanes, sterols) (Bouloubassi et al., 1997; Mead et al., 2005; Meyers, 1997), but many studies report only marine / terrestrial origin and do not distinguish further (Faust and Knies, 2019; Smeaton and Austin, 2022). Biomarkers have been used to distinguish between terrestrial, marine, and anthropogenic sources (e.g. Bulbul et al., 2021; Fang et al., 2014) in old and young sediments, and between different plant groups (Bush and McInerney, 2013; Fang et al., 2014).

N-alkanes are saturated hydrocarbons that can be used as a leaf wax biomarker. They are insoluble in water, chemically inert and relatively resistant to biochemical degradation (Eglington and Eglington, 2008). This allows them to be well preserved in sediments and as such, they are widely used as plant biomarkers (Bush and McInerney, 2013; Ficken et al., 2000; He et al., 2020) and for determining source contributions of organic matter to sediments (Chen et al., 2022). They are robust molecules that can be maintained in the fossil record for geological timescales (Lockheart et al., 2000; Logan et al., 1995). Generally, alkanes with more than 25 carbons are terrestrially derived, and those with fewer than 25 carbons are more likely to be from aquatic plants (Seki et al., 2010). C_{31} dominates in sediments when the primary vegetation is grasses, whilst C_{27} and C_{29} dominate where trees and shrubs influence sediments (Cranwell, 1973; Vogts et al., 2009). However, there can be large variation and discrepancies between different types of vegetation so caution should be used when using n-alkanes to identify specific plant species (Bi et al., 2005).

Stable isotope composition of n-alkanes ($\delta^{13}\text{C}$ and δD) has also been applied as a proxy to investigate environmental change and identify organic matter sources (Cooper et al., 2015; Liu et al., 2020; Meyers, 1994; Silva et al., 2012). $\delta^{13}\text{C}$ is an effective proxy because when there's no change in environmental conditions, the $\delta^{13}\text{C}$ values will still vary between plant types (Ankit et al., 2017; Liu and An, 2020). For example, coniferous and deciduous vegetation can have distinctly different isotopic $\delta^{13}\text{C}$ and δD signatures but this can differ depending on the abundance, geographic location and taxa (Schlanser et al., 2020). The $\delta^{13}\text{C}$ values, and

to a lesser extent δD values, of individual n-alkanes have been utilized in studies of plant wax, soil, and sediment (Pedentchouk et al., 2008; Sachse et al., 2006; Sikes et al., 2009). They have proved effective in identifying organic matter sources because stable isotope values vary according to the types of plants from which they derive (e.g., gymnosperms, angiosperms, aquatic plants) (Chikaraishi and Naraoka, 2003; Pedentchouk et al., 2008; Schlanser et al., 2020). The stable carbon isotope values of n-alkanes are primarily influenced by the method of CO_2 fixation and the source of CO_2 . C3 plants exhibit $\delta^{13}C$ values spanning from -24‰ to -34‰ , C4 plants display $\delta^{13}C$ values ranging from -6‰ to -19‰ , while algae demonstrate intermediate values ranging from -12‰ to -23‰ (e.g. O'Leary, 1988, 1981; Rao et al., 2017; Tieszen, 1991). Variations in hydrogen isotopes are attributed to fluctuations in the δD of plant source water, which correlates with geographic differences in precipitation δD , subsequent evapotranspiration, and biosynthesis (Hou et al., 2007; Sachse et al., 2006).

To aid identification of specific sources of OC, i.e. plant groups, and the presence of coniferous / deciduous inputs to the sediments, other biomarkers can complement bulk elemental and n-alkane data, such as terpenoids. Terpenoids are one of many lipid components that are useful in the sedimentary record, as many have links to specific biological origins (Brassell et al., 1983). Diterpenoids are known to predominantly originate from conifers, and triterpenoids from angiosperms (Brassell et al., 1983; Simoneit, 1977). They can maintain characteristic structures even with diagenetic alterations, so can be effectively used to suggest sources of organic material (Otto and Simoneit, 2001). Diterpenoids such as abietane and pimarane are well studied constituents of coniferous vegetation (Simoneit and Ikan, 2008). Dehydroabietic acid has been identified as a major component of coniferous resin and supportive tissue, and has been found in marine sediments from coniferous sources (Simoneit, 1977). $\delta^{13}C$ and δD signatures of n-alkanes and terpenoids can also be used to aid identification of source vegetation (Schlanser et al., 2020).

3.3 Study Area

Loch Creran, a fjord on the West Coast of Scotland, is the location for this study (Figure 3.1). It is 12.8 km in length, occupies an area of 13.3 km², and is relatively shallow with a maximum depth of 49 m. A catchment of 164 km² drains into the relatively well mixed and ventilated waters, which maintain mostly oxic conditions (Smeaton et al., 2017) as the fjord is flushed regularly (Edward and Sharples., 1986). The River Creran is the main inflow at the head of Loch Creran (Loh et al., 2010), which provides an average freshwater supply of $286.3 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ (Almroth-Rosell et al., 2012) into Loch Linnhe, making it a relatively enclosed system.

Within Loch Creran, there is a sill at Creagan that separates a smaller upper basin from the larger lower basins (Figure 3.1).

Upstream from Loch Creran sits a small freshwater loch, Fasnacloich, through which the River Creran runs (Figure 3.1a). The soil types for sampling sites are peaty and mineral podzols (Macaulay Institute for Soil Research, 1981). The geology of the Loch Creran catchment is metamorphic and igneous so there is minimal chance of petrogenic carbon being present (less than 0.1 % petrogenic C) (Smeaton et al., 2021). The catchment of Loch Creran has varied land use (Figure 3.1b) and forestry accounts for ~30 % of land cover (Marston et al., 2022), with broadleaf woodland accounting for ~14 % and coniferous woodland accounting for ~17 % (Figure 3.1b).

Previous work within this fjord has helped to better quantify organic carbon stored in sediments (Smeaton et al., 2021), and its terrestrial/marine origin (Loh et al., 2008b, 2008a; C Smeaton et al., 2021). Different techniques have been used to try to identify the source to the organic carbon within the sediments of Loch Creran: bulk organic carbon and nitrogen ratios, isotopic data ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$), as in Chapter 1 and other studies (Loh et al., 2008a; Smeaton et al., 2021; Smeaton et al., 2017), and lignin markers (S/V and C/V ratios) (Loh et al., 2010, 2008b). Much existing data in this location utilises surficial samples, highlighting very recent spatial variation, but not necessarily changes with depth / time, nor do they manage to identify plant source groups or whether surrounding forestry contributes to organic matter stored in the fjord sediments. As such, in this study we explore whether n-alkanes, n-alkane specific $\delta^{13}\text{C}$ biomarkers, and pine resins can help us to detect a forestry signal within the Loch Creran and its catchment, narrow down OC sources, and better understand (lateral) carbon transport from source towards sea.

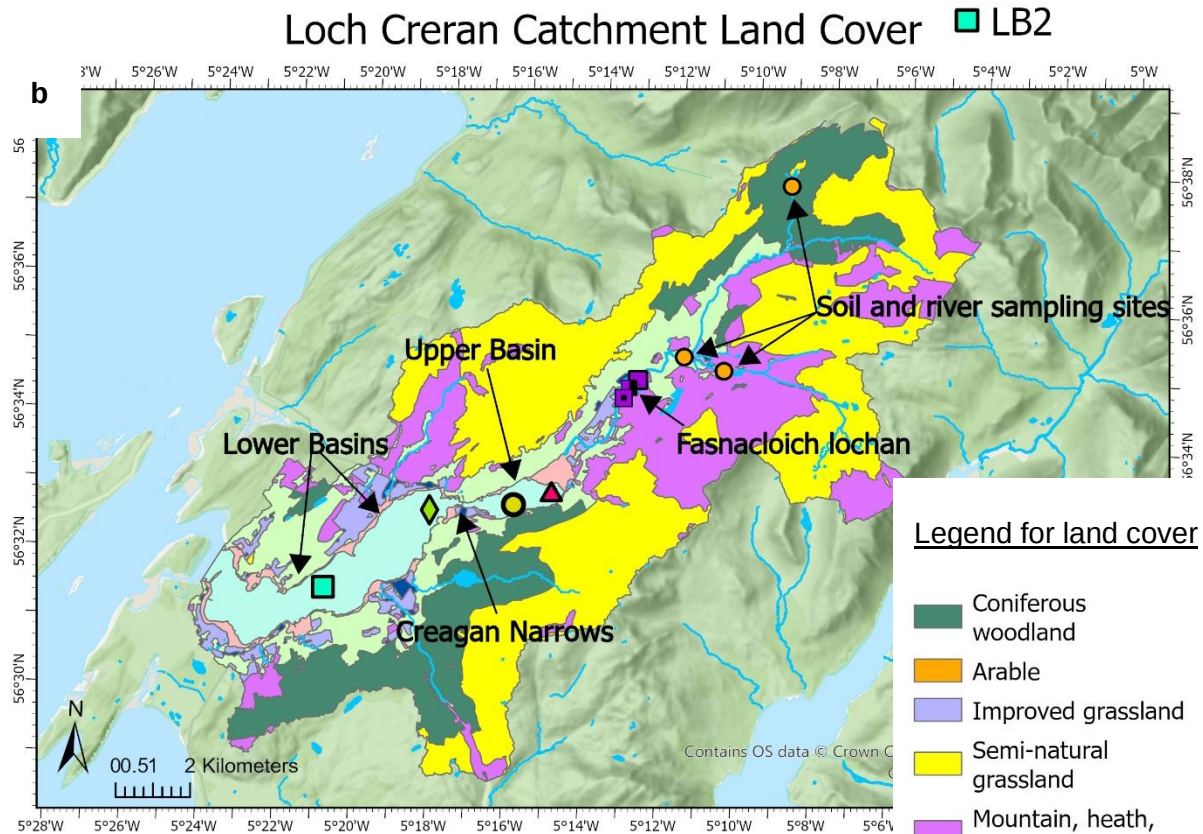
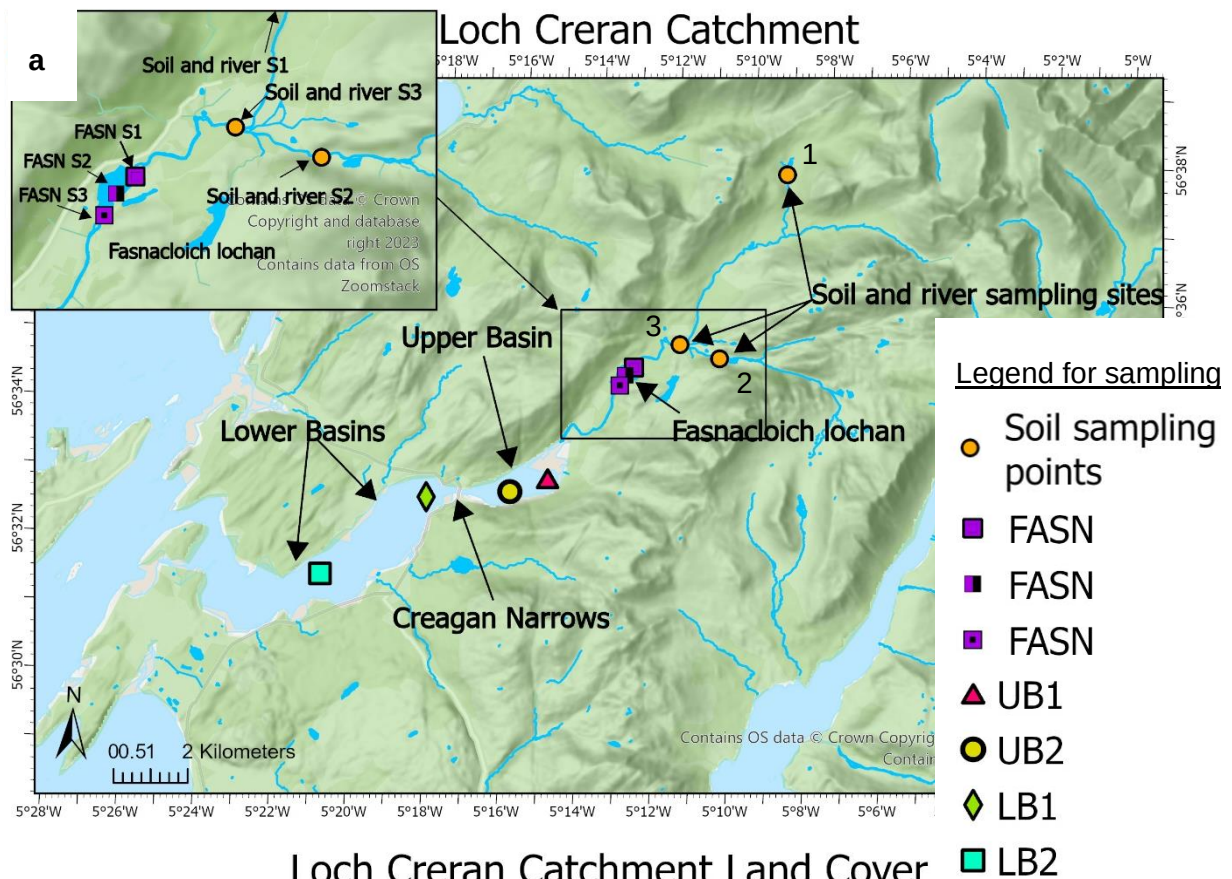


Figure 3.1: Maps of Loch Creran and its catchment (a) A map showing the topography, surface water, loch and sampling points. Sediment cores, freshwater sediment samples and soil and river sampling location are highlighted on the map. A cut out window provides a better view of the location of soil and river samples and Fasnacloich lochan samples (b) Land cover in the Loch Creran catchment showing different vegetation cover.

Mean rainfall and temperature for the region (West of Scotland) and the local area (Dunstaffnage) were recorded by the MetOffice (Hollis et al., 2019) (Table 3.1).

Table 3.1: The average temperature and rainfall for the region (West Scotland) and local area (Dunstaffnage) across seasons of sample collection 2021 – 2022.

		Dunstaffnage		West Scotland	
Year	Season	Average	Rain	Average	Rain
		degC	mm	degC	mm
2021	Summer	15.45 ± 1.62	67.20 ± 26.52	14.33 ± 1.40	65.00 ± 32.47
2021	Autumn	11.55 ± 3.05	203.47 ± 98.68	10.03 ± 3.35	187.03 ± 83.11
2022	Winter	6.22 ± 0.57	182.93 ± 57.47	4.77 ± 0.45	184.63 ± 78.38
2022	Spring	9.45 ± 2.28	92.80 ± 44.41	8.03 ± 2.51	96.33 ± 29.24

3.4 Methods

3.4.1 Sample Collection

3.4.1.1 Sediments

Sediment cores were collected in 2016, using a Sholkovitch corer (~50 cm long) from onboard the research vessel, RV Seòl Mara, in Loch Creran. Sediment cores were sliced at 1cm intervals and freeze dried. Full description of sample collection can be found in (Smeaton et al., 2021). These cores were selected to provide a transect from the head towards the mouth of the fjord, while avoiding aquaculture sites (Figure 3.1). Samples from the upper freshwater lochan, Fasnacloich, were collected in Spring 2022 along a three-point transect (Figure 3.1) using a Van Veen grab sampler.

3.4.1.2 Soil and vegetation

Soil samples were collected from three sites: S1 where River Creran and Ure meet, S2 River Creran, S3 River Ure (Figure 3.1). At the same sites, vegetation samples were collected. Soil cores were collected from each bank of the river, during each seasonal sample trip (omitting Autumn Site 3 due to high water levels, and with an augmented location for Site 1 in Spring due to snow that was approx. 2 miles downstream from the original Site 1). Cores were taken within 2 metre proximity to the river, two cores were taken within a metre of one another on each bank using a small metal hand-held soil corer (~23 cm in length) and stored in an Whirlpak bags. These samples were freeze-dried upon return to the laboratory, within 12 hours

of sample collection. 22 soil samples were collected and analysed for this study, covering three main locations in the catchment.

Plant leaf cuttings were collected across upper parts of the Loch Creran catchment at soils sites (Site 1-Site 3) around the River Ure, River Creran, and after both rivers merge during Summer 2021 and Spring 2022. These were collected to determine if biomolecular signatures can be attributed to deciduous and coniferous forestry in soils and sediments. These were collected in the same locations as soil cores. A total of 12 individual plant species were collected from the terrestrial environment (Table 3.2), covering several plant functional groups (trees, herbaceous perennials), which included natural and cultivated samples. Fresh and degrading tree leaf biomass were collected and homogenised to form samples representative of living and dead, coniferous and deciduous forestry. Vegetation samples are listed in Table 3.4. Samples were collected in combusted aluminium foil and placed into Whirlpak bags and frozen on return to the laboratory, within 12 hours of sample collection, before being freeze-dried, milled and stored in bags for analysis. We were unable to obtain aquatic plant samples in-situ and are using values from literature to inform source characteristics (Ficken et al., 2000).

To assess the seasonal variability in soils, the focus was on summer and winter samples, two opposing seasons that provide examples of changes in run off, decay and points in the growing season at the same sites due to the differences in light, temperature and rainfall (see below). There are complete and consistent data across these sites which made comparison easier than with Spring (augmented site) and Autumn (where river levels were too high to gain all necessary soil samples).

Table 3.2: A list of the types of vegetation samples collected in the Loch Creran catchment and used in this study.

Group	Plant description
Alnus glutinosa	Living deciduous (alder)
Alnus glutinosa	Dead deciduous (alder)
Picea sitchensis	Living coniferous

Picea sitchensis	Dead coniferous
Quercus	Oak
Betula	Birch
Ulex	Gorse
Hyacinthoides non-scripta	Bluebells
Poaceae	Grass
Poaceae + Bryophyta	Grass and moss
Bryophyta	Moss
Lichen	Lichen

3.4.2 N-alkane analysis and processing

Freeze-dried vegetation, soil and sediment samples were homogenized and stored in Whirlpak bags. The samples were weighed and extracted following the method in Planq et al. (2018). Briefly, the samples (~2 g) were extracted using dichloromethane (DCM): methanol (MeOH) (9:1) using a Dionex model ASE350 accelerated solvent extractor. Following evaporation of the solvent, the total lipid extract (TLE) vials were weighed and separated into neutral and acid fractions by elution through a LC-NH₂ SPE Silica gel column using DCM:Isopropyl alcohol (1:1), then 4 % acetic acid in diethyl ether, respectively. The neutral fraction was further separated into four sub-fractions (N1-N4) of increasing polarity using a silica gel column and hexane (N1), DCM (N2), ethyl acetate:hexane (1:3) (N3) and MeOH (N4). The N3 fraction was derivatised using 12 % (N,O-bis(trimethylsilyl)trifluoroacetamide) BTSFA and Pyridine and were heated to 80°C in the oven for 2 hours.

N-alkanes were identified and quantified using an Agilent 7890B Series GC coupled with a 5977A mass spectrometer detector with an electron impact (EI) ionisation source (GC-MS). Samples were dissolved in 150 µL DCM and a volume of 1 µL was injected and the inlet temperature was held at 315 °C. The following program parameters were used; there was a constant flow of 1.2 mL/min with an initial pressure of 24.8 psi, the oven was held at 60°C for 2 minutes, then raised to 120°C at 30 °C/min⁻¹, then increased to 310 °C at 5 °C/min⁻¹ and held for 33 minutes. The temperature in the transfer line between the GC and the MS was kept at 315 °C throughout. The MS source was set to 230 and the MS quad was set to 160.

The compound specific carbon isotope composition ($\delta^{13}\text{C}$) was measured on an Agilent 7890B Series GC system coupled with an Elementar GC5 furnace and IRMS. Samples were dissolved in 30 μL hexane and a volume of 2 μL was injected and the inlet temperature was held at 320°C. The following program settings were used: there was a flow of 1.2 mL/min with a pressure of 13.4 psi, the oven was held at 60 °C for 2 minutes, then raised to 120°C at 30 °C/min⁻¹, then increased to 330 °C at 5 °C/min⁻¹ and held for 15 minutes. The IRMS detector the GC was connected to a furnace with a temperature of 850 °C. The IRMS magnet settings used the following voltages: the accelerating voltage was 3991.18 V, extraction voltage 71.88 %AV, half-plate differential -42.78 V, Z-plates voltage -21.06. The current trap was set to 200 uA, electron volts at 100 V, ion repeller voltage was -8 V and the magnet current ran at 4000 mA.

Duplicate measurements were performed and averaged for six vegetation samples, six soil samples covering two seasons (Winter and Spring), three surficial freshwater sediment samples, twenty fjord sediment samples across different basins and depths.

Peak areas were measured using the Agilent MassHunter program and concentrations were calculated using a set of external calibrations constructed from a standard mix of eleven n-alkanes (these peaks are labelled and shown in B.1.0 External standard chromatograph). The stock solution of the external standard was 10 $\mu\text{g/mL}$. Calibration graphs were generated using three concentrations: 2.5 $\mu\text{g/mL}$, 5 $\mu\text{g/mL}$, 10 $\mu\text{g/mL}$. All concentrations were normalised to the weight of the sample. Compound classes analysed and used in this study were N1 (aliphatic hydrocarbons) to obtain n-alkane data and the N2 fraction (ketones, esters, aromatics) to obtain pine resin information. The instrumental limits of detection and quantification for n-alkanes can be found in Appendix B1.7, Table B.11.

3.4.2.1 N-alkane metrics

Several indices were calculated for N-alkanes (Table 3.3), to help determine the source of the organic matter and changes in the degradation of organic matter across samples.

Table 3.3: Details of n-alkane indices calculated for, and used in, this study.

Indices	Purpose	Equation	Value	Reference
Carbon preference index		$\text{CPI}_{\text{C16-C33}} = (\sum(\text{C}_{21} + \text{C}_{23} \dots + \text{C}_{31}) + \sum(\text{C}_{23} + \text{C}_{25} \dots + \text{C}_{33})) / 2 * \sum(\text{C}_{22} + \text{C}_{24} \dots + \text{C}_{34})$	>5 terrestrial ~1 petrogenic and marine	(He et al., 2020; Silva et al., 2012)

(CPI)				
Paq	Relative contribution of higher aquatic vs terrestrial plants.	$Paq = (C_{23}+C_{25})/(C_{23}+C_{25}+C_{29}+C_{31})$	Variable but generally: $<0.1 =$ terrestrial; $0.1 - 0.4 =$ emergent macrophytes; $0.4 - 1 =$ submerged / floating macrophytes	Ficken et al., 2000
Average chain length (ACL)	Weighted average number of carbon atoms of the higher plant between C23-C35.	$ACL_{C23-35} = \sum(C_n * n) / \sum(C_n)$		Rebolledo et al., 2019; Wang et al., 2018
Odd over even predominance (OEP)	Organic matter degradation.	$OEP = (C_{27} + C_{29} + C_{31} + C_{33}) / (C_{26} + C_{28} + C_{30} + C_{32})$	<5 material is more degraded.	Struck et al., 2020; Thomas et al., 2021

3.4.3 Isotopic and elemental measurements

Bulk $\delta^{13}C_{org}$, $\delta^{15}N$, Total N, Total C and Total OC were measured as per Chapter 1 (2.4.2). Briefly, freeze-dried, milled sediment, soil and vegetation samples were weighed into tin and silver capsules, for total and organic concentrations, respectively. Tin capsules were sealed after weighing, while silver samples underwent acidification using 1M HCl to remove inorganic carbon. $\delta^{13}C_{org}$, $\delta^{15}N$, Total N, Total OC were measured at James Hutton Institute Ltd. Values were determined using a Flash EA 1112 Series Elemental Analyser connected via a ConFlo III to a DeltaPlus XP isotope ratio mass spectrometer (IRMS) (all Thermo Finnigan, Bremen,

Germany). The $\delta^{13}\text{C}$ VPDB and $\delta^{15}\text{N}$ Air- N_2 values were normalized to their respective scales using international reference materials USGS40 and USGS41a (both L-glutamic acid obtained from International Atomic Energy Agency, Vienna, Austria and Reston Stable Isotope Laboratory, Virginia, USA). Additionally, the USGS40 was used as a reference material for both C and N concentrations, measured using the area output of the mass spectrometer. Running organic and total fractions independently prevents $\delta^{15}\text{N}$ and Total N values being altered by the acidification required for the OC analysis (Kennedy et al., 2005).

3.4.4 Statistical tests

Pearson correlation coefficient tests were performed in Microsoft Excel to determine the correlation between a number of variables to test whether relationships were significant. This was to help determine the main influences on OC abundance in soils and sediments. The function used all come as standard within the data analysis toolkit; PEARSON COUNT, TDIST. A P value of 0.05 or less was considered to be significant.

Three principal component analysis (PCA) tests was performed to identify similarities and / or differences between sediment core stations and samples, and to further investigate the controls on OC in this study. To explore these relationships, three PCA's was ran to provide a more in-depth explanation of the relationship between different variables. All values used in the PCA were standardised by using the 'scale' function which centres values around the means and is part of the R base package. Th following packages were loaded to enable analysis and visualisation; dplyr, fplot2, gridExtra,carData, car, factoextra, corrplot. PCA's included bulk data, biomarker measurements and indices details of these are shown alongside results.

3.5 Results

3.5.1 Organic carbon from catchment to fjord sediments

Soil site two has the highest average OC concentrations ranging from ~9-13 %, and site three the lowest with 3-5 % OC (Figure 3.2a). OC in lochan sediments (Figure 3.2b) increases from inflow (Site 1) towards outflow (Site 3). Surface fjord sediments exhibit lower OC concentrations than soils or freshwater sediments (Figure 3.2c) and these decrease further from UB1-LB2. UB1 has the highest concentrations averaging 5.4 % and LB2 has the lowest averaging 1.8 %.

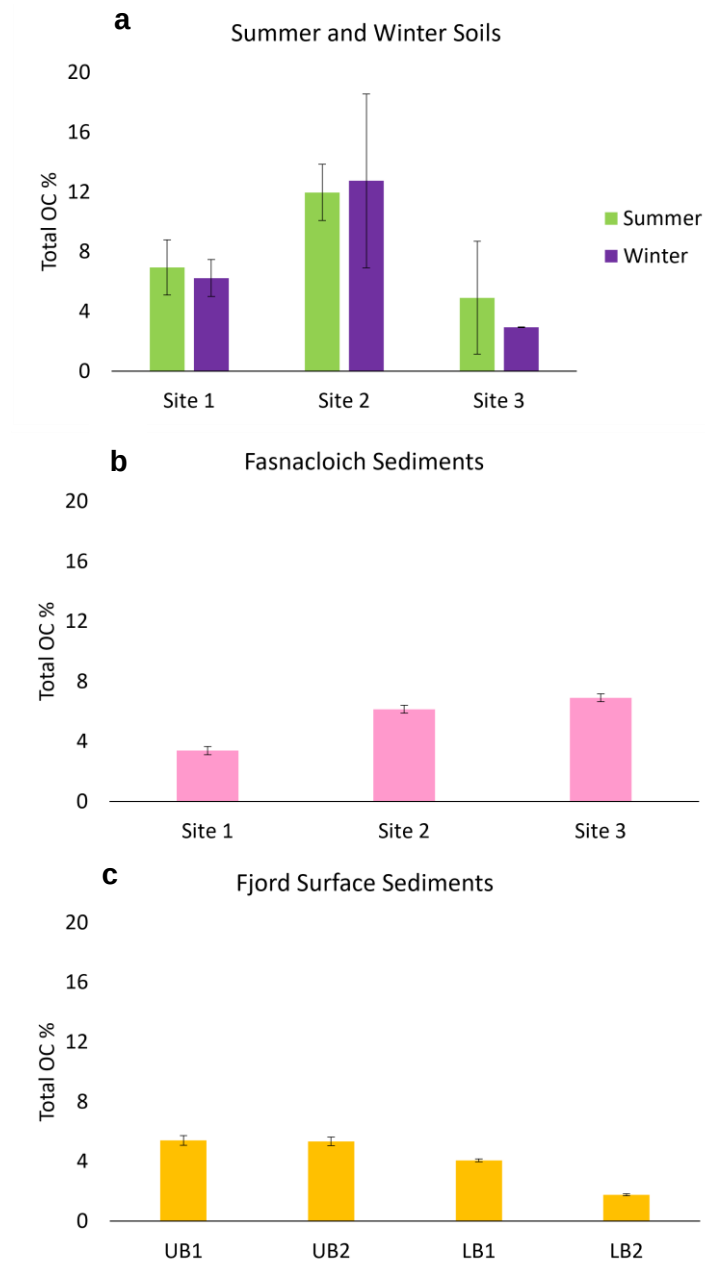


Figure 3.2: Bulk OC data in (a) summer and winter soil samples, (b) Fasnacloich lochan samples (c) Fjord surface sediment samples (<10cm). The values presented are averages; for soils this is the average of the soil samples across different riverbanks, and for fresh and fjord sediments this is the average of multiple sample measurements. The error for all samples is the standard deviation (stdev). For soils this was the stdev of the average values of the 2 riverbanks at each site, for the sediments this was the average stdev from 4 samples for UB1 and LB1 and 5 samples from UB2 and LB2.

3.5.2 N-alkane signatures

3.5.2.1 *Catchment vegetation*

N-alkane signatures for catchment vegetation samples were used to calculate different indices (Table 3.4), and C and N concentrations allowed the OC/N ratios to be determined. Living deciduous samples, of the dominant tree type in Soil Site S2 (alder), have a higher CPI (28) than their dead counterparts (12), and this difference is also reflected in the OEP values, (27 and 14 for living and dead respectively). The ACL remains the same in living and dead samples (27.5) but the total n-alkane concentrations differ significantly averaging 43 µg/g in living samples and 12 µg/g in dead samples. In living coniferous samples, the CPI and OEP are ~8 and 9 respectively however, these parameters could not be calculated in dead samples due to the absence of even numbered n-alkanes (as they were below limit of detection / quantification). The ACL remains similar 28.4 and 26.4 for living and dead conifer samples respectively, and the total n-alkanes are higher for the living material than the dead material, 5.6 µg/g and 2.4 µg/g respectively. This highlights some clear differences in living and dead deciduous and coniferous vegetation.

The majority of plant species collected have an ACL of 27-28, and the only samples to fall below that range are dead coniferous samples and birch samples, and above that range grass, moss and some perennials. Perennials exhibit some of the highest total n-alkane concentrations, while coniferous material (both in living and dead form) have the lowest concentrations.

Table 3.4: Bulk TC, OC, N, molar ratios and n-alkane indices for vegetation samples, providing common and Latin names

Group	Plant description	CPI	ACL	Paq	OEP	TAR	Total n-alkanes C ₁₆ -C ₃₅	Total C (% w/w)	Organic C (% w/w)	Total N (% w/w)	Molar OC/N
Alnus glutinosa	Living deciduous (alder)	28.10	27.48	0.27	27.31	297.77	43.42	48.04	41.04	2.04	23.45
Standard deviation		1.01	0.82	0.25	3.18	234.48	21.49	0.44	3.63	0.02	
Alnus glutinosa	Dead deciduous (alder)	12.22	27.55	0.30	14.76	89.84	12.18	48.88	46.46	1.07	50.87
Standard deviation		8.86	0.53	0.19	11.60	56.46	7.11	1.26	3.51	0.11	
Picea sitchensis	Living coniferous	7.92	28.41	0.51	9.11	25.76	5.60	47.57	42.20	0.82	59.70
Standard deviation		5.24	2.17	0.11	8.12	7.34	6.61	1.45	1.35	0.14	
Picea sitchensis	Dead coniferous	0.00	26.38	0.63	0.00	3.05	2.39	49.20	44.95	0.88	59.36
Standard deviation		0.00	1.17	0.25	0.00	4.14	2.92	0.62	1.86	0.28	
Quercus	Oak	10.75	27.53	0.35	9.82	233.67	25.50	43.64	34.38	3.29	12.20
Betula	Birch	45.93	25.57	0.95	39.14	28.98	86.05	45.87	41.35	1.86	25.98

Ulex	Gorse	11.71	27.23	0.37	11.41	26.53	48.72	44.35	42.78	2.03	24.55
Hyacinthoides non-scripta	Bluebells	19.49	28.55	0.28	21.66	2634.46	127.58	41.54	40.07	2.11	22.10
Poaceae	Grass	16.29	29.10	0.03	16.53	747.52	79.97	43.50	41.49	0.99	48.83
Poaceae + Bryophyta	Grass and moss	22.17	29.68	0.13	28.53	50.67	10.28	42.44	36.08	1.60	26.38
Bryophyta	Moss type	9.54	28.92	0.14	9.93	59.61	7.17	42.24	37.31	1.36	32.08
Lichen	Lichen	14.50	27.77	0.31	14.57	39.79	7.56	40.69	42.67	1.03	48.40

The relative abundance of carbon chain (C-chain) lengths between C₁₆-C₃₅ were calculated for dominant vegetation within the catchment (Figure 3.3a-d) and highlight where the dominant chain length differs and overlaps between samples: C₂₉ is dominant in grass, coniferous and alder samples, while C₂₇ is dominant in Birch samples. Even lower chain lengths, i.e. C₂₁, C₂₃ and C₂₅, are abundant in both coniferous and deciduous samples. Relative abundance of longer-chain lengths for other vegetation samples can be found in B.1.1 Relative abundance n-alkanes.

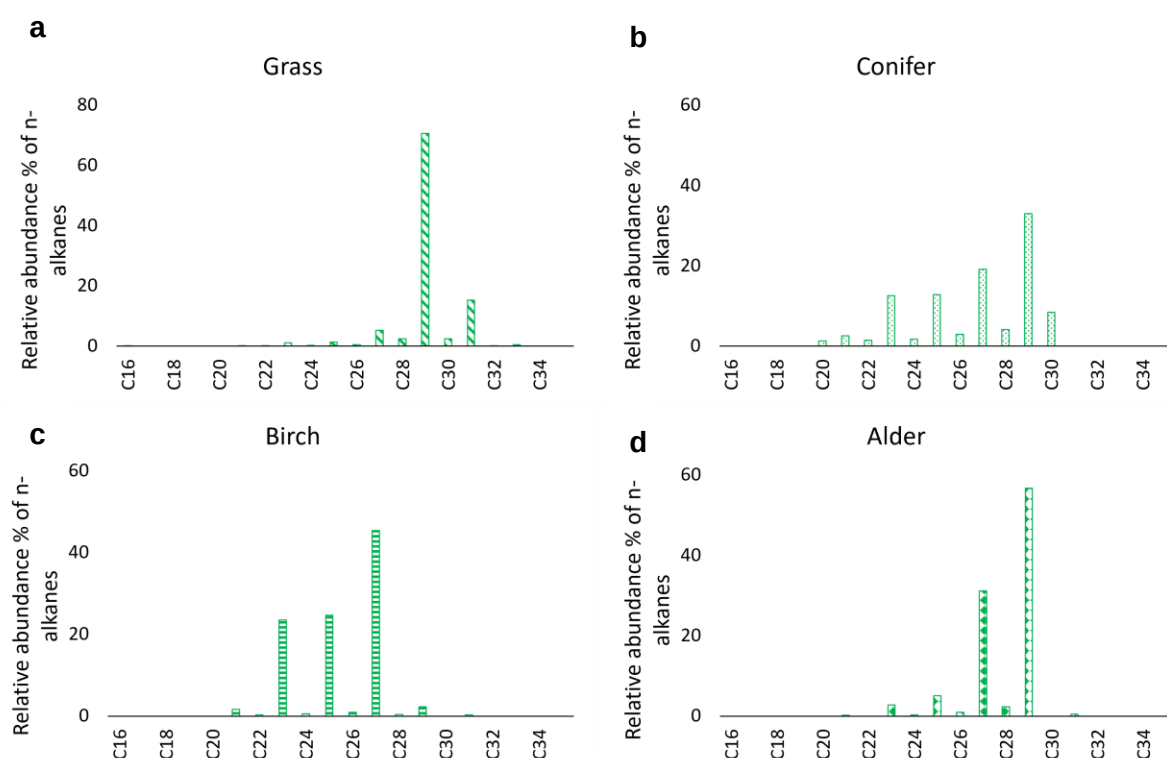


Figure 3.3: Relative abundances of n-alkane chain lengths C₁₆ – C₃₅ in (a) grass (b) coniferous (Sitka spruce) (c) birch (d) alder.

3.5.2.2 Soils and freshwater sediments

N-alkane measurements were used to calculate index values in soils and freshwater sediments (Table 3.5). The ACL in soil sites ranged from 27.99 to 29.23 across all sites in both seasons and 27.52 to 28.84 in freshwater sediments. Total n-alkanes (C₁₆-C₃₅) in soil sites ranged from 8-14 µg/g in soils and 13-24 µg/g in freshwater sediments. The range of total n-alkanes in soils and freshwater sediments is lower than vegetation samples, and the average ACL is slightly higher, falling within the same range of grass, moss and coniferous samples in soils and deciduous material in freshwater sediments.

Table 3.5: Bulk TC, OC, N and n-alkane indices for soil samples (summer and winter) and freshwater sediment samples

Site		CPI	ACL	Paq	OEP	TAR	Total n-alkanes C ₁₆ -C ₃₅ µg/g	Total C (% w/w)	Organic C (% w/w)	Total N (% w/w)	Molar OC/N
Summer S1	average	7.11	29.23	0.12	9.15	21.93	10.72	7.10	6.96	0.25	32.04
	standard deviation	0.62	0.27	0.06	0.99	9.56	0.44	1.89	1.83	0.07	
Summer S2	average	7.08	29.07	0.16	9.54	38.39	9.55	12.63	11.97	0.86	16.18
	standard deviation	0.23	0.02	0.09	0.55	4.90	6.88	2.17	1.89	0.26	
Summer S3	average	6.94	28.49	0.24	9.16	9.47	8.98	7.50	4.92	0.37	15.35
	standard deviation	0.13	0.02	0.03	1.11	3.06	7.00	1.38	3.77	0.10	
Winter S1	average	6.79	28.70	0.19	7.55	15.14	10.10	6.04	6.23	0.40	17.96
	standard deviation	0.54	0.11	0.03	0.91	12.19	2.41	1.19	1.23	0.09	
Winter S2	average	5.56	28.52	0.30	7.01	11.82	13.78	13.41	12.31	0.83	17.21
	standard deviation	0.10	0.47	0.11	0.22	2.99	5.28	7.03	6.43	0.46	
Winter S3	average	4.56	27.99	0.41	6.65	4.78	8.43	2.91	2.94	0.18	18.84
	standard deviation	0.06	0.22	0.01	0.49	1.32	2.82	0.36	0.03	0.02	

FASN S1 (Fr.Sed)		24.14	27.52	0.32	26.88	41.89	24.05	3.41	3.40	0.25	16.03
FASN S2 (Fr.Sed)		6.63	27.58	0.35	9.96	3.24	12.77	6.99	6.16	0.56	12.82
FASN S3 (Fr.Sed)		8.49	28.84	0.22	11.03	6.78	19.19	8.42	6.91	0.57	14.17

The relative abundance of chain lengths $C_{16} - C_{35}$ were calculated for all soil sites across two seasons and Fasnacloich sediments (Figure 3.4). In Site 1 soils (Figure 3.4a,d) C_{31} dominates in summer where we observe ~30 % abundance, this decreases in winter to ~23 %, where C_{29} becomes the dominant C-chain length at ~24 %. Lower chain lengths $C_{21}-C_{25}$ are also slightly elevated in winter in comparison to summer. In Site 2 soils (Figure 3.4b,e) C_{31} dominates across summer and winter, 30 % and 25 % respectively. This decrease in C_{31} from summer to winter is accompanied by an increase in lower C-chain abundance, particularly $C_{21}-C_{25}$. In Site 3 soils (Figure 3.4c,f) C_3 also dominates across summer and winter seasons, 23 % and 18 % respectively. Soil Site 3, across both seasons but particularly in winter, has the greatest abundance of lower C-chain lengths as C_{21} accounts for 6-8 % across summer and winter respectively, in comparison to 1-4 % in Soil Site 2 and 2-4 % in Soil Site 1.

From fresh plants to soils, CPI and OEP do not necessarily decrease in catchment samples (Table 3.4, Table 3.5) as observed in (Thomas et al., 2021). For example, in fresh Alder samples and corresponding Site 2 soil samples, CPI experienced little change from leaf to soil while OEP decreased, and in fresh coniferous samples and corresponding Site 1 soil samples CPI and OEP remained the same. However, this differs slightly between season as summer soils have higher CPI and OEP values than winter soils (Table 3.5).

A seasonal decrease in C_{31} is observed between summer and winter across all soil sites and aligns with an increase in the abundance of shorter C-chain lengths in winter. Both coniferous and deciduous sites have a higher relative abundance of longer C-chain lengths in comparison to Soil Site 3. Despite the differences between summer and winter n-alkane distributions, there is a greater difference in the relative distribution of n-alkanes between soil sites than seasons.

Fasnacloich samples were obtained in spring only. F1 (closest to the inflow) is dominated by C_{27} which accounts for 36% of all n-alkanes in the sediments, which is closely followed (31 %) by C_{29} . This varies downstream towards the outflow as F2 (middle of the waterbody) is dominated by C_{31} at 17 % closely followed by C_{20} at 16 %, showing large difference to F1 sediments and soils further upstream. Near the outflow (F3) C_{31} is most abundant accounting for 22 % of n-alkanes, while C_{27} and C_{29} account for 17 % and 19 % respectively. Fasnacloich also has peaks at C_{17} in F2 and F3 that are not observed in soil samples, suggesting different, maybe water-based vegetation inputs may be present.

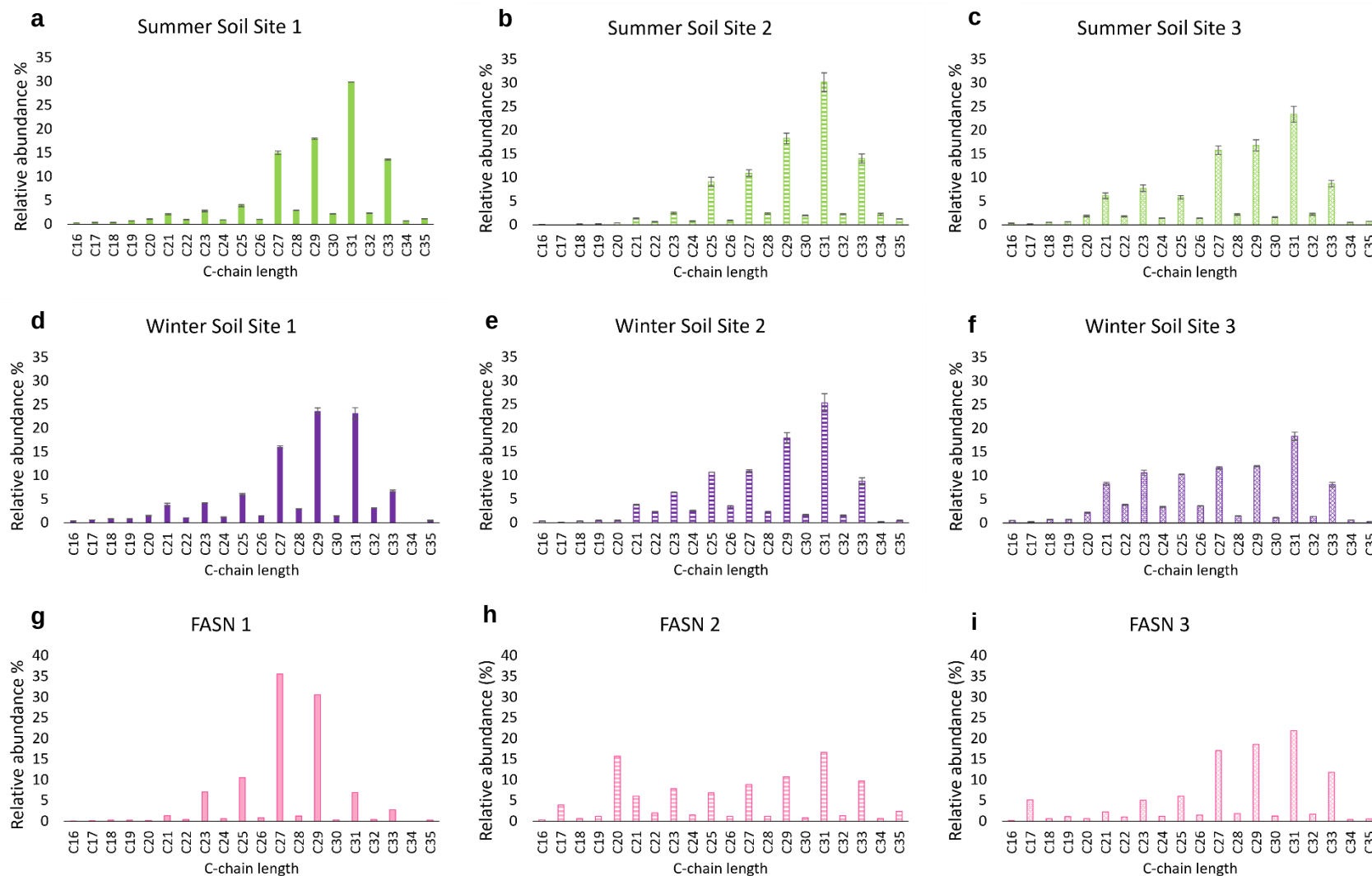


Figure 3.4: The relative abundance of *n*-alkane chain lengths for C16-C35 for (a) Site 1, Summer (b) Site 2, Summer (c) Site 3, Summer (d) Site 1, Winter (e) Site 2, Winter (f) Site 3, Winter (g) Site 1 Fasnacloch sediments (h) Site 2 Fansnacloch sediments (i) Site 3, Fasnacloch sediments (only collected in Spring). The error bars shown are based on the standard deviation of soils across both sides of the riverbank at each site.

3.5.2.3 Fjord sediments

N-alkane abundance was measured, and indices calculated for four sediment cores throughout Loch Creran to obtain spatial information, and with depth to gain a better understanding of temporal changes (Table 3.6). Total n-alkane values were calculated from C₁₆-C₃₅ and indices calculated accordingly. When an average is taken from all sediment depths within a core, we observe a decrease in total n-alkane abundance from UB1 to LB2, from 18.4 µg/g ± 4.7 to 5.6 µg/g ± 1.6 respectively.

Table 3.6: Bulk TC, OC, N and indices calculated from n-alkane data for all fjord sediment cores (UB1-LB2) across a range of depths.

<u>Sample</u>	<u>Depth (cm)</u>	<u>CPI</u>	<u>ACL</u>	<u>Pag</u>	<u>OEP</u>	<u>TAR</u>	<u>Total n-alkanes C16-C35</u>	<u>Total C (% w/w)</u>	<u>Organic C (% w/w)</u>	<u>Total N (% w/w)</u>
UB1 2.5	2.5	6.72	29.14	0.14	8.32	23.78	23.54	6.01	5.80	0.52
UB1 4.5	4.5	5.92	29.24	0.15	8.31	16.18	15.76	5.56	5.38	0.50
UB1 6.5	6.5	5.54	29.03	0.19	7.35	18.87	15.38	5.47	5.46	0.49
UB1 8.5	8.5	5.43	29.09	0.18	7.22	19.56	17.68	5.36	5.02	0.47
UB1 10.5	10.5	5.80	29.23	0.15	7.54	29.52	17.52	5.19	5.20	0.46
UB1 12.5	12.5	6.35	29.34	0.15	8.55	24.01	21.12	5.10	5.08	0.45
UB1 14.5	14.5	6.30	29.25	0.16	8.47	23.50	17.52	4.85	4.61	0.42
UB1 16.5	16.5	6.48	29.21	0.15	8.75	20.87	15.07	4.75	4.69	0.41
UB1 18.5	18.5	6.34	29.20	0.16	8.19	23.03	14.86	4.42	4.46	0.38
UB1 20.5	20.5	6.35	29.34	0.14	8.40	30.34	7.98	4.41	4.39	0.38
UB1 22.5	22.5	6.67	29.27	0.16	8.83	22.44	16.78	4.57	4.35	0.38

UB1 24.5	24.5	5.48	29.59	0.15	7.43	33.16	18.67	4.53	4.36	0.38
UB1 26.5	26.5	7.16	29.56	0.13	9.43	27.99	23.90	4.44	4.11	0.36
UB1 28.5	28.5	6.86	29.60	0.15	9.19	23.85	14.87	4.47	4.37	0.36
UB1 30.5	30.5	6.89	29.64	0.13	9.29	25.06	28.03	4.59	4.45	0.37
UB1 32.5	32.5	6.94	29.68	0.14	9.43	24.45	20.59	4.64	4.57	0.37
UB1 34.5	34.5	6.65	29.63	0.15	8.87	23.12	23.58	4.80	4.70	0.38
UB2 0.5	0.5	4.94	28.94	0.19	6.48	16.33	13.78	6.06	5.84	0.58
UB2 1.5	1.5	6.18	29.33	0.13	8.15	26.08	17.67	5.68	5.39	0.54
UB2 2.5	2.5	5.71	29.04	0.18	7.54	18.66	17.81			
UB2 3.5	3.5	4.08	28.51	0.33	5.81	7.40	16.65	5.98	5.46	0.54
UB2 4.5	4.5	5.52	28.93	0.19	7.19	14.63	14.55			
UB2 5.5	5.5	3.97	28.17	0.35	5.68	6.97	14.87	5.58	5.28	0.51
UB2 6.5	6.5	7.26	29.38	0.13	10.32	20.44	24.22			
UB2 7.5	7.5	6.05	29.11	0.14	8.20	22.98	17.61	5.75	5.13	0.52
UB2 8.5	8.5	5.99	29.13	0.17	7.64	20.45	19.23			
UB2 9.5	9.5	3.81	28.55	0.33	5.62	6.82	16.29	5.53	4.98	0.51
UB2 10.5	10.5	4.09	28.55	0.30	6.10	10.76	17.08			
UB2 11.5	11.5	4.40	28.63	0.32	6.60	9.28	17.05	5.43	5.10	0.50

UB2 13.5	13.5	6.61	29.24	0.16	9.16	22.53	20.83	5.38	5.01	0.50
UB2 15.5	15.5	5.85	29.28	0.15	7.96	17.60	24.81	5.72	5.23	0.53
UB2 17.5	17.5	6.85	29.31	0.14	9.54	21.61	15.55	5.13	4.85	0.46
UB2 19.5	19.5	6.31	29.23	0.16	8.15	21.07	20.01	5.03	4.80	0.45
UB2 21.5	21.5	6.04	29.06	0.18	7.95	16.98	17.51			
UB2 23.5	23.5	6.94	29.45	0.18	8.65	33.81	15.42	4.75	4.54	0.42
UB2 25.5	25.5	7.94	29.54	0.17	10.32	36.33	12.86	4.49	4.12	0.40
UB2 27.5	27.5	8.27	29.41	0.18	11.04	35.01	14.23			
UB2 29.5	29.5	4.61	29.00	0.25	7.02	18.85	16.62	4.70	4.22	0.42
UB2 31.5	31.5	6.58	29.20	0.21	8.27	30.89	13.11	4.60	4.11	0.40
UB2 32.5	32.5	5.46	29.24	0.15	7.18	18.66	16.18			
UB2 33.5	33.5	6.68	29.11	0.22	8.39	28.65	12.31	5.00	4.77	0.44
UB2 35.5	35.5	5.71	29.14	0.22	8.38	20.80	16.05	4.80	4.42	0.42
UB2 39.5	39.5	4.36	28.61	0.30	6.39	7.35	17.75	4.60	4.31	0.41
LB1 1.5	1.5	5.42	29.08	0.12	7.09	32.55	12.70	4.93	3.93	0.44
LB1 2.5	2.5	5.06	28.97	0.18	6.72	12.59	8.53	4.71	4.08	0.44
LB1 6.5	6.5	4.77	28.76	0.20	6.52	8.16	8.83	4.48	4.14	0.43
LB1 8.5	8.5	4.76	28.85	0.20	6.33	13.02	7.50	4.45	4.13	0.42

LB1 10.5	10.5	4.80	28.91	0.20	6.47	16.21	8.60	4.43	4.07	0.42
LB1 12.5	12.5	4.05	28.23	0.38	5.48	5.72	11.95	4.4	4.06	0.41
LB1 14.5	14.5	4.02	28.13	0.39	5.50	5.69	11.97	4.31	3.39	0.38
LB1 16.5	16.5	4.22	28.26	0.38	5.74	7.18	11.28	3.88	3.13	0.35
LB1 18.5	18.5	4.14	28.27	0.40	5.49	6.35	13.21	3.79	3.22	0.33
LB1 20.5	20.5	5.32	28.98	0.18	6.99	13.26	9.64	3.58	3.05	0.31
LB1 22.5	22.5	5.37	29.04	0.22	6.18	14.75	9.83	4.19	3.53	0.37
LB1 24.5	24.5	6.57	29.29	0.17	8.47	18.96	5.09	3.67	2.98	0.31
LB1 26.5	26.5	5.82	29.35	0.20	7.10	19.66	14.21	3.63	3.03	0.30
LB1 28.5	28.5	5.46	29.17	0.22	6.29	16.78	11.22	3.77	3.24	0.31
LB1 30.5	30.5	5.92	29.20	0.22	7.24	16.31	14.44	3.91	3.46	0.31
LB1 32.5	32.5	6.03	29.33	0.20	7.34	18.10	15.99	3.88	3.48	0.32
LB1 34.5	34.5	6.10	29.35	0.20	7.56	21.30	16.53	3.84	3.42	0.31
LB1 36.5	36.5	5.45	29.20	0.21	6.48	18.71	11.45	3.69	2.96	0.30
LB1 38.5	38.5	5.58	29.19	0.21	6.66	15.32	12.93	3.71	3.36	0.31
LB1 40.5	40.5	5.53	28.99	0.17	7.66	18.99	10.96	3.74	3.15	0.31
LB1 42.5	42.5	5.71	29.16	0.21	6.80	24.17	12.09	3.59	2.97	0.30
LB1 44.5	44.5	5.79	29.21	0.20	6.94	17.54	13.04	3.64	3.19	0.30

LB2 1.5	1.5	4.33	28.79	0.15	5.86	11.05	4.05	2.55	1.70	0.25
LB2 2.5	2.5	2.24	28.03	0.42	4.32	3.53	5.27	2.27	1.79	0.18
LB2 4.5	4.5	4.66	28.68	0.14	6.44	19.47	4.33	2.17	1.78	0.18
LB2 6.5	6.5	4.50	28.76	0.20	6.05	8.18	3.63	2.06	1.70	0.17
LB2 8.5	8.5	4.32	28.61	0.20	5.77	7.44	3.71	2.3	1.89	0.18
LB2 10.5	10.5	4.41	28.80	0.19	5.72	7.35	4.75	2.4	1.76	0.18
LB2 12.5	12.5	3.05	29.28	0.09	5.46	6.24	6.76	2.47	1.80	0.2
LB2 14.5	14.5	4.03	28.15	0.43	5.37	4.67	7.25	2.14	1.68	0.17
LB2 16.5	16.5	3.22	28.29	0.38	6.67	5.58	7.60	2.25	1.82	0.17
LB2 18.5	18.5	4.22	28.94	0.18	6.60	10.15	6.55	2.03	1.63	0.15
LB2 20.5	20.5	4.44	28.24	0.43	6.50	4.55	7.34	2.04	1.59	0.15

We do not observe a significant relationship between total OC and total n-alkanes when cores are analysed separately ($P > 0.05$) but when all cores are considered there is a significant correlation between these variables ($R = 0.755$, $P = <0.001$, Table 3.11). When these variables are plotted (Figure 3.5) similarities and differences can be observed in the downcore patterns. Downcore, n-alkanes have variable concentrations that do not necessarily decline with depth. Where OC decreases with depth throughout the sediment cores, n-alkane concentrations do not follow. In surface sediments (<10 cm) of UB1 and LB2 (Figure 3.5a,d) total OC and total n-alkane concentrations have similar trends however, in UB2 and LB1 (either side of the Cregan narrows sill) total OC and total n-alkane concentrations are inversely related (Figure 3.5b,c), where OC concentrations are higher n-alkanes are lower in concentration, and they then come together >10 cm. Overall, n-alkane concentrations are best aligned with OC concentrations in UB2.

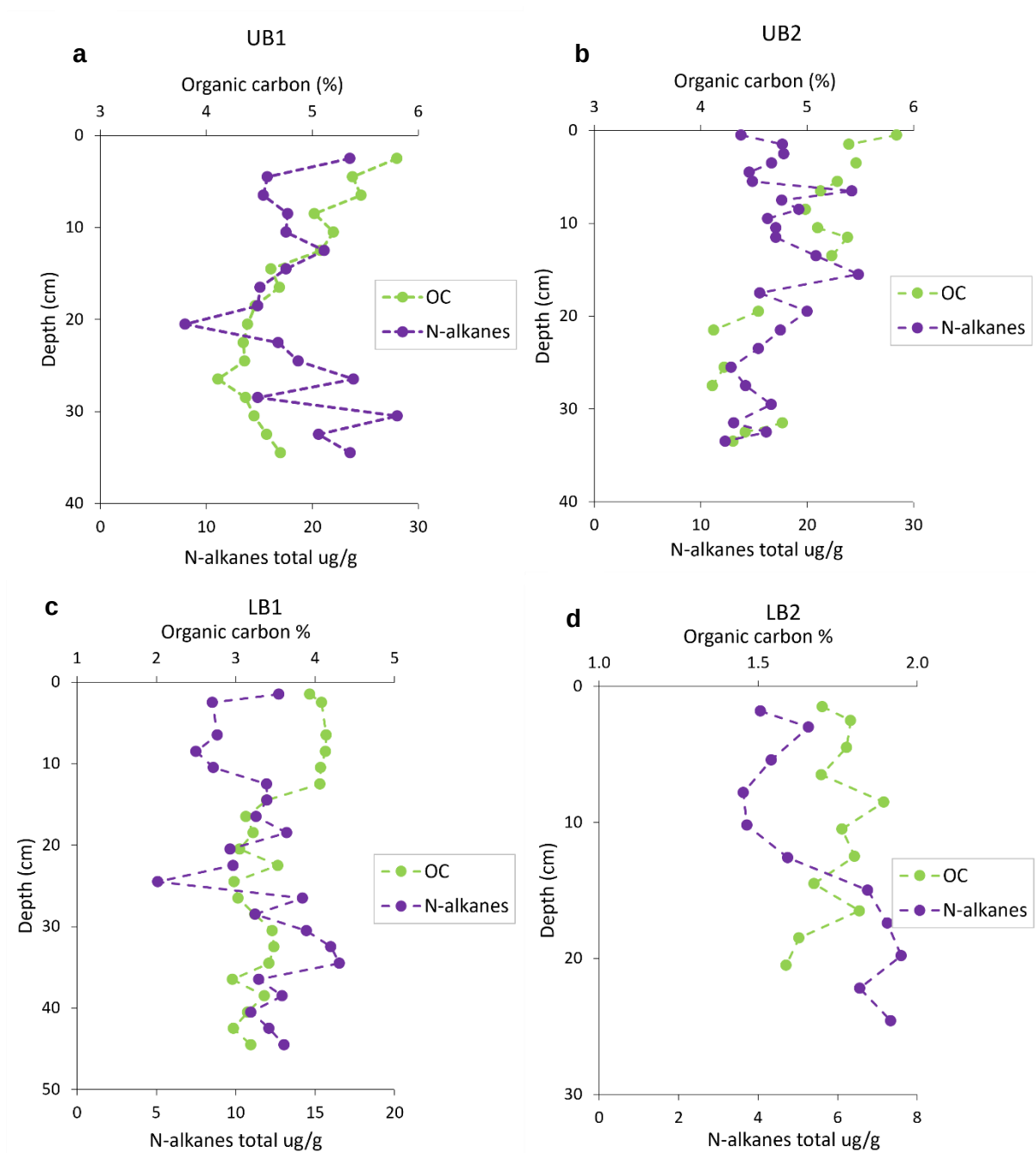


Figure 3.5: Organic carbon and *n*-alkane abundance plotted with depth for (a) UB1 (b) UB2 (c) LB1 (d) LB2. *N*-alkanes are represented by a purple line and points and organic carbon is represented by a green line and points.

To establish the main drivers behind the changes in *n*-alkane signatures with depth, changes in relative abundance of long-chain *n*-alkanes were calculated within sediment samples. Long-chain *n*-alkanes were considered to be C₂₅–C₃₅ and short-chains were C₁₆–C₂₄ (Figure 3.6) as per (Thomas et al., 2021). The relative abundance of long-chain *n*-alkanes ranges from 60 to 91 %. Long-chain abundance is most stable in UB1 where they account for 87-91 % of *n*-alkanes downcore. The relative abundance in UB2 is variable (74-90 %) until 14cm depth after

which long-chain abundance remains consistent at ~90 % until 35cm depth where it decreases to 77 %.

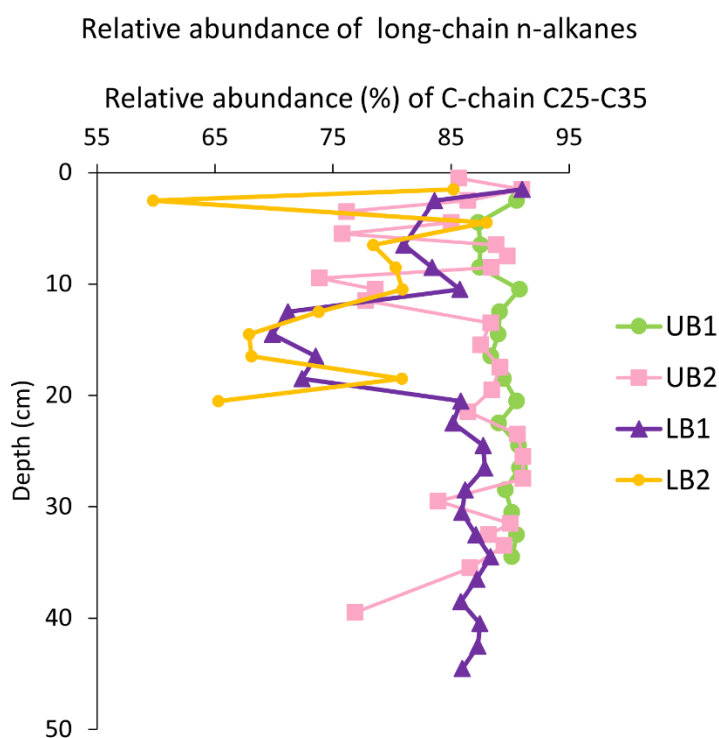


Figure 3.6: The relative abundance of long chain n-alkanes with depth for sediment cores UB1, UB2, LB1, LB2. In this case long-chain is inclusive of C25-C35.

LB1 and LB2 have much more variable long-chain abundance, and some of the lowest values. However, between 0-10 cm and 20-45 cm in LB1, the relative abundance of long-chain n-alkanes is between 78-91 %. We found no significant correlations between relative abundance of long-chain n-alkanes and n-alkanes, highlighting that changes in the distribution of n-alkane chain length is not necessarily correlated with n-alkane abundance (Table 3.11).

There is no evidence of linear degradation of n-alkanes with depth (Figure 3.5, Table 3.7). UB1 exhibits a weak positive correlation between depth and n-alkane abundance, UB2 has a weak negative correlation, while LB1 and LB2 show statistically significant positive correlations between depth and n-alkane abundance, showing that n-alkanes increase with depth. OEP is regularly used as a measure of degradation in soils and sediments, with values >5 being indicative of terrestrial vegetation and values <5 suggesting enhanced degradation or the presence of soils. OEP values vary downcore and with the exception of one sample in the surface sediments of LB2, all samples maintain an OEP >5 (Table 3.6). All sediments have positive OEP trends downcore, which is clear from the positive R values (Table 3.11).

The average total n-alkanes and relative abundance of long-chain n-alkanes for whole core and surface sediments (<10 cm) are summarised (Table 3.7) and compared to the relative abundance in freshwater sediments and soils.

Table 3.7: Average values for n-alkane parameters from vegetation, soil, freshwater and fjord sediment samples.

Core	Average total n-alkanes (µg/g)	Relative abundance of long chain n-alkanes (%) (C26 – C35)	Average total n-alkanes in surface sediments (µg/g)	Relative abundance of long chain n-alkanes in surface sediments (<10 cm) (%) (C26 – C35)
Deciduous trees	43.42 ± 21.49	90.23 ± 10.89		
Coniferous trees	5.60 ± 6.61	88.30 ± 11.16		
Soil sites	10.26 ± 1.90	83.46 ± 8.70		
FASN	18.67 ± 5.66	77.65 ± 15.11		
UB1	18.40 ± 4.70	89.48 ± 1.23	18.09 ± 3.77	88.2 ± 1.58
UB2	16.93 ± 3.06	85.58 ± 5.44	17.27 ± 2.97	84.10 ± 6.38
LB1	11.45 ± 2.75	83.61 ± 6.08	9.39 ± 2.28	84.76 ± 4.34
LB2	5.57 ± 1.56	75.31 ± 8.99	4.20 ± 0.66	78.33 ± 11.08

Studies have noted a clear decrease in the total n-alkane concentrations from fresh leaves to topsoil (~87 % decrease) (Thomas et al., 2021). In this study, total n-alkanes decrease from fresh leaves to soils (Table 3.7) e.g. total n-alkane abundance of alder leaves ~43.42 µg/g to ~10 µg/g in soils, but then total n-alkane concentrations increase in freshwater (~18.67 µg/g) and fjord sediments (18.40 µg/g in UB1) (Table 3.7). Varying changes (both increases and decreases) have been reported in the relative abundance of n-alkanes from vegetation to soils (Thomas et al., 2021) and the data in this study also shows variability depending on plant type and soil site. The relative abundance of long-chain n-alkanes generally decreases from fresh plants to soils (Table 3.7), and decreases from soils to freshwater sediments, increasing again

in fjord sediments where they decrease from UB1 to LB2 (Table 3.7). (Relative abundance for all individual samples can be found in B.1.1 Relative abundance n-alkanes).

3.5.2.4 Total lipid extracts

N-alkanes only represent a small fraction of the total lipids extracted from vegetation, soil and sediment samples (full TLE weights can be found in B.1.2 TLE weights). N-alkanes remain <1% of total lipids extracted (TLE) for all samples (vegetation, soils, sediments).

3.5.3 Pine Resin Data

We identified a coniferous biomarker, methyl dehydroabietate, an abundant spruce marker (Duce et al., 2015; Jablonský et al., 2015) which is present in soil and sediment samples in this study (Peak identification shown in B.1.3 Peak identification of methyl dehydroabietate) in low but quantifiable concentrations, and in coniferous vegetation samples obtained from the catchment and some moss from our coniferous soil site.

3.5.3.1 Vegetation samples

Methyl dehydroabietate is absent in all but a selection of coniferous samples (Table 3.8), which is in agreement with other studies that have used this compound as a coniferous marker (e.g. Azemard et al., 2016; Otto and Simoneit, 2001; Simoneit et al., 2018). On that basis it is used in this study as a marker representative of coniferous vegetation in this catchment. Concentration averages vary from ~0.5 – 8.14 µg/g in dead and living coniferous samples. The moss sample was taken from a coniferous tree stand, and as such, small pieces of coniferous material and soil were attached. The waxy resin is in both soils and coniferous vegetation so would coat other materials growing in the same space if they come into contact with coniferous material, especially decaying material.

Table 3.8: Concentrations of methyl dehydroabietate in vegetation samples.

<u>Group</u>	<u>Plant description</u>	<u>Site of collection</u>	<u>Methyl dehydroabietate µg/g</u>
Alnus glutinosa	Living deciduous (alder)	2	0
Alnus glutinosa	Dead deciduous (alder)	2	0
Picea sitchensis	Living coniferous	1	0.551 ± 0.707

Picea sitchensis	Dead coniferous	1	8.14 ± 11.22
Quercus	Oak	3	0
Betula	Birch	3	0
Ulex	Gorse	3	0
Hyacinthoides non-scripta	Bluebells	3	0
Poaceae	Grass	2	0
Poaceae + Bryophyta	Grass and moss	2	0
Bryophyta	Moss type	1	0.928
Lichen	Lichen	3	0

3.5.3.2 Soils and freshwater sediments

Methyl dehydroabietate concentrations from coniferous inputs are low but measurable in catchment soils and are only present in coniferous soils sites. Methyl dehydroabietate is present throughout different seasons (Figure 3.7a,b) and also downstream in freshwater sediments measurable near the inflow and outflow (Figure 3.7c).

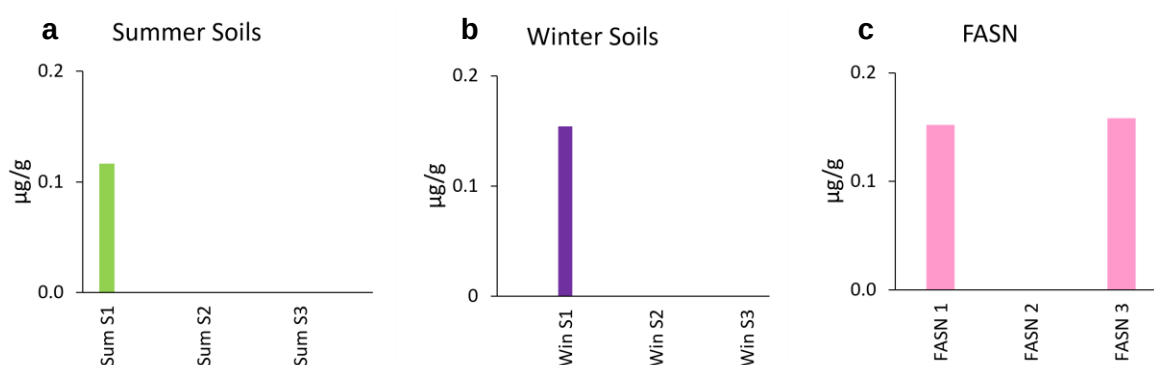


Figure 3.7: Concentrations of methyl dehydroabietate present in soil samples in (a) summer and (b) winter, and in (c) freshwater sediment samples.

3.5.3.3 Fjord sediment cores

Methyl dehydroabietate is observed in samples in all cores suggesting that it reaches the fjord from surroundings. It is most abundant throughout the depths of UB2 – LB2 (Figure 3.8). Cores UB2 – LB1 follow a similar pattern of methyl dehydroabietate with depth, with small peaks

around 10cm and 26cm. It appears to be absent in surface sediments in all cores except for LB2. Concentrations do not appear to decrease with depth in UB2 or LB1.

Surface sediments of UB1-LB1 have the highest OC concentrations, and methyl dehydroabietate concentrations increase as OC concentrations decrease downcore in UB2 and LB1, which is highlighted by the significant P values and negative R values associated with this relationship (Table 3.11).

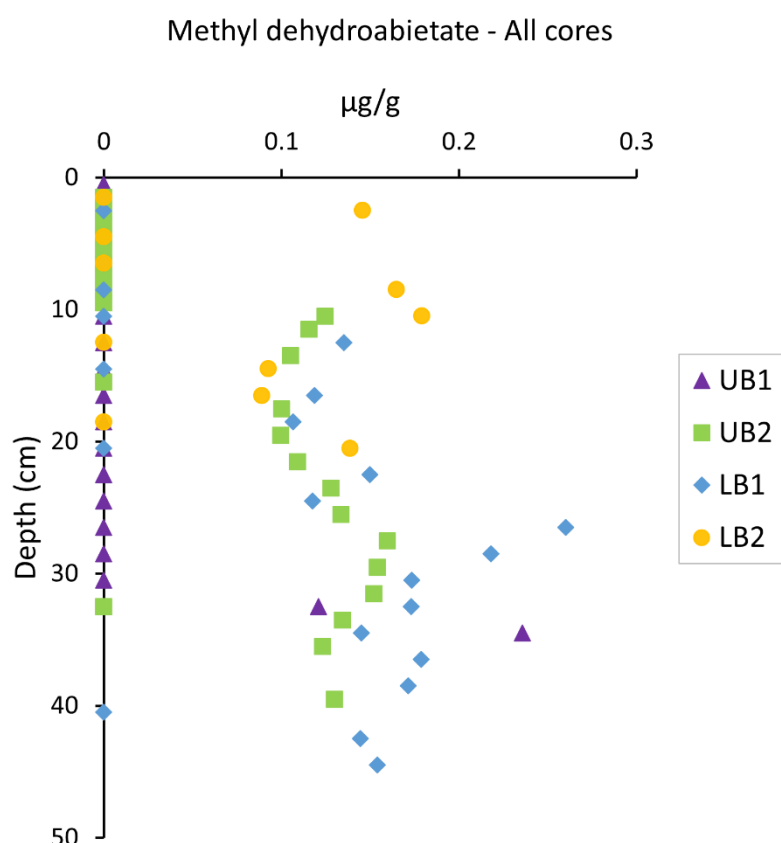


Figure 3.8: Concentrations of methyl dehydroabietate downcore in UB1 (purple triangle), UB2 (green square), LB1 (blue diamond), and LB2 (yellow circle).

3.5.4 N-alkane specific $\delta^{13}\text{C}$ composition from source-towards-fjord

3.5.4.1 Vegetation and soils

Living and dead vegetation samples can display different n-alkane specific $\delta^{13}\text{C}$ signatures (e.g. Nguyen Tu et al., 2004). In deciduous material, between C_{25} and C_{27} chain lengths, dead material is considerably more enriched in $\delta^{13}\text{C}$ (-30 ‰ in comparison to the living sample at -37 ‰) (Figure 3.9a). Similar observations could not be made for coniferous samples, as dead coniferous samples were below the limit of detection for $\delta^{13}\text{C}$.

When averaged values for odd-chained n-alkanes C₂₇-C₃₁ are considered, summer soils range from -35.07 ‰ to -37.6 ‰, and winter samples range from -34.5 ‰ to -36.4 ‰ but the larger differences can be observed between sites, as with n-alkanes. The most depleted $\delta^{13}\text{C}$ signatures are observed in Soil Site 1 (coniferous) with 33.4 ‰ to -38.5 ‰ in summer (Figure 3.9b), and -33.8 ‰ to -39.3 ‰ in winter (Figure 3.9c). Soil Site 2 and 3 (both with majority deciduous inputs) have closely aligned $\delta^{13}\text{C}$ signatures ranging from -32.5 ‰ to -36.7 ‰.

C₂₇ is the longest chain length present in all vegetation samples as well as soil samples, due to the absence of a $\delta^{13}\text{C}$ signatures for grass at C₂₉, grass, living deciduous and coniferous material for C₃₁ (Figure 3.9a). At C₂₇, coniferous samples exhibit a more depleted $\delta^{13}\text{C}$ signature

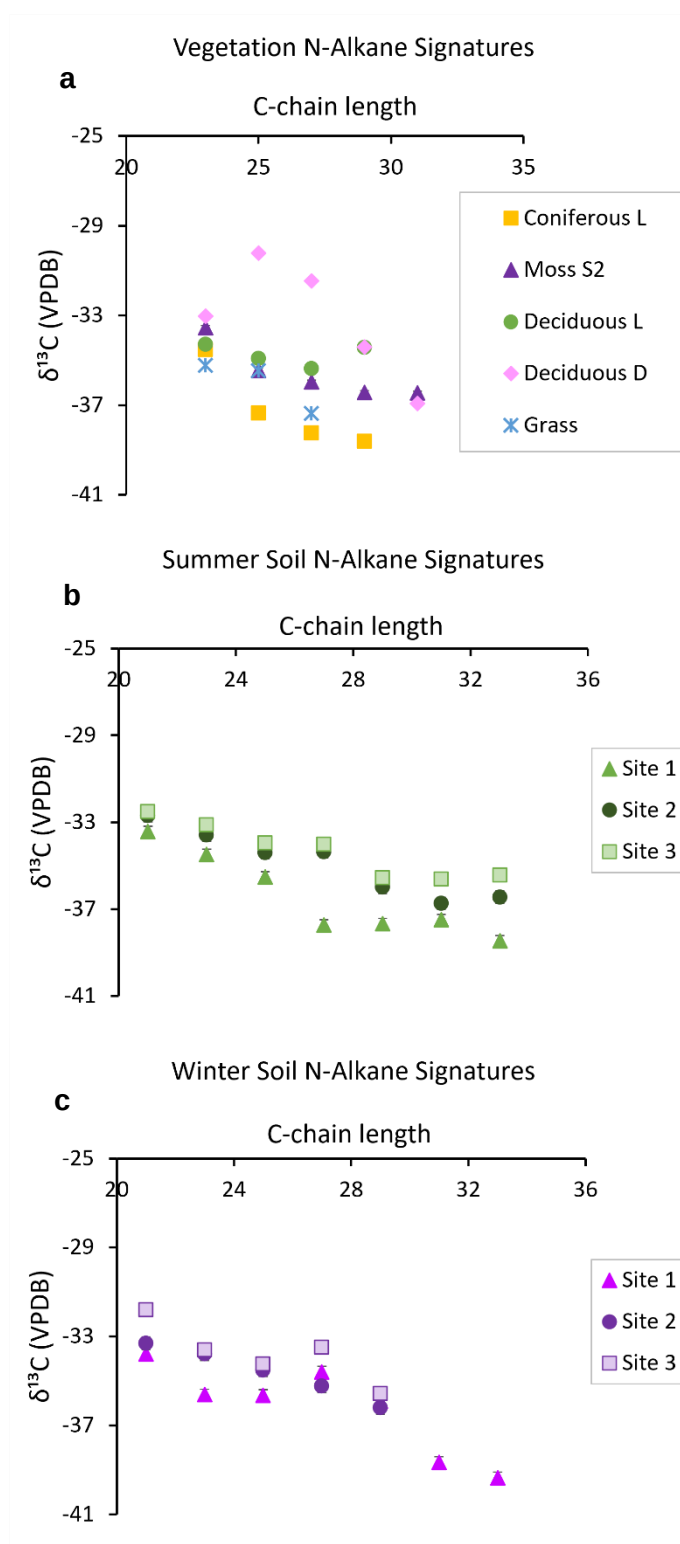


Figure 3.9: $\delta^{13}\text{C}$ signatures for (a) a selection of vegetation from the catchment of Loch Creran, (b) Soils across three catchment sampling sites in summer, (c) Soils across three sampling sites in winter.

(C_{27} ~ -38 ‰) in comparison to Site 2 and 3 soil samples (C_{27} ~ -34 ‰), but similar signatures when compared to grass (C_{27} ~ -37 ‰).

3.5.4.2 Fasnacloch and fjord sediments

N-alkane specific $\delta^{13}C$ signatures of sediments can be used to better characterise sedimentary OC (Fang et al., 2014; Mead et al., 2005). Sediments $\delta^{13}C$ signatures are within the range of vegetation sample values (~ -32.6 ‰ to -36 ‰) (Figure 3.10a-f). All sampling points within the small freshwater loch have similar values and follow the same trend of increasing depletion in $\delta^{13}C$ in longer chain lengths. FASN sites 1 and 3 are more depleted in $\delta^{13}C$ for C_{31} in

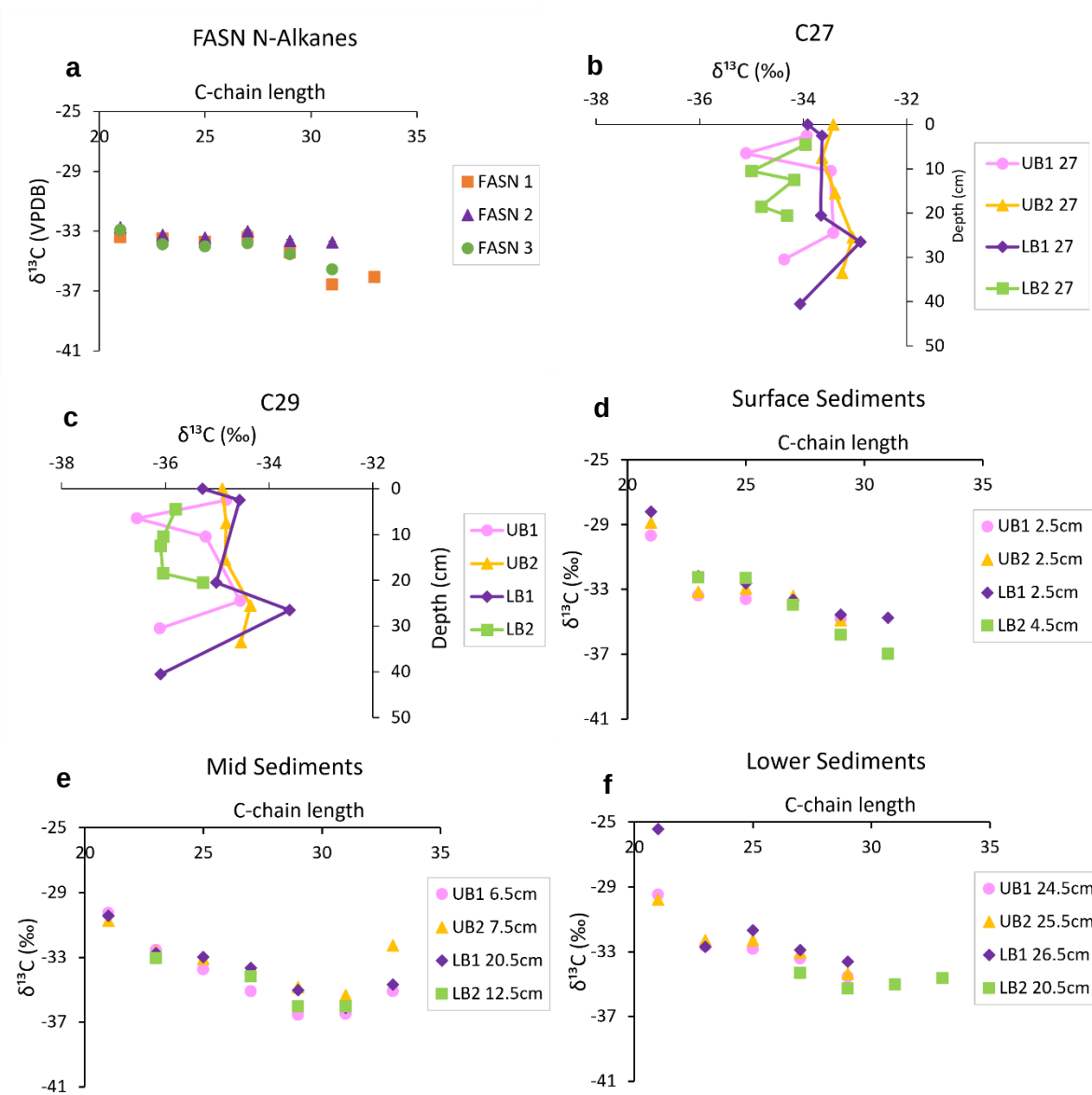


Figure 3.10: N-alkane $\delta^{13}C$ signatures for (a) freshwater sediments, (b) C27 in fjord sediment cores (c) C29 in fjord sediment cores (d) surface sediments (2-4cm) in fjord cores (e) mid-depth (6-20cm) sediments in fjord cores, (f) lower depth (20-27cm) sediments in fjord cores.

comparison to FASN Site 2, and FASN Site 1 is the only one of these sites that has a measurable $\delta^{13}\text{C}$ signature for C_{33} . No vegetation analysed had measurable amounts of $\delta^{13}\text{C}$ for C_{33} , but the depleted signatures at C_{31} (-36.6 ‰) are similar to deciduous values at the same chain length (-36.9 ‰). At C_{29} , all lochan sediment sites display similar $\delta^{13}\text{C}$ values $\sim$ -34 ‰, which is well aligned with isotopic measurements of living and dead deciduous material ($\sim$ -34 ‰).

In fjord sediments $\delta^{13}\text{C}$ values are variable downcore (Figure 3.10b,c). For C_{27} , UB2 has a consistently more enriched $\delta^{13}\text{C}$ signature (-33 to -33.6 ‰) and LB1 shows a similar trend (-33.6 to -34 ‰). LB2 has more depleted values (-33.9 to -35 ‰), and UB1 has the most variable range (-33.4 to -35.1 ‰). Comparatively, at C_{29} all values are more enriched in $\delta^{13}\text{C}$ (Figure 3.10c) but each core follows the same downcore trends as observed for C_{27} . When samples are compared across surface, mid, and deeper points within the sediments (Figure 3.10d,e,f), it is evident that surface sediments in cores UB1 – LB1 follow similar depletion trends while LB2 is depleted to a greater extent for chain lengths C_{29} and C_{31} . In mid and lower depth sediments (Figure 3.10e,f) all core samples remain aligned however, at lower depths (Figure 3.10f) LB1 shows a greater enrichment in C_{21} , and LB2 is the only core with quantifiable values for C_{31} and C_{33} .

Despite similar trends between $\delta^{13}\text{C}$ values in fjord sediments and C_{27} and long-chain n-alkane abundance there are no significant correlations (Table 3.11).

3.5.5 Climatic references for Loch Creran Catchment

Previous research suggests that temperature and precipitation can influence OC in soils and sediments and n-alkane properties (e.g. Kerr and Ochsner, 2020; Pedentchouk et al., 2008; Thomas et al., 2021; Wang et al., 2019, 2016). Seasonal temperature and rainfall data were obtained from the Met Office historical datasets. Monthly mean parameters were plotted against corresponding soil OC data to explore any influence that weather in the Dunstaffnage area may have on seasonal OC changes over a relatively short period of time (Figure 3.11). There is no indication that soil OC corresponds with precipitation changes (Figure 3.11a, b) across seasons or sites ($R^2 < 0.1$), but data does suggest that temperature and soil OC have a greater correlation ($R^2 > 0.95$ for Soil Site 2 and 3) (Figure 3.11b). There is no evident relationship between n-alkane concentrations and precipitation or temperature (Figure 3.11d,e).

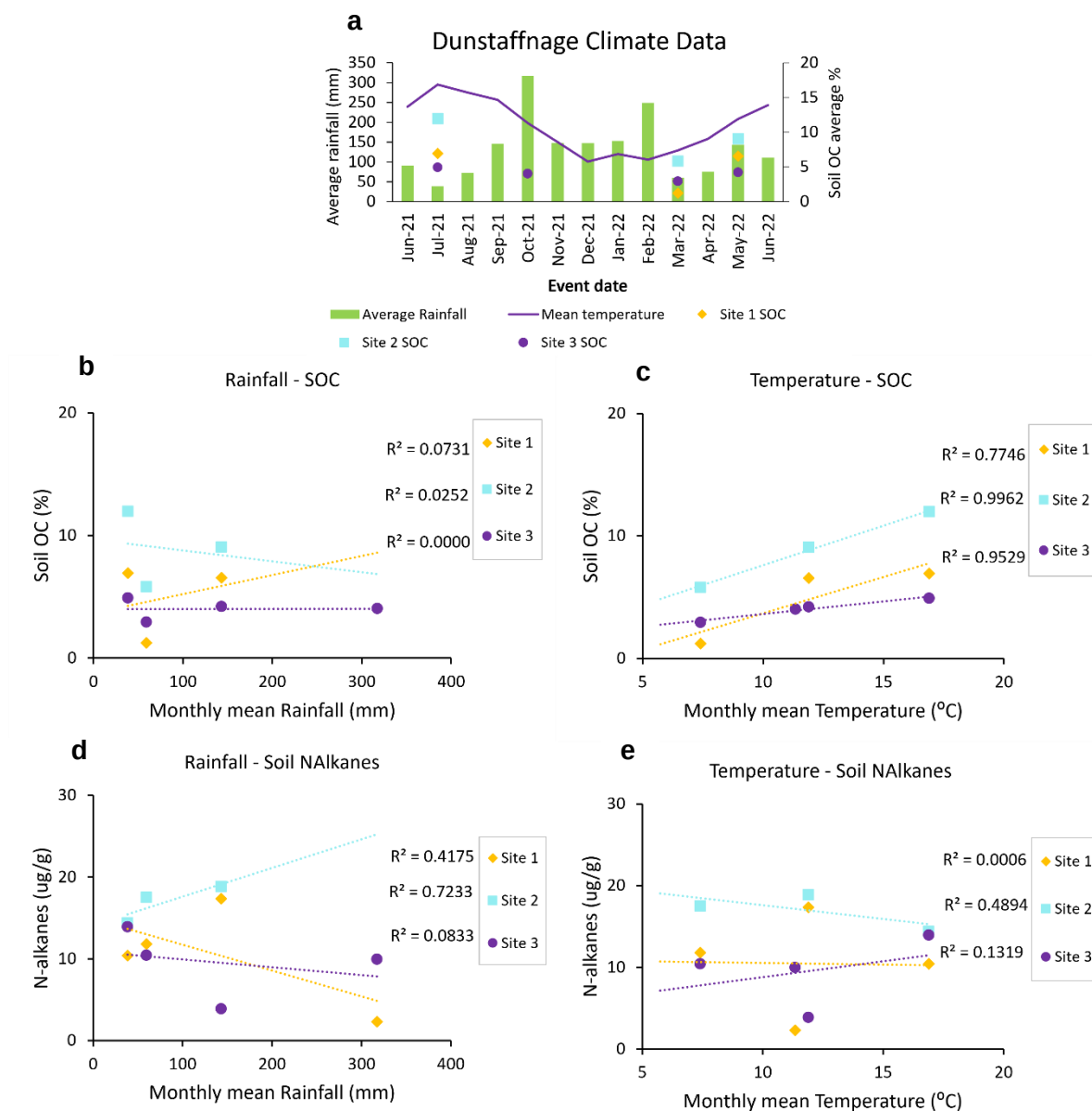


Figure 3.11: (a) Average rainfall (green bars) and mean temperature (purple line) during the sampling period June 2021 - June 2022. Specific sampling months indicated through points detailing Site 1,2,3 and average organic carbon % in the soil sites. Soil organic carbon is plotted against (b) rainfall (c) temperature and total n-alkanes for individual soil sites are plotted against (d) rainfall (e) temperature. Soil site 1 is represented by yellow circles, site 2 by blue squares, site 3 by purple circles.

3.5.6 Topography

The slope of the land surrounding Loch Creran is variable (Figure 3.12) and detailed in zonal statistics. Zonal statistics were used to calculate the slope (Table 3.9), elevation and bathymetric (Table 3.10) parameters within 200 m surrounding soil sampling points, within 500 m surrounding Fasnacloich sampling points and 1.5 km of core sampling points, the distance

covered was increased for grab and core points within the lochan and loch to include elevation of surrounding land.

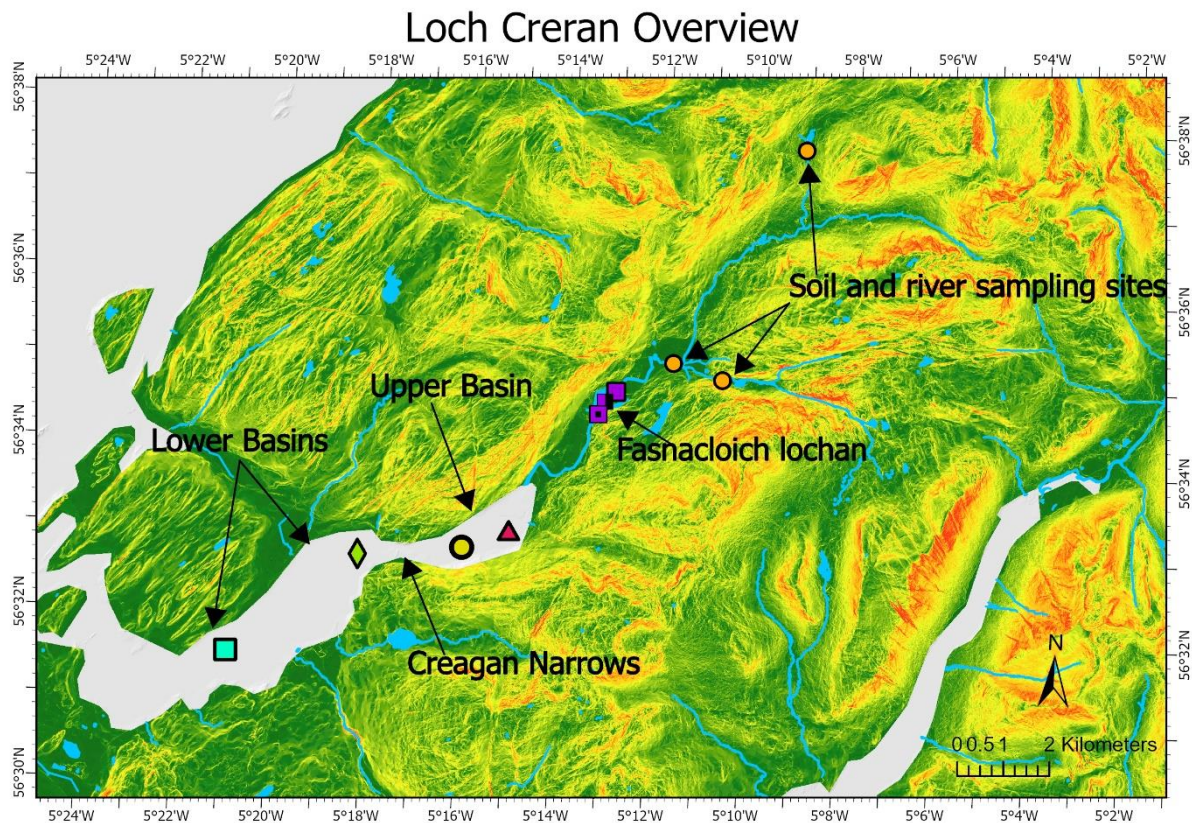


Figure 3.12: Overview of the slope surrounding Loch Creran and sampling points.

The range of slope for the soil sites shows Site 2 (deciduous) to have the largest increase in slope surrounding any soil sampling points (up to 68° difference), resulting in the highest mean of $19.3^\circ \pm 15.26$. In comparison, Soil Site 1 and Soil Site 3 had mean values of 8.9° and 2.9° respectively. Downstream, surrounding Fasnacloich lochan there is up to a 58° change in slope, and a mean of 7.7-10° slope. Surrounding fjord sediments have variable slopes (Table 3.9) that decrease from the upper to lower basins. UB1 and UB2 have mean slopes of 20.8-21.5°, in LB1 this decreases to 12° and LB2 8.2°.

Table 3.9: Slope values for soils, lochan and fjord sediments.

Type	Buffer	Sample	Min °	Max °	Range °	Mean °	Standard deviation	Median °
Slope	200m	Site 1 - River Creran	0.07	32.31	32.24	8.87	4.54	8.40
		Site 2 - River Ure	0.06	68.10	68.04	19.28	15.26	19.30
		Site 3 - River Creran + Ure	0.00	20.19	20.19	2.89	3.87	1.10
Slope	500m	FASN 1	0	44.47	44.47	7.66	8.04	5.14
		FASN 2	0	46.28	46.28	8.49	9.21	5.15
		FASN 3	0	57.58	57.58	10.03	10.60	5.97
Slope	1.5km	UB1	0	57.09	57.09	20.83	9.82	21.49
		UB2	0	57.09	57.09	21.51	8.90	21.95
		LB1	0	57.39	57.39	12.06	8.50	10.55
		LB2	0	53.83	53.83	8.25	7.59	5.76

The bathymetry of the sediments in the 200 m surrounding the sediment cores (Table 3.10) show UB2 to have the deepest mean at -25 m, and UB1 to be the shallowest at -6.9 m. LB1 and LB2 are -16 m and -19 m respectively.

Table 3.10: Bathymetry and elevation values for soils, lochan and fjord sediments.

Type	Buffer	Sample	Min (m)	Max (m)	Range (m)	Mean (m)	Standard deviation	Median (m)
Bathymetry	200m	UB1	-10.62	0.37	10.99	-6.86	3.07	-7.42
		UB2	-35.34	-10.10	25.24	-25.18	4.61	-24.85
		LB1	-22.81	-0.40	22.41	-16.03	3.45	-16.59
		LB2	-22.44	-14.44	8.00	-19.16	1.66	-19.58
Elevation	200m	Site 1 - River Creran	211.40	257.55	46.15	234.59	7.81	234.24
		Site 2 -River Ure	18.09	114.56	96.47	41.81	23.67	30.26
		Site 3 - River Creran + Ure	7.20	23.96	16.76	10.50	2.29	10.15
Elevation	500m	FASN 1 - 3	6.61	6.61	0	6.61	0	6.61
Elevation	1.5km	UB1	-1.13	487.56	488.69	109.15	123.21	63.46
		UB2	-1.13	452.90	454.03	115.93	122.25	70.99
		LB1	-1.13	224.53	225.66	34.82	48.68	9.13
		LB2	-1.14	93.75	94.89	10.83	18.24	-0.36

Soil Site 1 (River Creran, coniferous) has the highest elevation with a mean of 234.6 m above sea level, Soil Site 2 (River Ure) is significantly lower at ~42m and Soil Site 3 lower at ~10m. Downstream Fasnacloich is at an elevation of 6.6 m. The elevation noted for fjord sediment cores relate to the surrounding catchment within a 1.5 km circumference of the core sampling point to provide a reference of immediate catchment elevation. As observed in the mean slope measurements (Table 3.9), the catchment surrounding UB1 and UB2 has a considerably higher elevation (109-155 m) than the land surrounding lower basin cores LB1 and LB2 which is at 49 m and 18 m respectively.

3.5.7 Pearson Correlation Coefficients

Correlation coefficients were calculated for several variables (Table 3.11) that are referred to throughout the discussion. Significant correlations are highlighted in bold.

Table 3.11: Pearson correlation coefficients that test the strength of the correlation between variables within this study.

Variable 1	Variable 2	R value	P value
Total n-alkanes (vegetation)	Molar OC/TN (vegetation)	-0.422	0.172
Total n-alkanes (soils)	Molar OC/TN (soils)	0.059	0.856
Total n-alkanes (fr. sediments)	Molar OC/TN (fr. sediments)	0.985	0.109
Total C (vegetation)	Total n-alkanes (vegetation)	-0.263	0.408
Total C (soils)	Total n-alkanes (soils)	0.756	0.004
Total C (fr. Sediments)	Total n-alkanes (fr. sediments)	-0.633	0.563

Total C (core sediments)	Total n-alkanes (core sediments)	0.910	<0.001
Organic carbon % (vegetation)	Total n-alkanes (vegetation)	-0.041	0.900
Organic carbon % (soils)	Total n-alkanes (soils)	0.699	0.122
Organic carbon % (fr. Sediments)	Total n-alkanes (fr. sediments)	-0.691	0.515
Organic C % (fjord sediments)	Total n-alkanes (fjord sediments)	UB1 0.051 UB2 0.297 LB1 -0.226 LB2 -0.344 Overall 0.755	UB1 0.845 UB2 0.247 LB1 0.383 LB2 0.300 Overall <0.001
Long chain n-alkane % (fjord sediments)	Total n-alkanes (fjord sediments)	UB1 0.276 UB2 0.020 LB1 0.035 LB2 -0.622	UB1 0.301 UB2 0.923 LB1 0.879 LB2 0.041
Depth (cm) in fjord sediments	Total n-alkanes (fjord sediments)	UB1 0.278 UB2 -0.271 LB1 0.448 LB2 0.809	UB1 0.281 UB2 0.181 LB1 0.037 LB2 0.002
Depth (cm) in fjord sediments	Odd-over-even predominance	UB1 0.659 UB2 0.398 LB1 0.377	UB1 0.004 UB2 0.074 LB1 0.084

		LB2 0.505	LB2 0.113
Methyl dehydroabietate	Organic C % (fjord sediments)	UB1 -0.082 UB2 -0.840 LB1 -0.524 LB2 0.250 Overall -0.286	UB1 0.756 UB2 0.000 LB1 0.012 LB2 0.459 Overall 0.019
Methyl dehydroabietate	Long chain n-alkane % (fjord sediments)	UB1 0.236 UB2 0.163 LB1 0.174 LB2-0.468	UB1 0.360 UB2 0.426 LB1 0.439 LB2 0.146
Methyl dehydroabietate	Total n-alkanes (fjord sediments)	UB1 0.315 UB2 -0.345 LB1 0.514 LB2 0.073 Overall -0.982	UB1 0.218 UB2 0.084 LB1 0.014 LB2 0.831 Overall 0.329
$\delta^{13}\text{C}$ C ₂₇ (fjord sediments)	Long chain n-alkane % (fjord sediments)	UB1 0.918 UB2 0.356 LB1 -0.044 LB2 -0.037 Overall 0.332	UB1 0.028 UB2 0.569 LB1 0.943 LB2 0.923 Overall 0.153
$\delta^{13}\text{C}$ C ₂₉ (fjord sediments)	Long chain n-alkane % (fjord sediments)	UB1 0.811 UB2 0.708	UB1 0.095 UB2 0.180

		LB1 -0.219 LB2 -0.617 Overall 0.168	LB1 0.723 LB2 0.268 Overall 0.480
$\delta^{13}\text{C C}_{27}$ (fjord sediments)	Bulk isotopes	UB1 0.384 UB2 0.674 LB1 -0.234 LB2 -0.200 Overall -0.228	UB1 0.523 UB2 0.212 LB1 0.705 LB2 0.746 Overall 0.332
$\delta^{13}\text{C C}_{29}$ (fjord sediments)	Bulk isotopes	UB1 0.163 UB2 0.762 LB1 0.063 LB2 0.791 Overall -0.126	UB1 0.793 UB2 0.134 LB1 0.920 LB2 0.110 Overall 0.597
Organic carbon % (soils)	Catchment slope	0.998	0.034
Organic carbon % (soils)	Catchment elevation	-0.080	0.949
Organic C % (fjord sediments)	Bathymetry	0.178	0.822
Organic C % (fjord sediments)	Catchment slope (500m buffer FASN, 1.5km buffer fjord cores)	FASN 0.881 Cores 0.966	FASN 0.313 Cores 0.034

Organic C % (fjord sediments)	Catchment elevation (1.5km buffer fjord cores)	0.951	0.05
Terrestrial OC (fjord sediments)	N-alkane abundance (fjord sediments)	UB1 0.596 UB2 -0.440 LB1 0.507 LB2 0.172	UB1 0.012 UB2 0.067 LB1 0.016 LB2 0.613
Terrestrial OC (fjord sediments)	Long chain n- alkane % (fjord sediments)	UB1 0.194 UB2 0.109 LB1 0.492 LB2 0.071	UB1 0.456 UB2 0.667 LB1 0.020 LB2 0.836

3.5.8 Statistical analysis of biogeochemical data

PCA's included bulk data and biomarker measurements and indices and these are shown in Table 3.12 for the corresponding PCAs.

Table 3.12: Indication of what parameters were used in each of the 3 PCA tests.

PCA Test	ACL	OEP	Total n-alkanes C₁₆-C₃₅	Relative abundance of long-chain n-alkanes	Total Organic C	OC/TN	δ¹³C_{org}	OC Terr (FRUITS) %	Slope	TLE (g)	n-alkane % of TLE	Methyl dehydroabietate µg/g
A	X	X	X	X	X	X	X	X	X	X	X	X
B			X	X	X					X		
C			X	X	X							X

3.6 PCA - A

PCA-A enabled us to explore what parameters accounted for a majority of the variance in sediment core samples. Two principal components (PCs) accounted for 72 % of the variance observed in the sediment samples: PC1 60 % and PC2 12 %. The factors with positive loadings for PC1 were $\delta^{13}\text{C}_{\text{org}}$ and methyl dehydroabietate, the latter having a small loading on PC1 but the highest loadings in PC2 (Table 3.2, Figure 3.13a). All other variables presented negative loadings for PC1 (PC1 and DIM 1 are interchangeable units, as are PC2 and DIM 2), with the highest contributions (>9 %) from; Terrestrial OC values (calculated from FRUITS Bayesian model, Chapter 1), Total n-alkanes (between C_{16} - C_{35}), the isotopic composition of sediments $\delta^{13}\text{C}_{\text{org}}$, n-alkane % of TLE and the slope. Figure 3.13b provides a visual representation of the loadings and strengths where OC:TN, methyl dehydroabietate and TLE abundance are relatively weak, represented by purple lines. Positively correlated variables are positioned together, and negatively correlated variables are positioned on the opposite side of the plot. This suggests that $\delta^{13}\text{C}_{\text{org}}$ is negatively correlated with terrestrial OC (as measured by FRUITS) and this aligns with our interpretation of the data. However, methyl dehydroabietate is not shown to be well correlated (negatively or positively) with any other variables.

There is clear clustering (Figure 3.13c) between the different sediment cores, organised along the DIM1 axis (PC1) from UB1-LB2. As suggested from bulk results, the cores vary in OC abundance and slope around each basin, which are strong drivers in the core clustering (Figure 3.13a and b). This suggests that slope, basin position, and amount of terrestrial input (from FRUITS model, isotopic signatures and % n-alkanes) are highly correlated with OC content in fjord sediments. N-alkanes and OC show high correlation.

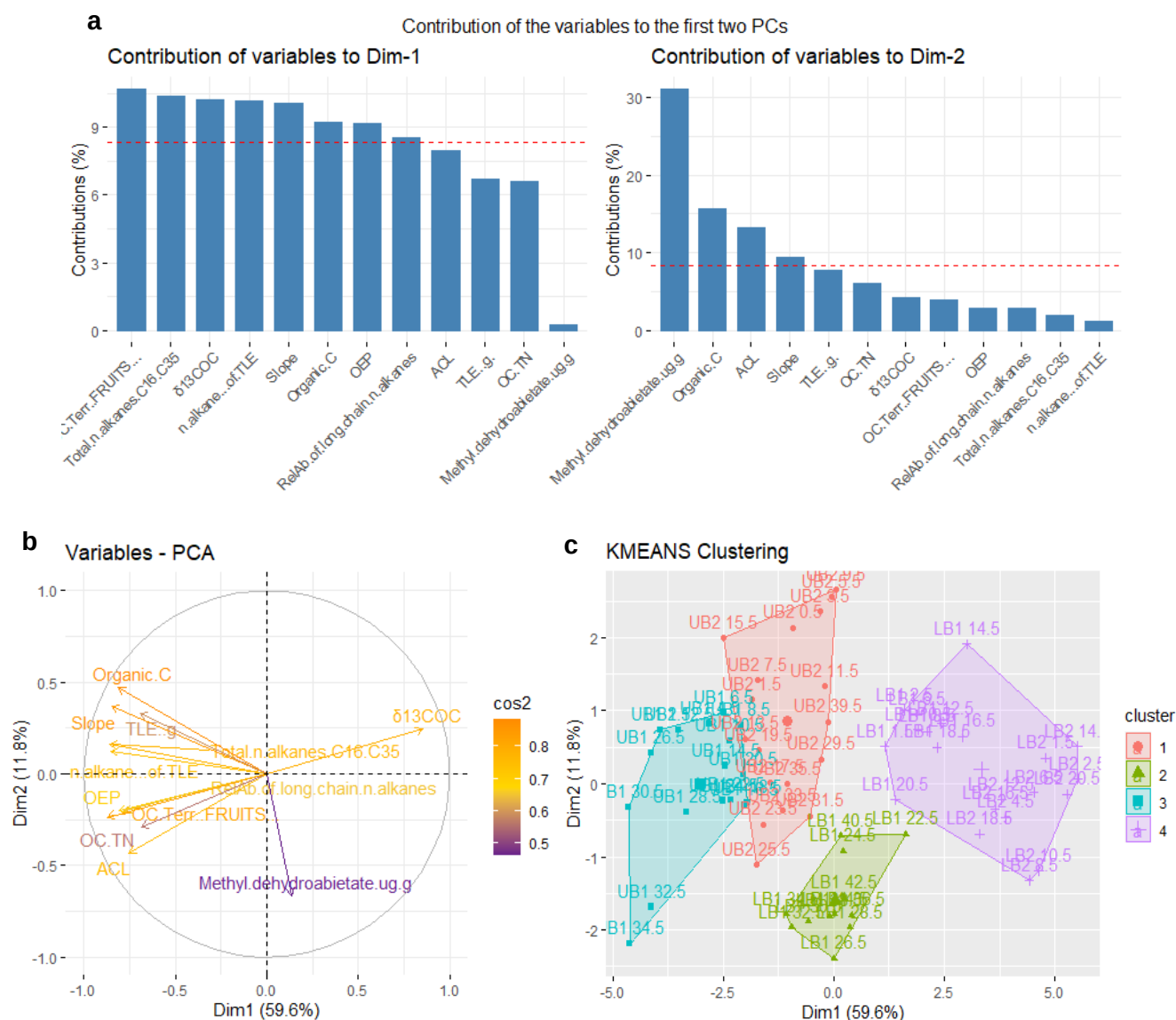


Figure 3.13: PCA - A results displayed (a) the contribution of each variable to PC1 and PC2 (b) Correlation, quality and strength of the variables along PC1 and PC2 on a $\cos^2$ (higher value = better representation) (c) KMEANS Clustering graph showing how samples are clustered with respect to PC1 and PC2.

3.7 PCA - B

PCA-B was ran to determine whether TLE, total n-alkanes, or the relative abundance of long-chain n-alkanes had a greater contribution / control on OC. N-alkanes only represent a small portion of total OC therefore it is useful to understand the correlation they may or may not have with OC. Two principal components were responsible for 84 % of the variance observed in these samples: 70 % for PC1 and 14 % for PC2. Of the parameters used, the total abundance of n-alkanes and total OC % each contribute to >25 % of the variance observed

for PC1 (Figure 3.14a) and the relative abundance of long-chain n-alkanes contributes >65 % of the variance observed in PC2. When variables are plotted against PC1 and PC2, the relative abundance of long-chain n-alkanes is found to contribute significantly across both PCs and is the only index that has a positive loading (Figure 3.14b). The relative abundance of long-chain n-alkanes is not as well correlated with total OC as total n-alkanes and TLE.

The clustering differs from the previous PCA test (Figure 3.14c), UB1 and UB2 have considerable overlap, showing limited differentiation in PC1 values, and some differentiation in PC2 contributions (Figure 3.14c). LB1 aligns more closely with UB1 and UB2 for both PC1 and PC2 contributions than LB2, showing a distinct separation between some of the lower basin core samples driven by the relative abundance of long-chain n-alkanes and OC content. This indicates that the variables may not exert the same influence on sediments in LB2.

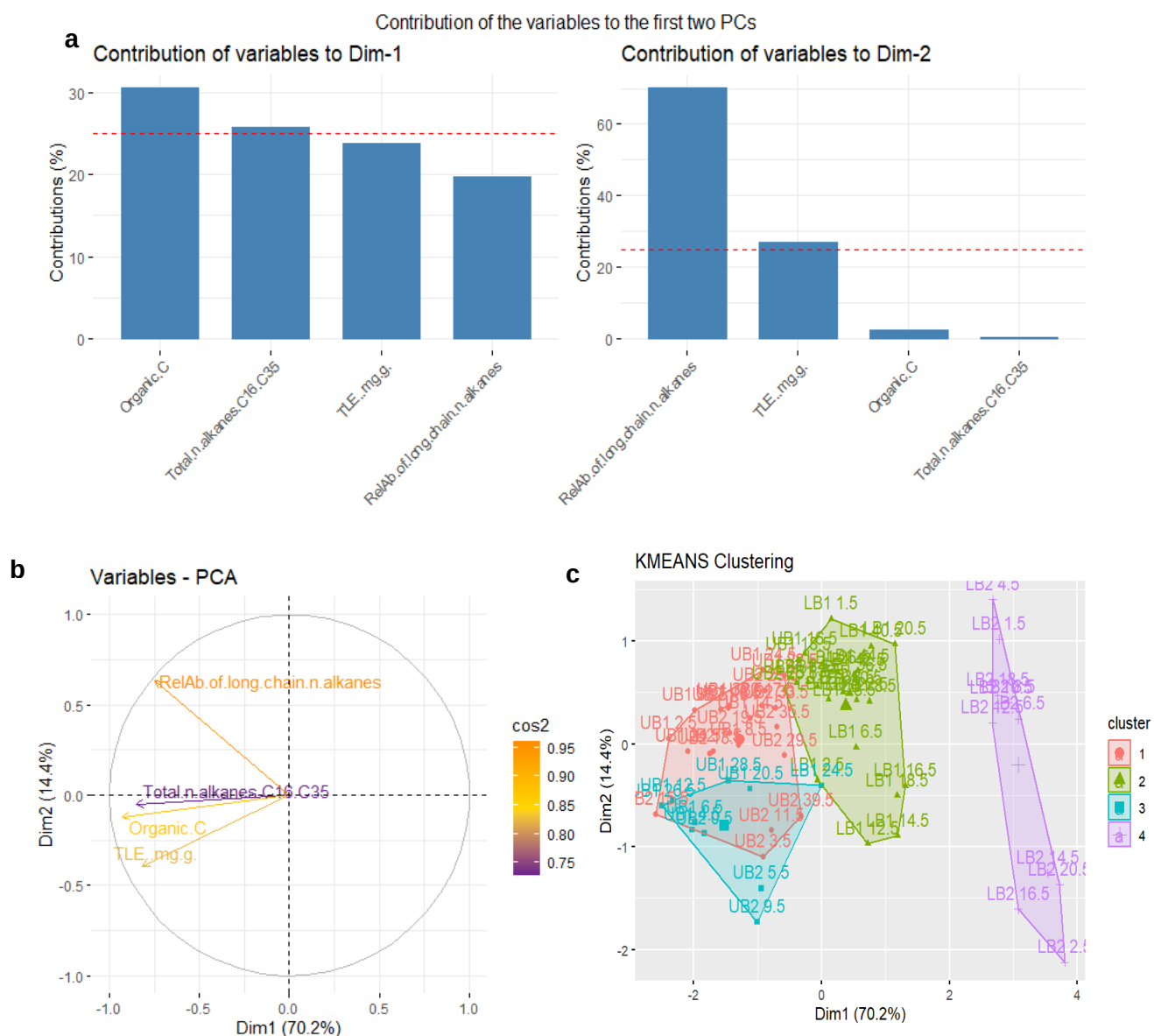


Figure 3.14: PCA - B results displayed (a) the contribution of each variable to PC1 and PC2 (b) Correlation, quality and strength of the variables along PC1 and PC2 on a cos2 (higher value = better representation) (c) KMEANS Clustering graph showing how samples are clustered.

3.8 PCA – C

PCA–C was ran to establish whether n-alkanes abundance, or the relative abundance of long-chain n-alkanes had a similar relationship with OC to methyl dehydroabietate. The aim of this analysis was to evaluate the similarities and differences between the n-alkane, specifically long-chain n-alkanes that are typical of terrestrial inputs, in comparison to the coniferous resin marker methyl dehydroabietate. Two principal components account for 82 % of variance: PC1 account for 58 % and PC2 accounts for 24 %. Total OC, total n-alkanes and the relative

abundance of long-chain n-alkanes each explain >25 % of variation observed in PC1, while methyl dehydroabietate explains >75 % of variation observed in PC2 (Figure 3.15a).

The total n-alkane abundance and relative abundance of long-chain n-alkanes are well correlated with total OC (Figure 3.15b) and while methyl dehydroabietate explains the largest portion of the variance for PC2, it is not well correlated with any other biomarker variable.

Generally, UB1 is strongly clustered in blue and UB2 and LB1 are largely clustered in red and green, respectively (Figure 3.15c) but there is some mixing of cores between different cluster groups. DIM1 is directed by total OC, the abundance of n-alkanes and the relative abundance of long-chain n-alkanes. DIM2 is driven by changes in methyl dehydroabietate. The red and green clusters have the strongest correlation with methyl dehydroabietate, and this can be observed by the positions of the clusters (Figure 3.15c) and the correlation directions (Figure 3.15b) suggesting that methyl dehydroabietate exerts a similar influence on the samples within these clusters.

DIM-1 has been dividing the clusters, and to some extent the basins, in previous PCAs (A and B), but less so in PCA-C, as all clusters are within the range of -2 to +2 (Figure 3.13c, 3.14c).

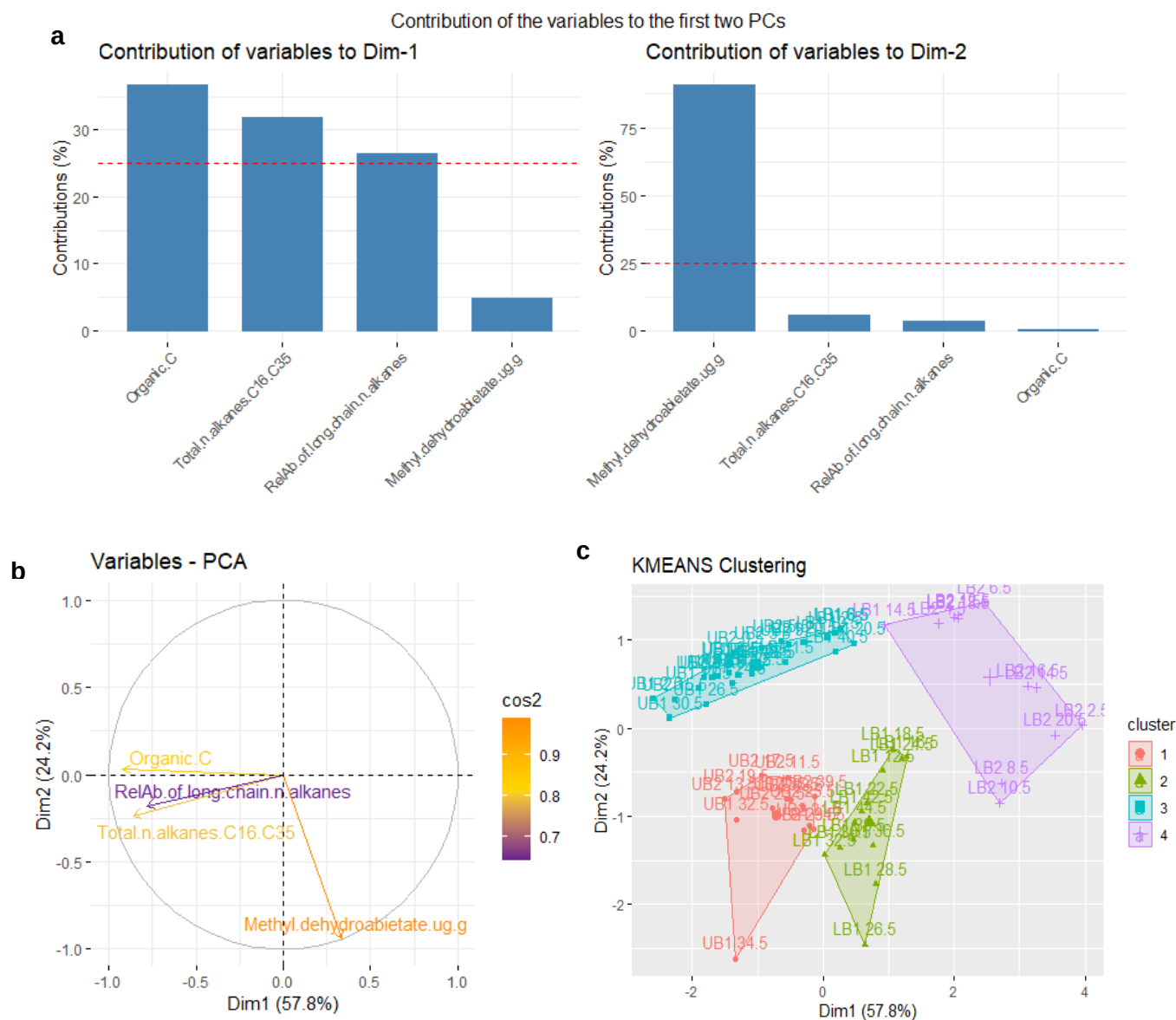


Figure 3.15: PCA - 3 results displayed (a) the contribution of each variable to PC1 and PC2 (b) Correlation, quality and strength of the variables along PC1 and PC2 on a cos2 (higher value = better representation) (c) KMEANS Clustering graph showing how samples are clustered.

3.9 Loadings Tables for all PCA tests

Table 3.13: Loading values for all PCA tests for PCA-A, PCA-B, PCA-C

	PCA - A		PCA - B		PCA - C	
Parameter	PC1	PC2	PC1	PC2	PC1	PC2
ACL	-0.2825	-0.3639				
OEP	-0.3032	-0.1694				
Total n-alkanes C16-C35 (µg/g)	-0.3224	0.1385	-0.5078	-0.064	-0.5652	-0.2400
Relative abundance of long chain n-alkanes	-0.2919	-0.1678	-0.4446	0.8381	-0.5146	-0.1805
Total Organic C	-0.3038	0.3958	-0.5536	-0.1579	-0.6063	0.0318
OC.TN	-0.2565	-0.2450				
δ ¹³ C _{org}	0.3196	0.2039				
OCTerr FRUITS	-0.3272	-0.1980				
Slope	-0.3172	0.3080				
TLE (g)	-0.2591	0.2774	-0.4878	-0.5181		
N-alkane %of TLE	-0.3187	0.1052				
Methyl dehydroabietate (µg/g)	0.0502	-0.5578			0.2195	-0.9533

3.10 Discussion

This research aimed to determine whether bulk geochemical measurements and biomarker data can provide a more in depth understanding of the sources of OC in soils, freshwater and fjord sediments in a mid-latitude fjord. We use n-alkanes, n-alkane specific ¹³C isotopes and a pine resin marker to better characterise inputs from the catchment to the fjord and can observe both spatial patterns and changes with depth in fjord sediment cores.

3.10.1 OC from catchment towards fjord

OC from catchment to fjord shows that the soils in Site 2 (deciduous, dominated by alder trees and grass), have the highest OC content of soil sites measured (Figure 3.2a). This is in agreement with observations across Scottish soils that show soils under woodland (Chapman et al., 2013), in particular deciduous woodland, store more OC than other environments, such as coniferous sites (Su et al., 2021). However, other studies have found coniferous forest soils can store more soil OC than deciduous soils (Andivia et al., 2016; Berger et al., 2002; Devi, 2021; Guedes et al., 2016; Jandl et al., 2021). This is due to the accumulation of OC forming under recalcitrant needles on the forest floor of the coniferous spruce forests (Achilles et al., 2021; Andivia et al., 2016), in comparison to deciduous forests that may have a similar litterfall to coniferous soils but a shallower layer of organic material due to the higher rate of decomposition and leaf litter turnover (Achilles et al., 2021; Trum et al., 2011). In this study, coniferous soil samples were taken from two riverbanks, one of which had experienced significant coniferous felling, and the other was densely planted with Sitka Spruce trees. Samples were obtained from the periphery of the coniferous forest, and this may explain the reduced OC content due to a shallower layer of litterfall, because this position has increased exposure to the elements (wind, run off) than the soils deeper in the forest.

It has been suggested that vegetation type may be one of the most important variables in the storage of soil OC because it has the ability to substantially change soil chemical properties (Marler et al., 2016; Shi et al., 2012). Soil OC stocks can be influenced by forest productivity, root depth, and decomposition of organic material (Andivia et al., 2016) and distribution of OC can also be influenced by forest floor vegetation such as mosses (Xiong et al., 2023), geographical location and elevation of a forest site, and soil type (Jandl et al., 2021). OC may be transported and accumulate at depth which varies with root systems, root type and root depth, and this differs amongst vegetation and tree species (Harrison et al., 2011). Forest soils are often cored to 50 cm, and some research has found a greater store of OC at depth (Chapman et al., 2013). The values of OC in this study are only representative of a small fraction (the upper 10 cm) of the OC present in soil.

In Scotland, 19 % of land is forested, and coniferous forests contribute up to ~71 % of forest cover (Forest Research, 2023), so the influence of vegetation and forest cover on soil OC is important to understand. In this catchment forestry accounts for ~30 % of land cover and coniferous forestry accounts for ~55 % of forest cover (Marston et al., 2022). Soil OC dynamics are known to vary depending on soil type, climate and vegetation characteristics (Gupta et al., 2007; Saiz et al., 2012) and so the influence of different tree species on soil OC is likely to vary with environment and latitude. The soil OC properties can often depend on soil type

(Andivia et al., 2016; Berger et al., 2002), and some studies find both deciduous and coniferous soils to have similar fluxes and stocks of carbon (Augusto et al., 2015). Soil Sites 1 and 2 are on peaty podzol soils, while Soil Site 3 is a mineral podzol (Macaulay Institute for Soil Research, 1981). It was not possible to find comparable studies that have focussed on the exact soil types and vegetation species we have in this catchment, so further work could be done within a Scottish context to build upon previous Scottish soil OC datasets (Chapman et al., 2013) and assess the soil OC stocks in our deciduous, coniferous and mixed forest environments on different soil types.

Riverbeds within the catchment were rocky with very coarse grained sediments, therefore there was a limited ability to obtain any organic material, and this is reflected in the bulk OC values obtained, ranging from 0.6 to 2.5 % (B.1.4 River bank sediments) and the absence of further organic measurements. OC measurements in the freshwater sediments of Fasnacloich (FASN) range from 3.4 - 6.9 % (Figure 3.2b) and this is where material has the opportunity to settle out before reaching the upper basin of Loch Creran. The River Creran flows through the small freshwater lochan and according to observations by the landowner, Fasnacloich has been losing depth due to sedimentation.

OC concentrations in surface sediments across the upper and lower basins (<10cm depth) are varied from 5.4 – 1.8 % (Figure 3.2c). They decrease between upper basin samples UB1 and UB2, towards lower basins LB1 and LB2. Overall, OC content is highest in forested soils (Sites 1 and 2), averages of 7 % and ~13 % respectively) and remains relatively high in FASN (up to ~7 %), decreasing towards LB2 where surface sediments hold an average of 1.8 % OC. The decrease in terrestrial OC from land towards the sea has been shown in Chapter 1 through bulk measurements and Bayesian mixing models.

3.10.2 N-alkane signatures from catchment towards fjord

3.10.2.1 *Catchment vegetation*

Catchment vegetation was analysed and n-alkanes in living (collected from live specimens) and dead (collected from the forest floor / no longer connected to origin plant) specimens showed differing concentrations and distributions of C-chain lengths across vegetation species around the Loch Creran catchment (Figure 3.3). While coniferous samples contained a greater range of lower C-chain n-alkanes (Figure 3.3b) in comparison to deciduous samples (Figure 3.3c,d), total n-alkane concentrations in living coniferous samples were significantly lower (0.3 – 10 µg/g) in comparison to in living deciduous samples (7 – 66 µg/g) which is consistent with other observations (Bush and McInerney, 2013; Diefendorf et al., 2011).

Degradation causes a decrease in n-alkane abundance between living and dead vegetation (Table 3.5), which has been observed in a variety of other studies as well (Thomas et al., 2021). The change in coniferous C-chain length distribution and abundance decreases to non-detectable values for several chain lengths in dead samples (Table 3.4 and B.1.5 All n-alkane data for living and dead vegetation samples) making dead material from some species difficult to detect using n-alkanes.

Despite some differences in type and abundance of dominant C-chain lengths between vegetation species and groups, there is an overlap between many, particularly in the dominance of C₂₉ which is observed across grass, coniferous and deciduous samples. The strong presence of C₂₉ in conifer samples has been found in a multitude of coniferous species (Diefendorf et al., 2015). A strong C₂₃ signature in Birch samples has been found in other *Betula* species, and the dominant C₂₇ chain length found in our birch samples agrees with those found in northern Scandinavia (Sachse et al., 2006). Hence, some sample measurements are observed to align with other studies. The ACL has also been observed to change with latitude in certain species (Sachse et al., 2006) so distributions of C-chain lengths can be variable across environments. The vegetation set presented is small but provides reference for differences across species within this catchment and highlights that there can be variability and crossover in dominant C-chain lengths between plant groups and species, which is found to be the case in other environments (Bush and McInerney, 2013). Thus, highlighting that C-chain length alone is not capable of identifying a range of individual vegetation species.

Seasonal differences were observed in plant n-alkane signatures, shown through the standard deviation of living and dead coniferous and deciduous samples (Table 3.4), differs from observations from larger sample sets where no variation was found seasonally (Bush and McInerney, 2013). This is likely due to differences in the ratio of components analysed, for example, if more bark than leaves are analysed in one sample in comparison to the other, the n-alkane signature would likely differ. Differences in bulk OC, N, $\delta^{13}\text{C}_{\text{org}}$ values for different parts of a plant have been observed previously (Smeaton and Austin, 2017) which was not fully accounted for during measurements. Samples were unlikely to experience significantly different growing conditions due to the small catchment area covered, so climate, sunshine, rainfall, temperature throughout the selected sites were likely similar, although forested sites would be likely to periodically experience large variations in light due to forestry activities over time (thinning, felling) or if they were on the periphery vs the centre of the forest as shading can affect soil temperature.

3.10.2.2 *From soil sites to Fasnacloich loch*

We observe a positive and significant correlation between TC stocks and total n-alkanes in soils but an insignificant relationship with OC (Table 3.11) and insignificant negative relationships between TC and OC in freshwater sediments and total n-alkane content (Table 3.11). This suggests that the abundance of OC is not the main control on n-alkane concentrations. Total n-alkane values in soils and freshwater sediments ($\sim 2 - 19 \mu\text{g/g}$ in soils and $19-24 \mu\text{g/g}$ in freshwater sediments) are significantly lower than concentrations observed in some vegetation samples, a result of the degradation of material from plant to soil (Thomas et al., 2021).

Comparing summer and winter, the variation in the abundance of n-alkanes across soil sites is slightly higher in Winter samples, varying from $\sim 4 - 14 \mu\text{g/g}$ in Summer and $\sim 6 - 17 \mu\text{g/g}$ in Winter (B.1.6 Total-alkanes in soils, for full dataset). The dominant C-chain length remains C_{29} across the three soils sampling sites regardless of dominant vegetation type or season (Figure 3.4 a-f). In general, we observe a greater difference across soil sites than seasons (Figure 3.4a-f) suggesting that seasonal changes are not the dominant control on soil OC.

The differences in n-alkane production in vegetation samples have been observed to transfer into soils (Otto and Simpson., 2005), and this can be seen to some extent within the soil samples of this study. The soil site with the highest n-alkane abundance coincides with the deciduous vegetation samples, which have been shown to have higher n-alkane abundance than coniferous vegetation samples and soil sites (Figure 3.2a,b). Despite coniferous samples having the lowest concentrations of n-alkanes by several orders of magnitude, the total n-alkane concentrations of the Site 1 soils (on both felled and planted banks) were not proportionately different to the vegetation and soil n-alkane abundance and proportions within other soils. This would suggest that there must have been significant contributions of coniferous material to the soil to accumulate to such (relatively) high n-alkane concentrations. Felled banks generally contained lower n-alkane concentrations than non-felled banks. Soil sites all exhibit a dominant chain length of C_{31} (with the exception of Soil Site 1 in Winter) (Figure 3.4) which is higher than the dominant chain length of the coniferous and deciduous woodland that occupies the soils sites.

Downstream, freshwater sediments demonstrate significant variation in n-alkane abundance over a small area (Table 3.5). A change in the dominant C-chain lengths is observed from FASN Site 1 (upstream) to FASN Site 3 (downstream) from C_{27} to C_{31} (Figure 3.4g-i) which is also reflected by an increase in the ACL (Table 3.5). The OEP for all FASN sites are >5 (Table 3.5), suggesting that there's not a considerable increase in degradation between Sites 1-3, therefore we propose that the difference in relative abundance of chain lengths is driven by a

change in the dominant OC source to the sediments. This may be due to material from different vegetation sources settling at different rates and locations within the sediments of this water body and this is likely influenced by different forms of vegetation growing within and around the loch. The Paq index is often used to distinguish plant sources (terrestrial, submerged, marine) as it highlights the proportion of aquatic macrophytes to the total plant community (Ficken et al., 2000). In freshwater sediments, Paq values fall within the range (0.1-0.4) (Table 3.4), which is indicative of a dominant source of emergent plants. Visual observations during sample collection corroborate the presence of emergent aquatic plants within the water body and deciduous woodland surrounding it.

3.10.2.3 *Variation in sedimentary n-alkane abundance and signatures*

3.10.2.3.1 Depth variation in n-alkanes from the head – mouth of the fjord

To understand what influence n-alkanes and OC may have on one another, patterns of total n-alkane distribution and bulk OC downcore were plotted and suggest that there may be links between, or a common control on the two variables (Figure 3.5a-d). Where n-alkanes and OC are the inverse of one another, this could indicate a source change or a different dominant influence. Total n-alkanes are variable with depth, showing that there are changes in sources / source proportions downcore, or that degradation has occurred periodically. N-alkanes are only a fraction of the extractable biomarkers present in these samples (<1 % of total lipid extracts from the samples), and because this is only a portion of the total carbon pool in the sediments, perfect alignment cannot be expected, but trends remain visible (Figure 3.5 a-d).

UB1 is likely the core that best represents the riverine inflow from Loch Creran due to its position at the head of the upper basin (Figure 3.1). Decreasing OC concentrations in the upper 7 cm of the core coincide with a decrease in n-alkane concentrations in the surface sediments (Figure 3.5a) and this is driven by a decrease in long-chain n-alkanes (Figure 3.6). However, the subsequent variability in n-alkanes downcore (20 – 35 cm) is not reflected in OC concentrations. UB1 is also the shallowest core site with respect to bathymetry (Table 3.10). The reason that variation in n-alkanes and OC is observed between upper basin cores, UB1 and UB2, could be due differences in bathymetry (-6.7 m for UB1 and -25.2 m for UB2). These bathymetric changes could mean that; accumulation rates in UB1 and UB2 are not equal, and that (terrestrial and marine) inputs will be observed at different scales in downcore profiles and sediments would experience different pressure and compaction at depth.

N-alkane and OC concentrations are best aligned in UB2 (Figure 3.5b). In surface sediments (upper 10 cm) inverse values suggest different controls however, below 11.5 cm changes in OC and n-alkane abundance are relatively well aligned (though statistically a weak, positive

correlation is present, $R = 0.297$, $P = 0.247$, Table 3.11). In particular, large changes in OC (>1 %) coincide with a large decrease in n-alkane abundance which was driven by a 63 % decrease in short chain n-alkanes and a 47 % decrease in long-chain n-alkanes. The inverse relationship in surface sediments can also be observed in LB1 (Figure 3.5c) but not LB2 (Figure 3.5d). While we observe no significant relationships in individual cores between n-alkanes and total OC (Table 3.11) we do observe a significant relationship between these variables when all cores are considered in one test, ($R = 0.75$, $P = <0.01$) showing that on larger scale these variables have a high correlation. This is corroborated by PCA tests A and B (Figure 3.13 and Figure 3.14) where n-alkanes are highly correlated with total OC. PCA-B suggest that total OC and total n-alkanes exert less influence on LB2 in comparison to cores in upstream basins (based on the weaker correlation (Figure 3.14c), which supports our findings of lower OC and terrestrial input in LB2 (Chapter 1).

It was estimated that 47 – 67 % of the OC in fjord sediments is of terrestrial origin (2.5.1), but the terrestrial OC data calculated by the Bayesian mixing model (that uses bulk OC, N and bulk isotopic values) does not necessarily reflect the same variability observed in n-alkanes. For UB1 and LB1 there are significant correlations between terrestrial OC and N-alkane abundance (UB1 $R = 0.596$, $P = 0.012$ and LB1 $R = 0.507$, $P = 0.016$) (Table 3.11), but this is not the case for UB2 or LB2. PCA-A corroborates this as n-alkanes were positively correlated with total OC, but variables with the capacity to indicate terrestrial inputs (terrestrial OC from FRUITS model, OC:TN ratio, relative abundance of long-chain n-alkanes, ACL) were separately correlated with one another, and with OEP, suggesting that OEP could indicate increases/decreases in terrestrial OC degradation in these sediments. Therefore, total n-alkane abundance may not correlate highly with terrestrial OC, but n-alkane indices that are more indicative of changes in terrestrial input do (ACL, relative abundance of long-chains) (Figure 3.13b) suggesting that terrestrial OC and n-alkanes are linked.

There are no dates for these specific cores at present, but there are other dated sediment cores within the fjord. Two cores have previously been dated in Loch Creran and highlight that there are not large differences in sediment accumulation rates across upper and lower basins (Smeaton et al., 2021). A twin sediment core for UB2 dates 27.5 cm with the year 1904, and sedimentation rates vary between $0.12 - 1.10 \text{ cm yr}^{-1}$, with more elevated sedimentation rates in more recent years. Comparatively, a sediment core taken from the lower basins below LB2, dates 27.5 cm at the year 1892, and sedimentation rates varied between $0.12 - 3 \text{ cm yr}^{-1}$. Sedimentation rates in LB2, although elevated in comparison to older samples, did not experience the same increase with recent time as those in the upper basin. The dates from these cores demonstrate that there is limited disparity in sedimentation rates and dates between upper and lower basins, and the dates provide a range in which our samples may

fall within. These dates are useful as they show that sediment samples are comparable across different basins and depths, as they represent a similar period of time.

There is no evidence of linear degradation of n-alkanes with depth in the sediment profiles (Figure 3.5a-d) or when assessing the changes in average n-alkanes between whole core and surface sediment total n-alkane and relative abundance measurements (Table 3.7). OEP is regularly used as a measure of degradation in soils and sediments, with values >5 being indicative of terrestrial vegetation and values <5 suggesting enhanced degradation or the presence of soils. OEP values vary downcore (Table 3.6) and with the exception of one sample in the surface sediments of LB2, all samples maintain an OEP >5. All sediments have positive OEP trends downcore, as evidenced by positive R values and significant P values for upper basin cores between depth and OEP (P-value = 0.04 and 0.06 respectively) (Table 3.11). This suggests that once in the sediments, n-alkanes are effectively preserved. However, there is variation with depth which could indicate that throughout time some sediments may have undergone more degradation than others or represent changes in input type / abundance over time, or a change in environmental conditions.

3.10.2.3.2 Spatial differences head – mouth

To better understand the spatial trends within the sediment cores the total and relative abundances of n-alkanes were calculated across sediment cores (Table 3.7). In UB1 and UB2 the average total n-alkane abundance in surface sediments is very similar to that of the whole core average. However, in LB1 and LB2 surface sediments, total n-alkane concentrations are lower than the whole core average, which may be indicative of decreased terrestrial inputs. N-alkane abundance is found to decrease by ~70 % from the head towards the mouth of Loch Creran (Table 3.6), which coincides with an increase in the relative abundance of short chain n-alkanes in sediments as we move further from the main riverine inflow. Shorter n-alkane chain lengths can be indicative of degradation (Thomas et al., 2021) or greater inputs from algae, bacteria and phytoplankton (marine sources) (e.g. Chevalier et al., 2015; Meyers and Ishiwatari, 1993; Sikes et al., 2009; Wang and Liu, 2012). The relative abundance of long-chain n-alkanes decreases by ~13 % in surface sediments from UB1 – LB2 (16 % when the whole core is considered), highlighting that marine inputs are contributing to increasing amounts of short-chain n-alkanes, buffering the decline in n-alkane abundance observed from the head to the mouth of the fjord.

There is a change in catchment slope and elevation from the head towards the mouth of the fjord. There is only one main riverine source to Loch Creran, but there is a considerable slope (up to 68 °) in some parts of the catchment, and elevation that ranges from 94m to 488 m in the land surrounding sediment cores that may influence the movement and storage of OC. As

such, we must also consider that material from non-riverine sources can influence the amount of OC transported and stored in different soil sites and sediments, i.e. material that is blown or washed through run-off into the fjord from the surrounding land (Tables 3.9 and 3.10). Pearson correlation coefficients facilitated the investigation of correlations between the slope of the surrounding land, bathymetry of the fjord and elevation of different sites and total OC and total n-alkane concentrations (Table 3.11). Positive and significant correlations are present between the catchment slope (surrounding 200 m) of soil sites and OC ($R= 0.998$, $P= 0.035$) and between sediment cores and OC content ($R= 0.966$, $P= 0.034$). The slope of the surrounding land of this fjord therefore has a significant correlation to the abundance of OC stored in both soils and sediments within this catchment, which aligns with the significant correlation observed between catchment elevation and OC around fjord cores sites ($R= 0.951$, $P= 0.05$). PCA–A also confirms that slope, TLE and total n-alkanes are positively correlated with sedimentary OC concentrations across fjord basins. Therefore, it is possible that one of the factors influencing the lower total OC (Figure 3.2) and terrestrial OC input (Chapter 1) observed from the head towards the mouth of Loch Creran is a decrease in terrestrial input as a result of reduced slope angles (and run off) from catchment surroundings.

The land cover surrounding the basins of Loch Creran varies (Figure 3.1b), alongside the slope from the head towards the mouth of the fjord (Figure 3.12). The southern bank is dominated by coniferous forestry around the upper basin, and to some extent lower basins, with the latter having an increased amount of deciduous woodland and grassland. The northern bank is more varied and dominated by deciduous woodland around the upper basin, and deciduous woodland, bog and grassland surrounding the lower basins. This increases the potential for differences in vegetation inputs to each basin. These changes in land cover are accompanied by a decrease in the slope of the land from upper to lower basin, which influences the volume of material that may run off the land into the fjord. For example, improved grassland occupies the (relatively flat) ground surrounding the lower basins (Figure 3.1b), so there may be a lower volume of run off from in comparison to the forested areas on steeper slopes further upstream.

No significant correlation has been identified between the bathymetry and OC in sediment cores, nor catchment elevation and soils (Table 3.11). The absence of a significant correlation between slope and OC stored around Fasnacloich lochan is most likely influenced by the small area the lochan covers, meaning there's little to no change in surrounding slope conditions from FASN Site 1 to FASN Site 3 within the lochan.

3.10.3 Pine resin data

N-alkane abundances, distribution and $\delta^{13}\text{C}$ signatures, provide an insight into some of the molecular changes that occur within catchment vegetation, soils and sediments. However, alone they are not able to provide clear evidence on the storage of organic matter from different plant groups in fjord sediments. As such, we identified a coniferous biomarker, methyl dehydroabietate, an abundant spruce marker (Duce et al., 2015; Jablonský et al., 2015) which is present in soil and sediment samples in this study (Figures 3.7 and 3.8) in low but quantifiable concentrations, and in coniferous vegetation samples obtained from the catchment and some moss from our coniferous soil site (Table 3.8).

3.10.3.1 *Vegetation samples*

Methyl dehydroabietate is absent in all but a selection of coniferous site samples and was thus selected as a marker representative of coniferous vegetation in this catchment. The concentrations vary from (0.05 – 8.14 $\mu\text{g/g}$) in dead and living coniferous samples (Table 3.8). The low concentrations observed are indicative of natural catchment inputs because more focussed human point sources from pine resin derived products such as essential oils and ship waterproofing etc. would likely yield higher concentrations.

3.10.3.2 *Soils and freshwater sediments*

Coniferous inputs are low but measurable in catchment soils and are only present in coniferous soil sites (Figure 3.7a-b). Concentrations of methyl dehydroabietate are comparable across soils and freshwater sediments (Figure 3.7c). The presence of methyl dehydroabietate in vegetation and soil samples suggests that abietanes from coniferous material undergo degradation in aerobic conditions into different compounds (i.e. different aromatic abietanes) (Otto and Simoneit, 2001; Simoneit et al., 1986). In Fasnacloich samples, methyl dehydroabietate is measurable in two locations near the inflow and outflow, indicating that this compound is transported from coniferous soil sites downstream through the lochan, as there is no coniferous woodland directly surrounding Fasnacloich lochan.

3.10.3.3 *Sediment cores*

Methyl dehydroabietate is observed in samples in all cores but is most abundant throughout the depths of UB2 – LB2 (Figure 3.8). UB1 has the fewest samples that contain the compound which could be due to its shallow position in the fjord (Figure 3.12). The position of UB1 being so close to the riverine inflow, may result in different accumulation rates to other cores which would explain the absence of methyl dehydroabietate until > 30 cm. Cores UB2 – LB1 follows a similar pattern of methyl dehydroabietate with depth (Figure 3.8) suggesting that concentrations in different basins are influenced by a common input. Methyl dehydroabietate appears to be absent in surface sediments in all cores except for LB2, the reason for this is

not clear. Surface sediments of UB1 - LB1 have the highest OC concentrations, and methyl dehydroabietate concentrations increase as OC concentrations decrease downcore in UB2 and LB1 which is evidenced by a significant correlation between the resin marker and OC in cores UB2 and LB1 ($P \leq 0.01$ and $P = 0.01$ respectively) and negative R values (-0.84 and -0.52 respectively) associated with this relationship (Table 3.11). Upper basin cores, UB1 and UB2, have insignificant positive ($R = -0.082$, $P = 0.756$) and significant negative correlations $R = -0.840$, $P = <0.01$) between total n-alkanes and methyl dehydroabietate respectively (Table 3.11). Alongside the differences in n-alkane abundance, these two core sites have different bathymetry and surrounding elevation, and likely accumulation rates, that may have contributed to the difference in both n-alkane and methyl dehydroabietate concentrations. In one of the lower basins, LB1, there is a significant positive correlation between total n-alkanes and methyl dehydroabietate concentrations ($R = 0.51$, $P = 0.01$), this is not observed in LB2.

Despite there being little coniferous forestry on the northern or southern banks in direct proximity to the fjord (dominated by deciduous woodland and grassland) (Figure 3.1b), coniferous signals remain present and stable in sediments. Between cores on either side of the Creagan Narrows there are significant positive and negative correlations (UB1 and LB1) between total n-alkanes and methyl dehydroabietate which may indicate that both slope and bathymetry might influence the different trends within these cores (Table 3.11). However, the decrease in slope (from $\sim 20^\circ - 12^\circ - 8^\circ$ in the upper basins to LB1 and LB2 respectively) does not correspond with a decrease in methyl dehydroabietate concentrations. The concentrations of methyl dehydroabietate in core sediments have likely been influenced by coniferous forests of the past, and paleo records from glens to the north and south of Loch Creran suggest that coniferous forests were present (Fyfe et al., 2013). It is unclear how quickly vegetation markers are eroded from the soil and how old the terrestrial material is without dating.

Relationships with n-alkane abundance show that fluctuations in methyl dehydroabietate concentrations are not necessarily represented by changes in n-alkane concentrations and when a correlation test is ran on all core samples together, an insignificant correlation is found ($R = 0.98$, $P = 0.33$). N-alkanes have relatively low concentrations within coniferous samples (Table 3.4) and the presence and/or increases in coniferous input to sediments may be missed if specific resin biomarkers are not utilised. PCA test A and C corroborates this as methyl dehydroabietate is not well correlated with any other variable tested (Figure 3.13b, Figure 3.15b) suggesting that biomarker indices do not reflect the same coniferous inputs as the pine resin. This is also reflected in the relationship between long-chain n-alkane abundance (typically associated with terrestrial inputs) and methyl dehydroabietate concentrations, where no significant correlations are observed (Table 3.11). As such, we propose that methyl

dehydroabietate can be used to track a different (coniferous) input to biomarker indices, and that changes in terrestrial signals observed from n-alkanes (and respective indices) are from other plant groups (e.g. deciduous forestry, perennial plants).

Methyl dehydroabietate has been identified in sediments in different environments spanning hundreds – millions of years confirming that it can be used as an effective tracer for coniferous inputs in sediments (Otto and Simoneit, 2001; Smittenberg et al., 2005; Stancampiano et al., 2023). Methyl dehydroabietate concentrations do not decrease with depth and are therefore a relatively robust proxy, able to withstand chemical changes, as suggested by (Simoneit, 1977), and is a stable component of the OC that remains well-preserved downcore. When OC concentrations decrease, methyl dehydroabietate does not. This compound is a derivative of abietane, but its presence in soil samples in this form suggests that there are no chemical transformations of this compound occurring during transport. The presence of methyl dehydroabietate provides evidence that the surrounding coniferous forestry does have an influence on fjord sediments composition, and that it can be effectively transported within this catchment to sediment and preserved over relatively longer timescale (>100 years).

3.10.4 Compound specific $\delta^{13}\text{C}$ from source-towards-sea

3.10.4.1 *Vegetation and soils*

$\delta^{13}\text{C}$ of different n-alkane chain lengths can be used for species and interspecies distinctions (Cooper et al., 2015; Pedentchouk et al., 2008) but overlaps can exist. In this study, as in Pedentchouk et al., (2008), C_{27} was the only long-chained carbon with $\delta^{13}\text{C}$ values in sufficient quantities to be measured in all vegetation samples (Figure 3.9). The $\delta^{13}\text{C}$ of n-alkanes can be sensitive to biological and environmental change (temperature, humidity and water availability) (Castañeda and Schouten, 2011; Hou et al., 2007; Meyers, 1997). The Loch Creran catchment is small, therefore we suggest that all plants would have experienced similar environmental conditions and that changes in $\delta^{13}\text{C}$ are reflective of physiological differences.

Living and dead deciduous samples exhibited different $\delta^{13}\text{C}$ signatures between C_{25} and C_{27} chain lengths, where dead material had considerably more enriched $\delta^{13}\text{C}$ values. Similar observations could not be made for coniferous samples, as dead coniferous samples were below the limit of detection for $\delta^{13}\text{C}$ (Figure 3.9a). Other studies have shown coniferous samples to be more enriched in $\delta^{13}\text{C}$ (~-30 ‰) in comparison to deciduous samples (~-32 ‰) (Chikaraishi and Naraoka, 2003; Pedentchouk et al., 2008; Schlanser et al., 2020), and some show similar $\delta^{13}\text{C}$ values (~-30 ‰) within mixed (coniferous and deciduous) forests in Scotland (Wiltshire et al., 2023). Coniferous $\delta^{13}\text{C}$ signatures in this study are from fresh samples and

are considerably more depleted than those of other studies, deciduous living/dead samples provide evidence that across a majority of C-chains, dead material becomes more enriched, which may account for the discrepancies between coniferous samples in this study relative to others (Figure 3.9a).

Some have used isotope specific $\delta^{13}\text{C}$ values to determine plant and tree species (Pedentchouk et al., 2008) while others suggest that they can only be used to determine differences in C3 and C4 plant groups (Cooper et al., 2015) but this may be dependent on the location of the samples, growing conditions, and species in question. The differences in $\delta^{13}\text{C}$ signatures may vary across modern and fossilised plants, and as a result of the environment in which they have grown and degraded.

Plant group determination is possible within this study as averaged $\text{C}_{27}\text{-C}_{31}$ $\delta^{13}\text{C}$ vegetation values (-38.4 to $\sim$ -34.2 ‰) fall within similar tree ranges to those in (Cooper et al., 2015) (-39.2 to -34.2 ‰). However, our grass samples have a signature that is not dissimilar to coniferous trees (-37.4 ‰), which fits within the range for graminoids (-37.5 to -33.8 ‰) (Cooper et al., 2015). Multiple studies show that there can be overlap between plant species and groups (Cooper et al., 2015; Struck et al., 2020), which can make it difficult to distinguish certain sources from one another. However, we can note from our study samples, that there is a difference in coniferous ($\sim$ -38 ‰) and deciduous ($\sim$ -34 ‰) $\delta^{13}\text{C}$ signatures, even if coniferous signatures may be confused with grass signatures due to overlap. A more extensive vegetation and soil sampling mission in this region could ascertain whether this distinction is consistent within a larger area.

Even when $\delta^{13}\text{C}$ signatures can distinguish between plant groups, it can sometimes be difficult to determine different dominant vegetation type and land uses from soil samples (Wiltshire et al., 2023). There are limited differences observed in $\delta^{13}\text{C}$ signatures in soils between seasons but more variability between sites (Figure 3.9c,d) as observed in n-alkane abundance (Figure 3.4a-f). Data suggests that a more depleted $\delta^{13}\text{C}$ signal in soils, in this catchment, aligns with coniferous inputs, as grass was present in all locations. This is in agreement with the $\delta^{13}\text{C}$ signatures observed in vegetation samples, where coniferous samples from Soil Site 1 exhibit a more depleted $\delta^{13}\text{C}$ signature (C_{27} $\sim$ -38 ‰) than deciduous samples (C_{27} $\sim$ -34 ‰), and similar signals to grass (C_{27} $\sim$ -37 ‰) (Figure 3.9a). The degradation of plant material can influence their $\delta^{13}\text{C}$ signatures and result in a depleted ^{13}C value of soils in comparison to plants (Fernandez et al., 2003) as is observed between vegetation and soils in this study. Land use, type of land cover, plant degradation, microbial activity and root respiration are just some of the processes that can influence the isotopic fractionation and signature of soils (Fernandez et al., 2003; Liu et al., 2018; Schweizer et al., 1999; Werth and Kuzyakov, 2010) which may

also explain why it is not straightforward to identify land cover from soil $\delta^{13}\text{C}$ signatures particularly when plants are in the same group (i.e. C3).

3.10.4.2 *Lochan and fjord sediments*

Downstream, freshwater sediment samples have $\delta^{13}\text{C}$ values within the range of vegetation sample values (~ -32.6 ‰ to -36 ‰) (Figure 3.10a). All sampling points within the small freshwater loch have similar $\delta^{13}\text{C}$ values and FASN Sites 1 and 3 follow the same trend of increasing depletion in $\delta^{13}\text{C}$ in longer chain lengths. Depleted signatures at C_{31} (-36.6 ‰) are similar to deciduous values at the same chain length (-36.9 ‰). At C_{29} , all lochan sites display similar $\delta^{13}\text{C}$ values ~ 34 ‰, which is well aligned with isotopic measurements of living and dead deciduous material (~ -34 ‰) (Figure 3.9a), confirming that all sediments sites have a relatively high contribution of deciduous material. FASN Sites 1 and 3 also contain coniferous material, as indicated by the presence of methyl dehydroabietate (Figure 3.7c) and it is likely that the depleted coniferous $\delta^{13}\text{C}$ signature (Figure 3.9a) is muted within Fasnacloich sediments as it is not the dominant vegetation input and due to the low concentration of n-alkanes from which we derive the $\delta^{13}\text{C}$ values. The more enriched $\delta^{13}\text{C}$ signatures are likely from deciduous material and may be influenced by the presence of emergent and submerged vegetation within this fresh waterbody, which can range from (-22 ‰ to -30 ‰) and (-14 ‰ to -30 ‰) respectively (Ficken et al., 2000). This would be expected given the surrounding vegetation of Fasnacloich is comprised of deciduous trees and grassy areas, and it is likely that any coniferous material has been transported from riverine inflow.

In fjord sediments $\delta^{13}\text{C}$ values are variable downcore (Figure 3.10b,c) with greater enrichment in UB2 and LB1 (generally) at both C_{27} and C_{29} suggesting similar influences on the specific isotopes which could be influenced by both terrestrial and marine inputs due to regular flushing of the fjord.

Surface, mid, and deeper points within the sediments (Figure 3.10d,e,f) follow similar depletion / enrichment trends while LB2 is depleted to a greater extent for chain lengths C_{29} and C_{31} . There is no linear increase or decrease in $\delta^{13}\text{C}$ enrichment / depletion downcore in sediments, providing no evidence of that certain components degrade downcore with changing conditions or time. To try and establish whether there are changes in input that might mask downcore changes in $\delta^{13}\text{C}$, correlations were investigated with relative proportions of long n-alkane distribution of C_{27} and C_{29} isotopic values, and bulk isotopes (Table 3.11). When comparing $\delta^{13}\text{C}$ values with C_{27} and C_{29} isotopic values throughout all sediments, there were positive but insignificant relationships ($R = 0.311$, $P = 0.153$ and $R = 0.167$, $P = 0.480$ respectively), and when this was broken down into individual cores different patterns were visible: positive correlations in the upper basin cores and negative correlations in the lower basin cores. This

indicates that isotopic enrichment coincides with an increase in the proportion of long-chain n-alkanes in the upper basin, but the opposite occurs in the lower basins, which may be influenced by a higher marine OC signal, particularly in LB2 (Chapter 1). There are no significant relationships observed between specific and bulk isotopes (Table 3.11) to link marine and terrestrial signatures.

Dead coniferous samples had no detectable $\delta^{13}\text{C}$ n-alkane signal, which is likely due to low n-alkane concentrations (Table 3.4), this may not be unusual in coniferous samples, as several coniferous species may have no detectable n-alkane signature at all (Diefendorf et al., 2011), which is why they may often be absent in n-alkane records in certain ecosystems (Diefendorf and Freimuth, 2017). As such, many methods commonly used to determine source inputs to sediment (bulk isotopes, ratios, n-alkane abundance and associated indices such as ACL, and proxies such as $\delta^{13}\text{C}$ n-alkane signatures) may all overlook the transport and storage of coniferous material.

3.10.5 Climate influence on soil OC

It is well established that climatic variables (such as temperature, precipitation) have an influence on soil OC (Chaplot et al., 2010; Chen et al., 2013; Doetterl et al., 2015; Luo et al., 2017; Mei-yan et al., 2013; Zhang et al., 2019). However, it is difficult to judge the influence of climatic parameters due to the absence of site-specific temperature and precipitation data within this study. Within a small catchment there are limited changes in latitude, altitude and environmental conditions, which are known to be linked with climate parameters over greater areas (Chen et al., 2013; Cong et al., 2016; Shi et al., 2012). In smaller catchments a multi-year dataset of vegetation and soil measurements would be particularly useful to unravel the role of weather and climatic variables (precipitation and temperature) over time. Seasonal soil samples can be compared to the precipitation and temperature data from the area (Figure 3.11). From limited single year measurements, there is an indication that soil OC has a greater correlation with temperature than precipitation (Figure 3.11) but without site-specific rainfall and temperature gauges, this is only a broad indication, and no significant values are observed between soil OC and rainfall / temperature or compound specific isotopic values and rainfall / temperature (Table 3.11).

Previous studies over larger areas, which have found changes in n-alkane indices, have been influenced by climatic parameters. For example, changes in ACL can reflect changes in temperature and precipitation and in turn water use efficiency of plants (Bush and McInerney, 2013; Sachse et al., 2006). Correlations between n-alkane concentrations and $\delta^{13}\text{C}$ have been

found with mean annual precipitation and temperature in other studies (Struck et al., 2020), and spatial and temporal variations in chain length distributions have been observed to correlate with growing season and temperature and the photosynthetic pathways of plants (Bush and McNerney, 2015), suggesting that there are likely seasonal and climatic influences that are not visible within this dataset. Without ages for multiple sample depths throughout cores, it is not possible to suggest the role of changing climate on sediment core datasets.

3.11 Conclusions

This research set out to determine whether the distribution and concentrations of biomarkers (n-alkanes and $\delta^{13}\text{C}$ n-alkanes) in vegetation, soil and sediments, are a useful tool, when combined with bulk geochemical data, for identifying the origin of terrestrial inputs in a mid-latitude fjord. Within this there were several objectives; to assess changes in n-alkanes from source towards sea, to establish whether n-alkanes and their specific $\delta^{13}\text{C}$ signatures could narrow down plant groups present in soils and sediments in this catchment, to explore whether a forestry signal could be detected in fjord sediments (and how well this material might be preserved), and to determine whether this dataset could help us to better understand the impact of forestry on carbon cycling in the fjord.

There are spatial and temporal changes in n-alkane abundance, distribution of chain lengths and $\delta^{13}\text{C}$ signatures across the source to sea continuum that improve our understanding of the molecular signal that is preserved in this fjord catchment and sediments from different plant groups. In vegetation samples we find $\delta^{13}\text{C}$ signatures to be distinct between deciduous and coniferous woodland, and grasses but this is only observed at a fresh plant level. In this catchment n-alkanes do provide more information on OC composition as the input of select plant groups can be observed in soil samples and freshwater sediments, i.e. the input of deciduous material to lochan sediments. However, in this instance these techniques did not necessarily enable the identification of specific vegetation species or different types of forestry in soils and sediments, due to a range of factors (decomposition, microbial activity and respiration) but a more extensive soil sampling survey and dating of individual core slices may help to unravel species specific patterns and how they have changed over time. Despite this, other correlations were revealed, such as the correlation between the slope of surrounding land with OC stored in both soils and sediments. It is therefore possible that the decreases in OC and terrestrial OC input in Loch Creran are influenced by both an increase in marine inputs and a decrease in terrestrial input as a result of reduced slope angles (and run off) from catchment surroundings, opposed to being solely a result of distance from riverine inflow and dilution.

Coniferous forestry inputs to sediment were identified using a pine resin marker, methyl dehydroabietate. This was a useful addition to the dataset and enables inputs of coniferous material to be followed from plant – soil – freshwater sediments – fjord sediments. There is no significant correlation between this compound and the abundance of long-chain n-alkanes (that are typically associated with terrestrial vegetation) which indicates that subtle changes in methyl dehydroabietate (that can indicate changing inputs) are hidden in bulk datasets. A majority of cores (with the exception of LB1) show no significant correlation between n-alkane abundance and methyl dehydroabietate highlighting that additional information on coniferous plant inputs can be gained when the n-alkanes are accompanied with pine resin markers across the source-to-fjord continuum.

The presence of both n-alkanes and methyl dehydroabietate downcore in fjord sediments show that these compounds (and coniferous and deciduous material) have been effectively transported to sediments through riverine inflow or run off over long periods of time. The presence of methyl dehydroabietate / coniferous sources is generally not reflected in n-alkane proxies and indices and may often be overlooked within soil and sediment profiles where resinous inputs are not monitored. There is no evidence of degradation of n-alkanes and methyl dehydroabietate in fjord sediments, suggesting that these compounds represent stable proxies that remain well-preserved downcore over time. This data enables a more detailed investigation of catchment inputs to sediments, and how surrounding vegetation can influence OC transport and storage.

Overall, the combination of biomarker (n-alkane and resin) data and bulk geochemical data has contributed towards a better understanding of OC composition, transport and storage from source-towards-sea in the Loch Creran catchment. Despite the limited geographic scale of this study, we observe interesting variations in abundance and distribution of n-alkanes, $\delta^{13}\text{C}$ values and resin markers that provide a greater insight into the origin of OC contributions, which can be applied elsewhere. Additional resin markers for tree species (i.e. Birch) could be incorporated into future studies, alongside $\delta^{13}\text{C}$ for resin samples to attempt to recognise the contributions of plant groups and species-specific inputs in more detail.

Chapter 4 Iron and carbon binding from source towards sea

4.1 Abstract

To better understand the role of reactive iron (FeR) in the preservation of organic carbon (OC) from source towards sea, we analysed total OC, Fe, N, $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ signatures, in soil and sediment samples. OC, Fe, N in water samples and FeR abundance and speciation, and OC-FeR complexation in samples from catchment soils, freshwater sediments and fjord sediments in Loch Creran. We estimate that 37 % of OC is bound to FeR in forested catchment soils, 41% in freshwater sediments, and ~16 % in fjord sediments. Sorption was found to be the dominant binding mechanism across all environments. Mössbauer analysis at 295 K and 4.2 K revealed that the primary FeR species in soil and freshwater sediment samples is ferrihydrite and a majority of samples also contained hematite. The common speciation and binding mechanisms throughout this catchment between OC-FeR complexes, alongside the abundance of particulate Fe throughout river and lochan sites suggest that a portion of the OC-FeR complexes found in fjord sediments are derived from catchment soils. We propose that OC-FeR complexes help to prevent flocculation across the salinity gradient from river to fjord and that the mutual preservation that the complexation offers protects both OC from degradation and FeR from transformation or dissolution. Overall, this study demonstrates that OC-FeR complexes play an important role in biogeochemical cycling, OC storage in forest soils, and OC transport and storage from source towards sea.

4.2 Introduction

A majority of the terrestrial organic carbon pool is stored in soils (Lal, 2004): it is estimated that ~1600 PgC is stored in soils which is higher than vegetation stores (570 PgC) and atmospheric reservoirs (780 PgC) (e.g. Bianchi, 2011; Burdige, 2005; Cai, 2011). Therefore, soils play an important role in global biogeochemical cycles as soil organic carbon storage is important for soil health and fertility and global carbon budgets (Gerke, 2022; Lal, 2004; Lal et al., 2013; Ma et al., 2023). Accumulation and burial of soil organic carbon isolates it from the atmosphere which changes the aerobic conditions and can slow / inhibit microbial decomposition (Chapricha and Marín-spiotta, 2014), and this can also be the case for eroded soils that are transported to sediments and stored. However, there are many controls on soil organic carbon formation and decomposition; oxygen availability, soil moisture, temperature, nutrient availability presence of bacteria and fungi (Chapricha and Marín-spiotta, 2014; Schmidt et al., 2011; Wang et al., 2019; Wei et al., 2019).

Despite the important role of soils in the global carbon cycle, the mechanisms by which soil organic carbon is stored are still not fully understood but it is clear that a portion of soil organic

carbon is stored through relationships with minerals (Han et al., 2016; Kaiser and Guggenberger, 2000; Kopittke et al., 2020; Wagai and Mayer, 2007; Ye et al., 2022; Zhao et al., 2016), as is the case in freshwater, estuarine and marine sediments (Barber et al., 2017; Faust et al., 2021; Lalonde et al., 2012; Shields et al., 2016; Wang et al., 2018). Research suggests that iron minerals play an important role in organic carbon storage, and an average of 20% of marine organic carbon is estimated to be bound to reactive iron (OC-FeR) (Lalonde et al., 2012), and a significant portion of soil organic carbon is bound to iron minerals. While soil OC-FeR complexation can be highly variable with values observed between 0 – 74 % of the total organic carbon (Ye et al., 2022; Zhao et al., 2016), on average it is thought that ~63 % of organic carbon may be bound to iron (and potentially aluminium) minerals in soils (Kramer and Chadwick, 2018). The amount of organic carbon bound in different environments can vary and may be influenced by soil type and texture (e.g. Bradley et al., 2005; Cai et al., 2016; Wiesmeier et al., 2012), surface area (e.g. Bi et al., 2023; Kaiser and Guggenberger, 2003), latitude (e.g. Zhao et al., 2016), pH (e.g. Ye et al., 2022), and land use and land-use change (Basile-doelsch et al., 2009; Bond et al., 2021; Giannetta et al., 2022; Longman et al., 2022), so OC-FeR complexation is likely to vary across different environments.

Despite our understanding of the role iron minerals play in terrestrial organic carbon storage in sediments globally (Shields et al., 2016; Zhao et al., 2018) and at the local scale (Chapter 1), it remains unclear whether OC-FeR compounds in soils are transported through waterways and runoff into sediments, and whether they can survive chemical changes along the way, or whether they are flocculated out as the salinity changes (e.g. Deng et al., 2022; Khoo et al., 2022). There are knowledge gaps across the source-to-sea continuum (Ward et al., 2017) and this includes the point along the journey from source-to-sea of OC-FeR binding for the complexes that are found in sediments (Faust et al., 2021). Inland waters can receive large amounts of terrestrially derived organic carbon and play a crucial role in the transportation and transformation of carbon from terrestrial to aquatic environments (Ward et al., 2017). Some studies have started to address this gap by investigating the lateral flow of carbon from soils via surface waters (Weyhenmeyer et al., 2012), coastal systems (e.g. Tao et al., 2022) and river sediments (Adame et al., 2012) to more marine environments, and others have focussed on the movement of iron across freshwater and saltwater gradients (Herzog et al., 2020; Herzog and Kritzberg, 2017; Krachler et al., 2015, 2016; Kritzberg et al., 2014). However, we are not aware of any studies at this time that have investigated the journey of OC-FeR complexes from a lateral source-towards-sea (soil to sediment) perspective within a catchment. It is suggested that iron is removed from the water column by flocculation where the salinity changes from fresh to saltwater (Boyle et al., 1977; Haese, 2006). However, a

series of studies have shown that OC-FeR complexes can make it is across changes in salinity (e.g. Herzog et al., 2020; Muller, 2018).

Despite the variety of research documenting OC-FeR associations in soils (e.g. Kopittke et al., 2020; Ye et al., 2022; Zhao et al., 2016) and sediments (e.g. Barber et al., 2017; Faust et al., 2021; Lalonde et al., 2012; Zhao et al., 2018), we still do not fully understand the mechanisms behind OC storage in soils and sediments. Furthermore, there is only a limited number of studies that try to establish a source-towards-sea approach for organic carbon-mineral associations, so questions remain over the longevity of these relationships downstream and the point at which they occur. This research investigates the differences in OC-FeR protection in soils and sediment across the land-sea interface and aims to gain a better understanding of the scale and dynamics of OC-FeR associations across the land-sea interface. We use a variety of biogeochemical techniques to determine concentrations of organic carbon and iron across soils to sediments, the speciation of iron in soils and sediments and the proportion of reactive iron bound to organic carbon within the catchment and sediments of Loch Creran, and whether this transect of measurements can provide insight into whether organic carbon – reactive iron complexes are transported from soil to sediment. Understanding the stability, transport and fate of organic carbon across the land-sea interface and in different environments will enable more robust carbon budgets to be calculated and could help inform management of different landscapes.

4.3 Study Site

Loch Creran and its catchment are the sampling locations explored in this study as per Chapter 1 and 2. In short, Loch Creran is a fjord on the West Coast of Scotland ~12.8 km in length and up to 49m deep. A catchment of ~160 km² drains into the fjord which is a relatively well mixed body of water with oxic conditions that is regularly flushed (Edwards and Sharples, 1986). There are multiple basins within the fjord that are separated by sills: UB1 and UB2 sit within the upper basin of the fjord, separated by a sill at Creagan Narrows from LB1, which is separated by a sill from LB2. The loch has a relatively enclosed system with one main inflow,

the River Creran (Loh et al., 2010) which passes through a small freshwater loch, Fasnacloich before entering the upper basin of Loch Creran (Figure 4.1).

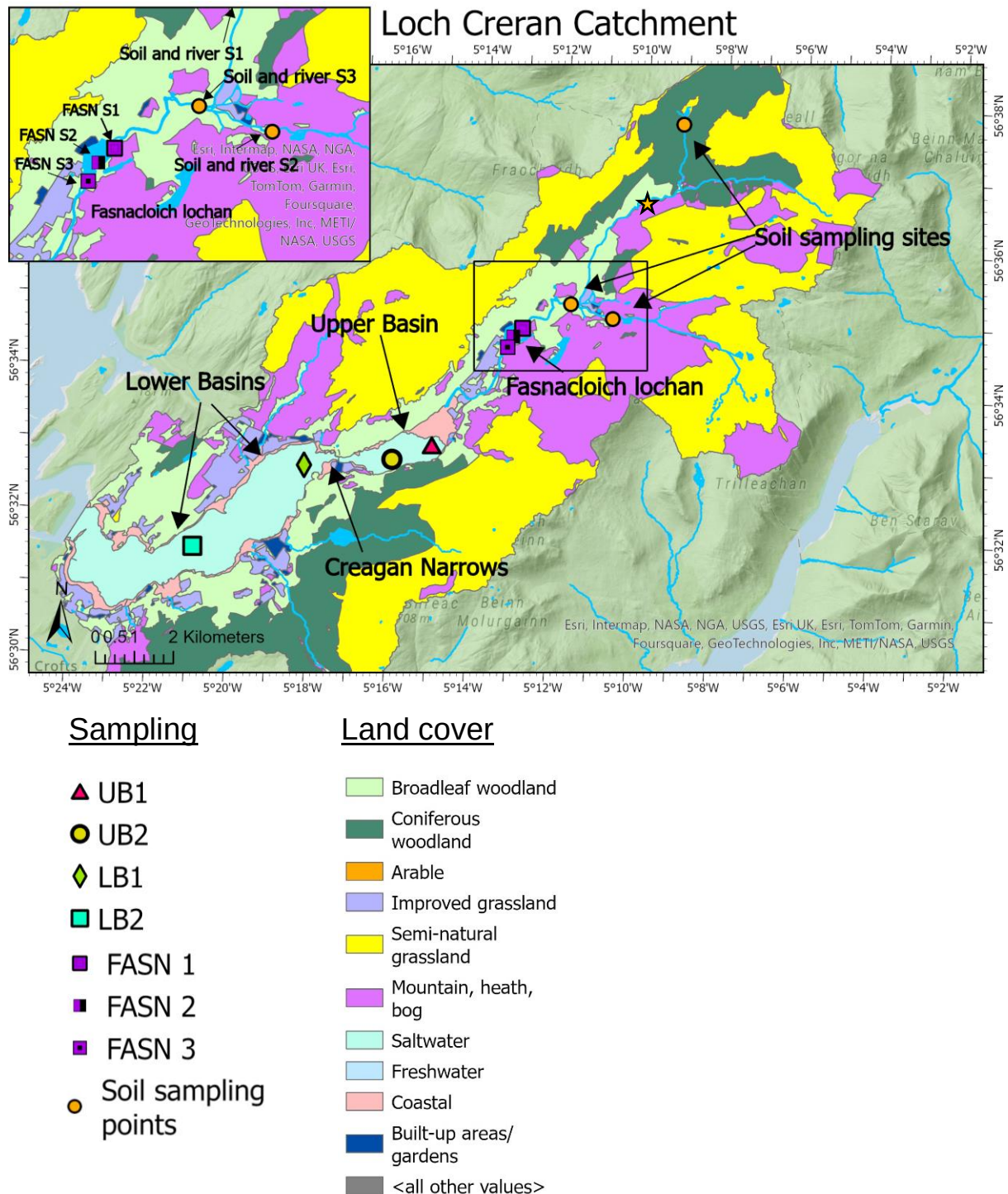


Figure 4.1: Map of Loch Creran and its catchment. Soil and river and sediment core sampling sites are marked. Zoomed in window provides a better view of Fasnacloich lochan sampling points and river/soil sampling points. The soil and river sampling points: river samples were taken within the river and soil samples were taken within 5m of the river sampling points on both banks of the river. The orange star represents the augmented sampling location for soil and river Site 1 during winter only.

The catchment is metamorphic and igneous with limited opportunity for petrogenic carbon input (less than 0.1 % petrogenic C) (Smeaton et al., 2021). Soil sampling sites (Site 1 - Site 3) are peaty and mineral podzols (Macaulay Institute for Soil Reserach, 1981) and land use is varied (Figure 4.1). Around 30 % of the Loch Creran catchment is forested with coniferous woodland accounting for ~17 % of the total land area.

4.4 Methods

4.4.1 Sample Collection

4.4.1.1 Soils

Soil samples were collected from three locations within the catchment (Figure 4.1): S1 where River Creran and Ure meet, S2 River Creran upstream before merging with the Ure, S3 River Ure) (Figure 4.1). Soil cores were collected from each bank of the river, during each seasonal sample trip (omitting Autumn Soil Site 3 due to high water flow, and with an augmented location for Winter Soil Site 1 due to snow, ~2 miles downstream of original site). Cores were taken within 2 metre proximity to the river, two cores were taken within a metre of one another on each bank using a metal hand-held soil corer ~23cm in length and stored in Whirlpak bags. These samples were freeze-dried upon return to the laboratory, within 12 hours of sample collection. 22 soils samples were collected and analysed for this study, covering three main points in the catchment.

Vegetation samples were collected at the same sites as soils. Plant leaf cuttings were collected across upper parts of the Loch Creran catchment at soils sites (Site 1 – Site 3) around the River Ure, River Creran, and after both rivers merge during Summer 2021 and Spring 2022. These were collected to determine if biomolecular signatures can be attributed to deciduous and coniferous forestry in soils and sediments. A total of 12 individual plant species were collected from the terrestrial environment (Chapter 2), covering several plant functional groups (trees, herbaceous perennials), which included natural and cultivated samples. Fresh and degrading tree leaf biomass were collected and homogenised to form samples representative of living and dead, coniferous and deciduous forestry. Samples were collected in combusted aluminium foil and placed into Whirlpak bags and frozen on return to the laboratory, within 12 hours of sample collection, before being freeze-dried, milled and stored in bags for analysis. We were unable to obtain aquatic plant samples in-situ and are using values from literature to inform source characteristics (Ficken et al., 2000).

4.4.1.2 *Water and particulate samples*

Water samples were collected using acid cleaned Nalgene bottles and acid cleaned cubitainers. Containers were held below the surface of the water and rinsed three times (discarding water downstream) before taking the sample, labelling and sealing bottles and storing them in the dark. Samples were kept in a cool and dark environment during transportation and were filtered within a 12-hour period from collection. Samples were filtered on to Whatman GF 0.45um 47mm filter paper, water was measured and stored in acid clean amber glass, and Nalgene, bottles for DOC and dissolved Fe respectively.. These water samples were stored in a constant refrigerated environment until use. Filters were stored for particulate analysis (elemental and isotopic) and frozen until use.

4.4.1.3 *Freshwater sediments*

Samples from the upper freshwater lochan, Fasnacloich, were collected in Spring 2022 along a three-point transect (Figure 4.1) using a Van Veen grab sampler. Samples were stored in Whirlpak bags and frozen within a 12-hour period of collection. Samples were then freeze-dried before analysis.

4.4.1.4 *Sediments*

Sediment cores were collected in 2016, using a Sholkovitch corer (~50cm long) from onboard the research vessel, RV Seòl Mara, in Loch Creran. Sediment cores were sliced using plastic implements at 1cm intervals and freeze dried. Full description of sample collection can be found in (Smeaton and Austin, 2019). Four cores are analysed in this study, two in the upper basin (UB1, UB2) and two across the lower basins (LB1 and LB2), positions of which are shown (Figure 4.1). These cores were selected to provide a transect from the head towards the mouth of the fjord, while avoiding aquaculture sites.

4.4.2 Bulk elemental and isotopic analysis

4.4.2.1 *DOC*

Filtered samples were all acidified with 25 microliters of 0.5 M HCl for 1 ml of sample and sparged for 30 seconds with oxygen in order to remove any potential carbonates. Samples were then analysed in triplicate for carbon (non-purgeable total dissolved organic carbon) which provided DOC values. The furnace of the TC/TN analyser (Thermalox, Analytical Sciences Ltd) was set at 685 degrees during this process.

4.4.2.2 *POC and PN*

Filters for POC, PN and particulate elemental analysis were frozen at -40°, before being defrosted and dried in an oven at +40° degrees. Sections of each filter were cut and weighed

into capsules and pressed to a smaller size analysis, for organic measurements samples within silver capsules were acid fumigated using concentrated HCl to remove carbonates before analysis (Harris et al., 2001).

Samples for PC and PN content were analysed at James Hutton Institute Ltd. using a Flash EA 1112 Series Elemental Analyser connected via a ConFlo III to a DeltaPlus XP isotope ratio mass spectrometer (Thermo Finnigan, Germany). USGS40 was used as a reference material for both C and N concentrations, measured using the area output of the mass spectrometer. Not all samples were successfully analysed due to issues with analysis (incomplete combustion / carry over with multiple samples during analysis). Successful measurements are reported but do not cover all seasons, hence seasonality is not discussed in depth. The issues from this analysis meant that there were not enough filters to covers seasonality in the particulate Fe analysis below (4.4.2.3).

4.4.2.3 Particulate elemental analysis

To analyse the elemental composition of particulate filters, microwave digestions were carried out on particulate filter samples to enable the elemental composition to be determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (iCap 6000 series ICP-OES from Thermo Scientific). The microwave digestion was carried out in a MarsXpress Microwave Digestion System from CEM, using program 'Soils 3C', based on the Mars 6 Method (CEM, 2023).

Briefly, 50% of each filter was weighed into separate Teflon microwave tubes, 1.5ml concentrated HCl was added to each tube using a graduated glass pipette and allowed to settle in a fume cupboard for 15 minutes. 3.5ml of concentrated HNO₃ was then added to each tube using a graduated glass pipette, swirled and left for a further 10 minutes until frothing had subsided. The lid was placed on the tube and the screw cap closed. Blank filters were ran in each batch. Tubes were placed in the microwave carousel and into the MarsXpress Microwave Digestion System. The program used was 'Soils 3C', based on the Mars 6 Method (CEM, 2023) which ramps up from room temperature to 210 °C over a period of 22 minutes at 75% of 1600W, and then maintains at a constant temperature of 210 °C for 20 minutes before cooling down. The digested material was then filtered (150 mm, Whatman No2) into 100 ml glass volumetric flasks. Samples were labelled and stored in acid cleaned plastic bottles before being ran on the ICP-OES. Acid blanks were used in every run as were estuarine sediment CRMs (Standard reference material 1646a, Estuarine Sediment, NIST).

Successful measurements are reported but do not cover all seasons.. Particulate matter in water samples was not even across seasons i.e. winter had very little and it was not possible to duplicate filters as a result. Some filters were split for POC, PC and isotopic analysis as

mentioned above, but the analysis was unsuccessful and there was not enough filter remaining to get an elemental profile. Hence, seasonality cannot be discussed for particulate Fe samples

4.4.2.4 Isotopic analysis of solid samples

4.4.2.4.1 Soil samples

Freeze-dried samples were weighed into capsules: ~12mg of milled sample were placed into the capsules. Tin capsules were sealed after weighing for total concentrations, while capsules for organic analysis underwent acid fumigation using concentrated HCl to remove inorganic carbon. Acid was carefully added to each of the silver capsules which were then dried at 40 degrees for up to 24 hours before being tested (additional HCl added and then re-dried for up to 24 hours), and then sealed and sent for analysis at the James Hutton Ltd.

4.4.2.4.2 Sediment samples

Freeze-dried samples were weighed into tin and silver capsules, for total and organic concentrations respectively. ~12mg of milled sample were placed in tin and silver capsules. Tin capsules were sealed after weighing, while silver samples underwent acidification using 1M HCl to remove inorganic carbon. Acid was carefully added to each of the silver capsules which were then dried at 40 degrees for up to 24 hours before being tested (additional HCl added and then re-dried for up to 24 hours), and then sealed and sent for analysis at the James Hutton Institute/Limited.

$\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}$, Total N, Total OC were measured at James Hutton Ltd. Values were determined using a Flash EA 1112 Series Elemental Analyser connected via a ConFlo III to a DeltaPlus XP isotope ratio mass spectrometer (all Thermo Finnigan, Bremen, Germany). The $\delta^{13}\text{C}$ VPDB and $\delta^{15}\text{N}$ Air-N₂ values were normalized to their respective scales using international reference materials USGS40 and USGS41a (both L-glutamic acid obtained from International Atomic Energy Agency, Vienna, Austria and Reston Stable Isotope Laboratory, Virginia, USA). Additionally, the USGS40 was used as a reference material for both C and N concentrations, measured using the area output of the mass spectrometer. Running organic and total fractions independently prevents $\delta^{15}\text{N}$ and Total N values being altered by the acidification required for the OC analysis (Kennedy et al., 2005).

4.4.3 Dithionite extractions

The concentrations of Fe-bound OC were determined by an established method of dithionite extractions as used by LaLonde et al. (2012), this method was previously used for sediment samples (Chapter 1). This extraction is designed to extract a majority of Fe oxides (goethite, hematite, ferrihydrite and others) while not affecting the Fe in clay minerals (Lalonde et al., 2012; Zhao et al., 2016). Like Lalonde et al. (2012), duplicates and controls were run for every sample.

Briefly, 250 mg of soil/sediment was combined with 15 ml solution of 0.27 M trisodium citrate and 0.11M sodium bicarbonate in a 30 ml centrifuge tube and mixed in a heated bath (80 degrees), 0.1 M sodium dithionite solution was added, and the solution was shaken at constant heat for 15 minutes. All chemicals used were analytical grade. All samples were run in duplicate with the triplicate sample acting as a control to quantify OC loss unrelated to the dissolution of Fe oxides, this enabled us to measure the amount of OC lost without the addition of dithionite to the solution. This control solution was buffered with sodium chloride to ensure the ionic strength mirrored that of the dithionite solution. Samples were then centrifuged at 6000 rpm for 10 minutes, initial supernatant was removed, then the sample was rinsed, vortexed and centrifuged at 6000 rpm for ten minutes. This rinsing was repeated three times for every sample, totalling an additional 15ml volume.

The post-extraction solid sample was analysed for $\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}$, Total N, Total OC at the University of St. Andrews using a Sercon Integra 2 EA-IRMS. The post-extraction supernatant was analysed for total Fe using inductively coupled plasma optical emission spectroscopy (ICP-OES) (iCap 6000 series ICP-OES from Thermo Scientific) at the University of Stirling. Speciation of this Fe pre and post extraction was measured using Mössbauer spectrometry which is detailed below.

This method for extraction was chosen based on its widespread use in different soil and sediment environments (Lalonde et al., 2012) enabling results to be compared to those of larger studies and datasets in different locations, and has remained consistent throughout chapters of this thesis for comparability within this catchment. There are multiple methods and chemicals that can be used to try and extract iron minerals in soils; sodium pyrophosphate, acidified hydroxylamine and inorganic dithionite (dithionite with a HCl rinse) (Coward et al., 2017; Wagai and Mayer, 2007). The amount of Fe extracted using these methods varies depending on soil type and depth but Fe extracted from the dithionite extraction method used here (Lalonde et al., 2012; Mehra and Jackson, 1958) and the inorganic dithionite method have not been found to produce statistically different results from one another, and have been found to extract greater amounts of Fe in surface (0-20cm) soils in comparison to other

methods listed above (Coward et al., 2017). Therefore, despite any noted flaws associated with the dithionite extraction method (i.e. the lack of correlation between extracted Fe and C, the extraction of less C than some other methods (Coward et al., 2017) and the inability to dissolve all FeR (Hepburn et al., 2020), the dithionite extraction method remains well-used, comparable and cost effective for Fe mineral extraction, with no clear successor / better alternative at present.

4.4.4 Mössbauer Spectroscopy

All pre and post extraction soil and sediment samples were analysed using a standard transmission Mössbauer Spectrometer (Wissel, Germany) with a ^{57}Co in Rh matrix radiation source in constant acceleration mode at the University of Stirling. Samples were weighed into acrylic glass discs (between 0.07-0.12 g) and sealed. Samples were measured at room temperature (295K), and a selection were also measured at 4.2K to establish the magnetic ordering of the Fe species present. Samples were cooled in a DRY ICE 4K Mössbauer Cryostat (ICEoxford, UK). Mössbauer spectra were produced after a period of analysis (2-4 days) and these were fitted using Recoil software using the Voigt-based fitting routine (Rancourt and Ping, 1991). Mössbauer spectroscopy allows for comparison between the relative contributions of Fe^{2+} and Fe^{3+} and facilitates the identification of specific Fe species (Gütlich and Schröder, 2012). Samples were analysed pre and post extraction to demonstrate the amount of reactive Fe dissolved/remaining and to determine which Fe species were preferentially dissolved by dithionite. The spectra were calibrated against a measurement of α -Fe foil (25 μm thickness) at room temperature.

4.4.5 XRD

Mineral composition was determined via X-Ray Diffraction (XRD) using a Panalytical X'Pert PRO PW3040/60 fitted with a PW 3050/60 goniometer in theta-theta configuration at the National Museums Scotland. 'Zero background' sample holders were used made from a single silicon crystal. Data was analysed using Profex software.

4.4.6 Statistical analysis

The Pearson Correlation Coefficient tests were performed in Microsoft Excel to determine correlations between different variables within this study. The functions used all come as

standard within the data analysis toolkit; PEARSON COUNT, TDIST. A P value of 0.05 or less was considered to be significant.

4.5 Results

4.5.1 Variation in bulk elemental composition in soils and freshwater sediments

4.5.1.1 *Soils and Freshwater Sediments*

Bulk organic carbon (OC) concentrations are highest in the deciduous Soil Site 2 and lowest in the mixed perennial / grass / deciduous downstream Soil Site 3 (Figure 4.2a). Freshwater sediments, only obtained in Spring, present increasing concentrations from inflow to outflow (Figure 4.2b). Fjord sediments (Figure 4.2c) (values obtained from Chapter 1), decrease from the upper basin, throughout the lower basins. From soils to fjord there is a general decrease in OC concentration: soils have the highest OC concentrations (ranging from 170 – 1154 µg/g) which decrease downstream in freshwater sediments (527 – 993 µg/g) and again in fjord sediments which range from (197 – 786 µg/g).

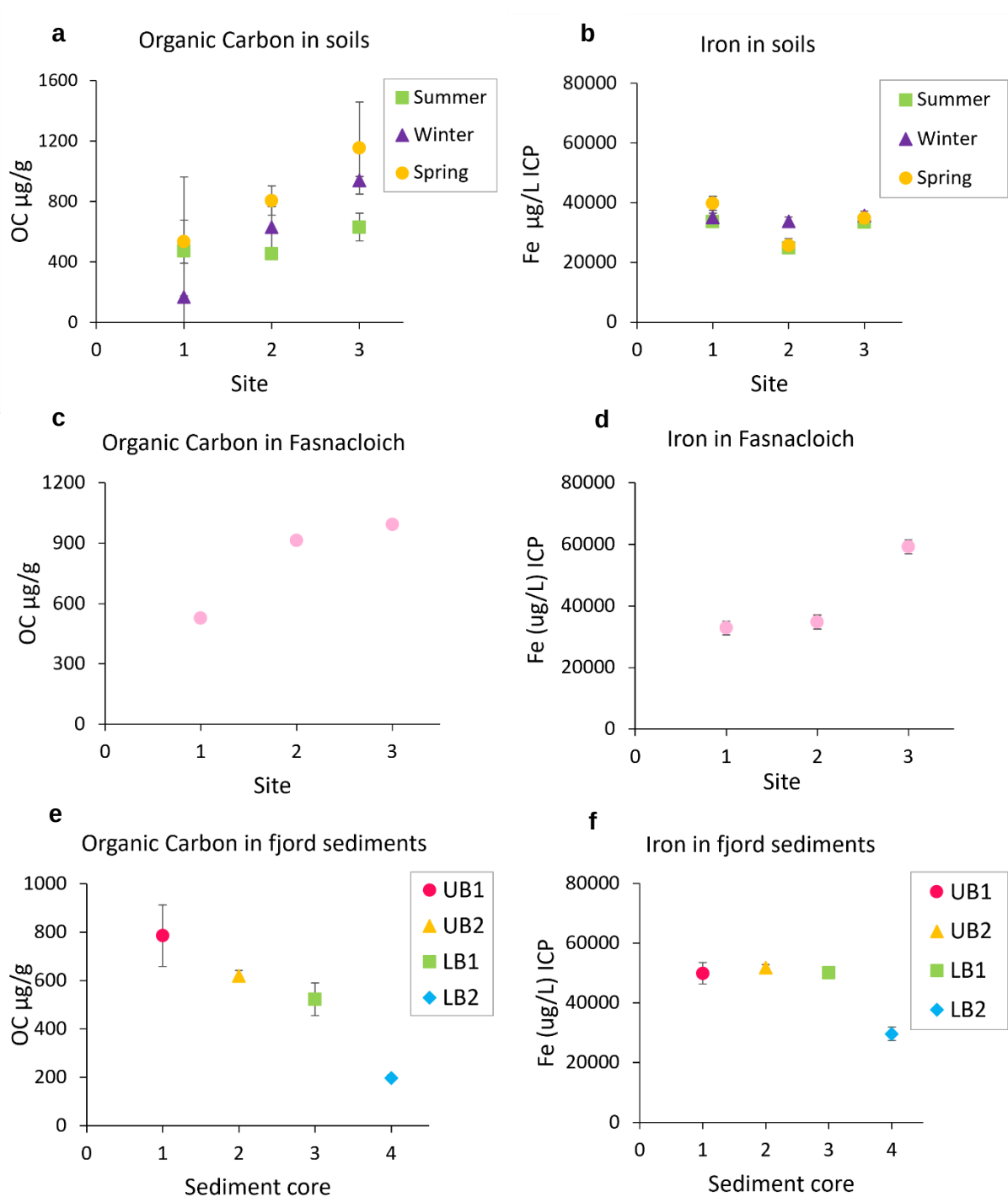


Figure 4.2: Bulk organic carbon and iron concentrations across soil, freshwater and fjord sediments. (a) Organic carbon % in soil samples (b) organic carbon % in freshwater sediments (c) organic carbon % in fjord sediments (d) soil Fe concentrations measured by ICP (e) Freshwater sediment Fe concentrations measured by ICP (f) Fjord sediment ICP concentrations measured by ICP, these values are an average of three depths in each sediment core. In soil samples, summer is represented by a green square, winter by a purple triangle, spring by a yellow circle. Bulk OC and Fe data for fjord samples has been obtained from Chapter 1 of this thesis).

Fe concentrations do not necessarily follow the same patterns as OC concentrations. In soil samples, Fe concentrations are highest in the coniferous Soil Site 1 and lowest in deciduous Soil Site 2, and there is very little seasonal variation in comparison to OC. Fe concentrations in sediments increase from inflow towards outflow in Fasnacloich by ~45 % (FASN Site 1 to Site 3) and remain relatively high in fjord sediments (Figure 4.2f). Fe concentrations remain ~50000 µg/L in the upper basin (UB1 and UB2) and in lower basin LB1, and only decrease in the basin closest to the mouth of the fjord.

OC:TN values for soils and Fasnacloich lochan sediments do not necessarily correlate with land cover but are known to vary across soil types and terrestrial and marine vegetation (Smeaton and Austin, 2017). In agreement with this study, coniferous samples in this catchment have higher OC:TN values than deciduous vegetation, and as sediment cores (Chapter 1) move closer towards the sea (LB2) a decrease in OC:TN values is observed (Figure 4.3).

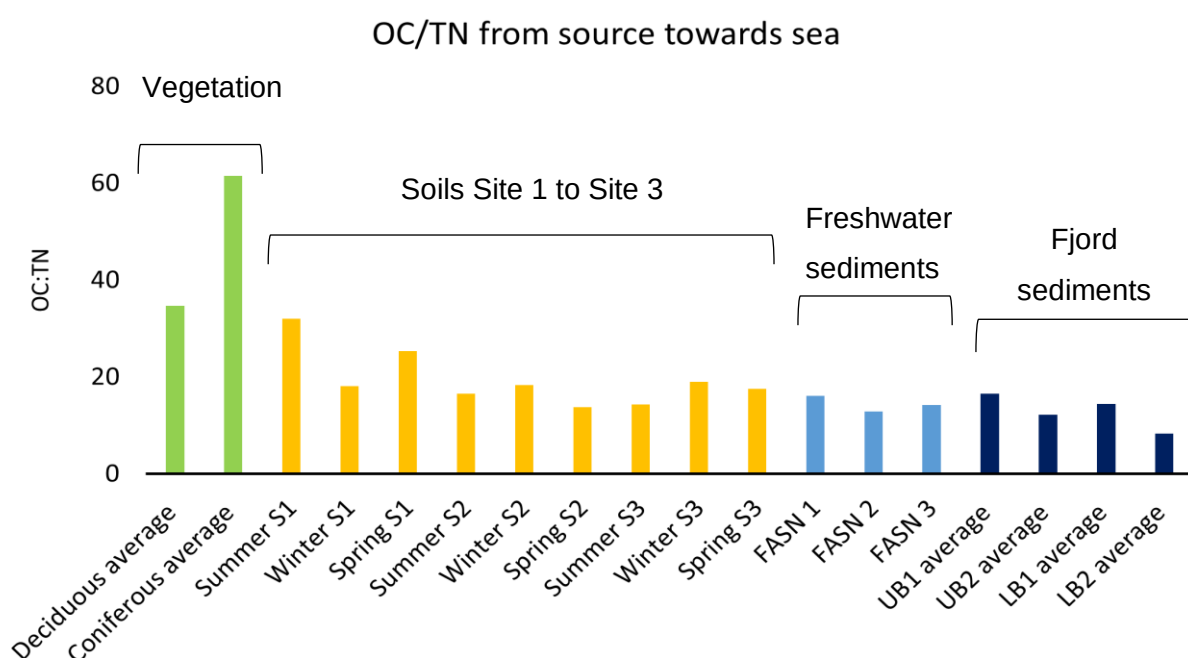


Figure 4.3: OC:TN variation from source towards sea. This covers average coniferous and deciduous values (green), soil samples across all sites and seasons (yellow), Fasnacloich lochan samples (light blue) and average fjord sediment values (dark blue).

The OC:TN ratios average to 25.12 ± 6.98 Soil Site 1, 16.20 ± 2.34 Soil Site 2 and 16.94 ± 2.39 Soil Site 3. Soil Site 1 has a generally higher OC:TN across seasons, but high variability, meaning there is seasonal crossover with other sites making it difficult to propose that the higher OC:TN observed is in relation to its coniferous land cover.

4.5.2 Transport of organic carbon and iron in river water

4.5.2.1 Dissolved

Dissolved OC (DOC) concentrations were most variable in Autumn (4378 – 7918 $\mu\text{g/L}$) and more stable in other seasons displaying relatively consistent values in spring (2427 – 2475 $\mu\text{g/L}$) and winter (1081 - 1204 $\mu\text{g/L}$) (Figure 4.4a). In spring summer there is a small increase in DOC from Soil/River Site 1 to Site 3 (1745 – 2770 $\mu\text{g/L}$). Both the increase in summer DOC between River Sites 1-3 and the decrease in DOC in River Sites 1-3 highlight that the DOC values observed in River Site 3 are not simply a mixture of the River Creran (River Site 1) and River Ure (River Site 2), but are likely influenced by inputs from land and exchange with the atmosphere. The DOC signal in Fasnacloich lochan is elevated in comparison to the River Creran (River Site 3) where values in spring are ~ 2575 $\mu\text{g/L}$ and lochan values are >4000 $\mu\text{g/L}$ (Figure 4.4c).

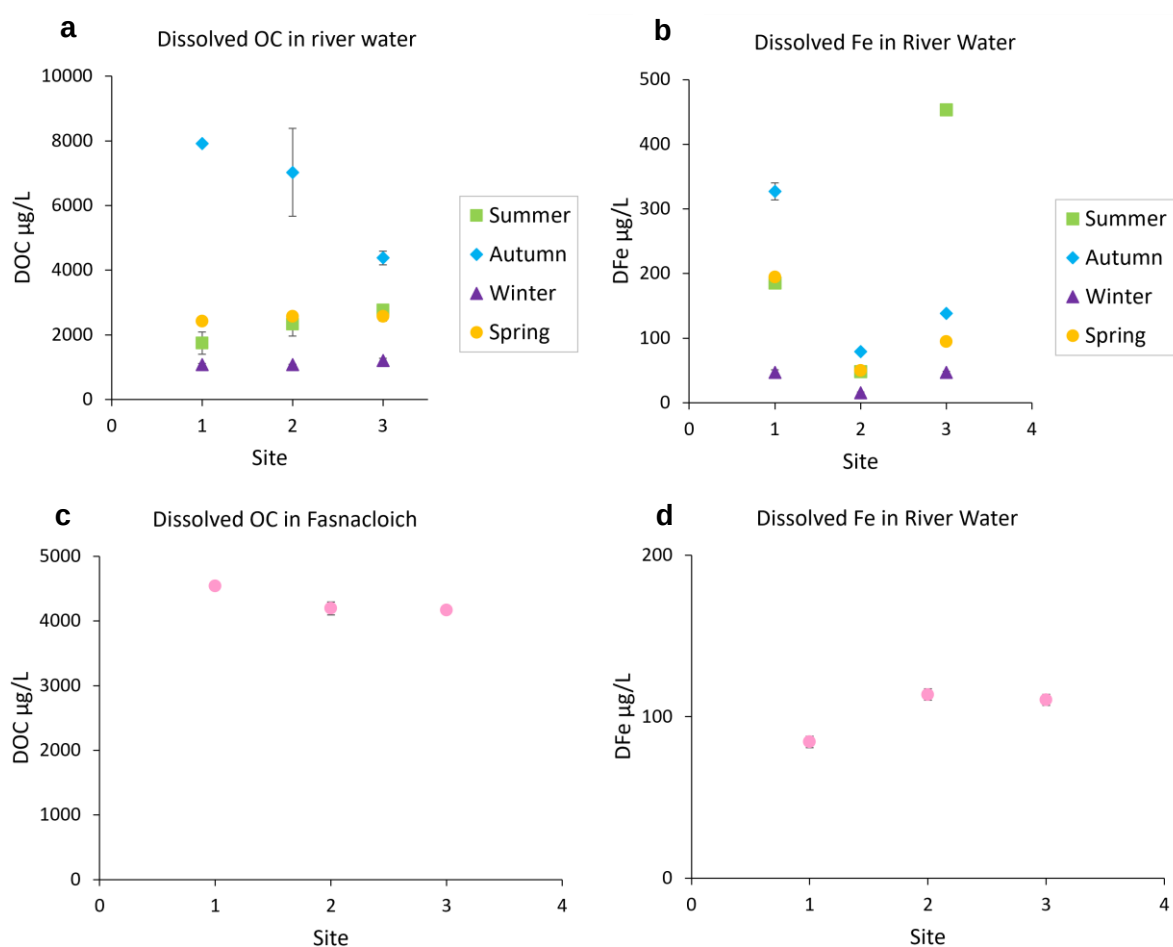


Figure 4.4: Dissolved OC concentrations in (a) river water across seasons and sampling sites (c) Fasnacloich lochan in spring. Dissolved Fe concentrations in (b) river water across different seasons (d) Fasnacloich lochan in spring. Errors are calculated based on the standard deviation of triplicate samples, but small errors are often obscured by points..

Dissolved Fe (DFe) concentrations in river and Fasnacloich samples are highly variable across seasons and sites. In samples taken across seasons, we observe less DFe in winter (averaging 36 µg/L), and similar spring values (113 to 103 µg/L respectively) in both river samples and Fasnacloich. With the exception of summer in River Site 3, all sites have the highest DFe in River Creran Site 1 (Figure 4.4b) while the River Ure, Site 2, has the lowest DFe concentrations across all seasons. Downstream of both in River Site 3, where the Creran and Ure meet, moderate values of DFe are observed ($\sim 93 \pm 2.4$ µg/L if the outlier is excluded) suggesting that the DFe signal from the River Creran is diluted by the River Ure, Site 3 has $\sim 50\%$ of the DFe signal of the River Creran upstream (Site 1). Dissolved OC concentrations in the lochan (Figure 4.4d) remain relatively consistent from the inflow from Loch Creran to the outflow ~ 100 µg/L. Overall DOC is considerably higher than DFe in both river and lochan waters.

Zonal statistics calculated from GIS slope measurements within the Loch Creran catchment (Chapter 2) were used to determine whether slope or elevation correlates with DOC or DFe, and no significant relationships were observed (Table 4.1). A correlation with elevation was only calculated for river/soil parameters because there is a difference in slope and elevation surrounding these sites, whereas the freshwater lochan is a small waterbody with no notable change in elevation or slope surrounding it (Figure 3.12, 3.5.6 Topography)

Table 4.1: Pearson Correlation Coefficient values for dissolved Fe and OC concentrations.

Parameter 1	Parameter 2	R value	P value
DFe	Slope	River / soil -0.920	River / soil 0.256
		FASN -0.969	FASN 0.158
DFe	Elevation	River / soil 0.414	River / soil 0.728
DOC	Slope	River / soil 0.739	River / soil 0.471
		FASN 0.914	FASN 0.265
DOC	Elevation	River / soil 0.655	River / soil 0.545

4.5.2.2 Particulate

Fe and C are also transported in particulate form throughout the catchment rivers. In contrast to the dissolved fractions, particulate Fe (PFe) is considerably higher in rivers than particulate total carbon (PC) (Table 4.2). This was also observed in soil samples (Chapter 2) but is not

as clear for PC. Despite seasonal variation (and therefore error) there is no overlap in PFe concentrations between river sites, showing distinct values. The particulate data highlights that a majority of Fe in the rivers is in particulate form, as this is much higher than its dissolved counterpart in both soils and lochan sediments (Figure 4.4b, d, Table 4.2). High concentrations of PFe are observed at River Site 1, lowest in River Site 2, and a mixture of both signatures is present downstream at River Site 3. Further downstream in Fasnacloich lochan, PFe concentrations are variable and highest at the riverine inflow, suggesting that a portion of the PFe may settle out in the freshwater sediments in particulate form contributing to the sedimentary Fe (Figure 4.2c) some of this Fe may then be reduced in the sediment (to Fe^{2+}) which would then be in a soluble form and could contribute to, and increase, the dissolved Fe pool. This could be due to a change in flow or chemical properties of the water, but elevated values near the outflow suggest that a portion of the particulate Fe may be remobilised or added to the water body from the surrounding catchment.

Total PC displays different patterns to Fe concentrations, as they are stable at River Sites 1 and 2, and higher at River Site 3 (Table 4.3). This would suggest that differing land cover and elevation have little influence on PC concentrations. This is confirmed with Pearson correlation coefficient values of $R = -0.804$, $P = 0.406$ for slope and soils, and $R = -0.574$, $P = 0.610$ for elevation and soils. However, there are clear indications that seasonality plays a role in PC patterns; summer 242 ± 2 ($\mu\text{g/L}$), autumn 229 ± 6 ($\mu\text{g/L}$), winter 21 ± 1 ($\mu\text{g/L}$), spring 88 ± 2 ($\mu\text{g/L}$). It is evident that there is a seasonal decrease in POC during winter and spring in comparison to summer and autumn. DOC is present in higher concentrations than PC so unlike Fe, C is more likely to be transported in dissolved form.

Table 4.2: Particulate averages across seasons for each of the river sampling sites (S1 - S3) and the Fasnacloich sampling sites (S1 - S3).

River Site	Total iron average (µg/L)	Total carbon (µg/L)
1 – River Creran	2430 ± 2533	134 ± 119
2 – River Ure	429 ± 236	133 ± 109
3 - Creran + Ure	744 ± 154	167 ± 133
FASN	792.80	202.30
	400.92	269.54
	961.40	255.71

4.5.2.3 Do dissolved and particulate samples provide insight into dissolution?

When PFe and DFe are plotted against one another across all available seasons, it suggests that there is a weak negative correlation (Figure 4.5a), which is confirmed by Pearson correlation coefficient tests, $R = 0.248$, $P = 0.426$, when lochan water samples are included and $R = 0.247$, $P = 0.593$, when lochan samples are excluded showing that there is more DFe there is more PFe, but this is not significant and likely skewed due the PFe value ~ 5300 µg/L. PC and DOC samples have significant positive trend (Figure 4.5b), $R = 0.647$, $P = 0.023$ indicating again that there's more PC when there's more DOC (so there are increases in both when there's more total C in the water column).

Fasnacloich lochan samples were collected in spring, alongside spring river samples, and thus offer a transect from source towards sea across one season. There is a strong and positive correlation between DFe and PFe in spring samples (Figure 4.5c) $R = 0.789$, $P = 0.062$ and a significant and positive correlation between DOC and PC in spring samples $R = 0.902$, $P = 0.014$ (Figure 4.5d).

If we consider the spring samples along a transect, the River Creran, River Site 3, flows in to and through lochan Sites 1-3. DFe and PFe align closely in River Sites 1-3 before reaching Fasnacloich lochan where there is some separation. River Site 3 is the product of the joining of River Site 1 (River Creran) and River Site 2 (River Ure). In Spring, River Site 3 (95 µg/L) is similar to but less than the average of River Site 1 and 2 (122.5 µg/L) (Figure 4.5e) indicating that some DFe is lost, probably through microbial action or precipitation. The precipitation data

shows River Site 3 PFe (635µg/L) is ~50 % of River Site 1 PFe concentrations (1208 µg/L), and this is also the case for DFe suggesting a ~50 % dilution from the River Ure input. However, this will be influenced by the volume of water and dilution factor for each river, and there may be various chemical processes en route from River Site 1 to Site 3.

Between Soil Site 3 and lochan Site 1 there is slight decrease in DFe and a small increase in PFe (Figure 4.5e), suggesting that a portion of the DFe may have precipitated out. Where PFe decreases in lochan Site 2, there is an increase in DFe, indicating that a portion of the Fe^{3+} has been reduced to Fe^{2+} , increasing the soluble dissolved fraction, or that some may have been deposited and buried. An increase in PFe at the outflow (lochan Site 3) is not accompanied by any change in DFe that may suggest an influx of PFe into the water column from sedimentary or terrestrial sources, or an increase in particle size through aggregation.

Spring concentrations of DOC in River Sites 1-3 are relatively stable in spring, while there is an increase at River Site 3 in PC (Figure 4.5f). As the increase in PC is not accompanied by any noticeable difference in DOC we suggest this may be due to terrestrial inputs of aggregation increasing particle sizes. There is an increase in both DOC and PC as the river enters Fasnacloich lochan Site 1 suggesting that there is a (relatively) Fe rich input likely from terrestrial surroundings into the lochan. PC increases between lochan Sites 1 and 2 by ~67 µg/L and DOC decreases by ~350 µg/L indicating that some of this DOC could be precipitated while a portion is lost, potentially through microbial action.

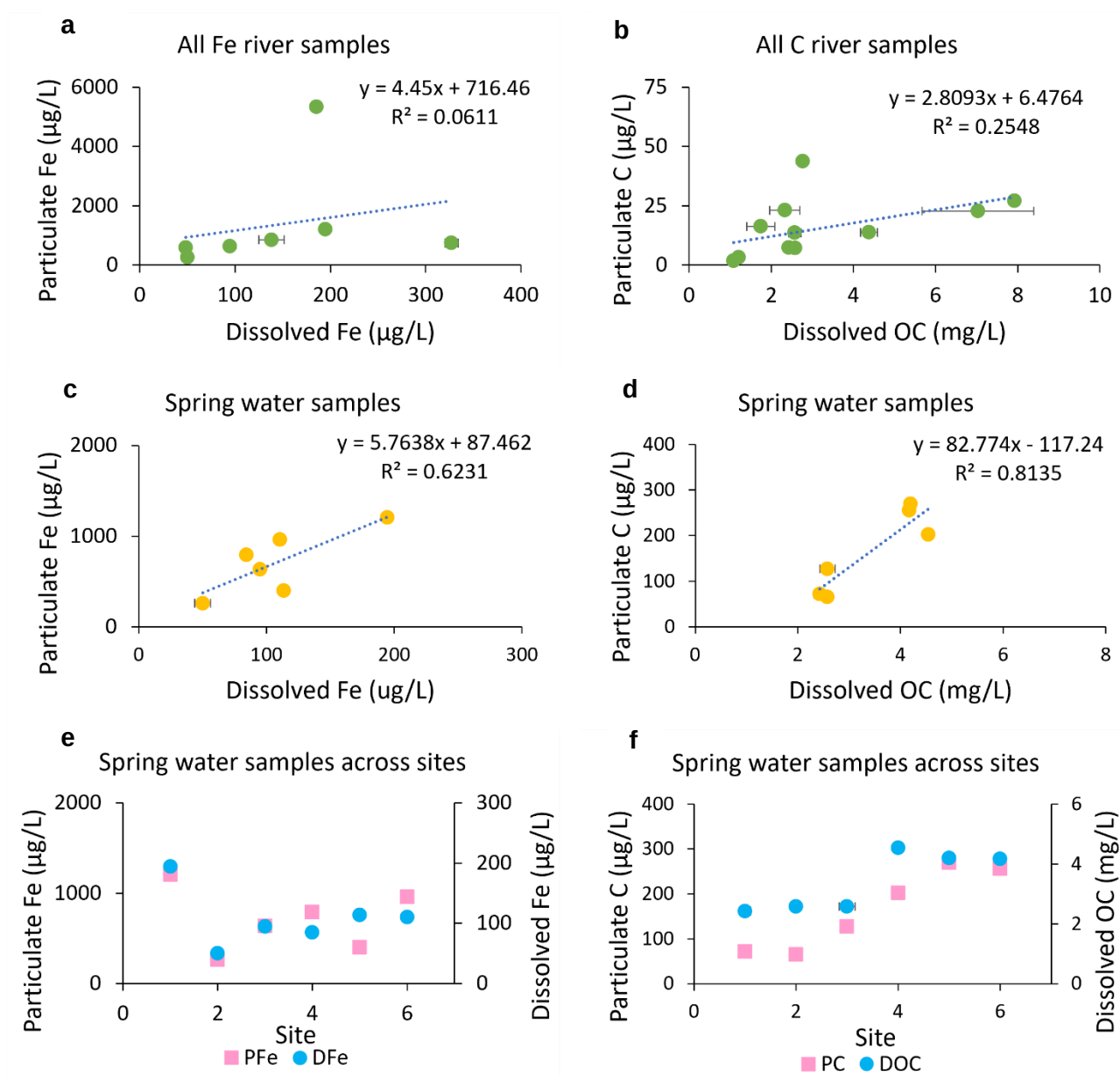


Figure 4.5: Dissolved and particulate river water samples (a) Dissolved and particulate Fe in all successfully measured PFe river samples (these means that all PFe samples are shown and corresponding DFe samples)(b)All dissolved and particulate C concentrations (c) Particulate and dissolved Fe samples in Spring transect only (inclusive of river water and lochan samples) (d) Particulate and dissolved C samples in Spring transect only (inclusive of river water and lochan samples) (e) Particulate and dissolved Fe across the Spring transect plotted according to site, where site 1-3 reflect the appropriate soil sites, and sites 4-6 represent lochan sites 1-3 (f) Particulate C and dissolved OC in Spring transect plotted according to Site as per (e).

When we evaluate the trends in PC and DOC across sites in different seasons, it shows a more complex seasonal picture, that is not possible to see through one season or seasonal averages (Figure 4.6). In summer and autumn DOC and PC follow the same sharp increasing and decreasing trends respectively, while spring and summer display lower DOC and PC concentrations and more muted trends of increasing PC and relatively stable DOC (Figure

4.6c,d). Unfortunately, the equivalent is not replicable for Fe due to analysis issues listed in methods (C.1.0 Particulate Fe, for all successfully analysed samples).

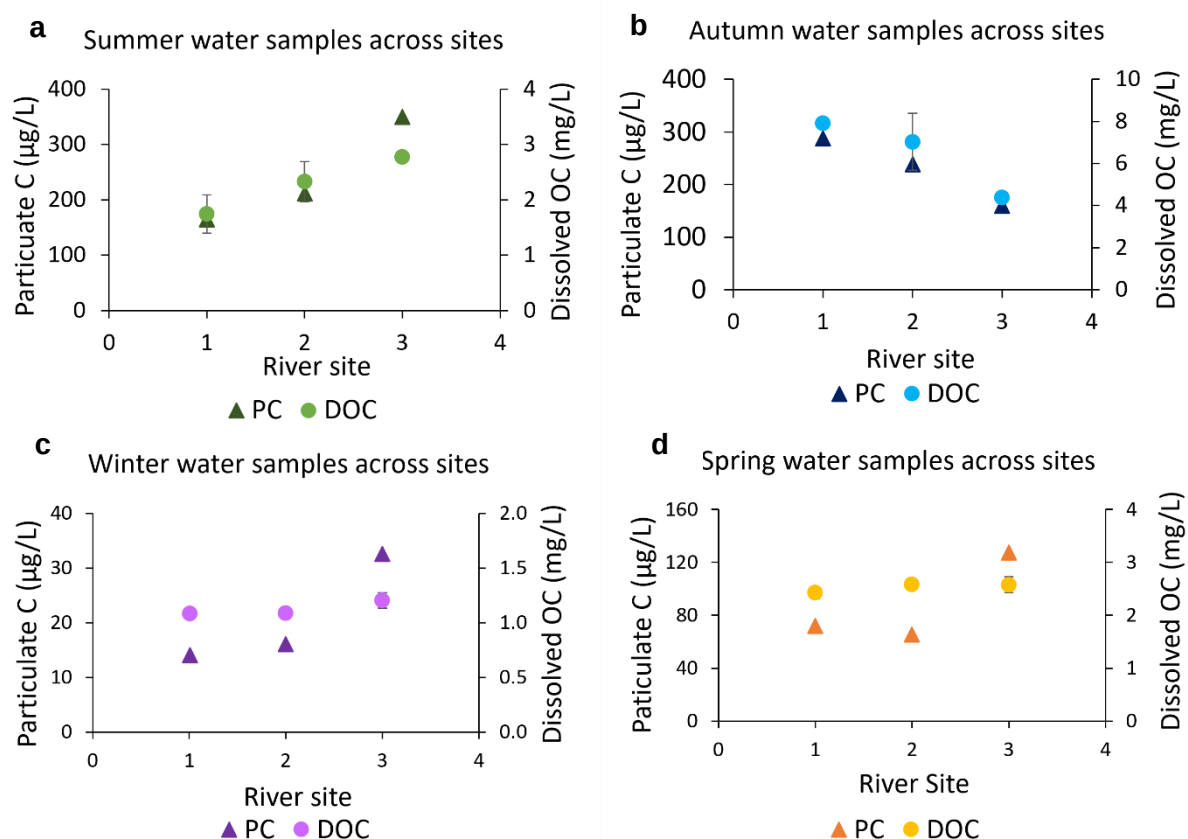


Figure 4.6: Concentrations of particulate and dissolved carbon across different seasons and sites (a) summer (b) autumn (c) winter (d) spring.

4.5.3 Isotopic $\delta^{13}\text{C}_{\text{org}}$ signatures from soils to sediments

$\delta^{13}\text{C}_{\text{org}}$ signatures in soils shows little seasonal or spatial difference, despite different land cover. This is distinctly different from the sediment $\delta^{13}\text{C}_{\text{org}}$ signatures, that are generally more enriched, especially with proximity to the marine environment (Figure 4.7a). The difference between lochan and fjord sediments highlights that regular flushing of the fjord has a large influence on the $\delta^{13}\text{C}_{\text{org}}$ values, making them generally more enriched by introducing more marine material. When plotted with $\delta^{15}\text{N}$ (Figure 4.7b), it is clear that both soil and freshwater sediment samples fall within mean terrestrial soil and vegetation values taken throughout the UK (Smeaton et al., 2022; Smeaton and Austin, 2022).

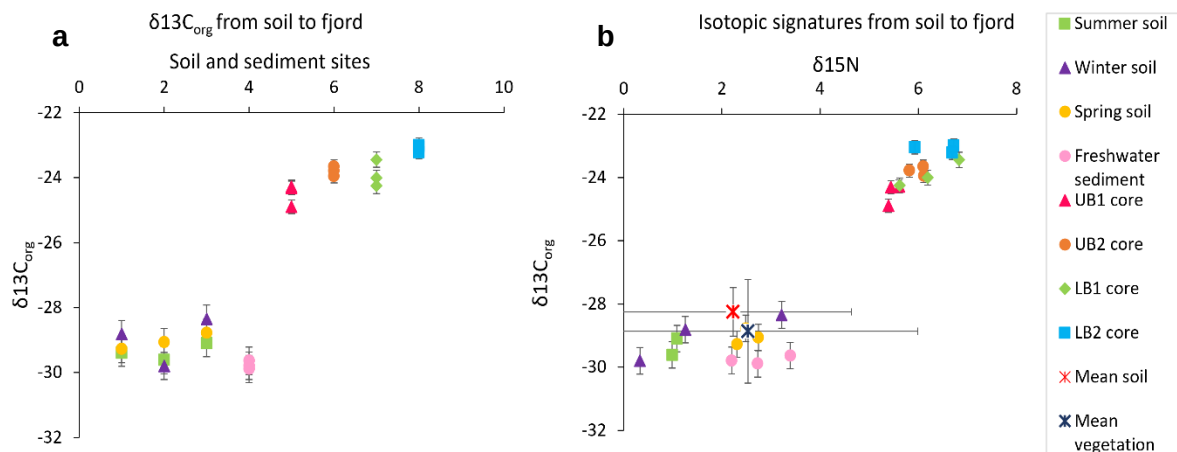


Figure 4.7: $\delta^{13}\text{C}_{\text{org}}$ measurements (a) per soil and sediment Site (soil and freshwater data from this chapter, fjord sediment data from Chapter 1) (b) against $\delta^{15}\text{N}$ showing soils, freshwater and fjord sediments and mean soil and vegetation data from Smeaton et al., 2022.

4.5.4 Organic carbon and reactive iron associations in soils and freshwater sediments

OC-FeR associations are variable in soils ranging from 4.5 to 74.6 %. In soil samples, coniferous Soil Site 1 displays high seasonal variability in OC-FeR complexes (75-29-54 % for Summer-Winter-Spring, respectively) (Figure 4.8a) which is reflected to some extent in the FeR concentrations, where there is a large decrease in FeR during winter (Figure 4.8b). Soil Site 1 has the highest (average) OC-FeR ~52 % and the highest (average) FeR ~14.5 %. Deciduous Soil Site 2 contains considerably lower OC-FeR concentrations in comparison to Soil Site 1 but shows similar seasonal variation through a large decrease in associations in winter (20-4-25 % for Summer-Winter-Spring respectively). This is the only site where spring associations are higher than summer. The FeR concentrations do not reflect the lower OC-FeR and are very similar to that of Soil Site 1 with an average FeR of ~14.3 % with very limited seasonal variation. FeR concentrations are lowest in Spring, where OC-FeR is the highest. It appears that forested Soil Sites 1 and 2 have similar seasonal variability even if concentrations differ. The same seasonal variations are not observed in Soil Site 3 as the OC-FeR is highest in winter (52-53-9 % OC-FeR for Summer-Winter-Spring respectively). The average OC-FeR values are in between that of Soil Site 1 and 2, averaging ~37.7 %. The FeR concentrations do not follow the same abundance pattern as OC-FeR concentrations, as Spring has the highest FeR but the lowest OC-FeR. Soil Site 3 has the lowest FeR content averaging ~10 %.

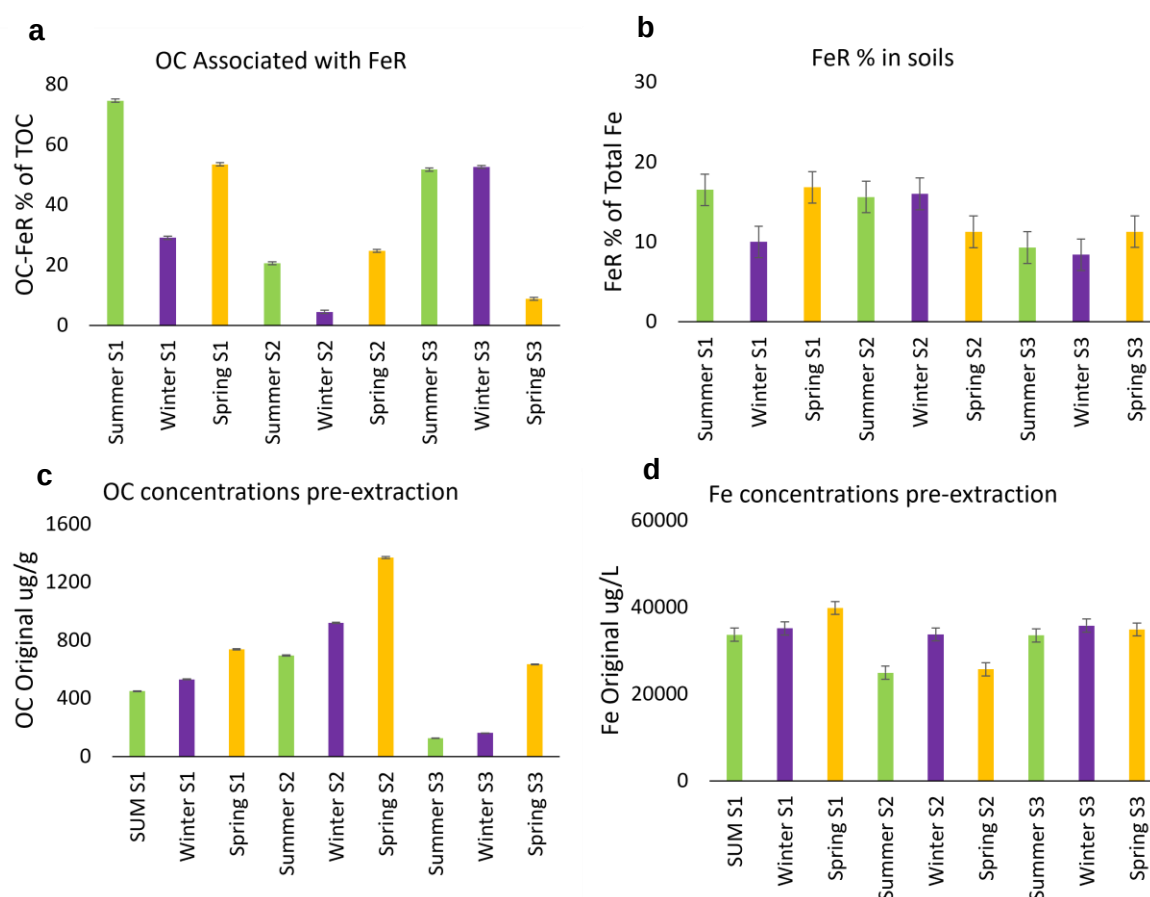


Figure 4.8: (a) OC associated with FeR in soils, values adapted to control values (b) FeR content in all soils sites (c) Original (pre—extraction) total organic carbon concentrations in soils (d) Original (pre-extraction) total iron concentrations (as determined by ICP). Colours in all soil samples highlight seasonal differences as per other graphs in chapter (green = summer, purple = winter, yellow = spring).

In the freshwater lochan, sediments have ~35 to 46 % OC associated with (a portion of) the FeR (Figure 4.9a). There is more OC associated with FeR closest to the outflow of the lochan, and this correlates with increased FeR present at the same site (Figure 4.9b). Unlike soil values (Figure 4.8c,d) the lochan OC-FeR concentrations align with the OC and Fe concentrations in sediments (Figure 4.9c,d) which may be indicative of the small spatial scale of the freshwater lochan and sample collection.

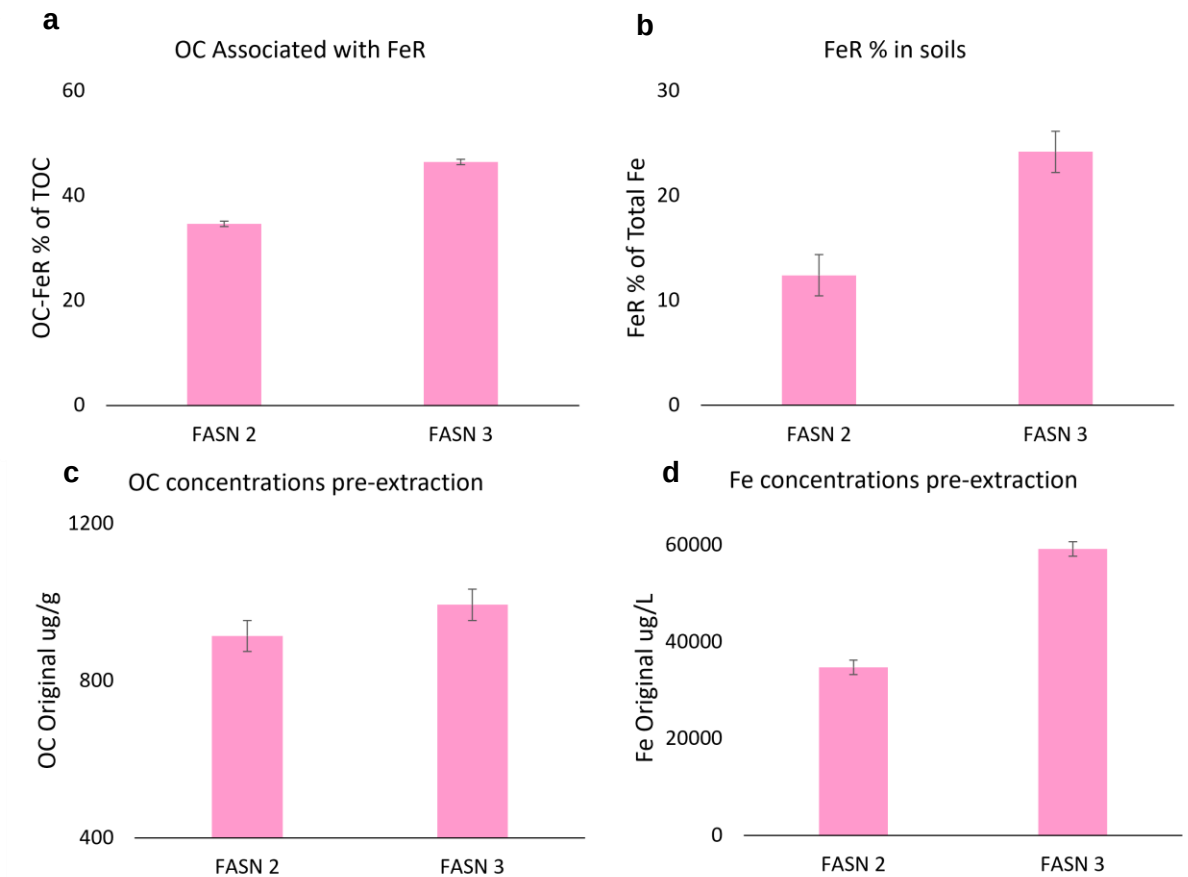


Figure 4.9: (a) OC associated with FeR in lochan sediments, values adapted to control values (b) FeR content in two sites (c) Original (pre—extraction) total organic carbon concentrations in lochan sediments (d) Original (pre-extraction) total iron concentrations (as determined by ICP).

Averages and standard deviation values were calculated for each soil and lochan site (Table 4.3) to highlight the differences in OC-FeR and FeR between sites: where there are large variations in OC-FeR, there may be minimal change in FeR concentrations.

Table 4.3: Table of OC-FeR and FeR averages across soil sites and Fasnacloich sediments.

Table of averages		
Sites	Average OC-FeR	Average FeR
Soil Site 1 (Creran)	52.40 ± 22.77	14.46 ± 3.86
Soil Site 2 (Ure)	16.61 ± 10.72	14.31 ± 2.64
Soil Site 3 (downstream)	37.72 ± 25.03	9.67 ± 1.47
All soils	35.57 ± 17.99	12.81 ± 2.72

FASN (all sites)	40.54 ±8.36	18.30 ± 8.33
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Furthermore, we calculated the concentrations of other elements extracted during the dithionite extraction such as aluminium, and found low but present amounts were dissolved (Table 4.4).

Table 4.4: Average Aluminium extracted from soil and sediment samples.

Site	Average Al % dissolved	Standard deviation	Average per Site %
Summer Soil Site 1	3.35	7.92	3.02
Winter Soil Site 1	2.33		
Spring Soil Site 1	3.38		
Summer Soil Site 2	3.41	4.08	3.67
Winter Soil Site 2	4.75		
Spring Soil Site 2	2.86		
Summer Soil Site 3	2.32	2.51	2.58
Winter Soil Site 3	2.13		
Spring Soil Site 3	3.29		
FASN 1	2.02	2.72	4.22
FASN 2	4.68		
FASN 3	5.96		

We calculated the Pearson Correlation Coefficient to investigate correlations between OC-FeR and other variables (Table 4.5). There are no significant correlations between OC-FeR and total OC, Fe, FeR or OC:FeR ratios suggesting that there may be relationships between these variables, but these individual variables are unlikely to be the dominant control on OC-FeR complexes.

A positive significant correlation is found between FeR and Al extracted, suggesting that there is a strong relationship between these variables and that Al may be released from FeR phases during the extraction (opposed to separate Al minerals) as Al can sometimes substitute for Fe

minerals (Jentzsch and Penn, 2006; Pinney and Morgan, 2013; Schwertmann et al., 1979). As such, we suggest that all OC released from the extractions were bound to Fe minerals.

Table 4.5: Pearson Correlation Coefficient R and P values for different variables in soil samples.

<u>Pearson Correlation Coefficient values</u>			
Variable 1	Variable 2	R-value	P-value
OC-FeR	Total OC	-0.54	0.14
OC-FeR	Total Fe	0.35	0.35
OC-FeR	Total FeR	0.03	0.94
OC-FeR	OC:FeR	0.36	0.34
OC-FeR	Fe 3+ pre extraction	-0.02	0.96
OC-FeR	Fe 3+ post extraction	-0.22	0.58
FeR	Fe 3+ pre extraction	0.33	0.39
FeR	Fe 3+ post extraction	0.40	0.29
OC-FeR	Al extracted	-0.45	0.23
FeR	Al extracted	0.80	0.01

4.5.4.1 Iron speciation

Mössbauer spectral parameters at 295K and 4.2K were used to determine the presence of dominant Fe minerals in soils, freshwater sediments, and fjord sediments (the latter being from Chapter 1).

Here we present an example of a room and low temperature soil sample and freshwater lochan sediment sample before and after extraction (Figure 4.10). In room temperature spectra FeR is within the Fe³⁺ phase (Figure 4.10 a,c,e,g, represented by grey lines), and spectra may, or may not have a sextet visible (Figure 4.10 a,c,e,g, represented by yellow lines). The Fe³⁺ phase incorporates Fe³⁺ that is in clay minerals, iron oxides, and superparamagenetic oxyhydroxides (as per Chapter 1), so only portion of the Fe³⁺ phase is FeR. As such, we do not expect all Fe³⁺ to be dissolved by the dithionite extractions (grey lines) but we do expect a large portion of the FeR sextet to be removed (yellow lines).

In Soil Site 2, before and after extraction, there is a visible Fe^{2+} , Fe^{3+} phases and a sextet (Figure 4.10a,c). The Fe^{3+} phase has reduced post extraction (Figure 4.10c) in comparison to the pre-extraction samples (Figure 4.10a) signalling FeR removal from the sample, but this is not clear in the FeR signal (yellow lines). Measurements at 4.2 K (Figure 4.10b,d) are below the magnetic ordering temperatures of Fe (oxyhydr)oxides, and we can therefore observe a clearer and more abundant six-line spectrum. Hematite is the present Fe phase at room temperature (Figure 4.10a,c), and ferrihydrite is the dominant phase at low temperature (Cornell and Schwertmann, 2003). Parameters do not perfectly align with ferrihydrite values (Cornell and Schwertmann, 2003) which indicates there may be other minerals present influencing the parameters, but that they are in lower quantities making them difficult to identify.

In the freshwater lochan Site 3 (Figure 4.10e-h), there is no sextet visible at room temperature, indicating that there are no minerals that can be magnetically ordered at high (room) temperature (such as Hematite) (Cornell and Schwertmann, 2003). There is a visible reduction in the Fe^{3+} phase (grey lines) at room temperature post extraction (Figure 4.10d,f)

Alike fjord sediment samples (Chapter 1) the dithionite extraction method (Lalonde et al., 2012) has not dissolved all FeR within samples (Hepburn et al., 2020, Fisher et al., 2020) which is evident by the presence of the magnetically order Fe at low temperature post extraction (Figure 4.10d,h). This remaining portion of FeR may still be bound to OC, therefore the OC-FeR pool may be underestimated in soils and freshwater sediments.

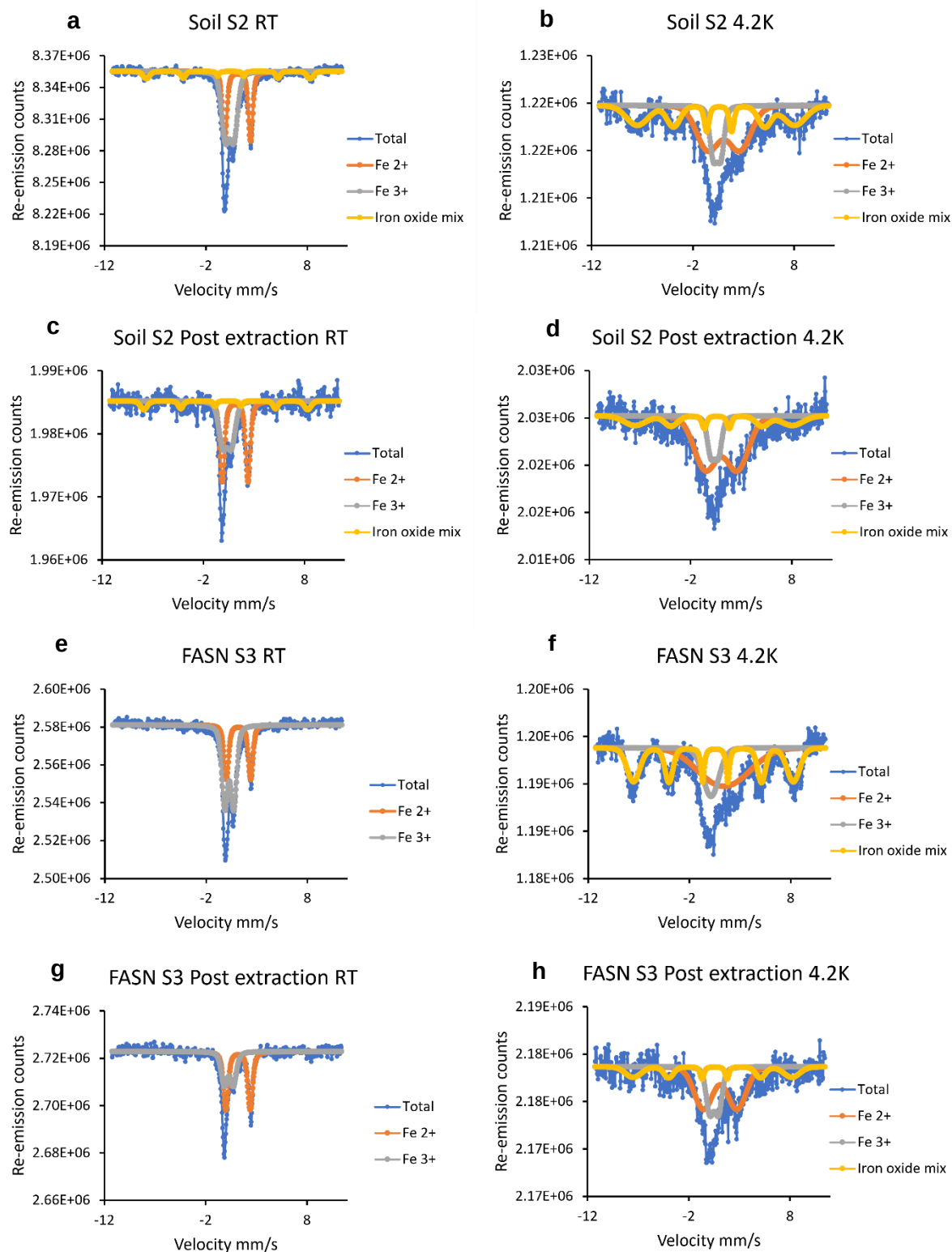


Figure 4.10: Mössbauer spectra examples for one soil and one freshwater sediment site (a) Soil site 2 pre-extraction at room temperature (b) soil site 2 pre-extraction at 4.2K (c) soil site 2 post-extraction at room temperature (d) soil site 2 post-extraction at 4.2K (e) Fasnacloch site 3 pre-extraction at room temperature (f) Fasnacloch site 3 pre-extraction at 4.2K (g) Fasnacloch site 3 post-extraction at room temperature (h) Fasnacloch site 3 post-extraction at 4.2K.

Low temperature measurements are available for winter samples; all Soil Sites (1-3) and one freshwater lochan Site (3). Room temperature Mössbauer measurements are available across all seasons to highlight pre and post extraction variation and any seasonal variation in magnetic ordering at room temperature (Table 4.6).

In Soil Site 1 (coniferous), we observe seasonal differences in Fe speciation (Table 4.6) covering magnetite, hematite and a non-descript fraction that could be superparamagnetic hematite or ferrihydrite (but the latter is difficult to identify at room temperature). In other Soil Sites, 2 and 3, hematite is the dominant form of Fe present at room temperature (295K) (Cornell and Schwertmann, 2003). This aligns with fjord sediments (Chapter 1), where hematite was also identified as the primary Fe mineral at room temperature.

At room temperature, we generally observe a reduction in Fe³⁺ phases post extraction (Table 4.6), these values include the iron oxide mix phase when present at room temperature.

Table 4.6: Results from room and low Mössbauer measurements for soils and Fasnacloch sediment samples.

			Pre	Post	Pre	Post			Pre	Post	
Site	Temperature	Oxidation state	δ	δ	Δ	Δ	H	H	%	%	Mineral
Summer S1	295 K	Fe 3+	0.366	0.366	0.847	0.847			33.9	29.3	
		Fe 2+	1.124	1.124	2.499	2.499			54.5	60.2	
		IOM	0.520	0.520	0.083	0.083	46.839	46.839	11.6	10.5	Magnetite
Winter S1	295 K	Fe 3+	0.358	0.358	0.906	0.906			53	38.5	
		Fe 2+	1.148	1.148	2.544	2.544			36.3	47.6	
		IOM	0.344	0.344	-0.118	-0.118	50.137	50.137	10.7	14	Hematite
Spring S1	295 K	Fe 3+	0.325	0.325	0.848	0.848			63.04	37.2	Superparamagnetic
		Fe 2+	1.162	1.162	2.470	2.470			36.96	62.8	
Summer S2	295 K	Fe 3+	0.365	0.365	0.762	0.762			60.6	39.9	
		Fe 2+	1.102	1.102	2.600	2.600			28.9	52.1	
		IOM	0.273	0.273	-0.111	-0.111	49.970	49.970	10.5	8	Hematite
Winter S2	295 K	Fe 3+	0.342	0.342	0.841	0.841			56.3	34.5	
		Fe 2+	1.154	1.152	2.464	2.464			31.6	53.2	
		IOM	0.286	0.286	-0.085	-0.085	50.096	50.096	12.1	12.2	Hematite

Spring S2	295 K	Fe 3+	0.387	0.387	0.789	0.789			49.7	35.1	
		Fe 2+	1.131	1.131	2.604	2.604			37.8	51.8	
		IOM	0.367	0.367	-0.090	-0.090	50.801	50.801	12.4	13.2	Hematite
Summer S3	295 K	Fe 3+	0.372	0.372	0.757	0.757			55.7	32.1	
		Fe 2+	1.106	1.106	2.619	2.619			32.9	50.5	
		IOM	0.313	0.313	-0.127	0.313	50.161	50.161	11.4	17.5	
Winter S3	295 K	Fe 3+	0.354	0.354	0.983	0.983			49.4	48	Hematite
		Fe 2+	1.154	1.154	2.585	2.585			39.7	35.5	
		IOM	0.329	0.329	0.106	-0.106	50.122	50.122	10.9	16.5	Hematite
Spring S3	295 K	Fe 3+	0.369	0.369	0.791	0.791			49	35.9	
		Fe 2+	1.113	1.113	2.587	2.587			33	50.1	
		IOM	0.424	0.424	-0.032	-0.032	49.665	49.665	17.9	14	Hematite
FASN 1	295 K	Fe 3+	0.365	0.365	0.793	0.793			49.9	35.5	Superparamagnetic
		Fe 2+	1.132	1.132	2.550	2.550			50.1	64.5	
FASN 2	295 K	Fe 3+	0.342	0.342	0.883	0.882			53.88	43.7	Superparamagnetic
		Fe 2+	1.150	1.150	2.558	2.558			46.12	56.3	
FASN 3	295 K	Fe 3+	0.300	0.300	0.893	0.893			64.5	40.3	Superparamagnetic
		Fe 2+	1.205	1.205	2.408	2.408			35.5	59.7	

Winter S1	4.2 K	Fe 3+	0.388	0.388	0.786	0.786			17	15.2	
		Fe 2+	1.063	1.063	3.258	3.258			44.6	62.8	
		IOM	0.448	0.448	-0.152	-0.152	48.164	48.164	38.4	22	Ferrihydrite
Winter S2	4.2 K	Fe 3+	0.497	0.497	2.428	2.428			45.7	46.8	
		Fe 2+	1.415	1.415	2.851	2.851			13.7	22.6	
		IOM	0.321	0.321	0.003	0.003	50.627	50.627	40.7	31	Ferrihydrite / akageneite
Winter S3	4.2 K	Fe 3+	0.330	0.226	2.374	1.840			45.4	46.1	
		Fe 2+	1.828	3.242	3.021	1.291			15.4	8.45	
		IOM	0.549	0.560	-0.199	-0.027	46.932	46.932	39.5	45.5	Ferrihydrite / Goethite
FASN 3	4.2 K	Fe 3+	0.521	0.521	0.900	0.900			16.8	23.9	
		Fe 2+	1.118	1.118	3.336	3.336			33.3	53	
		IOM	0.463	0.463	-0.098	-0.098	48.539	48.539	49.9	23.1	Ferrihydrite / akageneite

4.5.4.2 Fe 2+ changes from soil to sediment

There are subtle changes observed in Fe²⁺:Fe³⁺ ratios pre-extraction across seasons in soils and depths in sediment cores (Table 4.7) there is generally a lower Fe²⁺:Fe³⁺ ratio in soils, and a slightly higher ratio in sediments. This could be indicative of reduction as material moves downstream or indicates a change in Fe²⁺ mineralogy, but at different sediment core depths changes in Fe²⁺:Fe³⁺ may simply reflect variations in Fe²⁺ abundance and mineralogy at time of deposition due to variable environmental conditions over time.

The pre to post Fe²⁺:Fe³⁺ ratio generally increases in post extraction samples, reflecting the dissolution of Fe³⁺ during the dithionite extraction (Table 4.7). Mössbauer reveals that Fe²⁺ Δ parameters are relatively stable across seasons and Soil Sites, averaging 2.5, 2.56 and 2.6 across Soil Sites 1,2,3 respectively. In freshwater sediments this ranges from 2.4 - 2.56. Downstream in the sediments of Loch Creran, the Fe²⁺ Δ parameters range from 2.4 – 2.7. This may indicate that there is little change in Fe²⁺ mineralogy between sites. XRD was used to identify Fe²⁺ mineral phases but showed mainly Fe-free minerals quartz and feldspars derived from the rocky substrate (C.1.1 XRD measurements). The lack of distinct peaks in Fe²⁺ mineralogy may indicate that Fe²⁺ is in poorly crystalline clays.

Table 4.7: Room temperature Fe ratios and Fe²⁺ parameters across soil, freshwater and fjord sediment sites.

Sample			Fe2+ / Fe3+	Fe2+ / Fe3+	Fe2+ Δ	Fe2+ %	Fe2+ %
Soil / Core	Detail	Temperature	Pre	Post		Pre	Post
Site 1	Summer S1	295K	1.20	1.51	2.50	54.5	60.2
	Winter S1	295K	0.57	0.91	2.54	36.3	47.6
	Spring S1	295K	0.59	1.69	2.47	36.96	62.8
Average			0.78	1.37	2.5	42.59	56.87
Site 2	Summer S2	295K	0.41	1.09	2.60	28.9	52.1
	Winter S2	295K	0.46	1.14	2.46	31.6	53.2

	Spring S2	295K	0.61	1.07	2.60	37.8	51.8
Average			0.49	1.10	2.56	32.77	52.37
Site 3	Summer S3	295K	0.49	1.02	2.62	32.9	50.5
	Winter S3	295K	0.66	0.55	2.58	39.7	35.5
	Spring S3	295K	0.49	1.00	2.59	33	50.1
Average			0.55	0.86	2.6	35.20	45.37
Freshwater sediment	FASN 1	295K	0.48	0.81	2.55	50.1	64.5
	FASN 2	295K	0.39	0.67	2.56	46.12	56.3
	FASN 3	295K	0.55	1.48	2.41	35.5	59.7
UB1	2.5 cm	295K	0.69	0.96	2.59	40.7	49
UB1	10.5 cm	295K	0.75	0.94	2.62	43	48.4
UB1	24.5 cm	295K	0.83	0.84	2.69	45.5	45.7
UB2	7.5 cm	295K	0.63	0.90	2.58	38.6	47.4
UB2	15.5 cm	295K	0.75	0.85	2.60	42.96	45.9
UB2	32.5 cm	295K	0.53	0.35	2.63	34.8	25.8
LB1	0.5 cm	295K	0.65	0.98	2.62	39.39	49.4
LB1	20.5 cm	295K	0.76	0.77	2.61	43.03	43.6
LB1	40.5 cm	295K	0.85	0.85	2.42	46.07	45.9
LB2	4.5 cm	295K	0.74	0.95	2.58	42.5	48.6
LB2	12.5 cm	295K	0.72	0.94	2.41	41.9	48.4
LB2	18.5 cm	295K	0.67	0.73	2.60	40	42.1

4.5.4.3 Pre and post extraction $\delta^{13}\text{C}_{\text{org}}$

Isotopic values pre and post extraction vary between soil sites and seasons. All values have a standard deviation of 0.65 ‰ which means there's little distinction between values in close proximity (Figure 4.11). All soils and freshwater samples display more enriched $\delta^{13}\text{C}_{\text{org}}$ post extraction values post extraction (Figure 4.11). Considerable enrichment of $\delta^{13}\text{C}_{\text{org}}$ post

extraction indicates that isotopically depleted carbon has been removed during the extraction, but similar changes (to differing extents) can be observed in a majority of control samples. In summer (Figure 4.11a), winter (Figure 4.11b) and spring (Figure 4.11c) soils, Soil Site 2 shows the greatest alteration of the control samples (relative to the pre-extraction sample and Soil sites 1 and 3) while Soil Site 3 maintains the most distinct enrichment in pot extraction samples relative to the control. In Fasnacloich sediments, when error is considered, we only observe a distinct enrichment in $\delta^{13}\text{C}_{\text{org}}$ post extraction in Site 1, closest to the inflow.

Despite some differences in isotopic composition between the control and the post-extraction samples in some sites, it is evident that both the control and extracted sample become enriched as a result of the extraction process in many samples. Therefore, changes in $\delta^{13}\text{C}_{\text{org}}$ are not necessarily reflective of the original composition of the sample or what was bound to FeR but may actually reflect the isotopic fractionation that results from the method itself.

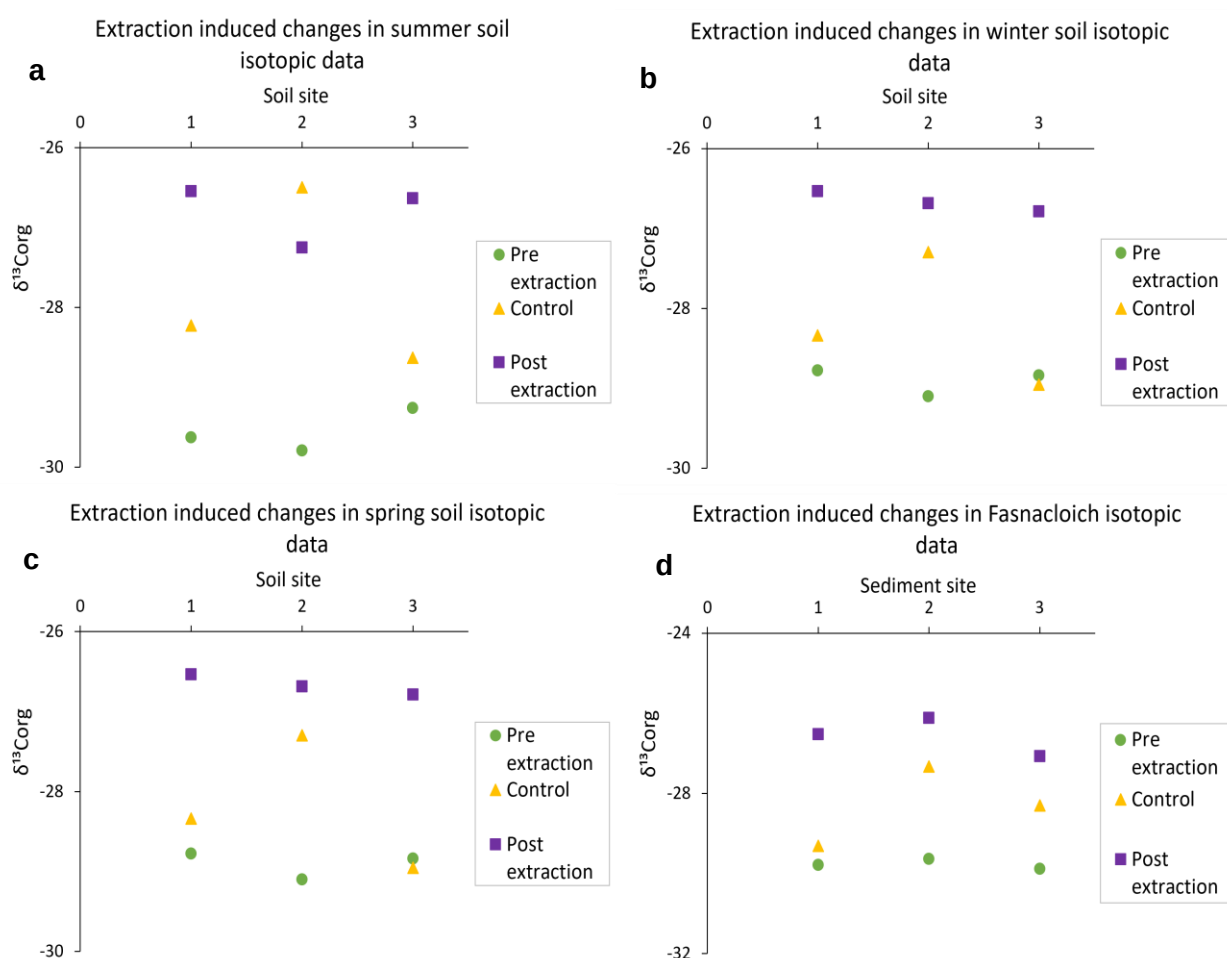


Figure 4.11: $\delta^{13}\text{C}_{\text{org}}$ pre and post extraction for (a) Summer soil sites 1-3 (b) Winter soil sites 1-3 (c) Spring soil sites 1-3 (d) Fasnacloich lochan sediments sites 1-3 (taken only in Spring). A standard deviation / error of 0.65 applies to all samples. Green circles represent pre-extraction samples, yellow triangles represent control samples and purple squares represent post-extraction samples.

4.5.4.4 Using OC:FeR molar ratios to determine binding mechanisms

To determine the dominant binding mechanism for OC-FeR complexes, OC (bound to FeR):FeR molar ratios were calculated (Figure 4.11). The main binding mechanisms for OC and FeR are sorption and co-precipitation (Kaiser and Guggenberger, 2000; Lalonde et al., 2012; Shields et al., 2016). An OC:FeR molar ratio <1 is indicative of sorption of organic matter onto FeR surfaces, and an OC:FeR molar ratio of 6-10 is representative of co-precipitation (Wagai and Mayer, 2007). The OC:FeR molar ratio is variable but all values are <2.2 . Winter samples maintain the lowest OC:FeR ratio in comparison to other seasons, and Soil Site 3 has the lowest OC:FeR ratio in comparison to other soil sites.

Sediment samples (presented in Chapter 1) (Figure 4.11) show that sorption is the dominant binding mechanism of sedimentary samples, as all sediments display OC:FeR ratios <1 . This

indicates that sorbed OC-FeR complexes are more likely to be successfully transported downstream than co-precipitated complexes, indicating that any co-precipitated samples in sediment are not likely to be suspended and transported due to changes in flow.

Table 4.8: OC:FeR molar ratios for seasonal soil samples and Fasnacloich sediments and fjord sediments.

Soil and lochan samples	OC:FeR Molar Ratio	Sediment samples	OC:FeR Molar Ratio
Summer Site 1	1.101	UB1 2.5	0.414
Winter Site 1	0.803	UB1 10.5	0.640
Spring Site 1	1.078	UB1 24.5	0.936
Summer Site 2	0.663	UB2 7.5	0.410
Winter Site 2	0.137	UB2 32.5	0.467
Spring Site 2	2.124	LB1 0.5	0.052
Summer Site 3	1.196	LB1 20.5	0.166
Winter Site 3	0.517	LB1 40.5	0.233
Spring Site 3	0.259	LB2 4.5	0.508
FASN 1	-0.772	LB2 12.5	0.234
FASN 2	1.336	LB2 18.5	0.666
FASN 3	0.579		

4.5.5 Influence of n-alkane signatures on OC-FeR association

We determined whether there were any significant correlations between the n-alkane abundance, chain length proportions and averages and OC-FeR binding and type of binding (OC:FeR ratios) in soils and freshwater sediments (Table 4.9, Table 4.10). There were no significant correlations between OC-FeR and n-alkane abundance, dominance of long-chain lengths or average chain lengths (Table 4.9).

Table 4.9: Pearson correlation coefficient values (R and P) for OC-FeR associations and different n-alkane variables

Soil sample	1	2	3	4
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	<u>OC:FeR % of TOC</u>	<u>Total n-alkanes C16-C35</u>	<u>Long chain n-alkanes C26 +</u>	<u>ACL</u>
Summer S1	74.59	11.03	82.61	29.04
Winter S1	29.09	8.4	73.81	28.62
Spring S1	53.49	9.07	84.22	29.69
Summer S2	20.62	4.68	89.96	29.06
Winter S2	4.45	10.04	65.5	28.19
Spring S2	24.74	13.11	93.44	29.61
Summer S3	51.72	4.03	76.14	28.51
Winter S3	52.62	6.44	61.13	27.83
Spring S3	8.83	10.17	75.11	28.66
R-Value		-0.147	0.06	0.133
P-Value		-0.707	0.878	0.733

However, two positive significant correlations were found between the OC:FeR and the dominance of long-chain lengths and average chain lengths (Table 4.10). This indicates that if there is any co-precipitation in soils, it is likely to occur with longer-chain n-alkanes, and as such a higher ACL also correlated positively with the OC:FeR molar ratio.

Table 4.10: Pearson correlation coefficient values (R and P) for OC:FeR molar ratio and different n-alkane variables

Soil sample	1	2	3	4
	<u>OC:FeR (binding mechanism)</u>	<u>Total n-alkanes C16-C35</u>	<u>Long chain n-alkanes C26 +</u>	<u>ACL</u>
Summer S1	1.1	11.03	82.61	29.04

Winter S1	0.8	8.4	73.81	28.62
Spring S1	1.08	9.07	84.22	29.69
Summer S2	0.66	4.68	89.96	29.06
Winter S2	0.14	10.04	65.5	28.19
Spring S2	2.12	13.11	93.44	29.61
Summer S3	1.2	4.03	76.14	28.51
Winter S3	0.52	6.44	61.13	27.83
Spring S3	0.26	10.17	75.11	28.66
R-Value		0.307	0.68	0.701
P-Value		0.422	0.05	0.035

There were no significant correlations between the amount of OC bound to FeR and n-alkane abundance, dominance of long-chain lengths or average chain lengths. However, two positive significant correlations were found between the OC:FeR and the dominance of long-chain lengths and average chain lengths. This indicates that if there is any co-precipitation in soils, it is likely to occur with longer-chain n-alkanes, and as such a higher ACL also correlated positively with the OC:FeR molar ratio.

4.6 Discussion

Many datasets exist for OC-FeR relationships in different environments (e.g. Faust et al., 2021; Lalonde et al., 2012; Shields et al., 2016; Zhao et al., 2018). However, few studies perform a transect from soil to sediment to show the distribution, changes and potential transport of OC-FeR compounds from source towards sea. As such our understanding of the origin of these compounds remains limited, with suggestions that complexes form at sediment-water interface, anoxic-oxic interface or that they might occur upstream (Barber et al., 2014; Faust et al., 2021; Lalonde et al., 2012). Results from this study have provided some insight into OC-FeR associations from soils to fjord sediments alongside changes in elemental

composition, mineralogy, and binding mechanisms to provide a better understanding of the binding location and transport of OC across the land-sea interface.

4.6.1 Variation of OC and Fe in soils and sediments

There is a general decrease in OC concentrations from soil samples to lower basin fjord sediments (Figure 4.2a, b, c). While elevation is not always thought to have a strong influence on OC concentrations (Bond et al., 2021), we find a significant relationship in soils and sediments to elevation and slope (Chapter 3: Table 3.11). Soil composition and properties are relatively location based; influenced by land use, environmental conditions and geology (Barré et al., 2017) while sediment composition is more heavily influenced by transport of material from upstream and surrounding catchments (Müller et al., 1998; Nadeu et al., 2015). In contrast to decreasing OC concentrations from source towards fjord, total Fe concentrations (calculated by ICP analysis) increase from soil to fjord sediments (Figure 4.2d,e,f), before decreasing at LB2, highlighting again that abundance of total Fe does not result in more OC stored.

Bulk molar OC:TN ratios can be used as predictors of soil properties and of land cover, litter inputs and organic matter decomposition, but can be influenced by environmental conditions (Blanco et al., 2023) and specific tree species (Cools et al., 2014). Some have found C:N ratios to correlate with forest cover, where n-fixing deciduous species may show a lower C:N, and evergreen species produce a higher C:N ratio (Cools et al., 2014). Sitka spruce, the dominant coniferous species in the Loch Creran catchment, can result in an N deficiency in soils (Taylor and Tabbush, 1990), which may account for the highest OC:TN ratios in the Loch Creran catchment being at Soil Site 1 (dominated by coniferous forest) with a ratio of ~25 (Figure 4.3). Lower OC:TN ratios are observed at Soil Sites 2 and 3 (~16-17) that have more deciduous and grass dominated land cover (Figure 4.3, Figure 4.1). This also aligns with OC:TN values for coniferous material in this study that are higher (~61) than deciduous material (~35), and in comparison to (deciduous) litterfall, spruce has been observed to have higher C:N values in other studies (e.g. Vesterdal et al., 2008).

Freshwater sediments have a lower average molar OC:TN of ~14 and this ratio is variable downstream from UB1-LB2 but moves from an average of ~17 to ~8 between the two extremes (UB1 and LB2). In sediments, this ratio can be indicative of marine and terrestrial inputs, with higher ratios from terrestrial sources (Chapter 1) (Bianchi et al., 2002; Smeaton and Austin, 2017). OC:TN ratios have frequently been used in fjord and marine sediments to identify the terrestrial / marine origin of OC (e.g. Bianchi et al., 2002; Perdue and Koprivnjak,

2007; Thornton and McManus, 1994), and as such fjord sediment cores show a decrease in OC:TN between UB1 and LB2 (Figure 4.3), but we did not find that it was possible to distinguish more specific sources from this proxy.

Bulk isotopic $\delta^{13}\text{C}_{\text{org}}$ signatures show soils and freshwater sediments to have significantly more depleted values than fjord sediments. Freshwater sediments have a terrestrial signal that is more similar to soils than fjord sediments (Figure 4.7) suggesting that regular flushing with marine waters in the fjord greatly enriches $\delta^{13}\text{C}_{\text{org}}$ values. Freshwater plants that we know to be present in Fasnacloich lochan (Chapter 2) do not have as large an influence on $\delta^{13}\text{C}_{\text{org}}$ enrichment as marine material.

We do not observe a significant correlation between the amount of FeR or total Fe on total OC, or OC-FeR complexes in soils or lochan sediments (Table 4.5), which is in agreement with other studies (Faust et al., 2021, 2020; Sirois et al., 2018) and fjord sediment results from Chapter 1.

4.6.2 OC-FeR associations in soils and freshwater sediments

The mean concentration of OC-FeR in catchment soils is 35.57% and ~40.54% in lochan sediments (Figure 4.8, Figure 4.9). This is variable between sites, with the coniferous Soil Site 1 having the highest OC-FeR abundance at 52.39 ± 22.77 %, and the deciduous Soil Site 2 having the lowest OC-FeR abundance at $16.61\% \pm 10.72$ (Table 4.3). Neither abundance of total OC or FeR abundance (Table 4.8c,d) follows the same pattern as OC-FeR (Table 4.8a), indicating that the factors controlling FeR and OC-FeR may be different. This is confirmed through R and P values (Table 4.5) that show weak and non-significant correlations between OC-FeR and total OC / Fe / FeR. Some studies suggest that there is a dominance of OC-mineral associations observed in soils with lower OC, while there is a dominance of plant residues in high-OC soils (Giannetta et al., 2022), but there is no indication of this from OC (Table 4.5) or n-alkane (Table 4.9) data from this study.

It has been established that organo-mineral associations can result in long-term soil OC protection (e.g. Hemingway et al., 2019; Kopittke et al., 2020; Schrumpf et al., 2013). There is limited evidence to suggest that differences in OC-FeR are driven by vegetation type, however there is evidence that soil pH can influence the concentrations of OC-FeR associations, and a lower pH of 3.5 - 4.2 may yield increased OC-FeR in soils (Ye et al., 2022). In this study the topsoil pH median across this catchment is 3.8 for Soil Sites 1 and 2, and pH 4 for downstream Soil Site 3. There is increased OC-FeR at Site 3 in comparison to Site 2 regardless of the higher pH therefore it may not be the dominant influence in this location as suggested by Ye

et al.,(2022). This is hard to establish without site and season specific soil pH values, so collecting this data would be beneficial in further land-sea studies. The difference in soil type from peaty to mineral podzol between upstream Soil Sites (1 and 2) and Soil Site 3 (Bibby et al., 1982) may have an influence on the different pH values. The extent to which minerals can bind to OC can be influenced by different factors such as mineralogy and the chemical properties of the soil (Han et al., 2016) so pH and the oxygen conditions within soils will play a role in OC binding capacity.

Coniferous sites generally have more acidic forest floor pH than deciduous sites and can have higher organic matter content. However, deciduous sites can more effectively transport forest floor OM into the topsoil and can have more acidic subsoils (Achilles et al., 2021, Burgess-conforti et al., 2019). In theory, more acidic soil pH could influence the Fe speciation and Fe³⁺ abundance and therefore FeR content of soils, but there is no evidence of this within sites because Soil Sites 1 and 2 (coniferous and deciduous cover respectively) have a similar average FeR content of 14.46 % and 14.31 % across seasons (Figure 4.8b). Regardless of the high FeR content, increased OM turnover and OC accumulation in the deciduous subsoils (Achilles et al., 2021, Burgess-conforti et al., 2019), Soil Site 2 has the lowest OC-FeR associations of any site. The absence of a significant correlation between FeR and OC-FeR (R value = 0.029, P value = 0.941) (Table 4.5) has been observed in other forest soils (Zhao et al., 2016) and sediment (Faust et al., 2021, 2020) studies suggesting that it is uncommon for abundance of FeR, or total Fe, to govern the type or quantity of OC-FeR associations in any a range of environments.

Across all soil sites there is an average of 35.6 % $\pm$ 12.8 % of OC-FeR in this mixed forest catchment, and this is well aligned with other forest soil estimates of 37.8 % OC-FeR (Zhao et al., 2016), suggesting that OC-FeR values in forest soils can be similar across different regions and environments. In comparison to other land uses / cover, i.e. grasslands at 13.6 - 15.8 % (Fang et al., 2018; Ye et al., 2022), peatlands up to 24 % (Huang et al., 2023), or soils in permafrost regions up to 14.8 % (Patzner et al., 2020), forested soils (across different latitudes) appear to have a higher concentration of OC-FeR. In this catchment, the amount of OC-FeR complexation increase in freshwater lochan sediments that contain an average of 41 % OC-FeR, and decreases downstream as fjord sediments contain an average of 16 % OC-FeR (Chapter 1). In comparison to marine sediments that contain on average 20 % OC-FeR (Lalonde et al., 2012), our research suggests that freshwater sediments and soils within a forested catchment contain higher OC-FeR associations than fjord / marine sediments.

Lochan sediments appear to act as an effective store of OC, with comparable OC concentrations to some of the catchment soil samples (Figure 4.2) around ~41 % of which is

bound to FeR (Table 4.3). Without lochan sediment cores, it is difficult to ascertain whether this lochan acts as a short-term or long-term carbon store, but it is evident that OC is stored in the lochan sediments high OC-FeR values within the lochan suggest that it filters out some OC-FeR complexes from the soil and catchment before they reach the fjord.

4.6.3 Binding mechanisms between OC-FeR

OC-FeR binding is mutually stabilizing as many iron oxides are not thermodynamically stable and can be reduced to soluble Fe(II) when free (Barber et al., 2017). It is possible for OC to remain sorbed to mineral surfaces throughout different oxygenation regimes and over long timescales making it one of the best methods of long-term OC preservation (Arnarson and Keil, 2007). The type of bond between OC and FeR can provide insights into how and where OC-mineral binding occurs and flocculation can be induced or deterred by the type of bond, coating extent and modification of surface charges between the two elements (Walch et al., 2022). OC binds to FeR through two main mechanisms: sorption and co-precipitation (e.g. Lalonde et al., 2012; Shields et al., 2016). OC:FeR molar ratios are between 0 - 2.1 for this study (Table 4.8a), and OC:FeR molar ratios are <1 for all extracted sediment samples (Table 4.8b). We thus show that sorption plays a dominant role in OC-FeR binding throughout this catchment, and across the land-sea interface. There may be small contributions from co-precipitation in soil and freshwater sediment samples (some OC:FeR value >1) that vary seasonally (winter ratios consistently remain <1).

Seasonal changes in OC:FeR binding mechanisms may be influenced by changes in temperature, precipitation, growth season or soil pH. During growing seasons (Spring, Summer) there is likely a greater influx of OC due to increased vegetation abundance. Some studies have found that higher pH favours sorption (Zhao et al., 2016), which may suggest that seasonal variations could be driven by changes in precipitation and run off that could influence the amount of H^+ exchange within the soils.

In Fasnacloch sediments, the variation in OC:FeR (S2 1.336 – S3 0.579) (Table 4.8) indicates that there can be differences in OC:FeR binding mechanisms even within small water bodies / areas. Lower OC:FeR values in lochan Site 3 coincide with highest total OC concentrations and a higher amount of OC-FeR complexation suggesting that sorption plays a larger role in OC-FeR binding towards the outflow to the fjord. The preference and dominance of sorption over co-precipitation is also found in the fjord sediments (Table 4.8), suggesting that any upstream coprecipitated complexes are not re-suspended or transported to fjord sediments.

This may also be influenced by particle size, as larger aggregates are more likely to settle out due to their weight instead of being transported.

There is a weak but positive correlation between the amount of OC-FeR and OC:FeR molar ratios ($R = 0.364$, $P = 0.335$), indicating there are slightly more OC-FeR associations where OC:FeR ratios are higher (around 1), but since this is not a significant correlation and OC:FeR values remain <2 across soils and sediments, it is unlikely that there is any true relationship in this catchment.

Variations observed in OC:FeR values show no clear pattern with Soil Site / dominant vegetation cover, confirmed by the absence of significant correlations between the abundance of long-chain n-alkanes, total n-alkanes or n-alkane average chain lengths (Table 4.9) which indicates that land cover / source vegetation does not control OC-FeR associations or binding mechanisms. OC:FeR molar ratios can be considered as guidance for binding mechanisms, but may not accurately represent the binding occurring in the soils and sediments as not all FeR is bound to OC, therefore this ratio will be influenced by 'free' FeR concentrations that may skew results.

When trying to determine specific sources of OC bound to FeR, we evaluated the isotopic composition of samples before and after extraction. Considerable alteration to the $\delta^{13}\text{C}_{\text{org}}$ isotopic signatures post extraction and for control samples (Figure 4.11) mean that it is not possible to assess whether enrichment and depletion of $^{13}\text{C}_{\text{org}}$ is indicative of isotopic fractionation as a result of preferential binding, or whether it is due to the alteration from the method itself. Therefore, these bulk isotopic changes from dithionite extraction cannot provide information on the origin of the OC bound directly to FeR.

4.6.4 The transport of C and Fe from source towards sea

When we consider the transport of OC and Fe from soils to sediments, the primary method of transport is through water. A majority of the Fe transported downstream in rivers is in particulate form, opposed to dissolved (Figure 4.5, Table 4.2), so may already have formed aggregates and compounds with other minerals and organic matter.

Some seasonal variation in DOC concentrations is observed, with weakest DOC signals observed in Winter (~ 1 mg/L), and highest in Autumn (~ 4 to 8 mg/L). This is likely to be influenced by changes in precipitation and runoff within the catchment and bacterial or chemical alteration (Bauer et al., 2013b). Spring-summer-winter values are within the ranges observed in mixed land use catchments, but autumn concentrations (>4 mg/L) exceed the

range others observed (Ritson et al., 2019) however, remain lower than concentrations observed in peaty forested areas where long-term DOC measurements averaged between ~9 – 14 mg/L (Shah et al., 2021). Increased DOC concentrations have been observed in forested catchments, particularly in areas of high upland conifer afforestation (Williamson et al., 2021) but generally effective forest management can help to mitigate increases in DOC from land to rivers (Shah et al., 2021). DOC concentrations in Fasnacloich varied between 4.1 - 4.5 mg/L and were collected in Spring, indicating that this lochan not only receives inputs from the River Creran inflow, as River Site 3 in Spring only contained ~2.6 mg/L, but also from immediate surroundings and in situ vegetation.

The transport of particulate material downstream depends on whether there is sufficient stream power, and material can be deposited and stored in stream sediments or lost to the atmosphere en-route (Worrall et al., 2017). Dissolved OC is present in higher concentrations than particulate C, which is the opposite to Fe (Figure 4.5, Table 4.2). Particulate C concentrations appear to be relatively consistent across river sites (Table 4.2) (with larger seasonal variations (Figure 4.6) indicating that seasonal increases in PC that could be influenced by increased soil erosion (Ciais et al., 2008). In this catchment the greatest PC concentrations are observed in summer and autumn which have opposing precipitation with the region averaging 91 mm rain in summer and 317 mm rain in autumn (Chapter 2, (Hollis et al., 2019)), yet PC remains higher in summer, indicating that temperature (aridity) (14 degrees in summer and 11 degrees in autumn) could influence the increase of PC in rivers, or other environmental conditions such as wind, growing season, litterfall, may play strong roles in PC concentration. While land use can influence and increase movement of PC (García-martín et al., 2023) the differences in PC do not appear to be site specific, therefore there's no indication of any relationship between land cover and PC outputs.

4.6.4.1 Can dissolved and particulate measurements provide insights into sedimentary C and Fe patterns?

Fe minerals are known to precipitate with, or attach to organic matter (sorption), which alongside other compounds can increase flocculation (Deng et al., 2022; Forsgren et al., 1996). Flocculation generally occurs where there is a change in salinity, and through chemical, biological and physical factors can exert stress on compounds resulting in aggregation or decay of suspended materials (Deng et al., 2022). Changes in salinity gradients are known to have an effect on Fe minerals (e.g. Herzog and Kritzberg, 2017; Linke and Gislason, 2018). A useful indication of the role of flocculation from fresh – brackish waters in this catchment would be the dissolved and particulate concentrations and ratios of OC and Fe in water and how these change from fresh to saltier water (Khoo et al., 2022). While riverine and lochan waters were sampled for this study, fjord waters were not, but they would provide a useful insight into

the role of flocculation in OC-FeR transport. Despite this, studies in other locations can provide reference to the ability of OC-FeR complexes to endure salinity changes in estuarine environments and be transported from upstream to downstream environments (Herzog et al., 2020; Herzog and Kritzberg, 2017).

We can use water and sediment samples from Fasnacloich lochan as an example of catchment processes at the land-sea interface between riverine inflow and marine influence (Figure 4.12). Fasnacloich has one main inflow (the River Creran) and one main outflow (to the upper basin to Loch Creran) and its contents are influenced by upstream riverine inputs (Chapter 2). Between lochan sampling Sites 1-3 there is an increase in PC and a decrease in DOC (Figure 4.12a,c) and at the same time there is an increase in both sedimentary OC and sedimentary OC-FeR complexes. Despite there being several DOC removal pathways - bacterial, atmospheric, physical – from this data we suggest that a portion of the increased sedimentary OC and OC-FeR is a result of DOC precipitation (some may also be lost to the atmosphere) and PC (which may or may not be bound to FeR) being deposited in sediments. In lochan Site 2 OC:FeR ratios are >1 indicating an increase in co-precipitation (Table 4.8) which coincides with an increase in sedimentary OC and OC-FeR of ~35 %.

A decrease in PFe at lochan Site 2 (793 – 401 $\mu\text{g/L}$) coincides with an increase in DFe (84 – 114 $\mu\text{g/L}$) which suggests that a portion of the PFe may have been reduced to Fe^{2+} , but this does not account for the total PFe loss. This PFe loss also coincides with an increase in PC, a decrease in DOC and an increase in OC-FeR which indicates that some of the PFe lost from the water column may have contributed to OC-FeR storage in lochan sediments. At lochan Site 3 there PFe, sedimentary Fe, sedimentary FeR and OC-FeR have all increased suggesting that there is a high rate of Fe input that is greater than the rate of deposition (Figure 4.12a, b, d).

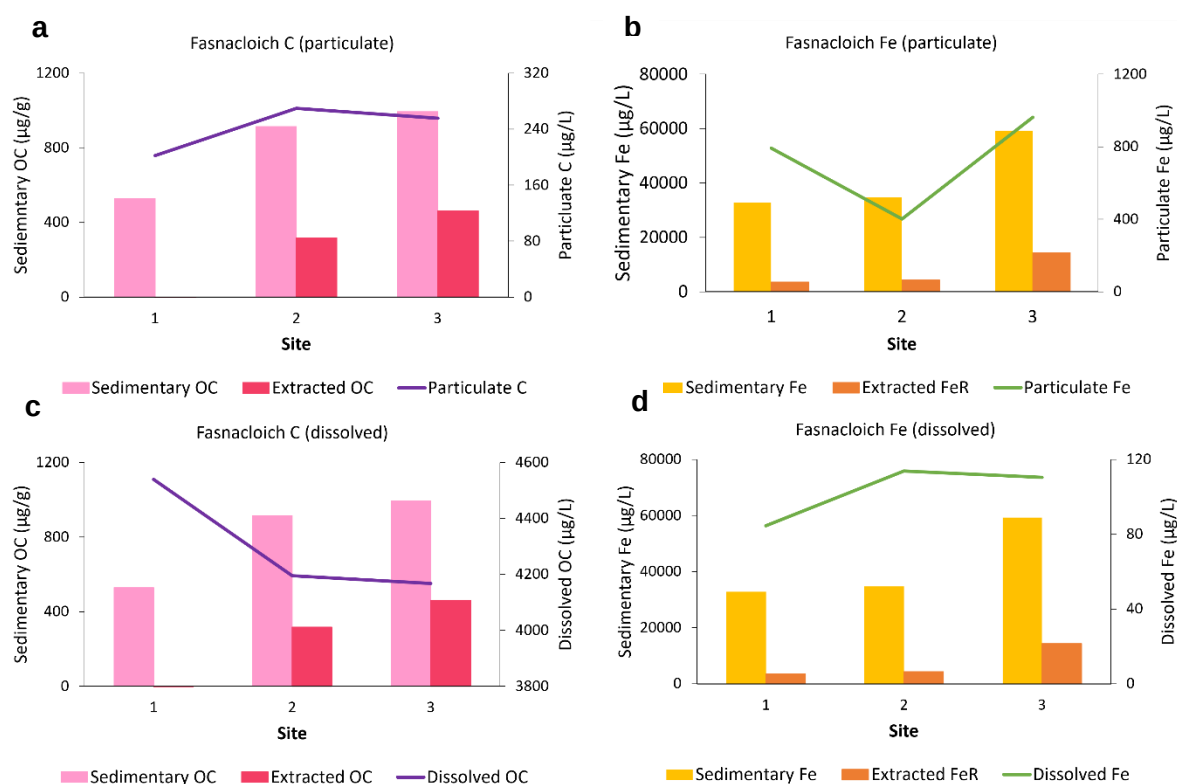


Figure 4.12: Sedimentary OC and Fe concentrations across Fasnacloich lochan sites plotted alongside (a) Particulate carbon (b) Particulate Fe (c) Dissolved OC (d) Dissolved Fe.

Due to limited particulate material, it was not possible to perform dithionite extractions on the suspended particulate fraction, which would have been a useful addition to this, and any other source-towards-sea dataset to inform the mechanisms supporting carbon transport and storage. In this catchment, Fe appears to be primarily transported in particulate form (Figure 4.4, Table 4.2), therefore the suspended concentrations of PFe likely play an important role in the transport of OC-FeR complexes downstream.

4.6.5 Insights into the journey of OC from Fe mineralogy

The speciation of Fe is dictated by environmental factors that can vary between seasons, locations (Dang et al., 2015; Öztürk and Bizsel, 2003) and changes in salinity gradients (Herzog et al., 2019; Herzog and Kritzberg, 2017; Ussher et al., 2007). Few studies utilise Mössbauer spectroscopy to analyse Fe speciation, especially across a gradient of source-towards-sea to assess the lateral transformations Fe may undergo, as presented here. Mössbauer data provided qualitative information on Fe speciation pre and post extraction while ICP analysis provided information on the quantitative changes in Fe content. Speciation of Fe was measured at room temperature (295 K) and low temperature (4.2 K) and each enable different Fe species to be identified (Figure 4.13).

Room temperature – 295K

Soil Site 1 – upland coniferous forest • Magnetite • Hematite	Soil Site 2 – deciduous forest • Hematite	Soil Site 3 – mixed deciduous use • Hematite	Fasnacloich • Superparamagnetic fractions • Ferrihydrite	UB1 • Hematite • Superparamagnetic fractions	UB2 • Hematite • Superparamagnetic fractions	LB1 • Hematite • Superparamagnetic fractions	LB2 • Hematite
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Low temperature – 4.2K

Soil Site 1 – upland coniferous forest • Ferrihydrite • Akaganeite	Soil Site 2 – deciduous forest • Ferrihydrite • Goethite	Soil Site 3 – mixed deciduous use • Ferrihydrite	Fasnacloich • Ferrihydrite • Akaganeite	UB1 • Ferrihydrite	UB2 • Ferrihydrite • Lepidocrocite	LB1 • Ferrihydrite	LB2 • Ferrihydrite • Goethite
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Figure 4.13: Mössbauer speciation of soil and lochan samples (data from this study) and fjord sediment samples (Chapter 1) (a) 295 K (b) 4.2 K.

The speciation of Fe^{3+} fraction is most varied in Soil Site 1, where we observe magnetite, hematite, ferrihydrite and potentially akaganeite across different seasons and temperatures (though akaganeite formation is less likely due to the conditions required for formation). The low temperature Mössbauer measurements enabled the identification of ferrihydrite due to magnetic ordering, and hematite was identified at room temperature (Cornell and Schwertmann, 2003). Ferrihydrite and hematite are present throughout all soil and lochan sample sites and are common in forest soils (Skerlep et al., 2022) but Fe species do not tend to be associated with specific land cover.

The similarities between upstream and downstream Fe^{3+} speciation (Figure 4.13), the dominance of sorption (Table 4.8) between soils and sediments, and the abundance of PFe (Table 4.2), suggest that a portion of the OC-FeR complexes in lochan and fjord sediments have been transported from upstream soil environments, and have been able to withstand the changing salinity downstream as observed in other studies (e.g. Muller, 2018; Zhao et al. 2023). The lack of co-precipitation in both soils and sediments suggests that dissolution and

co-precipitation before and after the salinity boundary play only a small role in the OC-FeR associations in this environment. OC and FeR may undergo dissolution, and reprecipitate before sorbing to one another post-salinity boundary, but it might be expected that this would cause changes in speciation of Fe from Ferrihydrite to a more stable form.

It was not possible to obtain detailed mineralogical information on the particulate / suspended sediment fraction in the rivers and lochan due to lack of particulate material. However, others have found ferrihydrite to dominate the reactive fraction of particulate Fe in rivers (e.g. Hirst et al., 2017) and have found quartz and phyllosilicates to dominate the suspended particulate matter fraction in rivers in different environments (Walch et al., 2022) which aligns with the mineral composition of our samples (C.1.1 XRD measurements).

4.6.5.1 Wider organo-mineral binding

We find the extraction method used (Lalonde et al., 2012) is not capable of dissolving all FeR from soils (this study) and sediments (Chapter 1) in agreement with previous research (e.g. Hepburn et al., 2020). Some suggest that this method could be capable of extracting more than just FeR, and that a portion of the OC thought to be bound to FeR could be bound to Al minerals (Hall and Thompson, 2022). Studies have found that OC can be bound to, and preserved by, both Al and Fe bearing minerals and complexes (e.g. Fang et al., 2018; Kramer and Chadwick, 2018; Tipping et al., 2002). To test this within our samples we monitored the amount of Al pre and post extraction.

We found that on average ~3 % Al was dissolved (corrected to control values) during dithionite extractions (Table 4.4), and that values have a significant correlation with the amount of FeR dissolved (Table 4.5). This correlation suggest that the Al has been released from dissolved FeR minerals (i.e. substituted for Fe in these minerals) and does not represent a separate pool of Al minerals OC binds to.

To speculate on the remaining OC stored in soils and sediments, it is likely that a portion of OC is associated with clay minerals (e.g. Han et al., 2016; Hedges and Keil, 1995; Sarkar et al., 2018), Fe can also be present in clays (Carroll, 1958) and FeR can play a role in the adhesion of OC to clay depending on conditions (Lalonde et al., 2012; Saidy et al., 2013).

When biomarker signatures were examined in Chapter 2, we found common n-alkane and pine signatures between soils and sediments, and signatures were relatively well-preserved with depth in sediment cores. While biomarker signatures can be altered across the aquatic continuum (Ward et al., 2017), these signatures may be preserved through both organo-

mineral complexes and incorporation into clays (C.1.1 XRD measurements). It has also been reported that terrestrially derived OC with high lignin content may have a stronger bond with Fe and Al oxyhydroxides due to the abundance of aromatic carbons that can complex with FeR (Kaiser and Guggenberger, 2000). This would support the results showing that there's a greater abundance of OC-FeR complexes in forest soils in this study, and that of (Zhao et al., 2016), in comparison to other land uses that may have less woody / lignin material.

To further explore the source-to-sea movement of OC-FeR complexes, a robust investigation of the PFe in rivers and freshwater bodies connected to fjord and marine environments would be beneficial. Evaluating the speciation and molecular composition of suspended particulate material can be difficult due to sample quantities and in some cases particle sizes, but synchrotron measurements would enable more detailed Fe information to be obtained for these samples as per (Schröder et al., 2016).

4.7 Conclusions

OC-FeR binding is higher in soils than in sediments within this forested catchment, with an average of ~37 % OC-FeR in soils and 16 % OC-FeR in fjord sediments within the same catchment. Forest soil values are similar to those found in other forested environments (Zhao et al., 2016) and higher than soils with different land cover such as grasslands 13.6 - 15.8 % (Fang et al., 2018; Ye et al., 2022), peatlands up to 24 % (Huang et al., 2023), or soils in permafrost regions up to 14.8 % (Patzner et al., 2020).

Data reveals that Fe is transported through freshwater sites primarily in particulate form and that ferrihydrite is the common dominant Fe species in soils, freshwater and fjord sediments indicating that some OC-FeR complexes may travel from source (surrounding terrestrial environments) to fjord sediments without extensive reworking. To account for the decrease in OC-FeR complexation found in fjord sediments in comparison to soils and freshwater sediments, we suggest that a portion of the OC-FeR complexes released from soils are buried in the freshwater fjord sediments, and a portion of the complexes that are transported downstream may be flocculated out at the salinity boundary. Sorption is the common binding mechanism throughout the catchment, indicating that it is capable of withstanding a certain amount of chemical change across the land-sea interface, as others have found (e.g. Krachler et al., 2015; Muller, 2018).

OC-FeR complexes, show no significant correlation to concentrations of total OC, Fe or FeR or Fe mineralogy. As such, more work has to be done to better characterise the main controls on OC-FeR complexation, particulate suspended material and the influence of seasonal

variables on the concentration of OC-FeR, total OC, and total FeR across the land – sea interface. While we observe a difference in OC-FeR concentrations between the coniferous and deciduous sites within this study, a more extensive soil sampling study would have to be undertaken to fully establish the variables that influence this. We conclude that FeR plays an important role throughout this catchment, and in the transport and storage of OC from source-towards-sea.

Chapter 5 Discussion and Conclusions

5.1 Summary and Key Results

This project set out to enhance our understanding of the mechanisms controlling organic carbon (OC) storage in fjord environments and to determine whether the range of biogeochemical methods selected could characterise the journey of carbon across the land-sea interface from forested catchments to fjord sediments. Fjords exist at the interface between land and sea and play a crucial role in the global carbon cycle through the uptake of CO₂ and the preservation of OC (Bauer et al., 2013a; Bianchi et al., 2020). Understanding their role in preservation of OC is of particular importance in Scotland's west coast which is home to at least 111 fjords (Edwards and Sharples, 1986). Despite multiple studies highlighting the efficiency of fjords in storing OC (Bauer et al., 2013b; Bianchi, 2011; Cui et al., 2022a; Craig Smeaton et al., 2021; Smith et al., 2015) and investigations of the organic carbon – reactive iron (OC-FeR) dynamics in sediments (Faust et al., 2021, 2020; Lalonde et al., 2012; Shields et al., 2016; Sirois et al., 2018), few explore OC-FeR relationships across the land-sea interface (Jilbert et al., 2018). In this thesis, Loch Creran on the west coast of Scotland is used to investigate movement of terrestrial OC from source to Fjord and the interactions between OC and iron (Fe) during this transition. Loch Creran is representative of fjords 'group 1', i.e. fjords that have had deeply glaciated basins and highly restrictive submarine geomorphology (creating basins) as calculated by Smeaton et al., (2017). This is the most common fjord type on the west coast of Scotland and is present in other temperate regions therefore making it an ideal study location.

Understanding the source-to-sea transport of OC from vegetation and soils to fjord sediments has been explored through all three data chapters of this thesis, and in doing so the three main objectives of this project have been achieved:

1. Determine how much OC in Loch Creran is bound to reactive iron and the broad origin of this material (Chapter 2).
2. Explore the role of catchment forest cover on the origin, transport and storage of OC in freshwater and fjord sediments (Chapter 3).
3. Investigate OC-FeR associations in catchment soils and contribute to a better understanding of where sedimentary complexes come from along a soil to freshwater sediment to fjord sediment transect (Chapter 4).

Chapter 2, the first study of its kind for Scotland's fjords, identified ~16% of OC was complexed with FeR in Loch Creran. OC-FeR complexation was greater in the upper basin in comparison to the lower basins. Chapter 2 highlights that mineral binding was spatially and temporally variable within surface sediments, which generally under-represent the amount of OC-FeR complexation buried at depth. Sorption is the preferential binding mechanism. There was a

decrease in FeR with depth which was often accompanied by an increase in OC-FeR associations highlighting that OC-FeR complexes may be preserved over unbound FeR and act as an important mechanism for carbon storage and FeR preservation. Ferrihydrite was identified as the dominant species of FeR using Mössbauer Spectroscopy and this remained the case throughout the sediment cores. Ferrihydrite is naturally metastable when it is not attached to OC, highlighting the stabilising effect of the OC-FeR associations on Fe. Results confirmed that dithionite extractions do not completely dissolve all FeR within the sediments suggesting that the role of FeR in OC preservation is underestimated when using this extraction technique. Isotopic signatures and model data show that a large portion of the OC stored within these sediments (43-73 %) is of terrestrial origin, indicating that the surrounding land has a large influence on OC input, and that some of the OC-FeR associations may have occurred before the sediment-water interface and were transported from upstream terrestrial environments.

Chapter 3 analysed bulk sediment used in Chapter 2 for biomarkers to better understand the terrestrial contributions to the sediments. Organic carbon (^{13}C) and nitrogen (^{15}N) isotopes were used to broadly identify terrestrial and marine inputs in Chapter 2, while n-alkanes and biomarker specific carbon isotopes used in Chapter 3 were able to distinguish differences in vegetation signatures. A difference in n-alkane specific $\delta^{13}\text{C}$ signatures between coniferous and deciduous material was observed for vegetation samples but was not visible in fjord sediments. Pine resin (methyl dehydroabietate) proved to be an effective coniferous marker as it was only present in coniferous soils and vegetation samples and could be seen in freshwater and fjord sediments. I therefore recommend that, in addition to n-alkanes, different resin markers be utilised where there's associations with specific plant groups / species when tracing OC sources. The presence of both n-alkanes and methyl dehydroabietate downcore in fjord sediments show that these compounds (and coniferous and deciduous material) have been effectively transported to sediments through riverine inflow and catchment run off and preserved over long periods of time.

Chapter 4 introduces soil and freshwater sediment OC-FeR data to provide a transect of mineral bound OC from land-towards-sea. I find soil in this mixed catchment to be consistent with other forested catchments at ~37 % OC-FeR and higher than other land uses (grasslands, peatlands). The primary binding mechanism in soils and freshwater sediments is sorption, as found in Chapter 2 for fjord sediments. In the Loch Creran catchment ferrihydrite was the dominant Fe species in soils, freshwater and fjord sediments. It is likely a portion of the OC-FeR in fjord sediments is directly transported from catchment soils through rivers and run-off. Binding mechanisms and iron speciation remain consistent across the transect and there are

relatively high particulate Fe concentrations transported downstream, supporting the notion that Fe may be complexed to organic matter before or within the rivers in this catchment.

5.2 Discussion

The main hurdle to a greater understanding of the transport and storage of OC across the land-sea interface is fragmented research disciplines and associated datasets. Currently, most disciplines operate in silos where research and management are 'terrestrial', 'freshwater', 'coastal' or 'marine' and few act across these boundaries. These silos exist across sectors and are well demonstrated when we consider the current designation and management of coastal / marine protected areas. The desired aquatic environment is given protected status with restriction for certain activities put in place, but there is little consideration for the land that surrounds it and flows into it. Water flows across systems connecting environments and habitats and carrying material (natural and anthropogenic) between them. In comparison to the large bodies of work that assess terrestrial (e.g. Wiesmeier., 2012, Andivia et al., 2016, Barré et al., 2017, Bradley et al., 2005, Chaopricha., 2014), coastal (e.g. Bauer et al., 2013; Bianchi et al., 2020; Smeaton et al., 2021, 2017; Smith et al., 2015) and marine (e.g. Burdige, 2007; Friedlingstein et al., 2023, 2019; LaRowe et al., 2020) OC, few studies assess the lateral movement of OC from source towards sea. A majority of studies focus on carbon stocks in soils and/or sedimentary environments but do not explore the journey of carbon—from one to the other. Often, the studies that quantify and characterise carbon do not necessarily investigate the mechanisms behind its transport and preservation.

A large proportion of organo-mineral binding research is conducted on surficial sediment samples (e.g. Lalonde et al., 2012; Wang et al., 2018; Zhao et al., 2018), prioritising spatial resolution over temporal resolution, which means that fewer studies identify the longevity of OC-FeR relationships and how they help to preserve OC with depth (and therefore generally with time). Using sediment cores, we explored the variation of OC-FeR associations with depth in a mid-latitude fjord to determine whether this relationship can withstand physical and chemical changes that may occur downcore and contributes towards long-term OC storage. OC-FeR complexation did not decrease with depth, suggesting little to no degradation of these compounds. When decreases in FeR were observed downcore, OC-FeR did not follow the same patterns suggesting that an increasing portion of Fe and FeR downcore may be comprised of FeR that is bound to OC. FeR effectively preserves OC downcore, but OC stabilises FeR, hence a mutual stabilisation relationship exists. This adds to other work in this field that has demonstrated long-term persistence of OC-FeR complexes in soils (e.g. Hemingway et al., 2019) and marine sediments (e.g. Faust et al., 2021; Longman et al., 2021).

Overall, OC-FeR in surface sediments likely lead to an underestimation of the role that FeR plays in OC stabilisation throughout the core, therefore we recommend that large spatial scale projects consisting of grab samples be accompanied by a small number of sediment cores to indicate whether OC-FeR contributes towards long-term carbon storage across a range of environments.

In terrestrial soils short cores (~20 cm) were collected that provided spatial resolution but not temporal resolution. Longer cores were not necessary for our line of enquiry into the contributions and origins of OC and OC-FeR in fjord sediments, and there is already considerable research on the presence of organo-mineral associations in soils and the ability of OC-FeR complexes to preserve older OC (e.g. Hemingway et al., 2019; Kaiser and Guggenberger, 2000; Kögel-Knabner et al., 2008; Kramer et al., 2012). The soils measurements in this study enabled the soil OC to be estimated in different areas of the catchment and the OC-FeR associations to be characterised in areas that were dominated by different land cover (deciduous, coniferous, mixed grassland). In agreement with previous research from other environments, we found an average of ~37 % OC-FeR in the Loch Creran catchment (Zhao et al., 2016) and this varied from 4-75 % across different soils sites and seasons (Chapter 3). Large variations in soil OC-FeR have been observed in other studies (Kramer and Chadwick, 2018; Zhao et al., 2016) in different soil types with a variety of land cover; forest soils ~37.8 % OC-FeR (Zhao et al., 2016), grasslands ~13.6 - 15.8 % (Fang et al., 2018; Ye et al., 2022), peatlands up to ~24 % (Huang et al., 2023), and soils in permafrost regions up to ~14.8 % (Patzner et al., 2020)). It has been suggested that OC-FeR relationships may be largely controlled by soil pH (Ye et al., 2022) that can be influenced by soil type and land cover. In this study, shallow soil profiles were used (<50 cm), but it has been estimated that up to 40 % of soil OC may be found at depths >1 m (Angst et al., 2016). Therefore, more research could be done to establish the controls on soil OC preservation at depth.

FeR and OC-FeR did not present similar trends in soils or sediments within this catchment suggesting that FeR was not the controlling factor for organo-mineral relationships in either setting (Faust et al., 2020, 2021; Sirois et al., 2018)). This does add to a greater question – what controls OC-FeR if not the availability of FeR in soils/sediments? As a pre-cursor, in Chapter 2, I explored whether the origin of the OC might influence the abundance of OC stored in soils or sediments. Using n-alkane abundance, a variety of n-alkane indices, specific carbon isotopes ($\delta^{13}\text{C}$) isotopes, resin markers and bulk geochemical techniques, a selection of vegetation, soil and sediment samples were characterised. The methods selected were able to help distinguish plant types in vegetation samples, and to some extent in soils and sediments. The dithionite extraction method led to considerable chemical augmentation of samples, as was visible in the isotopic fractionation of $\delta^{13}\text{C}$ in control and post-extract samples

(Chapters 1 and 3) meaning it was not possible to use this technique to distinguish the source of the OC bound to FeR. Post-extraction and control samples were not analysed for total lipid extract (TLE) or n-alkanes due to small sample sizes run for extraction. Instead, I focussed on exploring the role of TLE, n-alkanes and methyl dehydroabietate on total OC concentrations in soils, freshwater and fjord sediments. Slope, TLE and total n-alkanes were positively correlated with total OC concentrations across fjord basins. Variables with the capacity to indicate terrestrial inputs (terrestrial OC from FRUITS model, OC:TN ratio, relative abundance of long-chain n-alkanes, ACL) were correlated with one another, and with OEP, suggesting that OEP could indicate increases/decreases in terrestrial OC degradation in these sediments. Methyl dehydroabietate was not well correlated with any other variable and this suggests this resin marker tracks a different input (coniferous) in comparison to the n-alkanes and respective indices.

Chapter 4 investigated the origin of OC-FeR associations. The dominant binding mechanism between OC and FeR in Loch Creran sediments was sorption (Chapter 2). Previous work had suggested that the binding mechanism and lack of relationship with sedimentary FeR may indicate that complexes were formed before the sediment-water boundary (Faust et al., 2021). Chapter 4 focused upstream to gain a better understanding of where OC-FeR associations may originate. Sorption was the dominant binding mechanism observed in soils and sediments in this catchment, and Fe species were consistent throughout (mostly ferrihydrite and hematite). Fe species appeared to be slightly more varied in coniferous soils samples with some (seasonal spring and summer) OC:FeR values indicating more co-precipitation present (OC:FeR values >1 but <2), but this was not necessarily reflected in sediments. This suggested that OC-FeR species that were bound through co-precipitation or involved different Fe species were flocculated out across the salinity boundary, or provided a smaller contribution to sediments and were not visible amongst the signals from more dominant and sorbed Fe species.

I set out to investigate the interactions between OC and Fe in mid-latitude fjord sediments and found ~16 % of OC to be complexed with FeR in Loch Creran, which is comparable to the ~20 % average in marine sediments (Lalonde et al., 2012). OC complexed with FeR was considerably higher in upstream freshwater sediments (~41 %) and catchment soils (~37 %) therefore some of the OC-FeR may have been filtered out in the freshwater lochan before reaching the fjord sediments. The lower OC-FeR binding in sediments in comparison to soils may reflect the mixed terrestrial and marine inputs into the fjord basins and a decrease in OC-FeR complexes across the salinity boundary. As a majority of OC-FeR complexes in sediments are bound by sorption, it indicates that there are not considerable contributions from co-precipitation at sediment-water interface or across redox boundaries.

This work contributes to wider discussions on the extent of OC-FeR in terrestrial and coastal environments (e.g. Cui et al., 2022; Hemingway et al., 2019; Lalonde et al., 2012; Longman et al., 2022; Shields et al., 2016; Zhao et al., 2018, 2016) and the variety of research that starts to determine the source of OC in coastal and marine sediments (e.g. Faust et al., 2014; Gal et al., 2022; Smeaton and Austin, 2022). This thesis contributes to a small but vital and growing body of research working across the traditional terrestrial, freshwater, coastal and marine silos (Herzog et al., 2020; Jilbert et al., 2018; Krachler et al., 2010, 2016; Kritzberg et al., 2014; Muller, 2018). Each chapter of this thesis has contributed towards understanding the journey of OC in a mid-latitude fjord and its catchment, but there remains much work to be done.

5.3 Future Work & Recommendations

This project has been successful in estimating the amount of OC bound to FeR in mid-latitude fjord environments and highlighting the importance of flows from the land towards the sea. Globally, there is much to be done to gain a better understanding of the complex relationships between terrestrial and marine environments and the impact that changes in one location can have in the other, whether they are detrimental or beneficial, and how they will withstand changing climate conditions and human interactions.

5.3.1 Loch Creran Catchment

There are multiple effective ways to build upon this dataset compiled during this project:

Firstly, carbon or lead dating of core samples would be a highly beneficial addition and allow changes in sedimentary carbon stores to be aligned with past land use events that may provide greater insight into how the catchment has influenced these sediments in the past, and perhaps will in the future. Soil and sediment dating would also provide the opportunity to determine the age of OC bound to FeR and determine the age of the OC transported from terrestrial environments, and whether there is any preferential binding of young / aged carbon to FeR in sediments.

A more extensive vegetation and soil sampling regime would enable better characterisation of whole catchment vegetation and soil across different and distinct land uses, and OC-FeR relationships could be further characterised. In addition, exploration of different resin markers that may be representative of specific plant species would be particularly beneficial for characterising specific vegetation transport and storage downstream.

To improve the characterisation of particulate organic carbon (POC) within this catchment, more extensive POC collection and analysis would provide the opportunity to measure Fe speciation using a synchrotron as per Wood., (2020). This would provide insight into the species of Fe being transported downcore, and if enough material is present for further analysis, it would be beneficial to determine the OC and FeR relationships between particulate material in transit. A sediment trap could be beneficial if placed within fjord sediments close to the Fasnacloich outlet to determine the composition of material being transported downstream and the rate of accumulation of POC.

OC-FeR relationships could be analysed over a greater range of depths in the sediment cores to provide increased temporal resolution downcore. It is thought that the particle size and surface area of Fe oxides may influence OC-FeR associations when sorption is the dominant binding mechanism (Gu et al., 1995), which would be an interesting line of enquiry in this study catchment. Techniques such as Brunauer–Emmett–Teller could be used to obtain surface area to establish whether that has an influence on OC-FeR binding and survival across changes in salinity from soils to sediments.

Changes in land use can impact OC composition and transport. Within the Loch Creran catchment commercial forestry is present and could be used to investigate the impact of forest harvesting on the stability of organo-mineral associations in soils as it has been suggested that destabilisation can occur during large physical disturbance (e.g. Gabriel et al., 2018). Bulk geochemical and biomarker measurements could contribute to multiple objectives:

- the impact felling and harvesting events have on OC (dissolved and particulate) transport into surrounding waterways;
- whether destabilisation of OC-FeR occurs during events;
- if so, is there a corresponding increase in dissolved and particulate OC and Fe, and does this change the amount of co-precipitation of OC-FeR complexes?

Improved forest planting and harvesting techniques mean that the release of OC may not be substantial, but it would be useful to observe what scale of felling event can be observed in inland and fjord sediments and how large-scale land-use change may alter chemical conditions. This could provide a unique insight into the effectiveness of land management methods, particularly in terms of carbon transport and storage in coastal environments.

5.3.2 Scotland Source to Sea

A more extensive survey of soil speciation in mixed, deciduous and coniferous forests around Scotland, that encompasses different soil types would be beneficial to gain a better understanding of how land use, vegetation cover, pH and land use change can influence mineral binding from source towards sea in Scotland. This could build upon the Scottish soil OC comparison work of Chapman et al., (2013), that compared soil carbon stocks of different soil types and land cover in Scotland. This would be particularly beneficial if it encompassed research on root carbon transport and the influence of fungal networks on carbon transport within soils to establish what influences carbon transport and storage within soils at various depths, and the OC-FeR variability with depth.

It would be beneficial to run FeR extractions across a selection of Scottish fjord locations to investigate the spatial variation of OC-mineral binding and OC transport in order to calculate an average OC-FeR binding in Scotland's fjords. The methods used for datasets in this project could be applied to fjord samples previously collected across the west coast of Scotland (Smeaton et al., 2017; Smeaton and Austin, 2019, 2022). This would provide a dataset that may be capable of revealing the influence of land use and cover, soil type, latitude and other environmental factors on OC storage and organo-mineral binding for Scotland's coastline and this could be applied to many other coastal environments. Grab samples are easier and faster to obtain when covering many sample locations however, a selection of sediment cores should be taken alongside grab samples so that both spatial and temporal data can be obtained.

5.3.3 Recommendations

Measuring OC-FeR in surface sediments likely leads to an underestimation of the role that FeR plays in OC stabilisation throughout the core, therefore we recommend that large spatial scale projects consisting of grab samples be accompanied by a small number of sediment cores to indicate whether OC-FeR contributes towards long-term carbon storage across a range of environments. It is worth noting that the addition of sediment dating and porewater data to our dataset could provide a much more complete picture of changes in OC-FeR associations and sediment chemistry over time, but it was not within the scope of this project due to time constraints and sample collection prior to project initiation. When OC storage mechanisms are of interest, future core collection should aim to collect porewater to assess the influence of redox boundaries on OC preservation and Fe speciation.

Firstly, it would be appropriate to suggest that the catchments belonging to fjords with particularly vulnerable or protected coastal areas and / or quantified sedimentary carbon stores, are studied to provide a source-to-sea dataset that enables insight and understanding

of how flows from land are interacting with the coastal environment. This dataset could help to inform management plans for vulnerable coastal areas and provide information that could help to inform any plans for large-scale changes in land-use in these locations. Grab samples are easier and faster to obtain when covering many sample locations. However, a selection of sediment cores should be taken alongside grab samples so that both spatial and temporal data can be obtained.

The widely used dithionite extraction (Dithionite-citrate-bicarbonate) method for FeR extractions is sufficient for providing estimates of FeR, but does not allow true quantification of the FeR present in sediments, and as such the OC that is bound to it. Further development of the dithionite extraction method (Lalonde et al., 2012; Mehra and Jackson, 1958) is necessary as suggested previously by Fisher et al., (2020) and Hepburn et al., (2020).

To date, the OC-FeR relationship has primarily been explored in soils (e.g. Coward et al., 2017; Kaiser et al., 1996; Wagai and Mayer, 2007; Ye et al., 2022; Zhao et al., 2016) and surface sediments (Faust et al., 2020; Lalonde et al., 2012; Zhao et al., 2018), but more studies are needed using short sedimentary cores <50 cm to gain a better insight into the temporal changes in OC-FeR associations and the longevity of their relationship, as this study (Chapter 1) has contributed to (Faust et al., 2021). Even fewer have utilised longer gravity cores (3 to 12 m) to assess whether OC-FeR relationships can be detected over longer timescales and determine whether historical events (large-scale changes in land use and climate) are evident from downcore changes in organo-mineral relationships and OC and Fe concentrations. Different locations will have different sediment accumulation rates, so shorter cores may be able to provide millennial scale information where sedimentation rates are lower, therefore core length should coincide with depositional environment. To understand the mechanisms controlling coastal OC transport and burial, we must expand the global resolution of OC storage mechanisms across southern and northern latitude fjords.

It is regrettable that soil pH measurement were not successful in this project, despite calibrating different pH meters available, the values did not align between them, therefore there was no confidence in the measurements taken. This information could have provided valuable insights into the role of pH as a driver for OC-FeR in this catchment (Ye et al., 2022). It would also have been beneficial to have more accurate site-specific weather data (temperature and precipitation) for this study, to be able to assess whether changes observed in vegetation and soil biomarker data were driven by weather events. In future, weather gauges could be placed in sampling locations.

To fully utilise biomarkers to identify vegetation sources of OC in soils and sediments, it would be beneficial to gain a better understanding of the deterioration of compounds and how this

affects their chemical signatures and map these out for different plant species in different environments. A better understanding of their changing n-alkane and isotopic signatures will enable improved identification in soils and sediments.

5.4 Project challenges and limitations

This project faced considerable challenges within the initial two years due to the COVID-19 pandemic. Both field and lab work were delayed and the project goals had to be altered. Due to the reduced timescale for field and lab work, I had to make extensive adaptations and changes to this project and chose to sample only one field location, the Loch Creran catchment. Original plans for this project would have provided greater spatial resolution across different fjords/fjord catchments and the ability to contribute to slightly different questions surrounding OC-FeR relationships in mid-latitude fjords. As such, several of the areas suggested for future work above within this catchment and Scotland are based on the original questions and objectives of this project that were not able to be conducted due to significant restrictions: catchment sampling pre and post felling events, collection of sediment cores and catchment sampling across multiple Scottish fjords, a more extensive soil and vegetation sampling mission. Challenges extended beyond sample collection, as sample analysis was greatly impacted due to limited access to host and external facilities. Delays meant that the Mössbauer radiation source (^{57}Co in Rh matrix), deteriorated considerably during the months of inactivity, which required timescales for analysis and budgets to be redefined.

Multiple adaptations were made to this project that have resulted in positive changes; new collaborations, successful grant applications, increased knowledge base, new skills and different lines of scientific enquiry.

5.5 Source to Sea in Policy and Practice

There is an increasing need for more holistic research and management across the land-sea interface to address the nature-climate and biodiversity crises. When one part of the earth system faces significant challenges, the effects ripple throughout. For example, issues such as an increase in extreme weather events may lead to drought in one location, flooding in another, and the destruction of habitat networks that many species rely on. There is no one scientific discipline or sector that is equipped to address the environmental challenges we face, but when we combine skills, knowledge and resources, it can be done. Momentum is increasing for more holistic source-to-sea research and management across science, policy

and governance with considerable progress being driven by the Source-to-Sea Action Platform and partners (Mathews et al., 2023, 2019). On a governance level 'source-to-sea' relates to the connection of environmental systems; terrestrial, freshwater, coastal and marine, as well as the connection between sectors and stakeholders across these environments. In recent years a more holistic source-to-sea approach has been the centre of major international discussions at World Water Week, a dedicated UNECE workshop, and several COP events.

There are several projects throughout the UK that embody many aspects of the source-to-sea ethos, connecting stakeholders and considering upstream and downstream benefits e.g. MorPH 3C's project led by the Environment Agency, Dornoch Environmental Enhancement project led by Glenmorangie, Heriot-Watt University and the Marine Conservation Society (Kellock et al., 2023 and references therein). Though smaller river restoration projects also provide some excellent examples of holistic action, from re-meandering rivers, to riparian planting, removing artificial barriers, to species monitoring and catchment restoration, projects often managed river trusts (of which there are >20 in Scotland). While not all work entirely from land to sea, they capture and implement changes across different systems to make positive change for biodiversity and hydrological flow. Riverwoods is a larger river-based project that has potential to make source-towards-sea impact, it is a multi-stakeholder, multi-catchment project that aims to create a network of riparian woodland in Scotland and improve the health of rivers as a result (Ogilvy et al., 2022). A recent NatureScot Report was commissioned to highlight opportunities for more holistic management of Scotland's environmental resources and explore the challenges and benefits of a more connected approach (Kellock et al., 2023). I led this work through an internship during my PhD, assessing the need for (and interest in) more holistic management within Scotland, and brought together national and international stakeholders. To provide opportunity for funding mechanisms to finance source-to-sea action, Fisheries Management Scotland have been supported by a FIRNS bid (Facility for Investment Ready Nature in Scotland) to develop a 'source-to-sea' nature finance model that should provide opportunities to different sectors and disciplines to engage in collaborative and holistic action, management, and monitoring.

The findings of this research confirm that mid-latitude fjords are areas of significant OC storage, and that the surrounding catchment has an influence on the transport and storage of carbon within these environments. This is particularly useful when considering how land-use change may influence coastal carbon inputs and budgets, the benefits and value that coastal systems provide, and the need for more holistic management of protected areas. When coastal or marine areas are given a protected status, there is generally a lack of consideration for the land-sea flows surrounding that area and a lack of upstream – downstream monitoring. For example, there are many marine protected areas along Scotland's west coast but flows

across the land-sea interface are not monitored. Carbon, nutrients, pollutants, soil and sediments flow from land to sea (through freshwater systems and run off) and can be altered by land use, land use change and anthropogenic inputs and activities. A greater understanding of the biogeochemical mechanisms involved with the storage and transportation of carbon in coastal environments may contribute to decisions made on land-use change and management in coastal environments.

There should be a greater call for projects that connect datasets and disciplines across the land – sea interface, promoting collaboration and knowledge and data sharing across them to fully utilise datasets to answer complex cross-disciplinary questions.

5.6 Conclusions

Conducting a source-to-sea study utilising biogeochemical information across vegetation, soils, rivers and sediments I was able to contribute to a better understanding of the mechanisms that promote lateral carbon transport and the chemical changes that carbon complexes can withstand. In the Loch Creran catchment, OC-FeR complexes represent ~37 % of OC stored in soils and 41 % of OC in freshwater sediments in this catchment, while in Loch Creran sediments OC-FeR complexes represent ~16 % of OC. Fe is primarily transported through freshwater pathways in particulate form and ferrihydrite is found to be the dominant Fe species in soils, freshwater and fjord sediments indicating that some OC-FeR complexes may travel from source (surrounding terrestrial environments) to fjord sediments without extensive reworking. A portion of OC-FeR complexes are likely lost across the salinity boundary due to flocculation which would account for some of the decrease in OC-FeR complexation found in fjord sediments in comparison to upstream sites. There are both deciduous and coniferous inputs from the surrounding land into the fjord, determined by n-alkane indices and resin markers, highlighting the flows between different systems. I conclude that FeR plays an important role throughout this catchment in the transport and storage of OC from source-towards-sea.

Chapter 6 Thesis Appendix Document

Appendix A

This appendix relates to Chapter 2 datasets.

A.1.0 FRUITS model outputs

The terrestrial and marine value were calculated using the FRUITS Bayesian model as described in Chapter 2 of this thesis. N/OC, $\delta^{15}\text{N}$, $\delta^{13}\text{C}$ values were ran through the model using terrestrial soil and vegetation values separately, creating the averages and standard deviation values below (Table A.1).

Table A.1: Marine and terrestrial values as calculated from the FRUITS Bayesian model for full depth sediment cores across the fjord basins.

Sample	Depth	Marine		Terrestrial	
		Average %	Stdeva	Average %	Stdeva
UB1	0.50	69.56	1.57	30.44	1.57
UB1	2.50	69.75	1.70	30.26	1.70
UB1	4.50	65.80	1.58	34.21	1.58
UB1	6.50	65.76	1.48	34.24	1.48
UB1	8.50	65.88	1.70	34.13	1.70
UB1	10.50	63.75	1.61	36.26	1.61
UB1	12.50	65.84	1.54	34.16	1.54
UB1	14.50	65.32	1.46	34.69	1.46
UB1	16.50	65.02	1.65	34.99	1.65
UB1	18.50	64.09	1.52	35.92	1.52
UB1	20.50	64.68	1.46	35.33	1.46
UB1	22.50	65.53	1.68	34.48	1.68

UB1	24.50	64.48	1.63	35.53	1.63
UB1	26.50	64.99	1.55	35.02	1.55
UB1	28.50	66.93	1.63	33.07	1.63
UB1	30.50	68.58	1.72	31.43	1.72
UB1	32.50	69.06	1.69	30.95	1.69
UB1	34.50	71.33	1.86	28.68	1.86
UB1	36.50	73.37	1.76	26.64	1.76
UB2	0.5	56.74	1.27	43.27	1.27
UB2	1.5	57.08	0.95	42.92	0.95
UB2	3.5	58.85	1.43	41.15	1.43
UB2	5.5	58.97	1.43	41.03	1.43
UB2	7.5	59.09	1.83	40.92	1.83
UB2	9.5	56.18	1.37	43.82	1.37
UB2	11.5	55.19	0.62	44.82	0.62
UB2	13.5	54.99	1.87	45.01	1.87
UB2	15.5	55.62	1.18	44.39	1.18
UB2	17.5	55.23	1.20	44.78	1.20
UB2	19.5	56.28	1.84	43.72	1.84
UB2	23.5	57.58	1.49	42.43	1.49
UB2	25.5	59.43	0.78	40.57	0.78
UB2	29.5	55.16	1.06	44.84	1.06
UB2	31.5	55.61	0.71	44.39	0.71
UB2	33.5	58.99	1.34	41.01	1.34

UB2	35.5	56.26	1.63	43.75	1.63
UB2	37.5	56.29	0.57	43.72	0.57
UB2	39.5	55.83	1.97	44.17	1.97
LB1	0.5	51.77	0.94	48.24	0.94
LB1	2.5	50.98	1.04	49.03	1.04
LB1	4.5	51.49	0.91	48.52	0.91
LB1	6.5	52.05	1.02	47.95	1.02
LB1	8.5	51.80	1.06	48.20	1.06
LB1	10.5	50.70	0.99	49.30	0.99
LB1	12.5	53.23	1.15	46.78	1.15
LB1	14.5	52.50	1.24	47.51	1.24
LB1	16.5	53.35	1.07	46.66	1.07
LB1	18.5	55.33	1.20	44.68	1.20
LB1	20.5	57.00	1.33	43.00	1.33
LB1	22.5	54.07	1.03	45.94	1.03
LB1	24.5	59.93	1.15	40.07	1.15
LB1	26.5	60.99	1.29	39.01	1.29
LB1	28.5	61.57	1.42	38.44	1.42
LB1	30.5	63.10	1.51	36.91	1.51
LB1	32.5	63.87	1.48	36.14	1.48
LB1	34.5	63.69	1.37	36.31	1.37
LB1	36.5	62.88	1.46	37.12	1.46
LB1	38.5	62.74	1.47	37.26	1.47

LB1	40.5	65.10	1.48	34.90	1.48
LB1	42.5	63.11	1.32	36.90	1.32
LB1	44.5	61.77	1.39	38.23	1.39
LB1	45.5	60.49	1.47	39.51	1.47
LB2	0.5	49.43	0.84	50.58	0.84
LB2	2.5	48.85	0.79	51.15	0.79
LB2	4.5	48.46	0.98	51.54	0.98
LB2	6.5	46.13	0.83	53.87	0.83
LB2	8.5	46.61	1.00	53.39	1.00
LB2	10.5	44.17	0.70	55.84	0.70
LB2	12.5	49.20	0.99	50.80	0.99
LB2	14.5	43.44	0.75	56.56	0.75
LB2	16.5	52.55	0.95	47.45	0.95
LB2	18.5	51.51	1.29	48.49	1.29
LB2	20.5	45.20	1.36	54.80	1.36

The model outputs for surface sediments (<10cm) only are below (Table A.2).

Table A.2: FRUITS model outputs for fjord surface sediments. The percentage of terrestrial and marine material was calculated.

Sample	Depth	Marine		Terrestrial	
		Average %	Stdeva	Average %	Stdeva
UB1	0.50	69.56	1.57	30.44	1.57
UB1	2.50	69.75	1.70	30.26	1.70
UB1	4.50	65.80	1.58	34.21	1.58

UB1	6.50	65.76	1.48	34.24	1.48
UB1	8.50	65.88	1.70	34.13	1.70
UB2	0.5	56.52	1.12	43.48	1.12
UB2	1.5	56.97	1.12	43.03	1.12
UB2	3.5	58.35	1.17	41.65	1.17
UB2	5.5	58.93	1.39	41.07	1.39
UB2	7.5	58.87	1.20	41.13	1.20
UB2	9.5	55.83	1.34	44.17	1.34
LB1	0.5	51.77	0.94	48.24	0.94
LB1	2.5	50.98	1.04	49.03	1.04
LB1	4.5	51.49	0.91	48.52	0.91
LB1	6.5	52.05	1.02	47.95	1.02
LB1	8.5	51.80	1.06	48.20	1.06
LB2	0.5	49.43	0.84	50.58	0.84
LB2	2.5	48.85	0.79	51.15	0.79
LB2	4.5	48.46	0.98	51.54	0.98
LB2	6.5	46.13	0.83	53.87	0.83
LB2	8.5	46.61	1.00	53.39	1.00

A.1.1 Iron and sulphur XRF profiles

Samples were initially selected for FeR extractions by splitting the Fe and S profiles into three sections based on visible changes in Fe and Al data (A.1a-i). The cores with the highest Fe concentration within each of these sections was selected for extractions because they had the best chance of providing reasonable Mössbauer spectra before and after the extraction.

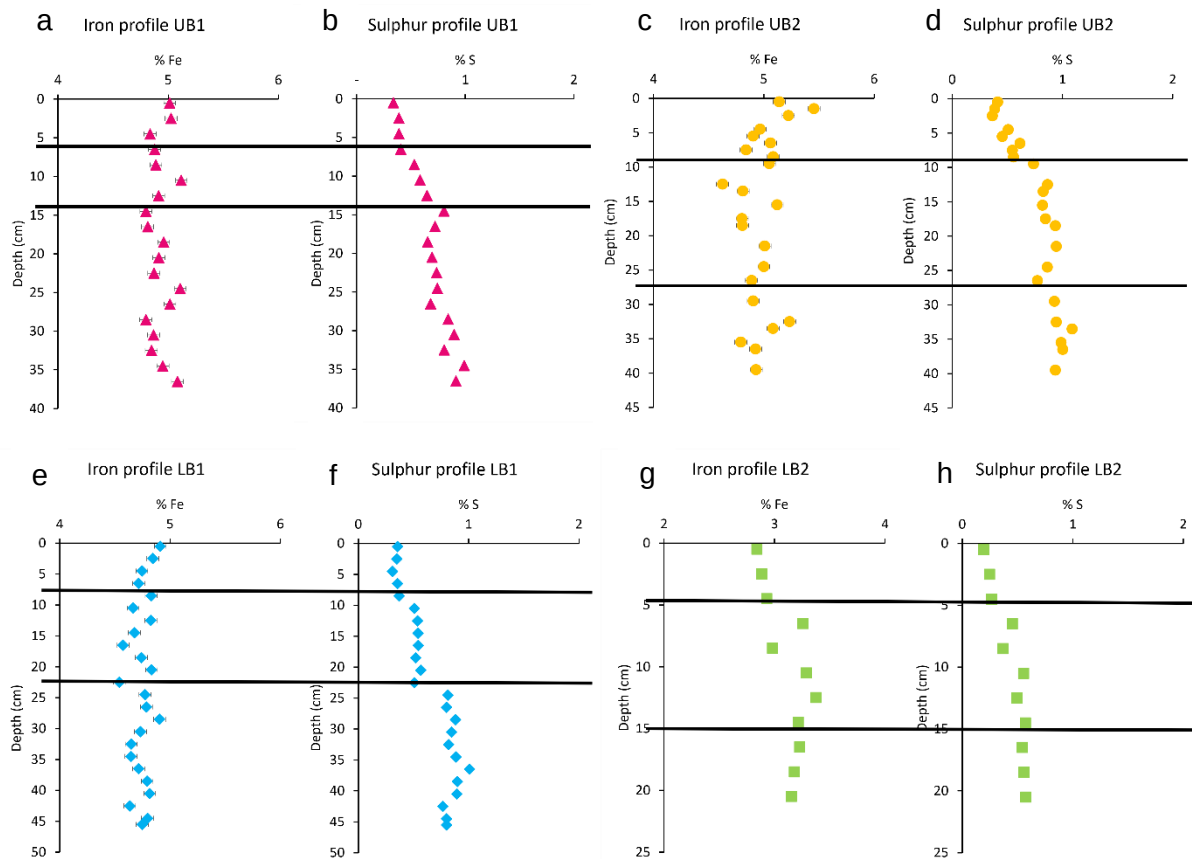


Figure A.1: Fe and S profiles downcore across the fjord basins. The sections they were separated into based on changes in concentrations is highlighted.

A.1.2 Mössbauer data

Mössbauer parameters are presented for room (295K) (Table A.3) measurements before and after extraction.

Table A.3: Mössbauer parameters for 295K. Three samples at different depths in each core have been analysed.

				Pre	Post	Pre	Post	Pre	Post	Pre	Post
Core	Depth (cm)	Temperature	Oxidation state	δ	δ	Δ	Δ	H	H	%	%
UB1	2.5	295K	Fe 3+	0.373	0.37621 7	0.698	0.75255 1			53.58	45.5
			Fe 2+	1.108	1.13694	2.589	2.60994			40.7	49
			IOM	0.325	0.32366 7	-0.054	-0.05501	49.746 4	49.7266	5.7	5.6
UB1	10.5	295K	Fe 3+	0.360	0.34404 4	0.760	0.82566 7			57	51.6
			Fe 2+	1.144	1.14915	2.618	2.58925			43	48.4
			IOM	-	-	-	-	-		-	
UB1	24.5	295K	Fe 3+	0.362	0.32792 4	0.660	0.76241 4			54.5	54.3

			Fe 2+	1.127	1.14943	2.686	2.60492			45.5	45.7
			IOM	-	-	-	-	-		-	-
UB2	7.5	295K	Fe 3+	0.365	0.35502 7	0.784	0.73838 3			53.4	47.9
			Fe 2+	1.135	1.12948	2.576	2.60009			38.6	47.4
			IOM	0.346	0.34566 1	-0.071	-0.06766	50.500 6	50.4779	8	4.7
UB2	15.5	295K	Fe 3+	0.345	0.27456 7	0.693	0.83080 7			57.04	54.1
			Fe 2+	1.125	1.17544	2.605	2.5363			42.96	45.9
			IOM	-	-	-	-	-		-	-
UB2	32.5	295K	Fe 3+	0.340	0.32708 6	0.657	0.77933 7			44.4	43.7
			Fe 2+	1.127	1.1588	2.632	2.56183			34.8	25.8
			IOM	7.799	1.13	4.635	0.19	68.221 6	68.22	20.7	30.43

LB1	0.5	295K	Fe 3+	0.369	0.35758 5	0.712	0.73178 7			52.6	47.3
			Fe 2+	1.128	1.13575	2.616	2.6021			39.39	49.4
			IOM	0.395	0.39453 8	-0.104	-0.10378	49.940	49.9395	8	3.3
LB1	20.5	295K	Fe 3+	0.357	0.36336 3	0.683	0.68969 9			49.95	52.5
			Fe 2+	1.128	1.12919	2.614	2.68606			43.03	43.6
			IOM	0.372	0.37161 2	-0.113	-0.11272	50.377 8	50.3778	7.02	3.9
LB1	40.5	295K	Fe 3+	0.238		0.843				53.93	
			Fe 2+	1.228		2.417				46.07	
			IOM	-		-		-		-	
LB2	4.5	295K	Fe 3+	0.405	0.38662 5	0.899	0.79309 1			44.9	41.3
			Fe 2+	1.142	1.13765	2.581	2.58506			42.5	48.6

			IOM	0.363	0.36306 5	-0.130	1.12996 3	50.231 8	50.2318	12.6	10.1
LB2	12.5	295K	Fe 3+	0.237	0.27532 7	0.862	0.90108 3			46.1	43.6
			Fe 2+	1.209	1.2156	2.414	2.39489 9			41.9	48.4
			IOM	0.310	0.30266 8	-0.093	-0.08446	50.025 3	50.0077	11.9	8
LB2	18.5	295K	Fe 3+	0.342	0.35125 1	0.658	0.69476 3			46.7	45.2
			Fe 2+	1.128	1.14039	2.597	2.58127			40	42.1
			IOM	0.402	0.40217	-0.113	-0.11271	50.197 7	50.1977	13.3	12.7

Low temperature measurements for all extracted sediment samples were also ran before and after extraction (Table A.4).

Table A.4: Low temperature Mössbauer measurement of sediment samples before and after extraction.

				Pre	Post	Pre	Post	Pre	Post	Pre	Post	
Core	Depth	Temperature	Oxidation state	δ		Δ / E for IOM		H		%		Mineral
UB1	2.5	4.2K	Fe 3+	0.46	0.52	0.89	0.91			11.6	13.7	
			Fe 2+	1.08	0.97	3.08	3.12			22.1	27.5	
			IOM	0.45	0.45	-0.07	-0.07	47.94	47.93	17.7	8.2	Ferrihydrite
			Background	1.03	1.26	8.07	6.86			49	50.7	
UB1	10.5	4.2K	Fe 3+	0.52		0.95				25		
			Fe 2+	1.04		3.39				25		
			IOM	0.37		-0.20		48.86		19		Ferrihydrite
			Background	1.03		9.42				42		
UB1	24.5	4.2K	Fe 3+	0.40		0.91				15.6		
			Fe 2+	0.73		3.25				25		
			IOM	0.40		0.00		46.73		24		Ferrihydrite

			Background	1.25		4.67				35		
UB2	7.5	4.2K	Fe 3+	0.23	0.22	0.88	1.54			18	20	
			Fe 2+	0.34	1.35	3.91	2.20			26	27	
			IOM	0.22	0.22	-0.03	-0.03	45.78	45.79	36	21.8	Lepidocrocite
			Background	2.13	1.09	3.44	5.83			21	31	
UB2	15.5	4.2K	Fe 3+	0.49		0.94				19.8		
			Fe 2+	0.73		3.70				25		
			IOM	0.51		-0.02		46.93		30.2		Ferrihydrite
			Background	1.62		4.77				25		
UB2	32.5	4.2K	Fe 3+	0.45		0.95				18.8		
			Fe 2+	0.94		3.19				20.2		
			IOM	0.47		-0.06		47.72		18.3		Ferrihydrite
			Background	1.10		4.97				42.7		
LB1	20.5	4.2K	Fe 3+	0.40		0.97				18.5		

			Fe 2+	1.14		2.99				16		
			IOM	0.43		-0.01		50.71		8.6		Ferrihydrite
			Background	1.05		5.63				56.9		
LB1	40.5	4.2K	Fe 3+	0.49		1.03				21.8		
			Fe 2+	0.88		3.55				20		
			IOM	0.40		-0.12		48.70		22.1		Ferrihydrite
			Background	1.05		4.60				36.1		
LB2	4.5	4.2K	Fe 3+		0.46		1.06				18	
			Fe 2+		1.03		3.19				31	
			IOM		0.73		-0.30		51		8.2	Goethite
			Background		1.21		7.24				43	
LB2	12.5	4.2K	Fe 3+	0.62		0.73				6		
			Fe 2+	0.03		0.84				10		
			IOM	0.53		-0.05		50.00		16.6		Ferrihydrite
			Background	1.02		3.85				68		

LB2	18.5	4.2K	Fe 3+	1.19		5.53				51.4		
			Fe 2+	1.53		2.69				12.6		
			IOM	0.55		-0.02		51.51		8.9		Ferrihydrite
			Background	0.35		1.48				27.1		

*LB1 0.5 cm is omitted at low temperature (4.2K) because the spectra was not well ordered and as such could not be characterised. This is likely due to a high amount of poorly crystalline Fe.

A.1.3 OC-FeR dataset

OC-FeR complexes were calculated, inclusive of control values (Table A.5).

Table A.5: Calculations for OC-FeR associations from pre extraction, control and post extraction OC data.

Sample	Depth	OC Pre	OC Control	OC Post	Controlled OC value	OC-FeR of total OC		FeR of total Fe	
	(cm)	Amount (µg)	Amount (µg)	Amount (µg)	Amount (µg)	%	Average error %	%	Standard deviation
SM2.16-01	2.5	910.00	679.59	522.79	156.80	17.23	0.39	14.91	0.98

SM2.16-01	10.5	792.00	571.37	389.07	182.30	23.02	0.39	10.88	6.85
SM2.16-01	24.5	656.00	512.01	283.64	228.37	34.81	0.39	8.32	6.27
SM2.16-03	7.5	630.66	562.67	440.33	122.34	19.40	0.39	10.94	0.80
SM2.16-03	15.5	633.66	593.00	634.54	-41.54	-6.56	0.39	8.94	3.14
SM2.16-03	32.5	593.34	518.61	445.85	72.76	12.26	0.39	5.52	3.06
SM2.16-06	0.5	601.00	458.65	437.76	20.89	3.48	0.39	14.77	4.72
SM2.16-06	20.5	478.00	276.48	246.59	29.89	6.25	0.39	6.32	1.37
SM2.16-06	40.5	489.00	264.20	230.70	33.50	6.85	0.39	5.47	4.40
SM2.16-08	4.5	199.60	165.67	109.47	56.20	28.16	0.39	7.17	9.82
SM2.16-08	12.5	208.18	175.76	145.91	29.85	14.34	0.39	7.30	6.94
SM2.16-08	18.5	184.79	159.83	91.81	68.02	36.81	0.39	6.70	4.40

Isotopic measurements for extracted samples are presented (Table A.6).

Table A.6: Isotopic $\delta^{13}\text{C}_{\text{org}}$ measurements for samples before and after extraction, inclusive of control values.

Sample	Depth	$\delta^{13}\text{C}_{\text{org}}$ pre	Control $\delta^{13}\text{C}_{\text{org}}$	$\delta^{13}\text{C}_{\text{org}}$ post
	(cm)	(‰)	(‰)	(‰)
SM2.16-01	2.5	-24.89	-24.85	-24.60
SM2.16-01	10.5	-24.28	-24.39	-24.42
SM2.16-01	24.5	-24.31	-24.45	-24.61
SM2.16-03	7.5	-23.78	-23.91	-23.86
SM2.16-03	15.5	-23.65	-23.79	-23.57
SM2.16-03	32.5	-23.95	-23.66	-23.43
SM2.16-06	0.5	-23.44	-23.55	-23.46
SM2.16-06	20.5	-24.00	-23.48	-23.11
SM2.16-06	40.5	-24.25	-24.11	-23.85
SM2.16-08	4.5	-22.97	-22.82	-23.57
SM2.16-08	12.5	-23.05	-22.55	-22.28

SM2.16-08	18.5	-22.92	-22.85	-22.42
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Appendix B

This appendix relates to Chapter 3 of this thesis.

B.1.0 External standard chromatograph

The standard used for GC-FIC and GC-MS (Figure B.1).

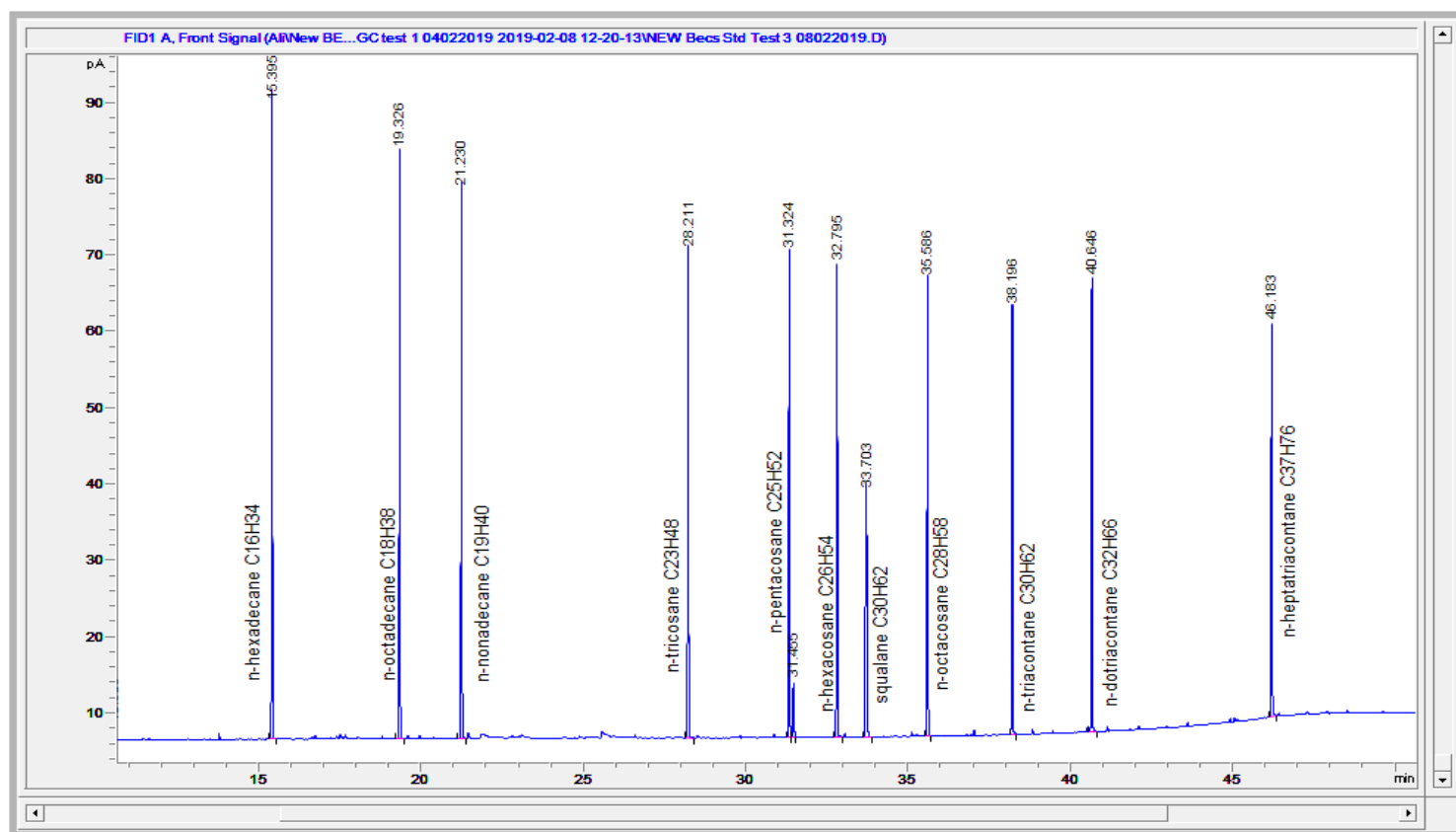


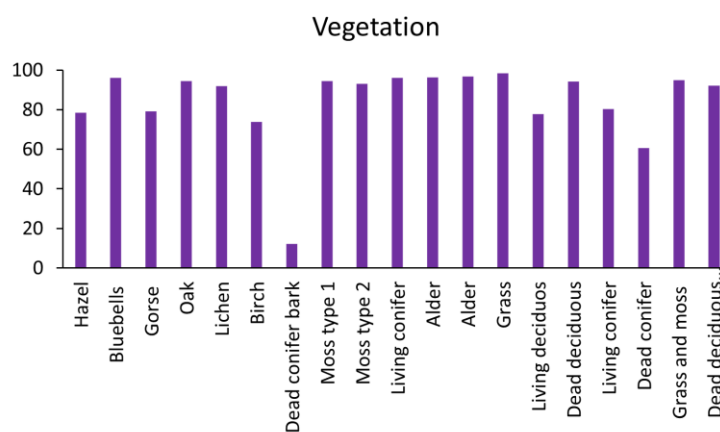
Figure B.1: The standard chromatogram consisting of 11 labelled peaks used for GC-FIC and GC-MS.

B.1.1 Relative abundance n-alkanes

The relative abundance of long-chain n-alkanes is presented for vegetation B.1, soils and freshwater sediments (Table B.2), fjord sediment cores UB1 (Table B.3), UB2 (Table B.4), LB1 (Table B.5), LB2 (Table B.6).

Table B.1: Relative abundance of long-chain n-alkanes in samples in vegetation samples

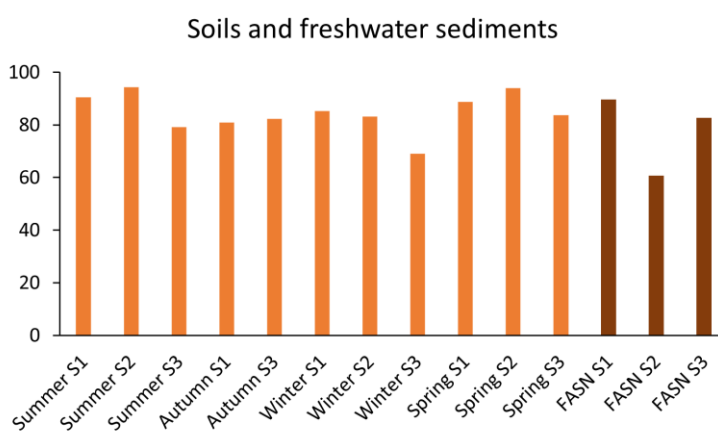
<u>Sample</u>	Relative abundance % long (C25 - C35)
Hazel	78.52
Bluebells	96.18
Gorse	79.06
Oak	94.43
Lichen	91.94
Birch	73.94
Dead conifer bark	12.16
Moss type 1	94.57
Moss type 2	93.03
Living conifer	96.19
Alder	96.35
Alder	96.68
Grass	98.45
Living deciduous	77.66



Dead deciduous	94.22
Living conifer	80.41
Dead conifer	60.65
Grass and moss	95.01
Dead deciduous leaves	92.10

Table B.2: Relative abundance of long-chain n-alkanes in soils and freshwater sediment samples

<u>Sample</u>	Relative abundance % long (C25 - C35)
Summer S1	90.56
Summer S2	94.42
Summer S3	79.21
Autumn S1	80.88
Autumn S3	82.36
Winter S1	85.22
Winter S2	83.09
Winter S3	69.13
Spring S1	88.81
Spring S2	94.02
Spring S3	83.72
FASN S1	89.60
FASN S2	60.65



FASN S3	82.70
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Table B.3: Relative abundance of long-chain n-alkanes in UB1

<u>Sample</u>	Relative abundance % long (C25 - C35)
UB1 2.5	90.57
UB1 4.5	87.32
UB1 6.5	87.49
UB1 8.5	87.41
UB1 10.5	90.81
UB1 12.5	89.14
UB1 14.5	89.00
UB1 16.5	88.37
UB1 18.5	89.45
UB1 20.5	90.58
UB1 22.5	89.05
UB1 24.5	90.75
UB1 26.5	90.79
UB1 28.5	89.60
UB1 30.5	90.16
UB1 32.5	90.57
UB1 34.5	90.17

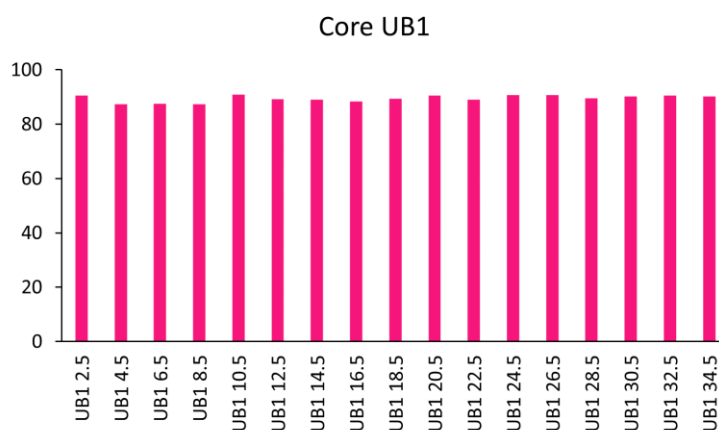
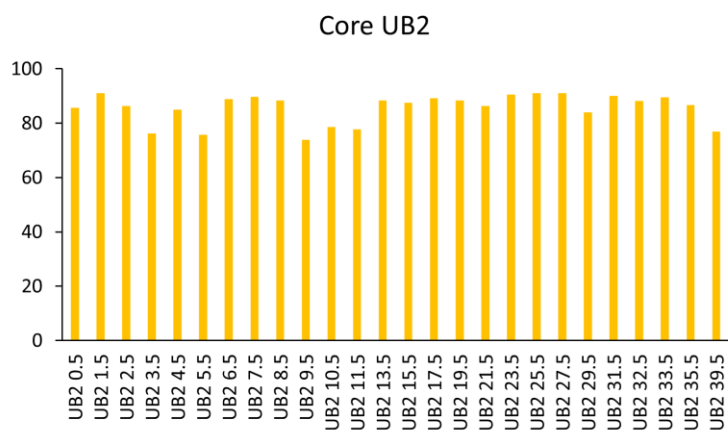


Table B.4: Relative abundance of long-chain n-alkanes in UB2

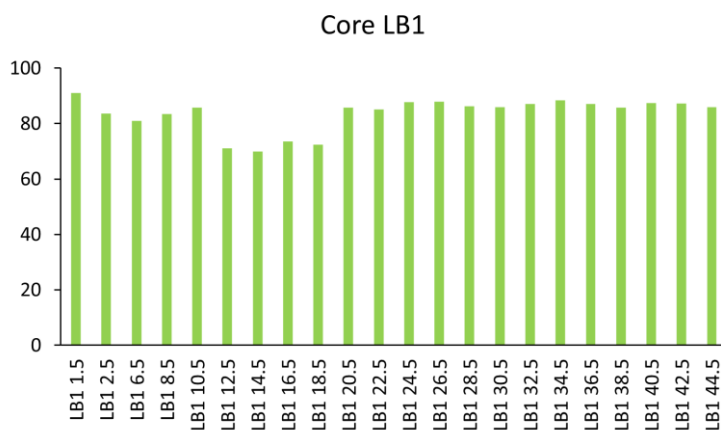
<u>Sample</u>	Relative abundance % long (C25 - C35)
UB2 0.5	85.64
UB2 1.5	91.03
UB2 2.5	86.42
UB2 3.5	76.18
UB2 4.5	85.04
UB2 5.5	75.81
UB2 6.5	88.82
UB2 7.5	89.77
UB2 8.5	88.43
UB2 9.5	73.84
UB2 10.5	78.59
UB2 11.5	77.76
UB2 13.5	88.36
UB2 15.5	87.52
UB2 17.5	89.17
UB2 19.5	88.44
UB2 21.5	86.43
UB2 23.5	90.63
UB2 25.5	91.08



UB2 27.5	91.08
UB2 29.5	83.91
UB2 31.5	90.03
UB2 32.5	88.15
UB2 33.5	89.50
UB2 35.5	86.60
UB2 39.5	76.86

Table B.5: Relative abundance of long-chain n-alkanes in LB1

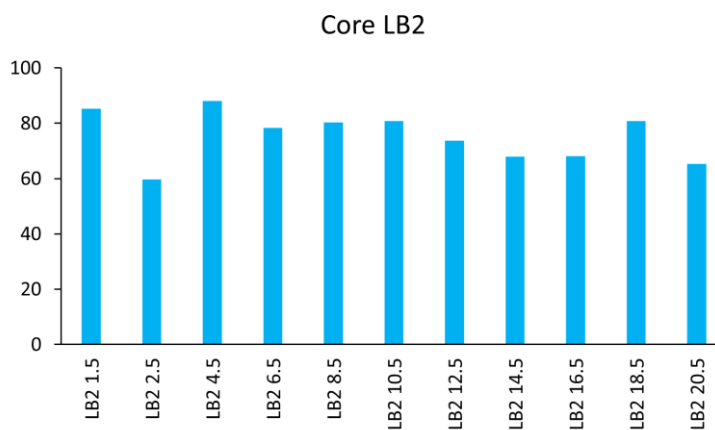
<u>Sample</u>	Relative abundance % long (C25 - C35)
LB1 1.5	91.03
LB1 2.5	83.61
LB1 6.5	81.00
LB1 8.5	83.40
LB1 10.5	85.74
LB1 12.5	71.17
LB1 14.5	69.87
LB1 16.5	73.52
LB1 18.5	72.39
LB1 20.5	85.84
LB1 22.5	85.18



LB1 24.5	87.71
LB1 26.5	87.86
LB1 28.5	86.18
LB1 30.5	85.92
LB1 32.5	87.09
LB1 34.5	88.34
LB1 36.5	87.16
LB1 38.5	85.82
LB1 40.5	87.43
LB1 42.5	87.26
LB1 44.5	85.95

Table B.6: Relative abundance of long-chain n-alkanes in LB2

<u>Sample</u>	Relative abundance % long (C25 - C35)
LB2 1.5	85.21
LB2 2.5	59.74
LB2 4.5	88.02
LB2 6.5	78.40
LB2 8.5	80.28
LB2 10.5	80.88
LB2 12.5	73.77



LB2 14.5	67.89
LB2 16.5	68.08
LB2 18.5	80.82
LB2 20.5	65.30

B.1.2 TLE weights

TLE weights are provided for all samples from vegetation, soils, river sediments, freshwater and fjord sediments (Table B.7).

Table B.7: Total lipid extract weights for all samples referred to within Chapter 3 of this study.

Depth (cm) / Detail	<u>TLE (g)</u>
Hazel	0.011682
Bluebells	0.013800
Gorse	0.007326
Oak	0.031000
Lichen	0.003915
Birch	0.010980
Dead conifer bark	0.047905
Moss type 1	0.008350
Moss type 2	0.004020
Living conifer	0.017900
Alder	0.006990
Alder	0.009156
Grass	0.011750

Living deciduous	0.020580
Dead deciduous	0.020146
Living conifer	0.020026
Dead conifer	0.010145
Grass and moss	0.019888
Dead deciduous leaves	0.019984
Summer Soil S1 average	0.009025
Summer Soil S2 average	0.013133
Summer Soil S3 average	0.008300
Winter Soil S1 average	0.010200
Winter Soil S2 average	0.010403
Winter Soil S3 average	0.005100
Spring Soil S1 average	0.016250
Spring Soil S2 average	0.012650
Spring Soil S3 average	0.014950
Spring Site 1 river sediment	0.000700
Spring Site 2 river sediment	0.000900
Spring Site 3 river sediment	0.001100
FASN S1	0.010400
FASN S2	0.010944
FASN S3	0.010934

UB1 2.5	0.007900
UB1 4.5	0.010000
UB1 6.5	0.009200
UB1 8.5	0.007200
UB1 10.5	0.007600
UB1 12.5	0.010200
UB1 14.5	0.006800
UB1 16.5	0.003600
UB1 18.5	0.004400
UB1 20.5	0.012400
UB1 22.5	0.005600
UB1 24.5	0.005600
UB1 26.5	0.012500
UB1 28.5	0.010080
UB1 30.5	0.007100
UB1 32.5	0.006000
UB1 34.5	0.007700
UB2 0.5	0.009700
UB2 1.5	0.007700
UB2 2.5	0.007700
UB2 3.5	0.006800
UB2 4.5	0.009000
UB2 5.5	0.007700

UB2 6.5	0.007500
UB2 7.5	0.007700
UB2 8.5	0.007400
UB2 9.5	0.008400
UB2 10.5	0.007300
UB2 11.5	0.006700
UB2 13.5	0.007600
UB2 15.5	0.009200
UB2 17.5	0.006500
UB2 19.5	0.007300
UB2 21.5	0.006300
UB2 23.5	0.006200
UB2 25.5	0.006000
UB2 27.5	0.014200
UB2 29.5	0.006400
UB2 31.5	0.005700
UB2 32.5	0.006900
UB2 33.5	0.006600
UB2 35.5	0.006400
UB2 39.5	0.005800
LB1 1.5	0.003700
LB1 2.5	0.007100
LB1 6.5	0.005300

LB1 8.5	0.004600
LB1 10.5	0.004700
LB1 12.5	0.005700
LB1 14.5	0.005000
LB1 16.5	0.005200
LB1 18.5	0.004700
LB1 20.5	0.003900
LB1 22.5	0.004800
LB1 24.5	0.012851
LB1 26.5	0.005400
LB1 28.5	0.005400
LB1 30.5	0.005000
LB1 32.5	0.004700
LB1 34.5	0.005600
LB1 36.5	0.005000
LB1 38.5	0.004600
LB1 40.5	0.003600
LB1 42.5	0.005200
LB1 44.5	0.004000
LB2 1.5	0.002500
LB2 2.5	0.003300
LB2 4.5	0.001700
LB2 6.5	0.002400

LB2 8.5	0.002400
LB2 10.5	0.002700
LB2 12.5	0.003200
LB2 14.5	0.002900
LB2 16.5	0.004600
LB2 18.5	0.002500
LB2 20.5	0.002900

B.1.3 Peak identification of methyl dehydroabietate

An example of identification of methyl dehydroabietate (Figure B.2) shows that the peak occurs at ~33.3 mins with a primary identifying peak of 239. Peak areas were measured using the Agilent MassHunter program.

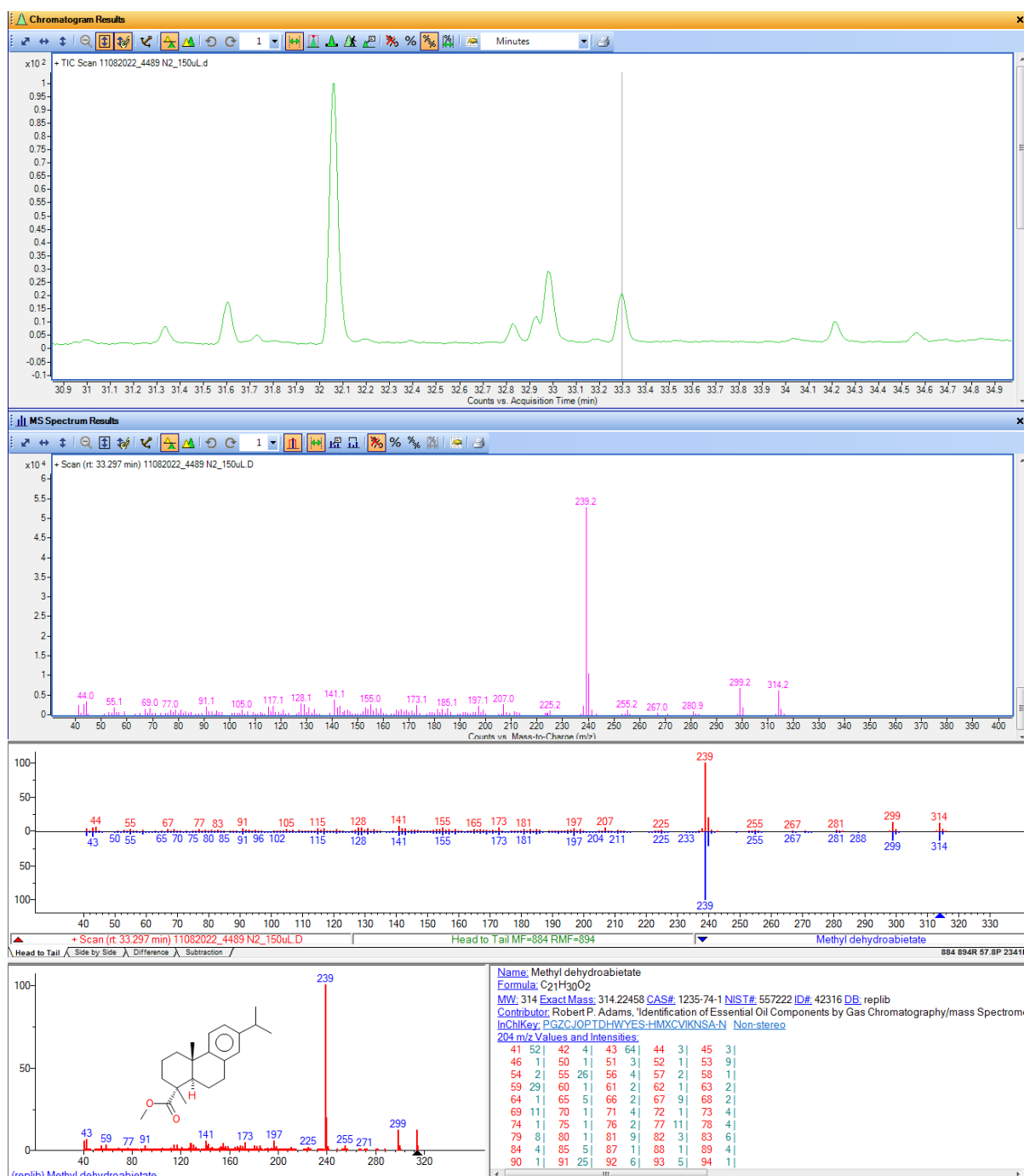


Figure B.2: Peak identification of methyl dehydroabietate.

B.1.4 River bank sediments

River bank sediments were very rocky with little collectable organic matter. The total C and OC is <1 % (Table B.8) which is lower than all other samples. OC% value for Spring Soil Site 1 is not correct as it cannot be higher than the total C value. Analysing samples with such low concentrations of carbon is difficult and therefore data from

Table B.8: Total carbon and organic carbon percentages in river sediments across three different river sites.

Sample	%C	%OC
Spring Site 1 Riv. Sed. (log)	0.26	2.52
Spring Site 2 Riv. Sed. (confluence)	0.55	0.84
Spring Site 3 Riv. Sed. (boulder)	0.86	0.64

B.1.5 All n-alkane data for living and dead vegetation samples

N-alkane concentrations were calculated for living and dead deciduous vegetation samples (Table B.9). Several coniferous chain lengths, primarily even C-chain lengths are absent in degraded coniferous material, meaning that proxies such as CPI and OEP were unable to be calculated for some samples.

Table B.9: N-alkane concentrations ($\mu\text{g/g}$) for chain lengths C16-C35 for living and dead deciduous and coniferous material

<u>Detail</u>	<u>C16</u>	<u>C17</u>	<u>C18</u>	<u>C19</u>	<u>C20</u>	<u>C21</u>	<u>C22</u>	<u>C23</u>	<u>C24</u>	<u>C25</u>	<u>C26</u>	<u>C27</u>	<u>C28</u>	<u>C29</u>	<u>C30</u>	<u>C31</u>	<u>C32</u>	<u>C33</u>	<u>C34</u>	<u>C35</u>
Living alder	0.05	0.00	0.00	0.00	0.00	0.16	0.02	1.94	0.25	3.37	0.48	22.55	1.33	35.31	0.11	0.42	0.00	0.20	0.00	0.00
Living alder	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.66	0.08	1.19	0.22	7.31	0.54	13.31	0.00	0.12	0.00	0.00	0.00	0.00
Living deciduous material	0	0	0	0	0.00	0.67	0.15	8.00	0.26	7.00	0.31	11.39	0.37	10.36	0.29	1.80	0.00	0.00	0.00	0.00
Dead deciduous material (alder)	0	0	0	0	0.00	0.10	0.11	0.43	0.36	1.07	0.63	5.21	0.85	7.14	0.39	0.78	0.14	0.00	0.00	0.00

Dead deciduous leaves (alder)	0	0	0	0	0.02	0.10	0.07	0.30	0.08	1.32	0.09	2.94	0.11	1.70	0.03	0.41	0.00	0.00	0.00	0.00
Living coniferous material	0.04	0.05	0.00	0.00	0.00	0.06	0.03	0.18	0.04	1.22	0.19	2.39	0.11	0.63	0.00	0.34	0.25	4.76	0.00	0.00
Living coniferous material	0	0	0	0	0.01	0.02	0.01	0.12	0.02	0.12	0.03	0.18	0.04	0.30	0.08	0.00	0.00	0.00	0.00	0.00
Dead coniferous material	0	0	0	0	0.07	0.02	0.00	0.03	0.00	0.05	0.00	0.05	0.00	0.06	0.00	0.04	0.00	0.00	0.00	0.00
Dead coniferous material	0.00	0.00	0.00	0.06	0.86	2.08	0.74	0.18	0.00	0.28	0.00	0.16	0.00	0.11	0.00	0.00	0.00	0.00	0.00	0.00

B.1.6 Total-alkanes in soils

The variation in total n-alkanes across the three soil sampling sites in summer and winter are presented (Table B.10).

Table B.10: Total n-alkane concentrations from summer and winter soil samples across Soil Sites 1-3

Soil Sample	<u>Total n-alkanes</u> ($\mu\text{g/g}$)
Summer S1	10.72
Summer S2	9.63
Summer S3	8.98
Winter S1	10.10
Winter S2	13.78
Winter S3	8.43

B.1.7 Limit of detection and quantification

The instrumental limits of detection and limit of quantification, LOD and LOQ respectively, can be found in Table B.11. This shows the values for all of the n-alkanes, and these can also be used for the pine resin and the same standards were used for all. These limits are based on 7 replicates.

Table B.11: Instrumental limits of detection and quantification for n-alkanes calculated from 7 replicate measurements.

N-alkane Compounds	Instrumental Limit of Detection (LOD) ($\mu\text{g ml}^{-1}$)	Instrumental Limit of Quantification (LOQ) ($\mu\text{g ml}^{-1}$)
n-C10	0.004	0.008
n-C11	0.004	0.009
n-C12	0.006	0.013
n-C13	0.011	0.024
n-C14	0.006	0.012
n-C15	0.006	0.013
n-C16	0.009	0.02
n-C17	0.006	0.012
n-C18	0.012	0.026
Phytane	0.012	0.025
n-C19	0.016	0.035
n-C20	0.022	0.047
n-C21	0.018	0.038
n-C22	0.019	0.042
n-C23	0.012	0.026

n-C24	0.031	0.066
n-C25	0.045	0.097
n-C26	0.004	0.009
n-C27	0.023	0.05
n-C28	0.028	0.061
n-C29	0.037	0.079
n-C30	0.076	0.164
n-C31	0.069	0.147
n-C32	0.044	0.095
n-C33	0.026	0.057
n-C34	0.015	0.032
n-C35	0.074	0.159

Appendix C

This Appendix relates to Chapter 4 of this thesis.

C.1.0 Particulate Fe

All particulate Fe samples that were successfully analysed are listed in Table C.1.

Table C.1: Successful particulate Fe concentrations across seasons from River Sites 1-3.

River Sample	Particulate Fe
	µg/L
Summer S1	5342.49
Summer S2	595.77
Summer S3	-
Autumn S1	740.28
Autumn S2	-
Autumn S3	852.85
Winter S1	-
Winter S2	-
Winter S3	-
Spring S1	1208.22
Spring S2	262.10
Spring S3	634.87

FASN 1	792.81
FASN 2	400.92
FASN 3	961.40

C.1.1 XRD measurements

XRD data was analysed using Profex software to determine minerals presented (Table C.2).

Table C.2: Minerals identified in soil and freshwater sediment sample, and a selection of fjord sediment samples from XRD analysis

Sample	Quartz	Labrad orite	Illite	Orthocl ase	Albite	Plagioclas e Andesine	Plagioclas e Bytownite	Anorthoclase	Anorthit e	Oligoclas e	Rwp	Rex p	X ²	Go F
Autumn S1	0.24		0.3	0.22	0.24						14.8	10.81	1.87	1.37
Summer S1	0.604		0.259			0.137					15.2	11.79	1.66	1.29
Winter S1	0.46		0.19	0.086	0.26						16.53	12.3	1.81	1.34
Spring S1	0.258		0.4			0.34					16.17	12.32	1.72	1.31
Spring S2	0.279		0.26			0.46					16.33	12.2	1.79	1.34
Summer S2	0.21		0.42			0.37					16.57	1213	1.87	1.37
Winter S2	0.492	0.34	0.17								16.88	12.45	1.84	1.36

Summer S3	0.507		0.306			0.187					17.42	12.88	1.83	1.35
Autumn S3	0.622		0.236			0.142					17.3	11.98	2.09	1.44
Winter S3	0.64	0.13	0.22	0.02							9.07	69.3	0.02	0.13
Spring S3	0.42		0.28		0.3						17.88	13.51	1.75	1.32
Soil averages	4.732	0.47	3.041	0.326	0.8	1.636								
FASN 1	0.39		0.27		0.26			0.085			18.15	12.88	1.99	1.41
FASN 2	0.242		0.521						0.236		15.87	11.43	1.93	1.39
FASN 3	0.31		0.489		0.17				0.03		13.76	11.76	1.37	1.17
Freshwater sediment averages	0.942	0	1.28	0	0.43	0	0	0.085	0.266					
UB1 2.5	0.288		0.544			0.168					14.58	10.95	1.77	1.33
UB1 10.5	0.3		0.469							0.231	14.73	11.45	1.66	1.29

UB1 24.5	0.253		0.462		0.063					0.22	16.51	10.85	2.32	1.52
UB2 7.5	0.355		0.41			0.18		0.05			14.65	11.55	1.61	1.27
UB2 15.5	0.316		0.385	0.072						0.227	14.05	11.22	1.57	1.25
UB2 32.5	0.305		0.45				0.25				14.77	11.67	1.60	1.27
LB1 0.5	0.31		0.54				0.15				8.32	69.51	0.01	0.12
LB1 20.5	0.381		0.517				0.1				14.79	12.4	1.42	1.19
LB1 40.5	0.372		0.387				0.24				15.18	12.12	1.57	1.25
LB2 4.5	0.485		0.182		0.14			0.2			16.77	12.31	1.86	1.36
LB2 12.5	0.488	0.224	0.232	0.057							16.12	12.15	1.76	1.33
LB2 18.5	0.497		0.31		0.059	0.13					16.01	12.35	1.68	1.30

The XRD measurements have been displayed visually as averages for each environment (Figure C.1).

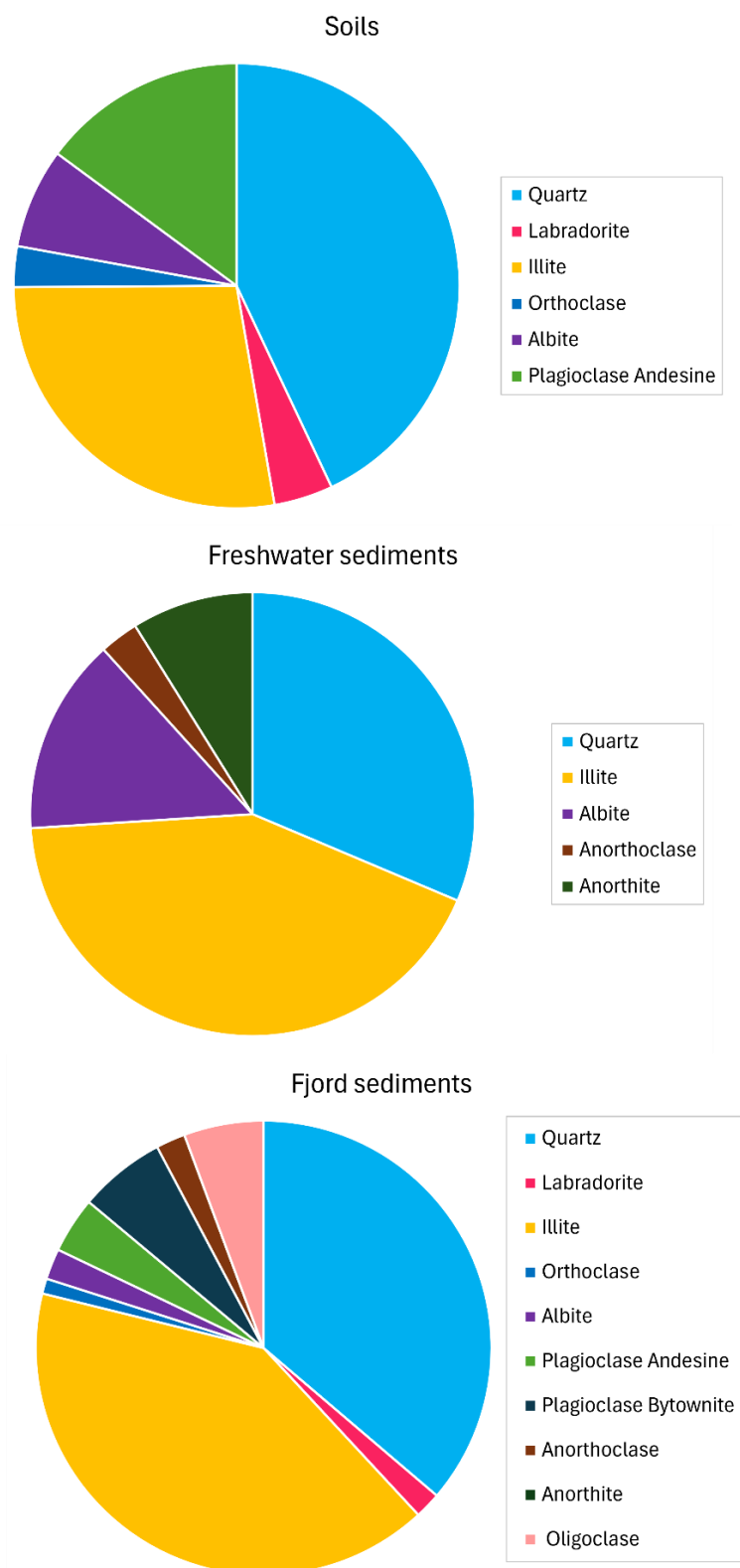


Figure C.1: Visual representation of the minerals, and quantities of the minerals present in soil, freshwater and fjord sediment samples.

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