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Abstract: Comparison of Diatom, Total Carbon, and Grain Size Proxies for Sea-Level Reconstruction

Catherine M. Kelham

Sediment lithology and biological assemblages from low energy intertidal environments (tidal flat to salt-marsh then upland communities) are valuable archives of relative sea level (RSL) information. Sediment organic matter and grain size are often recorded in addition to microfossil data to aid environmental interpretation. This study aims to assess use of sediment organic matter and grain size as indicators of former tidal level to aid diatom based RSL reconstructions.

This study firstly investigates modern (top 1cm) sediments from Loch Laxford in northwest Scotland. Grain size analysis in these sediments shows local processes are overprinting the general expected pattern of decreasing grain size away from the sea. Analysis of the modern total carbon distribution shows there a linear increase in percentage total carbon with elevation (r=0.92) between the low marsh and high marsh. Comparison of the modern total carbon distribution at a contrasting site, Beluga Slough in Alaska, shows the linear relationship still exists, but with lower total carbon values for equivalent elevations. This shows the importance of location, and climate, for total carbon distribution.

Secondly, this study applies the modern Loch Laxford total carbon – elevation distribution to reconstruct paleo marsh surface elevation (PMSE) and RSL at Loch Laxford, and in an older sediment sequence from Mointeach Mhor in western Scotland. These are compared with diatom based reconstructions from the same sites. Decomposition complicates the use of organic carbon as a sea-level proxy but does appear to stabilise. At Loch Laxford, this occurs after approximately 100 years. Sediment grain size appears to influence the total carbon value and should also be investigated. Total carbon has most potential as a sea-level proxy in sediments from the last millennium, where a local modern distribution is available and it is unlikely that large changes in grain size or volume, or organic matter accumulation have occurred.

Comparison of Diatom, Total Carbon and Grain Size Proxies for Sea-Level Reconstruction

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Department of Geography

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Abbreviations

Cal. year BP	Calendar years before present (1950)
d ¹³ C	Measure of the ratio of stable Carbon isotopes (¹³ Carbon : ¹² Carbon)
LOI	Loss on Ignition
m OD	Metres above Ordnance Datum
MHHW	Mean higher high water
MHWST	Mean high water spring tides
MLWST	Mean low water spring tides
MTL	Mean tide level (means high water and means low water)
HAT	Highest astronomical tide
m NAVD88	Metres above North American Vertical Datum of 1988
PIDS	Polarised Intensity Differential Scattering
PMSE	Paleo Marsh Surface Elevation
RMSEP	Root Mean Square Error of Prediction
RSL	Relative Sea Level (sea-level change relative to the present day)
SLIP	Sea-Level Index Point
SWLI	Standard Water Level Index

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Declaration

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Chapter 1: Introduction

Regional variations in relative sea-level change (RSL) help us understand how ice mass balances respond to climate and how these changes are translated in to sea level change at individual locations (Milne *et al.*, 2002). Records of rapid sea level change can help reconstruct earthquake histories and recurrence intervals (e.g. Hamilton and Shennan 2005, Hamilton *et al.* 2005). To understand the ice sheet histories, earth rheological properties, regional sea level variability and its drivers, as well as earthquake histories we need networks of regional RSL records that span though the Holocene and to present day (Milne *et al.*, 2002, Barlow *et al.*, 2013). Although RSL reconstructions do not give direct information on future sea level change, by understanding the mechanisms of RSL in the past, and using this data to develop earth property and climate forcing models, better predictions can be made.

Low energy intertidal environments (tidal flat to salt-marsh then upland communities) are valuable sea-level archives. Their sediment lithology and biological assemblages record both regional RSL and local, site specific, processes. In addition, they link present day RSL observations from tide gauges to longer term RSL trends (Barlow *et al.* 2013, Barlow *et al.* 2014, Long *et al.* 2014). Crucially for sea-level research, the tidal flat–salt-marsh–upland environment sedimentary characteristics and biological assemblages relate to their position in relation to tidal inundation duration and frequency, and therefore also elevation (van de Plassche 1986, Edwards 2007). Analysing the organic and minerogenic components of these low energy intertidal sediments in addition to their biological assemblages, such as diatoms and foraminifera, utilises these environmental gradients for RSL reconstruction.

Diatoms are common Holocene sea-level proxies, with good vertical zonation with elevation through the tidal flat—salt-marsh—upland environments (e.g.Nelson and Kashima 1993, Zong 1997, Zong and Horton 1998, Gehrels *et al.* 2001, Szkornik *et al.* 2006). They are not always present in Holocene sediments. In the fossil sediments, sections without diatoms can occur as diatoms are fragmented or poorly preserved (Zong 1997, Wilson and Lamb 2012). The breakdown of some species more than others can also lead to fossil assemblages being biased to more robust diatom species (Jones 2007). Using additional proxies to aid RSL reconstruct can avoid these problems and provide RSL information through fossil sediments where diatom assemblages cannot be used. A multi proxy reconstruction can also help to create more accurate and precise understandings of RSL change. Where multiple proxies are used to reconstruct change, all proxies should be considered equally (Birks and Birks 2006). Before this can be done, the proxies' relationship with the environment needs to be assessed.

1.1 <u>Aims and Objectives</u>

This project aims to investigate the use of sediment's organic matter and grain size distribution to aid diatom based sea-level reconstructions. To achieve this, the specific objectives are:

- To determine the relationship between organic matter, grain size distribution and elevation in the modern tidal flat–salt-marsh–upland system at two contrasting field sites – one in Scotland, the other one in Alaska.
- 2. To use the outcomes from the above to produce estimates of RSL change through a fossil core from the field site in Scotland.
- 3. Following reconstruction, to assess the relationship between modern and fossil salt-marsh organic matter.
- 4. To investigate a second fossil site using the same approach to test for regional applicability of this approach.

1.2 Thesis Outline

This thesis contains six chapters. Chapter 2 contains the background literature to the project. I focus on the distribution of organic matter and grain size in the tidal flat–salt-marsh–upland environment, their previous use, and how they are used in this study. I also review our current understanding of salt-marsh sediment decomposition processes. In Chapter 3, I describe the three study sites, and the laboratory and statistical analyses used in this investigation. The results from the modern sediments are presented and interpreted in Chapter 4, and from the fossil sediments in Chapter 5. In Chapter 6, I conclude the study by discussing the results in relation to the research aims and objectives.

Chapter 2: Project Background

This chapter outlines the scientific context for the study. Sediment grain size and organic matter are often assessed to help interpret sea-level records. In the field, the Troels-Smith Classification scheme is commonly used to record changes in stratigraphy resulting from changes in grain size or organic matter (Troels-Smith 1955). This classification scheme provides an objective quantification of a deposit's sediment characteristics (Long *et al.* 1999). Measuring organic matter and grain size can aid visual assessment of the sediment stratigraphy and help sea-level reconstruction by highlighting changes throughout the sediments (Long *et al.* 2010, Barlow *et al.* 2014).

In this chapter, I briefly review the main proxies used in sea-level studies. I explain the importance of tidal flat – salt-marsh – upland communities in sea-level studies and introduce microfossil based transfer function sea-level reconstruction. I then describe the distribution of grain size and organic matter across tidal flat– salt-marsh–upland systems and explain how they are used in this study. Lastly, I evaluate the organic decomposition processes occurring in tidal flat–salt-marsh–upland environments.

2.1 <u>Sea-Level Proxies</u>

In situ organic sediments , minerogenic sediments and morphological features whose formation was controlled by paleo sea-level can be used to reconstruct past changes. These are termed Sea-Level Index Points (SLIPs) and require a location, age, elevation and tendency (Shennan and Horton 2002, van de Plassche 1986). A SLIP may not have formed at Paleo Mean Sea level (PMSL) but its position is related to it. The indicative meaning relates the sample position to the tidal range so defining the vertical range at which it could occur in relation to a known water level, such as Mean High Water Spring Tides. From this we can measure RSL change (van de Plassche 1986). Uncertainties in the SLIP elevation can occur from tidal range changes, sediment compaction and the sampling processes (Shennan *et al.* 2006). The tendency of a SLIP describes whether it records an increase (positive tendency) or decrease (negative tendency) in marine influence. Changes in tendency direction indicate turning points in sea-level histories.

Examples of SLIPs come from a variety of features and sediment sequences. Isolation basins, for example in Greenland or the west coast of Scotland, record changes between marine, brackish and freshwater environments as RSL rises and falls. The height of the sill at the entrance to the basin controls tidal flooding into the basin and defines the SLIP elevation at the time when the basin is isolated or ingressesed (Long et al. 2011). Many proxies can be used to identify when the change occurred, for example microfossil assemblages, carbon to nitrogen ratios, organic matter, and changes between minerogenic and organic sediment (e.g. Long et al. 2011, Mackie et al. 2005). Tidal flat–salt-marsh–upland communities are another archive of RSL information. They record both regional RSL change and local, site specific processes through changes in their sediment lithology and biological assemblages. An alternative approach to reconstructing RSL is to use geomorphic features that formed at a known elevation in relation to a former sea level (Pirazzoli 2007). These can be erosional, such as sea arches, notches and benches or depositional, for example marine terraces or shorelines and microatolls. An example of this is from Smith et al. (2000), who use the altitudes of raised shorelines, each representing the height of former high water, and their extent to model patterns of Holocene crustal uplift in Scotland. The raised shorelines are distinguished morphologically as breaks of slopes at the back of former estuarine flats and can be dated using overlying peat.

Microfossil assemblages, such as diatoms, foraminifera, testate amoebae and ostrocods, can be used as sea-level proxies. For Holocene sea-level reconstructions, foraminifera and diatoms are the most common indicators, although testate amoebas can also produce accurate reconstructions (Gehrels, 2007, Gehrels *et al.* 2001). Diatoms and foraminifera are single celled organisms. Their abundance and distribution on salt-marshes is related to the environmental conditions in the tidal frame and this relationship can be used to infer paleo sea-level information. Both diatoms and foraminifera have a strong vertical zonation in salt-marsh environments (e.g. Hill *et al.*, 2007, Edwards *et al.* 2004, Horton *et al.* 1999, Zong and Horton, 1999, Zong and Horton, 1998) This vertical zonation has been used to suggest that environmental factors influencing their distribution are all related to tidal submergence and elevation relative to the tidal frame. Although foraminifera are good sea-level indicators, their distribution is limited to below HAT and so their use is

sometimes reduced when the fossil cores contain deposits from above this level (Gehrels *et al.* 2001). In addition, poor preservation of calcareous foraminifera in saltmarsh sediments and in faunal occurrences of some species causes problems for reconstruction (Gehrels *et al.* 2001). In this investigation, I have chosen to use diatom based reconstruction.

2.2 <u>Tidal flat–Salt-marsh–Upland Environments</u>

Tidal flat–salt-marsh–upland communities are low energy transitional environments separating the sea and land. Tidal flats are the lowest part of the transitional coastal environment. Landwards, are salt-marshes and above tidal influence, these develop into fresh water, upland environments (Allen and Pye 1992). Salt-marshes are vegetated areas of intertidal sediment (Boorman *et al.* 1998, Allen 2000). To form, salt-marshes require stable sediment where tidal exposure exceeds tidal submergence so that vegetation can establish (Boorman 2003). Sediment supply, organic material accumulation, tidal regime, relative sea-level (RSL) change, and wind and wave patterns all influence salt-marsh evolution (Allen and Pye 1992, Allen 2000). Importantly for sea-level research, the grain size, organic matter characteristics and biological assemblages from the tidal flat–salt-marsh–upland environments relate to their position in relation to tidal inundation duration and frequency, and therefore also elevation (van de Plassche 1986, Edwards 2007). Figure 2.1 shows a schematic diagram of a salt-marsh environment, with reference water levels and vegetation zones.



Figure 2.1: Schematic diagram of a salt-marsh environment showing zonations and reference water levels. (HAT – Highest Astronomical Tide, MHWST – Mean High Water Spring Tides, MTL – Mean Tide Level)

2.3 <u>Transfer Functions</u>

Transfer functions quantitatively predict an environmental variable as a function of biological data, and provide an estimation of the associated errors, (Birks 1995, Birks *et al.* 2010). In sea-level change studies, transfer function reconstructions produce sequences of sea-level index points which can help to build a detailed picture of sea level through time (Barlow *et al.* 2013).

Transfer functions development has two main steps. Firstly, using regression, modern day environmental data is expressed as a function of modern day biological data. This spatial relationship in the modern environment can be substituted for time as each assemblage in the vertical sequence is the outcome of horizontally adjacent depositional environments. In sea-level change studies, this microfossil assemblage data and their associated surface elevations often come from tidal flat–salt-marsh–upland environments. In the second step, the transfer function model uses the modern day relationship to produce quantities estimates of the environmental variable in the past from the fossil biological data. In this work, I use diatom based transfer functions reconstructions to compare with the sea-level estimates produced from organic matter and grain size distribution.

2.4 <u>Grain Size in Sea-level Reconstruction</u>

Sediment grain size influences its mobilisation, transport and deposition. The sediment sources dictate what sediment is available, and changes to the source can alter sediment type, effecting its mobilisation, transport and deposition (Allen and Pye 1992). Patterns of salt-marsh sedimentation and their relationship with elevation through the tidal flat – salt-marsh system have previously been investigated by Bartholomä and Flemming (2007) and Plater *et al.* (2011). Water velocity slowing over the tidal flat – salt-marsh surface causes a decrease in grain size from the sea and other large channels (Allen 1992, Adnitt *et al.* 2007). Sediment deposition as water velocities slow is aided by salt-marsh vegetation trapping suspended sediment (Allen 2000, Christiansen *et al.* 2000). Salt-marsh creeks also provide pathways for water and sediment to move through the coastal system and influence sediment deposition.

al. 2007). These deposition patterns should be identifiable in the fossil sediments as grain size distribution is not effected by preservation issues (Plater *et al.* 2011).

Rahman and Plater (2014) developed a conceptual mode (Figure 2.2) to shows how grain size distribution changes across the tidal flat - salt-marsh surface with elevation, excluding the effect of creeks in routing sediment. In the model, elevation is used as a function of tidal height and flow velocity.



Figure 2.2: A conceptual model of grain size distribution across salt-marsh varying with elevation because of tidal height and flow velocity. Figure adapted from Rahman and Plater, 2014, (Figure 2, p. 141). The solid curves in the tidal flat – salt-marsh system show the dominant expected percentage volume – grain size distribution whilst the dotted curves represent the contribution from the other deposition mechanism.

Sediment deposition varies in relation to the frequency and duration of tidal inundation. The conceptual model separates tidal deposition into simple 'fast tide' and 'slow tide' settings (Rahman and Plater 2014). As seen in Figure 2.2, this creates a pattern of percentage volume and grain size as the two different mechanisms vary over the marsh surface with elevation. 'Fast tide' dominates lower in the tidal flat - salt-marsh where a coarser, traction load is deposited. 'Slow tide' deposits are finer and occur higher in the tidal flat - saltmarsh where suspended load deposition dominates. Tidal velocity is only sufficiently low close to the high water level for fine suspended sediment to settle out, and remain on the marsh surface (Allen and Pye 1992). Table 2.1 summaries the characteristics of the two deposit types described in Rahman and Plater (2014). Higher in the marsh, grain size distribution is expected to be finer and more better sorted than lower in the marsh due to the changing dominance of the fast and slow tide deposition mechanisms. This information can give useful information on the relative position of samples. The two types of deposition will vary across the marsh surface, be influenced by tidal cycles and storm events, and change as the marsh evolves (Rahman and Plater 2014) but can give some indication of tidal flow and therefore relative elevation.

	Fast	Slow
Location on Salt-marsh	Lower	Upper
Method of Deposition	Traction	Suspension
Relative Grain Size	Coarser	Finer
Sorted	Moderate	Poor – Very poor
Skew	Larger finer proportion	Near symmetrical
Kurtosis ('peakedness')	Meso – leptokurtic	Meso - platykurtic

Table 2.1: Properties of faster and slower deposited sediment from Rahman andPlater (2014)

In this study, I use the 'fast tide' and 'slow tide' percentage volume – grain size curves described by Rahman and Plater (2014) to interpret the grain size distributions in the modern and fossil sediment samples. I also look at the sand, silt and clay grain size fraction.

2.5 Organic Matter in Sea-Level Reconstruction

The main primary producers in tidal flat–salt-marsh–upland systems are plants and algae (Adnitt *et al.* 2007). These produce organic compounds from carbon dioxide via

photosynthesis. Most plant species in the tidal flat–salt-marsh–upland transitional environment have zonations controlled by tidal flooding duration, and other biotic and abiotic factors including the rate of siltation, plant competition, and soil organic matter (Pielou and Routledge 1976, Vince and Allison 1984, Gray 1992). These zonations are shown in the previous schematic diagram - Figure 2.1. Typically , these vegetation zones change with surface elevation (Gray 1992). Organic rich peats tend to occur at the highest elevations at and above tidal influence. Seawards there is gradually less vegetation and more inorganic sediment (Lamb *et al.* 2006, Plater *et al.* in press). This vertical zonation of biological assemblages allows the tidal flat – saltmarsh – upland environments to be characterised using their organic matter (Edwards 2007, Plater *et al.* in press).

The position of changes in sediment organic matter in the modern day relative to a reference water level can provide useful markers in sea-level reconstruction. The distribution of plant species and peats in the modern low energy coastal environments and their subsequent identification in fossil sediments can provide useful information about the paleo environment (Behre 1986, Shennan 1986, Bos *et al.* 2012). Distinguishing between these deposits in fossil sediments helps to limit the sea-level position at the time the deposit formed and can aid paleo marsh surface elevation (PMSE) and RSL reconstruction.

Salt-marsh organic matter providence, and therefore position relative to sea level, has previously been characterised using δ^{13} C and carbon to nitrogen ratios (e.g. Chmura and Aharon 1995, Wilson *et al.* 2005a, Wilson *et al.* 2005b, Lamb *et al.* 2007). δ^{13} C is the stable carbon isotopic composition, expressed in parts per mil (‰), and calculated from the ratio of ¹³Carbon to ¹²Carbon. Certain plants species utilise either the C₄ or C₃ photosynthetic pathways. These have clear distinctions in δ^{13} C values. The photosynthetic pathway of C₄ plants enables them to survive in more saline conditions (Chmura and Aharon 1995). On tidal marshes the relative abundance of plants of each pathway type relates to its elevation above sea level (Lamb *et al.* 2006), and the fresh water fluvial input (Lamb *et al.* 2007). A lack of C₄ plants in many UK tidal flat–saltmarsh–upland systems reduces the δ^{13} C range, and therefore its use for distinguishing the sources of organic carbon (Wilson *et al.* 2005b, Lamb *et al.* 2006). Carbon to nitrogen ratios are also organic material source indicators. Some organic material, for example plankton, is nitrogen rich and therefore has lower carbon to nitrogen ratios (Tyson 1995). This can help distinguish sediments which have similar δ^{13} C values through time (Lamb *et al.* 2006). Unfortunately, selective degradation of plant material, for example cellulose, causes a negative shift in the δ^{13} C values (Ember *et al.* 1987, Tyson 1995). Similarly, in salt-marsh surface litter decomposition, nitrogen is initially lost more rapidly than carbon, leading to an initial increase in the carbon to nitrogen ration (Lamb *et al.* 2006). Subsequent loss of carbon through respiration, or increases in nitrogen from bacterial nitrogen fixation, then increases the carbon to nitrogen ratio (Wilson *et al.* 2005a, Lamb *et al.* 2006). These decomposition changes complicate the use of carbon to nitrogen ratios (Valiela *et al.* 1985, Ember *et al.* 1987, Lamb *et al.* 2006).

In this study, I examine the relationship between elevation and organic matter using total (organic) carbon and LOI in modern sediment samples rather than the organic material providence. I measure the organic matter incorporated in the sediment through below ground productivity of plants and accumulation of degraded plant material. This does not include the vegetation growing on the tidal flat–salt-marsh–upland surface. Organic matter measurements (Plater *et al.* in press). Loss of organic material through decomposition will result in decreases to the LOI and total (organic) carbon values.

2.6 <u>Decomposition of Organic Matter in salt-marshes</u>

The amount of organic material in fossil salt-marsh sediments depends on the amount of material entering the sediment record and the amount removed through decomposition processes. Salt-marshes have high primary productivity but only a small amount of organic matter is permanently accreted into the sediment (Howarth 1993). Organic material is degraded and lost above ground between the plants growing and the leaf litter entering the sediment. Modern sediment organic matter measurement in this study includes any below ground organic matter but not any plant material on the marsh surface. A second phase of organic material loss occurs in the sediment column as the organic material decomposes. This decomposition phase will cause a change between the modern and fossil organic matter values. In terrestrial peat land environments, decomposition can be tracked based on the position of the water table, inferred using C/N ratios or lipid biomarkers (e.g. Kuhry and Vitt 1996, McClymont *et al.* 2008). The position of the water table marks the transition between the acrotelm where aerobic decomposition occurs and the catotelm where slower anaerobic decomposition occurs (Kuhry and Vitt, 1996). Less decomposition therefore occurs when the water table is high, in wet climatic conditions, and faster rates occur during drier times with a lower water table (Ise *et al.* 2008, Biester *et al.* 2013). In salt-marshes using this technique is problematic due to the frequent tidal flooding changing the depth at which sediments are waterlogged.

In salt-marshes below the ground surface, organic matter is reworked and broken down by bacteria and fungi (Meyers 1997, Allen 2000). This can be aerobic, in the presence of oxygen, or anaerobic, without oxygen. The microbial processes that take act to break down organic matter in salt-marsh sediments have been reviewed by Howarth (1993) and are summarised here. Aerobic respiration only takes place where oxygen is available near the sediment surface. High oxygen usage near the sediment surface and poor oxygen diffusion through water logged sediment reduces the availability of oxygen in the sediment column and helps create anaerobic conditions (Howarth 1993). In anaerobic conditions, bacteria using sulphate as the oxidising agent break down organic compounds and dominate the decomposition process (Howarth 1993). Denitrification and iron, manganese, and methanogenesis reduction by bacteria are all minor organic decomposition processes in salt-marshes and use up little carbon.

Investigations into the depth, and time, over which salt-marsh organic matter decomposition occurs have mainly focused on sulphate reduction rates. Kostka *et al.* (2002) measured the sulphur reduction rate over multiple seasons at different locations across a salt-marsh in Georgia, Eastern USA. At the middle marsh site, sulphate reduction greatly reduces below the top few centimetres in both the summer and winter (see Figure 2.3). Their findings support Hines and Jones (1995) and Hines *et al.* (1989) who suggest, in a middle marsh type setting, maximum sulphate reduction occurs in the upper few centimetres and sulphate reduction experiences a rapid decrease with depth in non-bioturbated sites. Rapid initial decomposition is also supported by the buried litter bag experiments of Benner *et al.*

(1991). Their experiments of below ground *Spartina alterniflora* decomposition showed after 18 months only 45% of the original organic matter remains.



Figure 2.3: Sulphate reduction rate depth profile from Kostka et al. (2002), (Figure 7, p 61). Sulphate reduction rates were measured at three locations on the salt-marsh sites over five seasons (August 1997 and January 1998 displayed here). Symbols show duplicate samples, black line represents average. (See figure 7 in Kostka et al. 2002). The sulphate reduction rate greatly reduces below the top few centimetres.

In the bioturbated sites investigated by Kostka *et al.* (2002), the decrease in sulphur reduction rate with depth is less pronounced. They attribute this to the downward mixing of organic matter supplying more material for anaerobic respiration. Indeed, Howarth (1993) suggests the rate of sulphate reduction is strongly linked to the supply of organic material.

Temperature also has some effect on sulphate reduction rate. In the winter when temperature is lower, sulphate reduction rate decreases (Kostka *et al.* 2002, V.-Balogh *et al.* 2006). This single factor does not explain all the variability in sulphate reduction rates (Howarth 1993). Spatial and temporal differences in the sulphate reduction rates appear to exist on and between salt-marshes and will effect organic decomposition.

From these studies of below ground salt-marsh decomposition, there are two main mechanisms operating. Aerobic decomposition occurs near the surface and depends on oxygen availability. Anaerobic decomposition occurs below surface where sediments are waterlogged and oxygen cannot diffuse through the sediment. Sulphate reduction dominates anaerobic decomposition (Howarth 1993). Sulphate decomposition decreases with depth but is effected by organic material availability and temperature (Howarth 1993, Kostka *et al.* 2002, V.-Balogh *et al.* 2006). What depth decomposition occurs to, and how much decomposition occurs, appears to vary between seasonally and between salt-marshes (Howarth 1993, Kostka *et al.* 2002).

2.7 <u>Summary</u>

In this Chapter, I have shown organic material and grain size from tidal flat–salt-marsh –upland systems have the potential to be used as RSL indicators. Sediment grain size should show a trend of decreasing grain size, and larger 'slow tide' component with distance from the sea. Organic matter distribution in tidal flat–salt-marsh–upland systems relate to vegetation zonation and abundance. Decomposition of organic sediment complicates the interpretation of fossil organic matter. Few studies quantify the time over which decomposition occurs and therefore whether it can be accounted for in order to use organic matter as a proxy measure of sea-level change. The location of the field sites and the methods I use to measure organic matter and grain size are described in Chapter 3.

Chapter 3: Field Sites and Methods

This chapter introduces the field sites (3.2) and outlines the laboratory (3.3) and statistical (3.4) methods used to investigate the use of sediment's organic matter and grain size distribution to aid diatom based sea-level reconstructions.

This study uses three low energy intertidal field sites. The main field site is Loch Laxford in the North West Scotland. I use total carbon content, loss on ignition (LOI), diatom assemblages, and grain size data from the modern surface and core samples from this site. I use ordination methods to investigate what effect these environmental variables have on the diatom distributions in the modern environment. Fossil diatom assemblages from this site form an existing relative sea-level reconstruction (Barlow *et al.* 2014) and are compared with the alternative total carbon based RSL reconstruction. I also investigate total carbon and diatom assemblages at the contrasting modern field site, Beluga Slough in Alaska. Here I investigate the relationship between elevation and total carbon at a contrasting modern site. The secondary fossil field site is Mointeach Mhor in the West Scotland. I use a monolith from this site to investigate the regional applicability of using total carbon or grain size to help reconstruct RSL changes. I use grain size, total carbon, loss on ignition, and the diatom distribution data form this site. Both Scottish field sites were investigated previously and this study enhances the existing data.

To compare and combine data from multiple sites where tidal ranges differ, I converted metres above ordnance datum (m OD) or metres NAVD88 (m NAVD88) into standard water level index (SWLI) for each sample (n). I use the same conversion (Equation 4.1) as in the Northwest Scotland diatom data set (Barlow *et al.* 2013). Fossil material is plotted using core depth in centimetres where '0' is the upper surface of the core or monolith. Table 3.1 shows the tidal levels for each site. I convert PMSE to RSL using Equation 3.2.

$$SWLI_n = \frac{100(h_n - h_{MTL})}{h_{MHWST} - h_{MTL}} + 100$$

Equation 3.1: SWLI equation, h_n is the sample elevation (m OD), h_{MTL} is the local mean tide level elevation (m OD), and h_{MHWST} is the local mean high water spring tide. For Beluga Slough Mean Higher High Water (MHHW), the average of the higher high water height of each tidal day, rather than MHWST is used. MTL at any site accordingly has a SWLI value of 100 and MHWST or MHHW has a SWLI value of 200.

Site	Tidal Observation Location	MHWST	MTL	НАТ
Mointeach Mhor, Scotland ¹	Mallaig, Lochaber (8km North)	2.38 m OD	0.28 m OD	3.02 m OD
Loch Laxford, Scotland ¹	Loch Laxford	2.40 m OD	0.25 m OD	3.15 m OD
Beluga Slough,	Seldovia	3.89	1.42	5.34
Alaska ²	(25km South)	NAVD88 m	NAVD88 m	NAVD88 m

Table 3.1: Tidal levels for each field site, (¹Admiralty tide tables 2001, ²NOAA 2013)

 $RSL_n = sample elevation_n - PMSE_n$

Equation 3.2: Conversion from PMSE to RSL

3.1 <u>Study Sites</u>

3.1.1 Loch Laxford, Scotland

Loch Laxford is the main field site used in this investigation. It is located in the northwest Scottish highlands and is the northern most sea loch in the Northwest Scottish mainland (Figure 3.1). It incorporates the smaller Loch Dùghaill and Loch a' Chadh-Fi which branch from the northern edge of the main loch. The tidal sand flat–saltmarsh–upland system sampled are part of an 'embayment type marsh' (Allen 2000). It is located at the head of



Figure 3.1: Scottish field site locations. (Map from Digimap)

the Loch on the southern edge, in the small sheltered tidal basin Tràigh Bad na Bàighe (Figure 3.2). The northwest Scottish coastline is sparely populated and the surrounding vegetation is predominantly heather moorland. The saltmarshes in this area are unlikely to be affected by organic pollutant. This and its sheltered location make it a suitable field site for this investigation.

The lowest sample is from the sand flats and has an elevation of 1.24 metres OD. Across much of the site a small, approximately 10 centimetres, cliff exists between the tidal flat and salt-marsh. Above approximately 3.50 metres OD, there is an iris and freshwater heather community. MHWST at Loch Laxford is 2.40 metres OD, MTL is 0.25 metres OD and HAT is at 3.15m OD (*Admiralty Tide Tables* 2001). Spring tidal range at Loch Laxford is 4.2 metres.



Figure 3.2: Location of Loch Laxford tidal flat–salt-marsh–upland system in Northwestern Scotland.

Map B shows the location of Loch Laxford salt-marsh in Tràigh Bad na Bàighe inlet. Red box in Map A indicates location of Map B. In Map B, the surface sample transect location shown by black line, red spot marks approximate core location. (Maps A and B from Digimap). Panoramic image C shows the tidal flat—salt-marsh—upland heather and iris. The black line indicates surface sample transect location. Photograph taken from above the marsh facing south, Person for scale. Barlow *et al.* (2014) collected the surface samples and sediment cores and investigated the diatoms as part of their work on the 'North Atlantic sea-level change and climate in the last 500 years' (Barlow *et al.* 2014) and the Northwest Scotland training set (Barlow *et al.* 2013). The modern data contains 60 samples from the tidal flat, salt-marsh, and upland iris and heather communities. They have an elevation range of 3.74 and 6.40 NAVD88 metres. The core used in this project is LA-11-03(r) and was collected from the middle marsh zone with a core top elevation of 1.80 metres. It is an adjacent duplicate of the core LA-11-03 analysed by Cullen (2013) and (Barlow *et al.* 2014). It is referred to as 'LA-6' in the latter. The diatom assemblage counts, LOI data, modern sediment samples, and fossil cores have kindly been made available for this project. At this site, I measure total carbon and investigate grain size from the same surface samples used by Barlow *et al.* (2014) and in the duplicate fossil core. The Loch Laxford core has been radiocarbon dated at 4cm intervals to 44cm core depth. These dates are displayed in Table 3.2.

Sample code	Depth	Description	Dating Method	Reported ¹⁴ C age(s) + 1sd
				error
SUERC-35801	4.5 ±	Humin bulk	High Precision	108.68 ± 0.25 (% modern)
SUERC-35802	0.5		(HP) triplicate	108.82 ± 0.30 (% modern)
SUERC-35803				108.28 ± 0.27 (% modern)
SUERC-35804	8.5 ±	Humin bulk	HP triplicate	119.45 ± 0.32 (% modern)
SUERC-35805	0.5			118.96 ± 0.32 (% modern)
SUERC-35806				118.97 ± 0.29 (% modern)
SUERC-35807	12.5 ±	Humin bulk	HP triplicate	106.40 ± 0.29 (% modern)
SUERC-35811	0.5			106.38 ± 0.29 (% modern)
SUERC-35812				106.76 ± 0.26 (% modern)
SUERC-35813	16.5 ±	Humin bulk	HP triplicate	21 ± 20
SUERC-35814	0.5			92 ± 22
SUERC-35815				81 ± 22
SUERC-35816	20.5 ±	Humin bulk	HP triplicate	264 ± 21
SUERC-35817	0.5			249 ± 20
SUERC-35821				232 ± 20
SUERC-35834	24.5 ±	Humin bulk	HP triplicate	595 ± 21
SUERC-35835	0.5			606 ± 22
SUERC-35836				562 ± 21
SUERC-35837	28.5 ±	Humin bulk	HP triplicate	683 ± 21
SUERC-35841	0.5			664 ± 21
SUERC-35842				683 ± 21
SUERC-35844	32.5 ±	Humin bulk	HP triplicate	583 ± 21
SUERC-35845	0.5			581 ± 21

SUERC-35846				614 ± 21
SUERC-35847	36.5 ±	Humin bulk	HP triplicate	610 ± 20
SUERC-35851	0.5			586 ± 22
SUERC-35852				592 ± 21
SUERC-35853	40.5 ±	Humin bulk	HP triplicate	678 ± 21
SUERC-35854	0.5			658 ± 21
SUERC-35855				681 ± 20
SUERC-35856	44.5 ±	Humin bulk	HP triplicate	878 ± 21
SUERC-35857	0.5			853 ± 19
SUERC-35861				865 ± 20

Table 3.2: Loch Laxford core dates from Barlow et al. (2014) Table 2, p.10 Radiocarbon dates from Loch Laxford.

The age - depth model shows evidence of an erosional phase between 20 and 24cm depth (see Cullen 2013, Barlow *et al.* 2014 (supplementary information)). Figure 3.3 shows this. Barlow *et al.* (2014) suggest this hiatus represents a period of erosion at AD 1500 ± 100. The core is located at the seaward edge of a peat sequence. During the erosional period Barlow *et al.* (2014) hypothesis the marsh front moved close to the core location, then moved seawards towards the present day enabling a sediment record to accumulate before and after the erosional phase. The biostratigraphy does not show evidence of this sedimentation pattern.



Figure 3.3: Loch Laxford core age model showing non-continuous sedimentation. Figure from Barlow et al (2014) supplementary information, Figure 6:'BACON age model for core LA-6'

3.1.2 Mointeach Mhor, Scotland

Mointeach Mhor is located in Northwest Scotland, close to Arisaig in the western Highlands and approximately 8 km south of Mallaig (Figure 3.1). The monolith used in this investigation is from the northern section of a former tidal embayment, Mointeach Mhor (Figure 3.4). The sediments were exposed in 2001 during road construction. The northern Mointeach Mhor samples are believed to have formed in a more sheltered part of the wetland and therefore offer a better record of sedimentation compared to those in the southern part of the site (Shennan *et al.* 2005). Mointeach Mhor became a tidal embayment as rising sea level in the mid Holocene beached a dune ridge and inundated a wetland (Shennan *et al.* 1995, Shennan *et al.* 2005). Sea-level index points from this location, and surrounding area, show evidence for the Mid Holocene highstand reaching maximum elevation around 6.74 ± 0.2 metres above present at approximately 7600-7400 cal. year BP (Shennan *et al.* 2005). The sea-level highstand is thought to have extended for over 1000 years, with sea level within one metre of the maximum, and ended gradually around 5900 cal. Years BP (Shennan *et al.* 2000, Shennan *et al.* 2005).



Figure 3.4: Location of Mointeach Mhor and sediment monolith in North-western Scotland

Red box in Map A indicates location of Map B. Mointeach Mhor and the Monolith location shown in Map B. (Maps from Digimap).

Shennan *et al.* (2005) collected the sediment monoliths and examined the diatoms, LOI and grain size. This data and the sediment monoliths were kindly made available for this investigation. The monolith used has a top elevation (0 centimetres depth) of

9.37m OD. Diatoms were preserved only in the section between 20 and 50cm depth and this section is used in the investigation. The sediments are much older than Loch Laxford core sediment. The monolith was radiocarbon dated at 10 cm, 33cm, 46cm and 50cm (Shennan *et al.* 2005). The dates are summarised in Table 3.3.

Depth	Elevation	Lab code	¹⁴ C age BP ±	Age (cal. Years BP)		
(cm)	(m OD)		error	Median	Min	Max
10	9.27	AA54113	5771 ± 47	6575	6716	6452
33	9.04	AA54112	6499 ± 47	7394	7551	7309
46	8.91	AA54111	6786 ± 49	7635	7710	7515
50	8.87	AA54110	6836 ± 59	7671	7786	7580

Table 3.3: Mointeach Mhor dates from Shennan et al. (2005) Table 1 p.98 ' Sea- level index points and limiting dates from Arisaig, (a) Wetland site index points'

The closest port with tidal observations to Mointeach Mhor is Mallaig, approximately 8 km to the north. Here, present day MHWST is at 2.38 metres OD and MTL is 0.28 metres OD. Spring tidal range is 4.3 metres (*Admiralty Tide Tables* 2001).

3.1.3 Beluga Slough, Alaska

Beluga Slough is tidal area immediately east of the city of Homer. It is on the Kenai Peninsula, approximately 190km south of the city of Anchorage in south central Alaska. Beluga Slough is a tidal flat–salt-marsh system located seaward of the Sterling highway, to the south west of Beluga Lake. It is an 'embayment type marsh' (Allen 2000). Beluga Slough lies on the northwest side of Kachemak Bay, a large tidal bay off the south western side of the Cook Inlet. The location of Beluga Slough is shown in Figure 3.5.

The nearest port to Beluga Slough with tidal observation is Seldovia, approximately 25km to the south, bordering the southwest site of Kachemak Bay. Here, MHHW is 3.89 metres NAVD88, MTL is 1.42 metres NAVD88, and HAT is 5.34 metres NAVD88. Spring tidal range is 4.7 metres (NOAA 2013).





The Beluga Slough data contains 54 tidal flat and salt-marsh modern surface samples. They were collected in 2013 by Shennan *et al.* (unpublished data). The samples have an elevation range between 3.74 and 6.40 NAVD88 metres. At this site, I measure total carbon and investigate the diatom assemblages. The amount of sediment collected in each samples is small and so following the investigation at Loch Laxford, I chose to focus on total carbon and did not measure grain size or LOI at this site.

3.2 Laboratory Methods

Sample preparation followed standard methods. The data used in this investigation from each of the three field sites is summarised in the table below.

	Loch Laxford Modern	Beluga Slough Modern	Loch Laxford Fossil	Mointeach Mhor Fossil
Diatoms	Barlow <i>et al.</i> (2013)	This study	Barlow <i>et al</i> (2014)	Shennan <i>et</i> <i>al.</i> (2005)
Total Carbon	This study	This study	This study	This study
Nitrogen	This study	This study	Х	Х
LOI	This study and Barlow <i>et al.</i> (unpublished data)	-	Cullen (2013)	Shennan <i>et</i> <i>al.</i> (2005)
Grain Size	This study	-	This study	Shennan <i>et</i> <i>al.</i> (2005)

Table 3.4: Summary of the data used in this investigation. The data kindly supplied by others is as indicated; X indicates variable was not used in this investigation; - indicates variable was not measured in this investigation

3.2.1 Grain Size Analysis

Grain size analysis separates the minerogenic fraction into size categories. Results are expressed as a percentage of the total minerogenic component. To measure grain size the organic component must be removed from the samples. To do this, the organic material is digested using hydrogen peroxide. Once the organics are removed, the sample is centrifuged at 3700 rpm for 5 minutes. Each time the supernatant liquid decanted in order to remove any remaining hydrogen peroxide. Lastly, in the preparation stage, 20ml of distilled water is added to the sample along with 2ml of the deflocculating agent aqueous sodium hexametaphosphate. I use a Coulter I230 Laser Granulometer with Polarised Intensity Differential Scattering (PIDS) to measure the grain size. This machine can measure grain sizes between 0.04μ m and 2000 μ m. Sample properties are calculated from their diffraction of laser light and PIDS enables the measurement of submicron particles, as small as 0.04μ m (Blott *et al.* 2004). To analyse the data, I use the program 'GRADISTAT' (Blott and Pye 2001) and the Folk and Ward method to assess the skew, sorting and kurtosis.

I examine grain size distribution results in two ways. Firstly, I look at the three grain size fractions and their relationship with elevation. Secondly, I plot the grain size
results as percentage volume – grain size curves and compare them with the 'fast tide' and 'slow tide' deposits described by Rahman and Plater (2014).

3.2.2 <u>Organic matter</u>

Sediment organic matter is measured in two ways, by Loss on Ignition (LOI) and by using the total (organic) carbon content. LOI is a measure of the organic material. It includes all elements that form organic compounds, for example hydrogen, nitrogen, carbon, and oxygen. Total organic carbon is a measure of just the carbon in the organic material.

Total Carbon and Total Organic Carbon

Total carbon is a measure of the carbon proportion in the organic and inorganic material. It is measured as a percentage of the sediment dry mass. Total organic carbon is the difference between total carbon and total inorganic carbon.

For calculating both total carbon and total organic carbon, the samples are firstly dehydrated by freeze-drying. Samples are placed in a -60°C freezer for approximately 24 hours then moved to a pressurised hotplate system for the drying phase. As the pressure lowers and the samples warm, the frozen water in each samples sublimates and drains from the system. Once dehydrated, the samples are bore-milled into a fine homogeneous powder.

To measure total carbon between 1 and 12mg of each a sample is weighed into a tin capsule. The mass estimation depends on sample colour. Greyer samples generally indicate higher minerogenic component, so more sample is required to be within the machine detection limit. Total carbon is measured using a Costech Elemental Analyser with sphagnum reference material and calibrated using a sulphanilamide standard. The elemental analyser uses combustion and gas chromatography to calculate the amount of carbon present in each sample. This is converted to a percentage total carbon value using sample mass.

Inorganic carbon is calculated using titration with sodium hydroxide. This method has a detection limit of 0.5%. One gram of freeze-dried, bore-milled sample is added to a 250ml conical flask with 10ml of 1N Hydrochloric acid. Next, each flask is heated to 50°C and then cooled to room temperature. 50 ml of deionised water and

approximately 1ml of phenolphthalein indicator are then added. This solution is then titrated against 1N sodium hydroxide until a faint pink end-point is reached and the titre is recorded.

The titration technique for measuring inorganic carbon relies on a colour change that is obscured when using larger quantities of sediment. A selection of samples from Loch Laxford surface were analysed using this method. All were below the 0.5% detection limit. In the modern samples, total carbon is equivalent to total organic carbon. Inorganic carbon sources include carbonate ions, for example calcium carbonate, and bicarbonate ions. Some invertebrates with calcium carbonate shells, such as molluscs, do live on mudflats (Adnitt *et al.* 2007) . Their shells can be broken down into fine, mud sized particles by boring sponges and worms (Allen 2000) providing a potential source for inorganic carbon. Most carbon in tidal flat - salt-marshes - upland environments is expected to be organic. Samples from the other sites could not be investigated as the larger quantities of sediment required for inorganic carbon detection would obscure the colour change. An alternative method was not possible due to laboratory equipment constraints. I therefore use total carbon rather than total organic carbon throughout this investigation.

<u>Nitrogen</u>

Nitrogen is measured in the samples at the same time as the total carbon in the modern surface samples, using the Costech Elemental Analyser with sphagnum reference material and calibrated using a sulphanilamide standard. It is used in the statistical analysis ordination of surface data.

Loss on Ignition

LOI is a measure of the organic matter as a percentage of the dry mass. It was measured using the method of Heiri *et al.* (2001). Each sample is oven dried to remove moisture then burnt in a furnace at 550°C for four hours. The dry weight minus the remaining ash is the LOI organic matter value. Barlow et al (unpublished data) measured Loch Laxford Surface LOI for forty-three of the sixty surface samples. The Loch Laxford core LOI is from the adjacent duplicate core and was measured by Cullen (2013). To check between the cores, 10 samples at 7cm intervals (excluding 21cm depth as it is within the erosional hiatus) in the LA-11-03(r) core were also analysed. Mointeach Mhor LOI was measured by Shennan *et al.* (2005).

3.2.3 Diatom analysis

All diatom preparation and identification used standard methods (Palmer and Abbot 1986). The diatom samples from Loch Laxford marsh surface form part of the North West Scotland diatom training set (Barlow *et al.* 2013). The Loch Laxford core diatoms are from the adjacent duplicate core (LA-6) to the one used for the carbon and nitrogen analysis (LA-11-03(r)). This core was investigated by Barlow *et al.* (2014). Mointeach Mhor diatoms were examined by Shennan *et al.* (2005). Diatoms from Beluga Slough surface were investigated as part of this project. Each sample contains 250 diatoms, except at Mointeach Mhor where poor preservation of diatoms have prevented this. Diatom counts from Mointeach Mhor contain between contain 103 to 115 diatoms.

3.3 <u>Statistical Analysis</u>

3.3.1 <u>A Total Carbon Model</u>

I use a simple linear regression model (Equation 3.3) to describe the relationship between surface total carbon and elevation, from the sand flats to high marsh environment, at Loch Laxford. From this relationship in the modern day, total carbon measurements in the core can be related to a paleo marsh surface elevation (PMSE). This relationship relies on the assumption that this relationship at the surface between elevation and total carbon has not changed, and that the fossil values have not undergone any post depositional processes.

elevation = $(m \times \% \text{ total carbon}) + c$

Equation 3.3: Linear regression equation between elevation and total carbon, m = gradient, c = y intercept

The model performance is assed using the squared correlation (r²) and model residuals. The r² indicates the fraction of the explained variance. In a model where there is a good agreement between observed and predicted values, the r² will be closer to one. The model residuals are the difference between the actual elevation and

predicted elevation. They are plotted against actual elevation to assess model output. Any structure in the residuals suggests the model does not account for all the controlling, or partially controlling factors.

Model errors are calculated from the regression standard error multiplied 95% confidence level (1.96). Unlike the diatom transfer function errors of prediction, these errors are not cross validated, or sample specific and therefore are likely to be an underestimate of actual model error.

I use model developed from the Loch Laxford modern total carbon values and elevation to produce PMSE and RSL estimates using the Loch Laxford and Mointeach Mhor fossil samples.

3.3.2 Ordination

Ordination is a method of measuring the strength of the relationship between biological and environmental data. It is useful here to investigate what effect total carbon and grain size have on the diatom distributions. In ecological systems, large numbers of abiotic factors, or environmental variables, impact species abundance and distribution. Ordination is a set of multivariate techniques that arrange species data along axes to detect possible underlying structure so that these influences can be assessed (ter Braak 1995, Lepš and Šmilauer 2003, Birks 2010).

Ordination can be either indirect or direct. In indirect ordination methods, patterns in the species data are used to maximise the variance explained by each axis without knowledge of the environmental data. In direct ordination methods, the environmental data is used to explain patterns in the species data and maximise the variance explained by the axes (ter Braak and Prentice 1988, ter Braak 1995, Lepš and Šmilauer 2003, Birks 2010). The methods names are summarised in table 3.5.

	Indirect	Direct
	(unconstrained)	(constrained)
Linear	Principle Component Analysis (PCA)	Redundancy Analysis (RDA)
Unimodal	Correspondence Analysis (CA)	Canonical Correspondence Analysis (CCA)
Unimodal - Detrended	Detrended CA	Detrended CCA

Table 3.5: Summary of ordination methods

The ordination models were run using CANOCO, version 4.55 (ter Braak and Šmilauer 1997). To choose an appropriate method, the species response to the environment needs to be identified. This can be unimodal or linear. It is assessed using the 1st axis gradient length of the species data with a detrended model (Lepš and Šmilauer 2003). If the detrended correspondence analysis (DCA) first axis gradient length greater than three standard deviation units, the distribution of species along the first axis indicates unimodal methods are most appropriate (ter Braak and Prentice 1988). Using this information, I can select the most suitable constrained, or direct, ordination model. This type of model can simultaneously analyse the species and environmental data. I also run partial direct analyses to describe the variance in the data set accounted for by each of the environmental variables.

3.3.3 <u>Diatom Transfer Function Development</u>

At Loch Laxford, I use a published sea-level reconstruction, developed using transfer function techniques by Barlow *et al.* (2014). At Mointeach Mhor, I develop a diatom transfer function in order to compare the reconstruction methods.

As described in Chapter 2, there are two steps to creating a transfer function model. Firstly, using regression, modern day environmental data is expressed as a function of modern day biological data. Secondly, the relationship between the modern biological data and environmental is used to produce quantities estimates of the environmental variable in the past from the fossil biological data.

In the first step, I use the Northwest Scotland diatom training set (Barlow *et al.* 2013) to quantify the modern relationship between the diatom assemblages and elevation. This training set contains samples from nine tidal flat - salt marsh - upland sites in western and northern Scotland. A training set requires a balance between high predictive powers, where there is a large range of modern analogues for the fossil data, and high precision, where the errors between observed and predicted values are low. I have chosen to use a regional training set rather than a local training set as it has better analogues for the fossil assemblages. This is compensated by lower precision as there is greater variability in diatom assemblages with elevation due to the importance of other factors across multiple sites (Horton and Edwards 2005). As tidal ranges differ between sites, elevation is standardised to SWLI using equation 3.1.

To use an appropriate transfer function model, the species response to the environment needs to be assessed. Species response to an environmental variable can simply be characterised by either a linear model, where the species increases or decreases along a gradient, or by unimodal model, where there is a species optimum along the gradient. This is assessed using detrended ordination techniques. Detrended Canonical Correspondence Analysis (DCCA) of the Northwest Scotland Diatom data set by Barlow *et al.* (2013) shows that a unimodal transfer function approach is most appropriate.

To develop this transfer function I used the program 'C2' (Juggins 2011). I have chosen to use the unimodal transfer function model 'Weighted Averaging – Partial Least Squares' (WA-PLS) (Birks 1995). The first component of WA-PLS is the same as the Weighted Averaging model. This uses an abundance weighted elevation average of every sample where each diatom species is found (species optima) to predict fossil elevation. In the WA-PLS method, each subsequent model component uses the residual structure in the species data to update the species optima and improve the relationship between the predicted and observed marsh surface in the weighted average prediction (ter Braak and Juggins 1993, Birks 1995).

Removing samples can improve model predications. For example, if the environmental range of the fossil samples is known, using modern samples from the same environment can the increase the linearity between the observed and predicted and increase the predictive ability of the transfer function model (Hamilton and Shennan 2005). At Mointeach Mhor, this is not the case. I have decided to leave all samples in the training set as they show the natural variety of the modern sampled environment (Barlow *et al.* (2013).

The number of components selected in the model depends on model performance. I use the cross validation methods, bootstrapping, to randomly resample the data in order to calculate a standard error of prediction for each sample (Birks 1995). RMSEP summarises the model's predictive power; a lower RMSEP indicates better performance. r²Bootstrapped is the squared correlation of observed versus predicted using the resampled data sets. In a model where there is a good agreement between observed and predicted values, this will be closer to one and there will be a linear relationship between the observed and predicted values. The model residuals, the difference between the observed and predicted elevation, also help to assess model output. Structure in the residuals suggests the model does not account for all the controlling, or partially controlling factors. Increasing the number of components should improve model prediction. As more components are included, the model becomes less directly affected by the species-elevation relationship. Successive model components therefore are only selected if there is greater than 5% improvement in RSMSEP values and only up to three components are used (Birks 1998, Barlow *et al.* 2013). Using these criteria, I can select an appropriate model component.

The modern day relationship between the biological data and environmental can be used to produce quantities estimates of PMSE using the fossil diatom assemblages from Mointeach Mhor. A vital consideration for a transfer function model is that it makes ecological and statistical sense and the result must be considered for reliability (Birks 1998). Comparing RSL past observations, for example from tide gauges, with the predicted value is a good assessment of transfer function reliability. Where this is not possible, as for Mointeach Mhor, the Modern Analogue Technique can provide a measure of reliability by comparing how similar fossil assemblages are to modern day assemblages (Birks 1995). The Modern Analogue Technique produces a minimum dissimilarity coefficient which is a measure of similarity between the fossil biological assemblage and the weighted mean of the ten most similar modern biological assemblages and their associated environmental data (Birks 1995). A lower minimum dissimilarity coefficient indicates a closer match between fossil and modern data. I follow the method of Watcham et al. (2013) who distinguishes between good and close modern analogues at the 5th percentile and considers modern analogues poor when they are beyond the 20th percentile.

3.4 <u>Summary</u>

In this chapter, I described the three field sites. The main field site is Loch Laxford in North West Scotland. The contrasting modern site is Beluga Slough in Alaska, and secondary fossil site is Mointeach Mhor in Western Scotland. I have also explained the laboratory methods and statistical analysis methods used in this study. I present the results from the modern and fossil sites in Chapters 4 and 5 respectively.

Chapter 4: Results - Modern Sediments

This chapter presents the results from the two modern sites. The main site is Loch Laxford in northwest Scotland and the secondary site is Beluga Slough in Alaska. At Loch Laxford, there are 60 surface sediment samples. These have an elevation range between 1.24 and 3.65 metres OD and come from sand flat, salt-marsh, upland iris and heather vegetation zones. I measured total carbon, nitrogen, LOI, and grain size in these samples. I measured inorganic carbon in a selection of samples across the zones. Diatom assemblages were recorded from the samples shown by Barlow *et al.* (2013). At Beluga Slough, there are 54 surface sediment samples. These come from between 3.74 and 6.40 metres NAVD88. I record total carbon, nitrogen, and the diatom assemblages in these samples. Insufficient sediment quantity prevented grain size and LOI being analysed at Beluga Slough.

4.1 Organic Sediment – Loch Laxford

I measure the organic matter in the modern sediments at Loch Laxford using LOI and total carbon. Inorganic carbon at Loch Laxford surface was below the detection limit, suggesting that at Loch Laxford total organic carbon is equivalent to total carbon.

Figure 4.1 shows the LOI and total carbon plotted against elevation at Loch Laxford. The samples are colour-coded based on their surface vegetation zone. Samples from the transition between two zones are coloured according to the upper vegetation zone. Both LOI and total carbon increase linearly with elevation and then flatten around 2.60 metres ordnance datum (m OD). At elevations above 2.60 metres, organic matter is close to maximum possible values. LOI values are between 90 and 100% and total carbon at these elevations is about 40%. This is the maximum value expected for organic carbon, based on the relative atomic mass of carbon within a simple carbohydrate molecule ((CH_2O)n) from photosynthesis (Veres 2002, Plater *et al.* in press). The flattening of the graph at maximum values occurs in iris and heather samples, between MHWST (2.40 m OD) and HAT (3.10 m OD). At these maximum values, it is likely that elevation (or tidal inundation and frequency relating to elevation) is no longer limiting vegetation cover and therefore the organic matter. Figure 4.2 shows the relationship between LOI and total carbon.



Figure 4.1: Loch Laxford surface LOI (circles) and total carbon (diamonds) plotted against elevation. Samples are coloured according to their surface vegetation zones. Samples from the transition between two zones are coloured according to the upper vegetation zone.



Figure 4.2: Loch Laxford surface Total Carbon plotted against LOI

Both LOI and total carbon are strongly positively correlated with elevation. Using all the surfaces samples for total carbon r(58)=0.92, p<.001 and for LOI, r(58)=0.87,

p<.001. The coefficient of determination (r^2 value), which represents the percentage of the data that can be explained by the linear relationship between elevation and either total carbon or LOI, is higher for total carbon (r^2 =0.85) than LOI (r^2 = 0.75). Furthermore, LOI has some known methodical errors, which are described further in chapter 6. For these reasons, I have chosen to focus on total carbon rather than LOI in this investigation.

4.2 <u>Organic Sediment – Beluga Slough</u>

At the second field site, Beluga Slough, I measure total carbon as a proxy for organic matter. Again there is a significant correlation between total carbon and elevation (52) =0.39, p<.001. Although a linear relationship does exist, this is a weaker relationship than at Loch Laxford. Figure 4.3 shows total carbon plotted against elevation at Beluga Slough. Several sites on the Beluga Slough salt-marsh, in particular the two samples from above HAT, have total carbon values much lower than expected for their elevation . These are highlighted in Figure 4.3.



Figure 4.3: Beluga Slough surface total carbon against elevation. Labelled samples highlighted in red show samples with lower total carbon values than are expected for their elevation.

4.3 Organic Matter – Comparison Loch Laxford and Beluga Slough

Figure 4.4 shows total carbon from the two surface field sites plotted against elevation in SWLI. This is a method to standardise the water levels between sites with difference tidal ranges. Equation 3.1 shows the conversion between elevation metres and SWLI. Both Loch Laxford and Beluga slough have linear relationships with elevation, but relationship is stronger with better clustering of samples at the former. Total carbon at Beluga Slough is consistently lower than total carbon at Loch Laxford at the equivalent SWLI elevation.



Figure 4.4: Loch Laxford and Beluga Slough Total Carbon plotted against elevation in SWLI (Standard Water Level Index).

Elevation in SWLI units accounts for the different tidal ranges between sites and so allows data from multiple sites to be meaningfully combined. MTL at any site has a SWLI value of 100 and MHWST or MHHW has a SWLI value of 200.

4.4 <u>Grain size distribution – Loch Laxford</u>

I present the grain size distribution results in two ways. Firstly, I present the sand, silt, and clay grain size fractions and their relationship with elevation. Secondly I plot the grain size results as percentage volume – grain size curves and compared with the 'fast tide' and 'slow tide' deposits described by Rahman and Plater (2014).

Figure 4.5 shows the grain size fractions potted against elevation. At low elevations, on the sand flat and low marsh, there are larger proportions of sand (>60%). In these low elevation samples, the sand fraction sand decrease whilst the silt and clay fractions increase with elevation. Above approximately 1.60 m OD sand and silt fluctuate with no clear trend with elevation.



Figure 4.5: Loch Laxford modern Grain size fractions plotted against elevation.

Figure 4.6 shows the percentage volume – grain size curves for the surface samples separated into the surface vegetation zones. The upland iris and heather samples are not shown in this way as the conceptual model developed by Rahman and Plater (2014) is for intertidal deposits. The lowest surface samples from the sand flat and low marsh are composed of fine sands, are poorly to very poorly sorted, have mixture of skew from symmetrical to very fine and are leptokurtic to mesokurtic in shape.



Figure 4.6: Percentage Volume- Grain size curves for Loch Laxford surface. Grain size (φ) uses Gradistat scale; dotted lines show sand, silt, and clay fractions. Insert (from Rahman and Plater, 2014) shows idealised 'fast tide' and 'slow tide' transport shapes.

Figure 4.7 shows the grain distribution properties against elevation. The sand flat and low marsh percentage volume – grain size curve is most similar in shape to the 'fast tide' deposits described by Rahman and Plater (2014) and seen in the insert in Figure

4.8. In the mid-marsh and high marsh, samples are poorly to very poorly sorted with a symmetrical to very fine skew. The majority of samples have a mesokurtic distribution. There is large variability in particle size distribution between individual sites, especially in the mid and high marsh sample. Some sites from these zones have the same shaped percentage volume – grain size curve seen in the low marsh and sand flat. Others have a greater 'slow tide' component.





Grain size distribution at Loch Laxford does not show a strong relationship with the elevation (Figure 4.5). The 'fast tide' and 'slow tide' percentage volume - grain size curve (Figure 4.6) do show some change between 'fast tide' and 'slow tide' style deposits but there is large variability between individual sites in the mid and high marsh. There is too much variation between sites to use these curves to separate samples according to where they formed in the tidal flat–salt-marsh system.

4.5 <u>Correlation with Environmental Variables – Loch Laxford</u>

Table 4.1 shows the Pearson's correlation matrix for all the surface samples. Table 4.1 shows clay and elevation have a weak negative correlation over the whole elevation range. As seen in figure 4.5, clay forms a small percentage of the grain size distribution. Five of the six highest elevation samples from the iris and heather environments contain less than 2.6% clay, below the average 3.8% for all the samples. Table 4.1 also shows sand and silt are not correlated with elevation.

	Elevation	Total Carbon	LOI	Sand	Silt
Total Carbon	r=0.92,				
	p<.001				
	r=0.87	r=0.94			
LOI	p<.001	p<.001			
Canad	r=0.0031	r=-0.17	r=-0.22		
Sand	p=.981	p=.202	p=.091		
C:1+	r=0.044	r=0.21	r=0.25	r=-0.997	
SIIL	p=.739	p=.114	p=.052	p<.001	
Class	r=-0.34	r=-0.20	r=-0.10	r=-0.79	r=0.74
Ciay	p=.008	p=.135	p= .429	p<.001	p<.001

Table 4.1: Pearson's correlation (r) matrix for all the surface samples, n = 60, elevation range 1.24 to 3.65 metres OD. Correlations where p<0.01 are highlighted

Although there is a good correlation between total carbon and elevation over the whole elevation range, Figure 4.1 shows the linear relationship between increasing total carbon with elevation breaks down above the high marsh. I have therefore also looked at the linear section of the distribution between the sand flat and high marsh. Table 4.2 shows the correlation with the upland iris and heather samples excluded. The grain size factions, with the exception of clay over the whole elevation range, do not show any correlation with total carbon or elevation.

	Elevation	Total Carbon	LOI	Sand	Silt
Total Carbon	r=0.96				
	p<.001				
LOI	r=0.90	r=0.93			
	p<.001	p<.001			
Sand	r=-0.07	r=-0.23	r=-0.28		
	p=.620	p=.096	p=.041		
Silt	r=0.10	r=0.26	r=0.30	r=-0.998	
	p=0.490	p=0.060	p=.027	p<.001	
Clay	r=-0.18	r=-0.07	r=0.03	r=-0.82	r=0.78
	p=.190	p=.630	p=0.818	p<.001	p<.001

Table 4.2: Pearson's correlation (r) matrix for the surface samples between sand flat and high marsh, n = 54, elevation range 1.24 to 2.68 metres OD. Correlations where p<0.01 are highlighted.

Table 4.2 show the grain size fractions do have a correlation with total carbon. The five samples from the sand flat and low marsh, where there is very low total carbon (<10%), shown a positive correlation between the silt fraction and total carbon; and negative correlation between the sand fraction and total carbon. In the higher sections of the marsh, there is a mixture of particle size proportion with similar total carbon values.



Figure 4.8: Loch Laxford Sand and silt fractions plotted against total carbon values. The five circled samples are from the sand flat and low marsh. They show a change in total carbon with grain size. This is not seen in the non-circled samples.

4.6 <u>Total Carbon Model</u>

Using the relationship at Loch Laxford between total carbon and elevation, I develop a simple linear regression model to estimate marsh surface elevation from total carbon. As seen in Figure 4.1, a linear relationship between the two variables exits between the sand flats and high marsh. In the iris and heather samples, total carbon remains around 40% despite further increases in elevation. I have therefore limited the regression equation by excluding total carbon values and elevations from the iris and heather samples. Using the Loch Laxford surface distribution, samples with total carbon vales of 40% could have formed at elevations in the high marsh and above. The model will predict high marsh values for these values. This must be considered when using the model to reconstruct paleo marsh surface elevation (PMSE).

The relationship between the modern day elevation in metres (OD) and percentage total carbon is described by the regression line '*elevation* = 0.04 % TC + 1.15' (2 d.p.), (with elevation in SWLI units '*elevation* = 1.68 % TC + 141.91 (2 d.p.)').

The observed and predicted values (Figure 4.9) show a linear relationship. The lower part of the model on the sand flats and low marsh is less well constrained with fewer samples. This is a limitation of the model and more samples from these elevations would improve it. The observed and predicted values show the model will under predict these low elevation samples.



Figure 4.9: The observed elevation (m OD) plotted against predicted elevation (m OD) using the Total Carbon model. The grey dashed line shows where predicted elevation = observed elevation



Figure 4.10: The observed elevation (m OD) plotted against the observed-predicted residuals for the Total Carbon model.

Structure in the residuals suggests the model does not account for all the controlling or partially controlling factors. Figure 4.10 displays the model residuals and show a scattered distribution with little structure.

The total carbon model errors are calculated from 95% confidence limits of the model standard error value. For this model, where percentage total carbon is used to predict elevation, standard error = ± 0.11 m, 2 d.p.) (± 5.14 SWLI, 2 d.p.) and the model errors are ± 0.22 m, 2 d.p. (± 10.06 SWLI, 2 d.p.).

4.7 <u>Modern diatom distributions – Loch Laxford</u>

The modern diatom distribution at Loch Laxford (Figure 4.11) shows a change in diatom assemblages with elevation. As expected, at higher elevation there are more salt intolerant diatoms. Transfer functions quantify this relationship between the diatom assemblages and elevation to produce PMSE reconstructions.

Ordination is a method of measuring the strength of the relationship between the diatom assemblages, elevation, and the other environmental variables. It is useful here to investigate what effect total carbon and grain size have on the diatom distributions.





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At Loch Laxford, I use the indirect ordination method DCA to assess the diatom species gradient length and select a suitable constrained ordination model. Indirect methods spread species data to maximise the variance explained by each axis without the environmental data (Lepš and Šmilauer 2003). The DCA output shows the gradient length of the first axis is 5.909 standard deviation units, indicating unimodal ordination methods are appropriate (ter Braak and Prentice 1988). The constrained ordination models use the environmental data to explain the variance in the diatom species data. The environmental data included in the analyses are elevation, sand, silt, clay, total carbon, and nitrogen.

I chose to use Canonical Correspondence Analysis (ter Braak 1986) for its ability to simultaneously analyse the unimodal species data with the environmental data. In this model, species assemblage data is directly related to known environmental variables. I also ran partial CCAs to describe the variance each environmental variable can explain. The significance if the constrained ordination is tested using Monte Carlo permutation tests (499 unrestricted permutations).



Figure 4.12: Relationship between environmental variables at Loch Laxford Surface

Figure 4.12 shows the relationships between the environmental variables. The eigenvalues measure the amount of variance an ordination axis explains. Larger values indicate the axis is more important (Lepš and Šmilauer 2003). The CCA first axis eigenvalue is high (0.743, p=0.002), suggesting it represents a strong gradient of variability. It is most closely orientated with elevation (Figure 4.14). As is larger than the second axis eigenvalue (0.41, p=0.002), it is more important in explaining diatom species distribution.

Table 4.3 shows the partial CCA results. The partial CCA results shows the amount of total variation the selected environmental variable explained. It includes both the unique effects of that single variable on the diatom distribution and the compound effect of other variables along that gradient. The total of the partial effects is the total explained variance. The p-value refers to whether the partial effect of the variable is significant (p<0.05) using Monte Carlo permutation tests. The six environmental variables investigated at Loch Laxford together explain 40% of the surface diatom assemblages. Typically, environmental variables only explain a fifth to half of the variance in the diatom assemblages (Zong and Horton 1999, Horton *et al.* 2006, Roe *et al.* 2009). The cause of the remaining fraction is unclear but possibilities include random variation or autocorrelation (Horton *et al.* 2006, Szkornik *et al.* 2006). Of the six environmental variables, elevation, plus the effects of elevation confounded with the other environmental variables, explains the most variation (18%, Table 4.3) in the diatom assemblage data.

Environmental variable	Partial effect (% total variance)	p value	Variance inflation factor
Elevation (m OD)	18	0.002	9.47
Nitrogen (TN) (%)	9	0.002	8.30
Total Carbon (TC) (%)	6	0.002	20.91
Silt (%)	5	0.002	0
Clay (%)	2	0.022	3.87
Sand (%)	-	1.0	4.13

Total explained variance: 1.533 (40%), Total variance: 3.796

Table 4.3: Loch Laxford Surface Partial CCA results

Table 4.3 also shows the variance inflation factor. This a measure of the uniqueness of information provided by that environmental variable about the sample. An inflation factor of one implies that the variable contains unique information about the assemblage. At Loch Laxford, total carbon has the highest inflation factor implying it does not provide unique information. Pearson's correlation analysis of the environmental variables in section 4.5 confirms inter correlations exist and are strongest between elevation and total carbon. The effects of carbon on the diatom assemblages operates along the same gradient as elevation.

With environmental variables that total one hundred percent, CANOCO does not calculate the inflation factor of the last inputted category. Due to this silt has an

inflation factor of zero and sand has a low inflation factor with respect to clay, elevation, nitrogen and carbon. Sand and silt are strongly negatively correlated (Table 4.1 and 4.2). The partial effect and variance inflation factor results show that once elevation has been included, total carbon explains very little additional variation.

Total carbon has little effect in explaining the diatom species distribution once the influence of elevation has been included. The grain size fractions also only explain only a small fraction of the variation in diatom species data. These results confirm that including the geochemistry data does not change elevation, and the effects of elevation confounded with other environmental variables on that gradient, from being the primary control on diatom species distribution at Loch Laxford.

4.8 <u>Modern diatom distributions – Beluga Slough</u>

The modern diatom distribution at Beluga Slough (Figure 4.13) shows a change in diatom assemblages with elevation. As expected, at higher elevation there are more salt intolerant diatoms. At Beluga Slough, there is a dominance of the diatom *Navicula cari var cincta*, particularly between 3.80 and 4.70 metres NAVD88.

At Beluga Slough, the environmental variables are total carbon and nitrogen. I use the indirect ordination method DCA to assess the diatom species gradient length and select a suitable constrained ordination model. The DCA axis one length is 3.945 indicating unimodal ordination models are appropriate. As before, I therefore use the direct ordination method CCA.







CCA shows that the first axis eigenvalue is high (0.516, p=0.002) and is closest aligned to elevation (Figure 4.13). The second axis eigenvalue is lower (0.126, p =0.0640). It also does not separate the species any more than randomly selected data (p>0.05). Figure 4.14 shows this relationship between the axis and environmental variables.



Figure 4.14: Relationship between environmental variables at Beluga Slough analysed using CCA.

Table 4.4 shows the CCA output. The total amount of variance explained (18.5%, table 4.4) is lower than at Loch Laxford (40%, see table 4.3). Grain size was not measured in the Beluga Slough samples. With fewer variables included in the ordination, the explained variance is likely to be lower. Elevation also accounts for a lower percentage of the diatom assemblage variation at Beluga Slough than at Loch Laxford.

Environmental variable	Partial effect (% total variance)	p value	Variance inflation factor
Elevation (m OD)	11.9	0.002	1.28
Total Carbon (%)	4.5	0.002	7.56
Nitrogen (%)	2.1	0.250	6.85

Total explained variance: 0.697 (18.5%), Total variance: 3.773 *Table 4.4: Beluga Slough Partial CCA results*

Total carbon has the highest inflation factor implying it does not provide unique information. This inflation inflation factor is lower than at Loch Laxford (c.f. 20.9%) and as seen previously in sections 4.2 and 4.3 the relationship between elevation and total carbon is less strong at Beluga Slough. From the variable included in the

ordination, elevation appears to have the largest effect on species distribution. Total carbon is the second most important but explains only a small prortion of the variance (Table 4.4). Nitrogen has a p value greater than 0.05 indicating that some of the oredination model's random permutations can explain the same amount of variability as the measured nitrogen.

These results confirm elevation, and the effects of elevation confounded with other environmental variables on that gradient, as the primary control on diatom species distribution at Beluga Slough.

4.9 Surface Results Summary

I have shown modern organic matter between the sand flat and high marsh has a strong linear relationship (r=0.92). Between the MHWST and HAT, the carbon content does not increase despite further increases in elevation. This relationship between organic matter and elevation also occurs at Beluga Slough. Here the total carbon values are lower at the equivalent SWLI elevation and do not show the flattening with elevation seen in the iris and heather samples at Loch Laxford.

Grain size distribution at Loch Laxford does not show a strong relationship with elevation. Analysis of the percentage volume - grain size curves shows the sand flat and low marsh samples have a 'fast tide' shape. This represents greater deposition by traction, where sediment is rolled along the surface by the water (Rahman and Plater 2014). In the mid and high marsh samples, the curves indicate more 'slow tide' deposition. This represents the greater contribution of suspended sediment, which settles onto the salt-marsh surface as water velocities decreases (Rahman and Plater 2014). Some mid and high marsh samples have the 'fast tide' style volume- grain size curves that are seen on the low marsh and sand flat. Although there the percentage volume- grain size curves show, some relationship with elevation at Loch Laxford, there is too much variation between sites to use the percentage volume - grain size to indicate where samples formed in the tidal flat –salt-marsh system. Comparison of the grain size and total carbon show that they are not correlated except in the five sand flat and low marsh samples where total carbon is low (<10%). Using the relationship between organic matter and elevation between the sand flat and high marsh, I have developed a total carbon model to reconstruct PMSE and RSL from fossil total carbon values. I apply this model in Chapter 5 to the Loch Laxford and Mointeach Mhor fossil samples.

Chapter 5: Results - Fossil Sediments

This chapter presents the fossil sediment results from Loch Laxford in Northwest Scotland and Mointeach Mhor in Western Scotland. The fossil results from Loch Laxford are from a 66 centimetre core, taken from the mid marsh, with a core top elevation of 1.80 metres OD. This core has been dated to 44 centimetres and shows an erosional hiatus between 20 and 24 centimetres depth (Barlow *et al.* 2014), (see Table 3.2 and Figure 3.3). The results from Mointeach Mhor are from a sediment monolith, dating from the mid Holocene. At this time, sea level was higher than present. The monolith has a top elevation of 9.37 metres OD and the sediments within it record the mid Holocene sea-level highstand. Diatoms were only preserved in the section between 20 and 50 centimetres depth. I use this 30 centimetre section in the investigation.

At both sites, I investigate total carbon, LOI, and grain size. I use the Loch Laxford surface total carbon – elevation linear regression model, developed in Chapter 4, to predict PMSE at each site using the fossil total carbon values. Lastly, at each of the sites, I compare the total carbon PMSE and RSL predictions to diatom transfer function -based PMSE and RSL predictions from Loch Laxford and Mointeach Mhor.

5.1 Loch Laxford

The Loch Laxford core samples are from a mid-marsh core with a core top elevation of 1.80 metres OD. In this section, I present the total carbon, grain size, and LOI results. I also use the modern day total carbon – elevation linear regression model to estimate PMSE using the fossil total carbon values. LOI was measured by Cullen (2013) from a duplicate core. This duplicate core is referred to as LA-6 in in Barlow *et al.* (2014) and was radiocarbon dated at four centimetre intervals from the surface to 44 centimetre core depth. The dating showed an erosional hiatus between 20 and 24 centimetres, which lasts approximately 400 years from around 1800 AD to 1400 AD. I have therefore divided the results from the core into an upper section, above the erosional hiatus from the surface to 20 centimetre core depth, and a lower section, between 24 centimetres to the base of the core. The Loch Laxford diatom based transfer function reconstruction I use in this section was developed by Barlow et al.

(2014) using the duplicate fossil core. It provides a quantitative PMSE and RSL reconstruction to 44 centimetres core depth.

5.1.1 Organic matter

I measure both LOI and total carbon in the Loch Laxford fossil samples to assess the organic matter. The results are shown in Figure 5.1. Both show higher organic matter in the upper part of the core compared to the lower section below the erosional hiatus. In the upper part of the core LOI and total carbon decrease with depth. Total carbon shows little change down core whereas LOI shows some larger fluctuations, for example at 50 centimetres depth. It then also decreases to the base of the core.



Figure 5.1: Loch Laxford fossil environmental variables (%) plotted against core depth. Note different scales between total carbon and LOI, sand and silt, and clay. The fossil total carbon values are coloured according to which modern vegetation zone their modern analogues are from. (Sand flats <5%, Low marsh 5-11%, mid marsh 11- 24%. Maximum fossil total carbon values are 21%. This is below the transition between modern Loch Laxford mid and high marsh total carbon values (between 24 and 29%), see section 4.1)

The surface sample, with an elevation of 1.80 metres OD has a LOI of 60%. This is expected based on the surface LOI distribution (Figure 4.1). The total carbon value (12.30%) is much lower than expected (~17%) from the modern total carbon distribution. It is also lower than the fossil total carbon values from 1 to 10 centimetres core depth.

5.1.2 Grain Size

Figure 5.1 also shows the sand, silt, and clay fractions plotted through the core. Like in the modern samples from Loch Laxford, there is little clay. The upper part of the core contains higher percentages of silt and lower percentages of sand than the lower part of the core. The surface sample has a larger proportion of sand and lower proportion of silt compared to the samples below it.

The fossil percentage volume – grain size curves (Figure 5.2) show a change in shape between the upper and lower parts of the core. The upper section is more similar to the modern day mid marsh and high marsh samples whilst the lower section has a more peaked distribution and is more similar to the modern low marsh and sand flat samples (see Figure 4.10).



Figure 5.2: Loch Laxford fossil percentage volume and grain size distribution at 5 centimetre intervals in the upper and lower sections of the core.

As a hiatus of about 400 years, splits the upper and lower parts of the core, I have viewed the percentage volume – grain size curves from the upper and lower section separately. The upper section curves are similar to each other with no change down core. In the lower section, the curves from 55, 60 and 65 centimetre depth have a larger coarse component than those below them. The other curves from the lower section, between 25 and 50 centimetres core depth, are similar and again do not have a pattern with core depth. Rahman and Plater (2014) suggest no up core trend in percentage volume- grain size curves is indicative of sedimentation matching sea-level rise. Over the erosional hiatus, this core is thought to have been close to the active marsh front, and shows the transition between the non-eroded upper marsh and eroded lower marsh (Cullen 2013, Barlow *et al.* 2014). The change between the percentage volume- grain size curves in the upper and lower parts of the core supports a change in salt-marsh deposition environment before and after the hiatus.

5.1.3 <u>Comparison between fossil environmental variables</u>

In the fossil core from Loch Laxford, the sand and silt grain size fractions are correlated with total carbon. Figure 5.3 shows the positive correlation between total carbon and silt and negative correlation between total carbon and sand. The lower part of the core has lower total carbon values, higher sand and lower silt than the upper part. This differs from the modern day environment where only the sand flat and low marsh samples, (total carbon is below 11%), have a correlation with sand and silt values (Figure 4.12).



Figure 5.3: Loch Laxford fossil sand and silt plotted against total carbon.

5.1.4 Comparison between modern and fossil organic matter

Comparing the distribution of total carbon values between the fossil and modern environments shows no fossil value exceeds the modern day mid marsh values. The maximum fossil total carbon value is 21%. This is below the transition between mid



Figure 5.4: Loch Laxford Modern and Fossil Total Carbon distribution from the upper and lower parts of the core. Modern samples are coloured by their vegetation zone. and high marsh total carbon values (between 24 and 29%). Figure 5.4 shows the modern total carbon distribution and the fossil total carbon distribution for the upper and lower parts of the core.

As all the fossil total carbon results have mid marsh or lower values, I can use the sand flat to high marsh, total carbon- elevation model developed from the modern Loch Laxford sediments to estimate PSME. By comparing total carbon reconstruction with a diatom-based reconstruction, I can see whether the

diatoms also show the same trend and assess the total carbon model.

5.1.5 <u>RSL reconstructions</u>

In this section, I use the Loch Laxford modern sand flat to high marsh total carbon – elevation linear regression model to produce PMSE and RSL estimates based on the Loch Laxford fossil total carbon values. I compare this to an existing, published diatom based transfer function reconstruction by Barlow *et al.* (2014) and investigate the differences between them. Diatom errors are bootstrapped and sample specific one sigma error. The total carbon reconstruction uses 95% confidence limits of the model standard error. They are both likely to be an underestimate of the true error.

Figure 5.5 shows the PMSE plotted against core depth. The surface sample has lower than expected total carbon for its elevation and is under predicted by the model. The total carbon PMSE is generally lower than the diatom reconstruction. This is also seen in the relative sea-level reconstruction (Figure 5.6) where the lower total carbon PSME results in higher reconstructed RSL.



Figure 5.5: Loch Laxford fossil PMSE reconstructions to 44 centimetre core depth using the Total carbon model (blue) and diatom transfer function reconstruction (from Barlow et al. 2014) (green).

In the top fifteen centimetres, until around 1900 AD, the two reconstructions show similar fluctuations with overlapping error bars but diverge with core depth. Below 15 centimetres core depth, the reconstructions differ. In the lower section of the core, the diatom and total carbon PMSE consistently differ, with some overlap in the reconstruction errors.



Figure 5.6: Loch Laxford fossil RSL reconstructions using the Total Carbon surface linear regression model (blue) and diatom transfer function reconstruction (green)





As seen in Figures 5.5 and 5.6, the total organic matter reconstruction shows good agreement in trend with the diatom transfer function reconstruction, particularly in the lower section of the core, but under predicts the absolute values. To compare the diatom transfer function and total carbon model reconstructions, I plot the difference between the two PMSE reconstructions against core depth (Figure 5.7). A positive difference between the reconstructions shows the diatom PMSE is greater than the total carbon PMSE. Error are cumulative errors from the two PMSE reconstructions, $(\sqrt{e_a^2} +$

 e_b^2), and are 0.42 metres at Loch Laxford.

In the upper part of the core, the difference between the reconstructions increases with core depth. The surface sample shows a greater variation between the reconstructions. It is caused by a low total carbon value and under prediction of the surface elevation by the total carbon model. The mean difference and standard deviation between the reconstructions in the upper section is 0.28 ± 0.16 meters. In the lower part of the core, below the erosional hiatus, the differences between the reconstructions do not have a trend with core depth. They have higher mean differences and smaller standard deviations between the reconstructions (0.37 ± 0.09 metres) than in the upper part of the core. The lower part of the core also has higher sand proportions than the upper part of the core.

Comparison of the differences between the reconstructions and total carbon PMSE predictions (Figure 5.8) shows there is a systematic relationship between them. The difference is larger when the total carbon PMSE, and therefore the total carbon value, is lower. The diatom PMSE does not show a correlation with the differences between the reconstructions (Figure 5.8).



Figure 5.8: Loch Laxford fossil PMSE reconstructions and difference between the reconstructions for A. the total carbon PMSE reconstruction and B. the diatom PMSE reconstruction. The black line shows where the two reconstructions have the same value. Errors are PMSE prediction errors for each reconstruction and the cumulative errors used in Figure 5.7 for the difference between two reconstructions.

5.1.6 Loch Laxford Fossil Summary

The differences between the reconstructions increase with depth through the upper section of the core (Figure 5.7). Figures 5.5 and 5.6 shows the diatom transfer function and total carbon model predictions have separated by 15cm core depth, or 100 years. As the total carbon values decrease, the difference between the reconstructions increases (Figure 5.8.A). In the lower, older section of the core the diatom and total

carbon reconstruction show a similar trend. The differences between the reconstructions are more consistent (figure 5.7) and have a mean difference of 0.37 metres with a standard deviation of 0.09 meters.

Samples from the upper and lower sections of the core both show total carbon values decrease as silt decreases and sand increases (Figure 5.3). The lower section of the core contains more sand than the upper section (Figure 5.1). Whether the difference between the reconstructions in the lower section of the core is also affected by sand is unknown due to the erosional hiatus.

5.2 Mointeach Mhor

The Mointeach Mhor samples are from a sediment monolith dating from the mid Holocene high stand. The monolith sediments have a top elevation of 9.37metres OD. Investigations into the mid Holocene high stand duration at Mointeach Mhor and the surrounding area suggest the high stand in this area extended for over 1000 years and ended gradually (Shennan *et al.* 2000, Shennan *et al.* 2005). These sediments are approximately 7000 to 6000 years older than the fossil sediment core from Loch Laxford. The monolith was taken from the northern part of a former tidal embayment. This is believed to have resulted from rising sea level breaching a dune ridge and inundating a wetland during the mid-Holocene (Shennan *et al.* 1995, Shennan *et al.* 2005).

The sediments used in this investigation come from 20-50 centimetre depth. In this section, I present the total carbon, grain size, and LOI results. LOI, grain size and diatom assemblages were investigated by Shennan *et al.* (2005). I use the fossil total carbon results and fossil diatom assemblages to develop PMSE and RSL reconstructions.

5.2.1 Organic matter

At Mointeach Mhor, I use total carbon and LOI to measure organic matter. Figure 5.9 shows these plotted against depth. The organic matter shows three sections. Between the base of the monolith at 50 centimetres and 48 centimetre depth , LOI has a gradual decrease in value while total carbon shows mid marsh values. Between 47 and 28 centimetres, both LOI and total carbon have low values. LOI values have a range of 6.35% and 21.92%. Total carbon has a range of 2.87% and 11.47%. The upper section occurs from 28 centimetres to the top of the sampled section at 20 centimetres depth. Here, LOI and total carbon have higher, mid marsh type values.

I have categorised the Mointeach Mhor fossil total carbon values according to the modern Loch Laxford tidal flat – salt-marsh – upland vegetation zone analogue values. This does not account for a difference in climate at the time the fossil Mointeach Mhor sediments formed compared to the modern day samples at Loch Laxford.


Figure 5.9: Mointeach Mhor fossil environmental variables (%) plotted against core depth. Note different scales between total carbon and LOI, sand and silt, and clay. The upper, middle and lower sections described in the text are shown. The fossil total carbon values are coloured according to where in the modern day their analogues (Sand flats <5%, Low marsh 5-11%, mid marsh 11- 24%. Maximum fossil total carbon values are 26%. This is in the transition between mid and high marsh total carbon values (between 24 and 29%).

5.2.2 Grain Size

The sand, silt, and clay fractions are shown plotted against depth in figure 5.9. The clay fraction is low, less than 20% in all the samples, and shows similar trends to the silt fraction down the monolith. The grain size, like the organic matter, also shows three parts to the monolith sediments. At the section boundaries at 48 centimetres and 27 centimetres there are shifts in the sand, silt and clay fractions. In the middle section, where total carbon and LOI have lower values, there are higher sand values and lower silt values. The upper and lower sections, where total carbon and LOI are higher, have lower sand and higher silt values.

Figure 5.10 shows the percentage volume – grain size curves though the monolith. The samples from the middle section of the monolith have a larger 'fast tide' component using the criteria from Rahman and Plater (2014). The sample at 49 centimetres is more similar to the upper samples at 20 and 24 centimetres depth. These have a larger finer component, and a mixture of 'fast tide' and 'slow tide' characteristics. The percentage volume –grain size curves show clear differences between the middle, and the upper and lower sections of the monolith, indicating changes in grain size deposition through time.



Figure 5.10: Mointeach Mhor fossil percentage volume and grain size distribution through the monolith

5.2.3 <u>Comparison between fossil environmental variables</u>

In the fossil sediments from Mointeach Mhor, changes in sand and silt coincide with changes in total carbon. Figure 5.11 shows the correlation between percentage sand and silt, and total carbon in the monolith. There is a positive correlation between silt and total carbon and a negative correlation between total carbon and sand.



Figure 5.11: Mointeach Mhor silt and sand plotted against total carbon.

5.2.4 Comparison between modern and fossil organic matter

I have compared the Mointeach Mhor total carbon values to the modern day Loch Laxford values. I have used the modern Loch Laxford distribution as it is likely to have a more similar total carbon distribution than the Alaskan site, Beluga Slough.



Figure 5.12: Loch Laxford Modern and Mointeach Mhor Fossil total Carbon distribution. Modern samples are coloured by their vegetation zone. The maximum fossil total carbon value at Mointeach Mhor is 26%. This is between modern day Loch Laxford mid and high marsh values. Figure 5.12 shows the Loch Laxford modern total carbon distribution and the fossil Mointeach Mhor total carbon distribution.

As all the fossil total carbon results have mid marsh or lower values, I can use the total carbon- elevation model from the modern Loch Laxford sediments to estimate PSME. By comparing total carbon reconstruction with a diatom-based

reconstruction, I can assess whether the diatoms also show the same trend and assess the total carbon model.

5.2.5 <u>RSL reconstructions</u>

In this section, I produce diatom and total carbon RSL reconstructions. The diatom based reconstruction uses the fossil Mointeach Mhor diatom assemblages. These are quantitatively related to elevation using a transfer function. Low numbers of diatoms were present in the sediment and the assemblage counts only contain 103 to 115 diatoms. This is below the recommended 250 (Battarbee 1986). The total carbon reconstruction uses the Loch Laxford surface sand flat to high marsh total carbon – elevation linear regression model. Lastly, I compare the two reconstructions and investigate the differences between them.

Following the method outlined in Chapter 3, I use the WA-PLS model with bootstrapping cross validation methods to develop the transfer function. The training set used is the Northwest Scotland diatom training set (Barlow *et al.* 2013). In component 1 (Figure 5.13), the lower SWLI values cannot be predicted well by the model. This is shown by a distortion from the linear trend and structure in the residual plot in Figure 5.14. In the subsequent components, the structure in the residuals is used to improve the model prediction and this distortion decreases. Components 2 and 3 of the regional model have a linear relationship between predicted and observed and less residual structure (Figure 5.13). Table 5.1 summarises the performance of the training set. Component two has a greater than 5% improvement in RMSEP value compared to the 1st component (see Birks 1998, Barlow *et al.* 2013). The 3rd component has an increase in RMSEP compared to the 2nd component, indicating a decrease in model predictive power despite a higherR²_{bootstrapped} value.

Model	# samples	SWLI range	Component	$R^{2}_{bootstrapped}$	RMSEP (SWLI)	% change	MAT DC percentile	
						RMSEP	5 th	20 th
Regional WA-PLS	215	100- 280	1	0.72	19.53		68.61	119.00
			2	0.78	18.53	5.14		
			3	0.80	19.66	-6.11		

Table 5.1: Output from the local and regional diatom training set models - WA-PLS model performance statistics and MAT dissimilarity coefficients are calculated in C2 (Juggins, 2011)





Component two

Component one

Figure 5.13: The observed SWLI - predicted SWLI (A) and observed SWLI - residuals plots (B), using the WA-PLS transfer function model for the regional diatom training set, components one, two and three. The blue circled area in component one observed SWLI - predicted SWLI highlights where the observed values are poorly predicted by the model. This improves in the subsequent components and there is a clear decrease in residual structure between components one and two.

I have chosen to use the 2nd component to reconstruct RSL using the Mointeach Mhor fossil diatom assemblages. To assess the reliability of the transfer function, I use the modern analogue technique to compare how similar fossil and modern assemblages are. Using the minimum dissimilarity coefficients 5th and 20th percentile thresholds, the regional model has close modern analogues for three of the twenty samples and no good modern analogues (Figure 5.14). This may be due to a lack of preserved diatoms, leading to low diatom counts in the Mointeach Mhor samples. In these data sets, non-analogue species are not a problem. 24 out of the 26 (92%) fossil diatom species from Mointeach Mhor are found in the modern Northwest Scotland diatom training set. The two fossil diatom species not in the modern diatom training set account for just 1% of the total fossil diatoms from Mointeach Mhor.



Figure 5.14: Modern Analogue Technique - Regional Minimum Dissimilarity Coefficient. Red lines indicate position of 5th and 20th Percentile. Good modern analogues are below 5th, close are between the 5th and 20th and poor greater than 20th percentiles.

I produce PMSE estimates for Mointeach Mhor using the regional model, component 2 and the Mointeach Mhor fossil diatom assemblages. I convert PMSE in SWLI to metres OD using the reverse SWLI calculation (Equation 3.1). I can then calculate RSL using Equation 3.2. Model errors are from the corresponding bootstrapped standard error.

The total carbon model uses the Loch Laxford surface linear regression model to estimate PMSE. As tidal ranges differ between the sites the regression equation is in SWLI units. This is converted to metres using the reverse SWLI calculation (Equation 3.1). RSL is calculated using Equation 3.2. Figure 5.15 shows the two PMSE reconstructions and Figure 5.16 shows the RSL reconstructions.



Figure 5.15: Mointeach Mhor fossil PMSE reconstructions using the total carbon model (blue) and diatom transfer function reconstruction (green).

The total carbon and diatom PMSE and RSL predictions are similar from 27 centimetres to the top of the sampled section and from the base of monolith to 48 centimetres. In the middle section, between 47 and 28 centimetres, the reconstructions differ. This section has lower total carbon values then the upper and lower sections, causing the total carbon model PMSE prediction to be lower and therefore the RSL higher.

Despite poor modern analogues and low diatom counts for the assemblages, the diatom RSL prediction shows steady (between 6.88 ± 0.49 to 7.34 ± 0.49 metres) RSL through the mid Holocene highstand. Maximum sea level predicted by the diatom transfer function (7.34 ± 0.49 metres) is a little higher and occurs later (~7200 cal. year BP) than predicted by the existing sea-level index points from the northern section of Mointeach Mhor (6.74 ± 0.20 metres, at ~7600-7400 cal. year BP). Steady RSL, within a metre of the maximum, is as predicted by sea-level index points from the local area

and northeast Scottish highlands (Shennan *et al.* 2000, Shennan *et al.* 2005). The diatom reconstruction differs from the total carbon reconstruction which shows a rapid increase in RSL to 7.50 ± 0.21 metres around 7600 cal. year BP and maximum RSL of 7.72 ± 0.21 metres at approximately 7200 cal. year BP.



Figure 5.16: Mointeach Mhor RSL reconstructions to using the Total Carbon surface linear regression model (blue) and diatom transfer function reconstruction (green).



Figure 5.17: Mointeach Mhor difference between the PMSE reconstructions with monolith depth.

To investigate the cause of the differences between the reconstructions, I have plotted the differences between the two reconstructions against depth (Figure 5.17). A positive difference between the reconstructions shows the diatom PMSE is greater than the total carbon PMSE. The differences between the diatom and total carbon reconstructions between 20 and 27 centimetres depth have an average difference of 0.11 metres with a standard deviation of 0.09 metres. Between 48 and 50 centimetres depth, the mean is -0.05 metres and the standard deviation is 0.01 metres. The negative mean shows

the total carbon model predicts higher PMSE than the diatom model. The difference is small compared to the middle section where the mean difference between the reconstructions is 0.46 metres, with a standard deviation of 0.12 metres. The errors seen in Figure 5.17 are cumulative from the two Mointeach Mhor PMSE reconstructions, ($\sqrt{e_a^2} + e_b^2$). They are between 0.52 and 0.56 metres.

Comparison of the differences between the reconstructions and total carbon PMSE predictions show there is systematic difference between them (Figure 5.18). The differences between the reconstructions are larger when the total carbon PMSE, and therefore the total carbon value, is lower (Figure 5.18). Like in the Loch Laxford core, the differences between the reconstructions do not correlate with the diatom PMSE (Figure 5.18).



Figure 5.18: Mointeach Mhor fossil PMSE reconstructions and difference between the reconstructions for A. the total carbon PMSE reconstruction and B. the diatom PMSE reconstruction. The black line shows where the two reconstructions have the same value. Errors are PMSE prediction errors for each reconstruction and the errors from the difference between two reconstructions.

5.2.6 Mointeach Mhor Fossil Summary

Unlike at Loch Laxford, the reconstructions do not show an increase in offset between reconstructions with depth, or a consistent difference between the reconstructions. In the upper and lower sections of the Mointeach Mhor sediment monolith, the difference between the reconstructions is very small, whilst in the middle section the difference between the reconstructions is much larger.

Mointeach Mhor is a former tidal embayment, created as tidal water breached a coastal sand dune system (Shennan *et al.* 1995, Shennan *et al.* 2005). The sediments used in this investigation are from the northern section of the embayment which was thought to be more sheltered and so less effected by the fossil dune ridge (Shennan *et al.* 2005). Despite this, the sediment record shows an influx of sand in the middle section. The grain size – percentage volume curves show a larger 'fast tide' component in this part of the monolith, also indicating a change to coarser grain deposition. This middle section is the most sandy and is also where the differences between the reconstructions are larger (mean difference is 0.46 metres), and the total carbon values lower (Figure 5.9). Like at Loch Laxford, sand and total carbon has a negative correlation in all of the Mointeach Mhor fossil samples (Figure 5.11). The influx of sand and lower total carbon values suggests site selection is an important consideration for using total carbon as a sea-level proxy. This is discussed further in Chapter 6.

5.3 Fossil Result Summary

In this chapter, I have used the modern Loch Laxford total carbon – elevation relationship to produce quantitative estimates of RSL using the fossil total carbon values at Loch Laxford and Mointeach Mhor. The diatom transfer function reconstruction generally predicts higher PMSE than the total carbon model reconstruction. The exception to this is in the lowest three samples, between 50 and 48 centimetres monolith depth, at Mointeach Mhor. Here the total carbon model PMSE reconstruction is between 4 and 7 centimetres higher than the diatom transfer function model.

At Loch Laxford, the differences between the reconstructions increase with depth then stabilise in the lower part of the core. In the lower section of the core at Loch Laxford there is good agreement in trend between the diatom and total carbon reconstruction. At Mointeach Mhor, the differences between the two reconstructions are small in the upper and lower parts of the monolith but differ in the middle, sandier, section, between 47 centimetres and 28 centimetres. By comparing the Loch Laxford and Mointeach Mhor fossil total carbon, total carbon reconstruction, diatom reconstruction and particle size results I have made two observations.

Firstly, low total carbon predicts of PMSE, and low total carbon values, coincide with greater difference between the reconstructions. Figures 5.8A and 5.18A show the relationship between total carbon PMSE and the difference between the two PMSE reconstructions. As the total carbon PMSE decreases, the difference between the models increase. This is most obvious in the upper section of the Loch Laxford core. Here, as the total carbon PMSE reconstruction decreases with depth, the differences between the two reconstructions increase. A low total carbon PMSE reconstruction indicates a low total carbon value. The modern day total carbon – elevation model has few low marsh and sand flat samples. In the modern samples, it under predicts these samples by a mean of 7 centimetres. This will account for some of the total carbon model under prediction in the fossil samples with low total carbon values but not all of it.

Secondly, low total carbon values, and larger differences between the reconstructions, also coincide with higher proportions of sand. This is clearest at Mointeach Mhor, where the reconstructions are similar in the upper and lower parts of the monolith but differ in the middle section. In this section there is more sand and the total carbon values are lower (Figure 5.11). It also indicated by a larger 'fast tide' component in the central monolith section at Mointeach Mhor (Figure 5.10). This relationship is also seen at Loch Laxford where total carbon decreases as sand increases (Figure 5.3). The impact of sand on total carbon values is discussed further in Chapter 6.

Chapter 6: Discussion and Conclusions

In this chapter, I address the four research aims outlined in Chapter 1 using the results from the modern and fossil sediments described and interpreted in Chapters 4 and 5 respectively. Lastly, I conclude the project by considering the use of total carbon and grain size in aiding diatom based sea-level reconstructions

6.1 <u>Objective one</u>

'To determine the relationship between organic matter, grain size distribution and elevation in the modern tidal flat—salt-marsh—upland system at two contrasting field sites – one in Scotland, the other one in Alaska.'

6.1.1 Organic matter

The modern organic matter at Loch Laxford shows a strong linear relationship with elevation between the sand flat and high marsh (r=0.92). Above the high marsh, between MHWST and HAT, the total carbon values reach a maximum, at which they stabilise. At Beluga Slough, there is also a linear relationship between total carbon and elevation, but there are lower total carbon values for similar elevations on the tidal flat– salt-marsh surface compared to Loch Laxford. In addition, the total carbon values do not reach same maximum threshold and stabilise with elevation. Taking more samples above and below HAT at Beluga Slough would help ascertain whether a similar relationship with elevation exists here. Total carbon at Beluga Slough may stabilise at lower total carbon values, as there is less organic material on the salt-marsh, or they may stabilise at the same maximum value as at Loch Laxford, but at higher relative elevations.

In this study, I chose to focus on total carbon rather than LOI to assess organic matter. Total carbon has a stronger linear relationship with elevation in the modern samples than LOI. In addition, LOI has as a proxy for sediment organic matter has some known methodical errors. LOI assumes that burning sediment will cause a sample mass change from just the organic sediment loss and the minerogenic material is not effected, or contributing to the sample mass change (Plater *et al.* in press). This is not true under all conditions. The sediment grain size, loss of chemically bound water, destruction of inorganic or elemental carbon, and remaining ignition residue can all influence LOI (Ball 1964, Veres 2002, De Vos *et al.* 2005). The effects of these will carry through and influence any estimation of organic carbon made using LOI (Mackereth 1966, Håkansson and Jansson 1983). In addition, measurements of LOI can differ with sample size and furnace times (Heiri *et al.* 2001).

The lower total carbon at Beluga Slough compared to at Loch Laxford may be explained by the difference in growing season between the two sites. In Scotland, the average growing season is from 240 to 270 days (Sniffer 2014). In the Anchorage area of Alaska, 190km to the north of Beluga Slough, the average growing season is approximately 120 days (Alaska Botanic Garden, 2014). This shorter growing season in Alaska may account for lower tidal salt-marsh productivity and less biomass accumulation, leading to lower total carbon values at Beluga Slough when compared to Loch Laxford. If the growing season, and therefore the climate, is important in determining the relationship between elevation and total carbon, this may have implications for using fossil total carbon values.

At Beluga Slough, several samples including the two from above HAT have total carbon values much lower than expected for their elevation (see figure 4.3). The low total carbon values are more noticeable at higher elevations but may also occur lower in the marsh. These low values are likely due to ice rafting of salt-marsh sediment (Shennan, personal communication). Ice rafting occurs as ice freezes to the salt-marsh surface. As the ice moves, with the tide or as the ice weakens in spring, it rips sediment from the salt-marsh. The ice then deposits the sediment above or below their original elevation (Hardwick-Witman 1986, Hamilton *et al.* 2005). Hamilton *et al.* (2005) investigated this process in Alaska at Girdwood and Ocean view salt-marshes. They found large sediments blocks transported up marsh, from the tidal flat to the vegetated marsh, by the ice. As the ice melts this tidal flat sediment is deposited on the vegetated marsh surface. Although the water can disperse thin layers of sediment, large blocks remain and are gradually incorporated into the organic sediment (Hamilton *et al.* 2005). Samples from the vegetated marsh area where this process has occurred would have locally lower total carbon and nitrogen values.

The difference in growing season and total carbon between the two sites has important implications for using fossil total carbon, or organic matter, to reconstruct tidal flat–salt-marsh–upland surface elevation. Figure 6.1 illustrates the possible effect of three climatic or site specific processes on modern total carbon - elevation distribution. The blue line represents the observed total carbon distribution at Loch Laxford. Here, total carbon values increase with elevation until they reach a threshold where they stabilise. The green line represents a different location where there is a similar linear trend, and potentially a maximum threshold exists. This would be a Beluga Slough type scenario, although I have not identified a maximum threshold in the samples investigated at this site. A final scenario, shown by the red line, may also exist. Here, the relationship is still linear but the slope differs. Again, a potential maximum threshold could exist.



Figure 6.1: Schematic diagram illustrating the possible effect of three climatic or site specific processes on the modern total carbon distribution with elevation.

A number of questions regarding the relationship between total carbon and elevation still exist. Investigating total carbon distributions at more sites will help to answer these. I have shown the relationship between total carbon and elevation to differ at contrasting sites. This does not prevent the total carbon – elevation relationship from being used. Instead, it suggests that local investigations should take place so that the most suitable distribution can be used. This assumes that the relationship between total carbon and elevation at each site has not changed through time meaning recent, last millennium sediments, will be most appropriate.

6.1.2 Grain size

Grain size distribution and the percentage volume- grain size curves at Loch Laxford do not show a strong relationship with elevation.

At Loch Laxford, the salt-marsh is characterised by a dense network of creeks. Creeks on the salt-marsh are important water and sediment pathways. As water leaves the creeks, reduced current velocities and sediment retention by vegetation causes coarser sediment deposition close to the creek banks (Adnitt *et al.* 2007). The dense network at Loch Laxford may be locally increasing the coarser sediment at higher elevations and influencing the spatial pattern of particle size distribution across the salt-marsh surface. A similar pattern was observed by Allen (1992) on the reclaimed Elmore salt-marsh in the Severn Estuary. On the Elmore salt-marsh, the sediment grain size generally decreases away from main tidal channel but is locally affected by sedimentation around former creeks. The creeks at Loch Laxford may explain some the variation in grain size proportions and grain size - percentage volume curves between nearby samples on the salt-marsh surface. This theory may also explain why the 'fast tide' style percentage volume–grain size curves, associated with lower marsh settings, occur in the mid and high marsh.

The dense creek network at Loch Laxford appears to be an important local factor for sediment distribution. The effect of creeks are not included in the simple conceptual model by Rahman and Plater (2014) and they recognise this as a limitation to their model. Change in sediment source over time will also have some impact on the grain size deposited on the salt-marsh surface. I believe from the modern particle size investigation at Loch Laxford, there are too many local effects between samples to use the grain size distribution or percentage volume - grain size curves to indicate where samples formed in the tidal flat- salt-marsh system.

6.2 <u>Objective two</u>

'To use the outcomes from the above to produce estimates of RSL change through a fossil core from the field site in Scotland.'

Using the modern Loch Laxford total carbon – elevation linear regression model, I have produced PMSE and RSL reconstructions for the Loch Laxford fossil sediments. In the upper part of the core, the total carbon model and diatom transfer function reconstruction show similar fluctuations with over lapping error bars but they diverge with depth. The difference between the reconstructions stabilises after approximately 100 years and there is an agreement in trend between the two reconstruction methods.

In the lower section of the core, the diatom reconstruction and total carbon reconstruction show similar trends but total carbon under predicts the diatom reconstruction. Total carbon could be useful as part of a multi-proxy approach to sealevel reconstruction, but this under prediction needs to be acknowledged. I have investigated some reasons for this under prediction through assessing the relationship between modern and fossil salt-marsh organic matter.

6.3 <u>Objective three</u>

'Following reconstruction, to assess the relationship between modern and fossil saltmarsh organic matter.'

Decomposition of organic matter is one process that can lower the total carbon value between the modern day and fossil sediment. As reviewed in chapter 2, there are two main processes of decomposition occurring in salt-marshes. These are aerobic decomposition, which occurs near the surface, and anaerobic decomposition, where sulphate reduction dominates. Studies of sulphate reduction in salt-marshes indicate a strong time component. Initially decomposition processes have a high reaction rate, which decreases with depth below ground (Kostka *et al.* 2002, Hines and Jones 1995, Hines *et al.* 1989).

The sulphate reaction rate is limited by metabolizable organic matter rather than by sulphate for the sulphate reduction (Howarth 1993, Kostka *et al.* 2002). As sulphate concentrations are high in salt-marshes (Howarth 1993), a higher rate of reaction, and therefore more decomposition, should take place where there is more organic matter available. The amount of decomposition occurring therefore should be proportional to the amount of organic material available. A proportional loss would cause a gradient change in the elevation – total carbon relationship between the modern and fossil values (Figure 6.2). Sulphate concentrations were not measured at Loch Laxford or Mointeach Mhor. Upon reflection, measuring the sulphate concentration may help to provide a better understanding of the decomposition processes. As the metabolizable

carbon is used up and the sulphate reduction rate decreases to zero, the net decomposition effect will stabilise with depth.



Figure 6.2: Schematic graph of the modern and fossil total carbon distribution if the change between modern and fossil (decomposition loss) is proportional to the original amount.

At Loch Laxford, the diversion of the diatom transfer function and total carbon model predictions suggests the decomposition rate has stabilised by 15cm core depth, or 100 years. In the lower section of the core, there are similar differences between reconstructions throughout the core (mean difference 0.37 metres), supporting organic decomposition has stabilised.

At Mointeach Mhor the sediments are 6000 to 7000 years older than at Loch Laxford. Decomposition studies on salt-marshes suggest that the decomposition decreases with depth, and therefore time (Hines *et al.* 1989, Hines and Jones 1995, Kostka *et al.* 2002). I therefore expect a difference between the reconstructions throughout the monolith. This is not the case. In the upper and lower sections, the difference between the reconstructions is small (mean difference 0.11 metres and -0.05 metres respectively), whilst in the middle, section the difference between the reconstructions is much larger (mean difference 0.46 metres).

The differences between the reconstructions at Loch Laxford and Mointeach Mhor increase with low total carbon values (Figure 6.3). If the organic material loss is just proportional to the organic carbon, this is unexpected (see figure 6.2). Another

process must also take place to cause greater differences between reconstructions with lower total carbon values.



Figure 6.3: Loch Laxford fossil (A) and Mointeach Mhor fossil (B) total carbon values plotted against the difference between the diatom transfer function and total carbon model PMSE reconstructions. The difference increases as the total carbon value decreases.

6.3.1 The effect of sand on total carbon values

From the Loch Laxford and Mointeach Mhor fossil results, I observed low total carbon values, and larger differences between the reconstructions, also coincide with higher proportions of sand (Figure 6.4).

In the modern samples at Loch Laxford, sand and total carbon have a negative correlation only in the low marsh and sand flat, where sand is high (>60%) and total carbon is low (<10%). This negative correlation does not occur in the samples from higher in the tidal flat – salt-marsh – upland system. Modern samples from the mid marsh and above can have high total carbon and high sand content. Conversely, in the fossil samples at Loch Laxford total carbon and sand have negative correlation (Figure 6.4). This happens in all the samples, not just those with total carbon values below 10%. At Loch Laxford, a change appears to take place between the modern and fossil that reduces total carbon values more if there is more sand in the sediment matrix.

In the Mointeach Mhor fossil samples, I observe a similar pattern where total carbon and sand have a negative correlation. Here the differences between the diatom transfer function and total carbon model PMSE reconstructions are greater and the total carbon values are lower, when there is a higher sand content.



Figure 6.4: Total carbon and sand at Loch Laxford and Mointeach Mhor.

Total carbon is measured as a proportion of the freeze-dried mass of the sample. Increasing the minerogenic sediment input will cause lower total carbon values. The input of sand from the former barrier system at Mointeach Mhor may be contributing to the lower carbon value in this way. At Loch Laxford, the lower section of the core is sandier than the upper part (see Figure 6.4), but whether, or how much, this is contributing to the lower total carbon values in the lower section of the core is unknown due to the erosional hiatus.

An explanation for the correlation between high sand and low total carbon seen in fossil sediment, but not the modern distribution is the different porosity and permeability of sediment types (Howarth 1993, Tyson 1995). Coarser, sorted sandier sediments will have greater permeability compared to a mixture of finer silts and clays (Tyson 1995). With more space between the grains, oxygen can reach deeper into the sediment. The supply of oxygen into the sediment will result in more rapid and greater aerobic decomposition lower in the sediment column. With air reaching further into the sediment, the rate and amount of aerobic decomposition will increase. The duration sediments are exposed to air depends on tidal flooding frequency as well as distance from creeks (Howarth 1993). These temporal and spatial effects will cause differences across as well as through salt-marsh fossil sediment. This process occurs in marine sediments where the availability of oxygenated water lowers the boundary between the oxygen rich layer and oxygen poor layer, where anaerobic reduction reactions dominate (Fenchel and Riedl 1970). Andrews et al (2000) have also previously pointed to increased oxidation of sulphides in coarser grained, sandier, sediment in the Humber Estuary. Currently we need more experimentation and data, including sulphate concentration measurements, to explore this theory further and ascertain if this process is occurring in salt-marsh sediment.

In marine continental margins, high sand and low carbon is also linked to grain size surface area. Clay and silt have a larger surface area to volume ratio and so can have a proportionally greater covering of organic matter than sand. Greater organic material can therefore accumulate in the fossil sediment surrounding silt and clay than surrounding sand (Keil and Hedges 1993, Mayer 1994, Tyson 1995). This process suggests sediment grain size is a physical limiting factor for incorporating organic material into sediment. Salt-marshes are only water covered for part of each day. Whether this process is occurring on salt-marshes, and how important sand is in regards to decomposition remains unknown.

Enhanced decomposition in sandier sediment, relative increases in minerogenic sediment inputs, and grain surface area controlling organic material deposition all provide reasons for lower total carbon values in sandy fossil sediments. Due to the decrease in the total carbon value, the total carbon reconstructions are likely to differ from diatom based reconstructions. Site selection therefore appears an important consideration in using total carbon as a sea-level proxy. Sites with influxes of minerogenic sediment input, like the sand at Mointeach Mhor, should be avoided when using total carbon as a sea-level proxy.

Particle size did not have a large effect on the diatom assemblages when measured in the surface samples at Loch Laxford. PCCA shows all combined effect of particle size explains 7% of the variance compared to the 18% explained by elevation. The effect of sand on the fossil diatom assemblages is unknown but the controlling factors explaining the diatoms distribution and assemblage variance are assumed not to change between modern diatom training sets and fossil diatom assemblages. 6.3.2 How much organic decomposition takes place in salt-marsh sediments The organic material decomposition taking place in salt-marsh sediments through time will depend on what factors are limiting the reactions. Aerobic decomposition takes place where air can access the sediment. As discussed above, the amount of sand in the sediment may alter the air space and locally increase this process (Tyson 1995, Howarth 1993). Changes in the rate of decomposition from aerobic decomposition are likely to affect recently deposited sediments, near the ground surface. Anaerobic decomposition takes place where no oxygen is available. Sulphate reduction by bacteria is the dominant anaerobic organic material mechanism in saltmarsh sediments (Tyson 1995). The sulphate reduction rate decreases with depth but also depends on the amount of organic material available (Hines *et al.* 1989, Hines and Jones 1995, Kostka *et al.* 2002, V.-Balogh *et al.* 2006). The sulphate reaction rate also appears to vary between sites and with temperature (Howarth 1993, Kostka *et al.* 2002). These two decomposition mechanisms and contributing factors will cause saltmarsh decomposition to vary spatially and through time.

As decomposition lowers the organic material, fossil measurements with low organic material may simply indicate more of the original organic material has been lost. A greater offset would exist between a diatom and total carbon sea-level reconstruction where this has taken place. This effect of decomposition lowering fossil organic matter values will have implications for other studies that use these values, (for example saltmarsh sediment decompaction or estimates of salt-marsh carbon storage), and needs to be considered. In salt-marsh sediment decompaction, decreased fossil organic matter matter could result in sediment sequences being under decompacted, which would have a knock on effect on RSL data.

At Loch Laxford, the deviation of the diatom transfer function results and total carbon model predictions suggests the decomposition rate has stabilised by 15cm core depth, or around 100 years ago. In the lower section of the core, both the total carbon and diatom transfer function models show little change in PMSE. There are similar differences between reconstructions throughout this core section, supporting the theory that organic decomposition has stabilised. The mean difference between the reconstructions in the lower section, where the proportion of sand is stable and there is little change in PSME, is 0.37 metres with a standard deviation of 0.09 meters. Using

the Loch Laxford modern total carbon – elevation relationship, a change of 0.37 metres is equivalent to a change in the original total carbon value of around 9%. As decomposition rates appear to have large variation between sites, this value is specific to Loch Laxford.

6.4 Objective four

'To investigate a second fossil site using the same approach to test for regional applicability of this approach.'

I used the Loch Laxford surface total carbon model to reconstruct PMSE and RSL at the second fossil site, Mointeach Mhor. Mointeach Mhor is a former tidal embayment in western Scotland, approximately 170 kilometres south-southwest of Loch Laxford. The fossil sediments used in the reconstruction date from the mid Holocene sea-level highstand. This is thought to have lasted for over 1000 years, ending gradually around 5900 cal. year BP (Shennan *et al.* 2005). They are approximately 7000 to 6000 years older than the fossil core from Loch Laxford.

The total carbon model and diatom transfer function PMSE and RSL reconstruction differ in the middle, sandier, section of the studied fossil sediments. They show close agreement in the upper (20 -27 centimetres depth), and lower (48 to 50 centimetres depth) monolith sections. The mean difference between the reconstructions the upper and lower sections are 0.11 metres and -0.05 metres respectively. As the sediments are older at Mointeach Mhor than at Loch Laxford, I expect there to be a difference between the reconstructions due to decomposition of organic material throughout the monolith. The mean differences from the upper and lower sections show that this is not the case.

As discussed in the previous objective, since decomposition lowers the fossil sediment total carbon value, the total carbon value at Mointech Mohr must have originally been higher. The change between the Loch Laxford modern distribution and Mointeach Mhor modern values combined with decomposition lowering fossil total carbon values is such that in the upper and lower sections, the Loch Laxford modern total carbon – elevation relationship gives a good estimate of Mointeach Mhor PMSE and RSL. The middle section at Mointeach Mhor has larger differences between the diatom transfer function reconstruction and the total carbon reconstruction. If the modern Mointeach Mhor total carbon values were originally higher, this middle section indicates greater decrease in total carbon values has occurred than is currently estimated.

Figure 6.5 illustrates the possible total carbon distributions at Mointeach Mhor in comparison to those at Loch Laxford. The blue lines represent the Loch Laxford total carbon distribution in the modern day (solid line) and in the fossil (dotted line) where decomposition reduces the total carbon value proportionally from its original value. The orange line represents the potential modern (solid line) and fossil (dotted line) total carbon distribution Mointeach Mhor. The fossil total carbon distribution at Mointeach Mhor is also based on decomposition reducing the total carbon value proportionally from its original value. The modern distribution (solid line) shows total carbon was likely higher at Mointeach Mhor than at Loch Laxford for the same intertidal elevation. The Mointeach Mhor fossil values are similar to the Loch Laxford modern distributions.



Figure 6.5: Schematic graph of the possible Mointeach Mhor total carbon elevation distribution in comparison to the Loch Laxford total carbon – elevation distribution. The fossil distributions at both sites show organic material loss that is (linearly) proportional to the original (modern) total carbon value. The grey circled highlights the where the Mointeach Mhor fossil and Loch Laxford modern distributions are similar – the scenario believed to be occurring at Mointeach Mhor. This explanation for the similar total carbon vales at Mointeach Mhor relies on three assumptions. Firstly, that the diatom transfer function reconstruction is accurate secondly, that there is no inorganic carbon at Mointeach Mhor contributing to the total carbon value and thirdly that organic decomposition is occurring and lowering the total carbon value between the modern (original value) and fossil (present value).

The potential difference in modern total carbon distributions between the sites or through time complicates the regional applicability of the Loch Laxford total carbon model. Under the scenario described above, the Loch Laxford total carbon model is not suitable to be used at Mointeach Mhor as the modern total carbon –elevation distribution has changed. Further investigation is required in order to attain whether the Loch Laxford total carbon distribution is applicable to nearby sites where more recent fossil sediment sequences are available

6.5 <u>Conclusions</u>

As discussed, the effect of decomposition and changes in grain size volume or type complicates the use of total carbon as a sea-level proxy. The results from Loch Laxford suggest total carbon stabilises after approximately 100 years. This is likely to be site specific as the rate of decomposition is affected by temperature and the amount of organic material available (Howarth 1993, Kostka *et al.* 2002, V.-Balogh *et al.* 2006). The total carbon - elevation distribution varies between modern sites and through time as climate variations alter organic material accumulation. In the Loch Laxford reconstruction, total carbon under predicts actual values but the agreement in trends means organic matter and total carbon could be useful as part of a multi-proxy approach to sea-level reconstruction.

At Mointeach Mhor, sand appears to have a large effect on the total carbon values. I have suggested this may be caused by the input of sand from the former barrier decreasing total carbon values. I have also suggested the negative relationship between total carbon and sand seen at Loch Laxford and Mointeach Mhor in the fossil samples may result from enhanced aerobic decomposition in sandier sediments or grain size surface area influencing organic material deposition. Sediment sequences interrupted by inputs of sand should be avoided when using total carbon as a sea-level proxy. Grain size therefore needs to be assessed to see whether fossil sediments are suitable to use total carbon as a sea-level proxy.

For these reasons, I believe that total carbon has most potential as a sea-level proxy in sediments from the last millennium, where a local modern distribution is available and it is unlikely that large changes in grain size or volume, or organic matter accumulation have occurred.

Where the diatom and total carbon reconstructions exist together, the relationship between them can be investigated (Figure 6.6). Using this relationship, the total carbon value may be semi empirically calibrated and used to provide a PMSE and RSL estimate. In this way, the direction of change in the total carbon values, rather than their absolute value is being used. This is the same approach that carbon to nitrogen ratios and $d^{13}C$ are used as RSL indicators in tidal flat –salt-marsh – upland environment sediment sequences, for example in the work of Meyers (1994), Wilson *et al.* (2005b) and Lamb *et al.* (2006).



Figure 6.6: Schematic diagram of the relationship between total carbon and PMSE reconstructions using diatom.

To integrate the total carbon data into a multi-proxy sea-level reconstruction one approach is to measure total carbon between dated levels. In records where no microfossils are preserved, or in records where they were not initially assessed, this would provide a rapid assessment of change. One example where this may be used is in sediments from the Humber Estuary. In the Humber Estuary at Paradise Farm, work by Metcalfe *et al.* (2000) uses the radiocarbon dated transgressive salt-marsh peat to clastic sediment transition, which has a known altitude relationship with sea level, as a SLIP. Investigating the organic material in the salt-marsh sediments below this transition should provide further information about the history of the salt-marsh and evolution of Humber Estuary through the Holocene. This method of interpolating between dated levels using organic matter may enhance our current understanding of existing records but currently needs more investigation.

Finally, this project has shown organic matter has the potential to be used as a sealevel indicator to aid diatom based reconstructions. Analysis of grain size patterns over the tidal flat - salt-marsh environments at Loch Laxford shows the influence of local processes overprinting the expected pattern with elevation. In fossil sediments, sediment grain size appears to influence the total carbon value. Grain size investigations provide necessary information as to whether fossil sediment is suitable for total carbon to be used as a sea-level proxy. The effect of decomposition also complicates the use of organic carbon but these effects do appear to stabilise over time.

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