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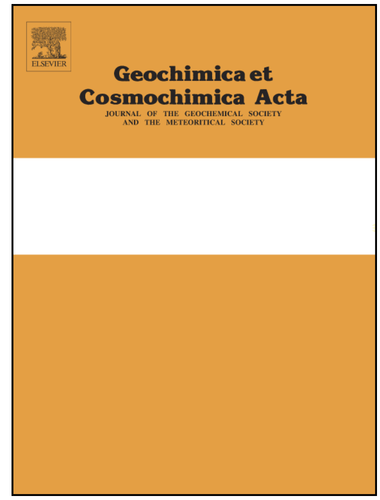

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PII: S0016-7037(17)30462-3
DOI: http://dx.doi.org/10.1016/j.gca.2017.07.038
Reference: GCA 10400

To appear in: *Geochimica et Cosmochimica Acta*

Received Date: 24 January 2017
Revised Date: 23 June 2017
Accepted Date: 24 July 2017

Please cite this article as: Wilson, G.P., On the application of contemporary bulk sediment organic carbon isotope and geochemical datasets for Holocene sea-level reconstruction in NW Europe, *Geochimica et Cosmochimica Acta* (2017), doi: http://dx.doi.org/10.1016/j.gca.2017.07.038

On the application of contemporary bulk sediment organic carbon isotope and geochemical datasets for Holocene sea-level reconstruction in NW Europe

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Keywords: Stable carbon isotope; Organic geochemistry; Sea level changes; North West Europe; Holocene; Estuary; Coastal wetland

Abstract

Bulk organic stable carbon isotope ($\delta^{13}C$) and element geochemistry (total organic carbon (TOC) and organic carbon to total nitrogen (C_{org}/N_{tot})) analysis is a developing technique in Holocene relative sea-level (RSL) research. The uptake of this technique in Northern Europe is limited compared to North America, where the common existence of coastal marshes with isotopically distinctive C_3 and C_4 vegetation associated with well-defined inundation tolerance permits the reconstruction of RSL in the sediment record. In Northern Europe, the reduced range in $\delta^{13}C$ values between organic matter sources in C_3 estuaries can make the identification of elevation-dependent environments in the Holocene sediment record challenging and this is compounded by the potential for post-depositional alteration in bulk $\delta^{13}C$ values. The use of contemporary regional $\delta^{13}C$, C/N and TOC datasets representing the range of physiographic conditions commonly encountered in coastal wetland sediment sequences opens up the potential of using absolute values of sediment geochemistry to infer depositional environments and associated reference water levels. In this paper, the application of contemporary bulk organic $\delta^{13}C$, C/N and TOC to reconstruct Holocene RSL is further explored. An extended contemporary regional geochemical dataset of published $\delta^{13}C$, C/N and TOC observations (n=142) from tidal-dominated C_3 wetland deposits (representing tidal flat, saltmarsh, reedswamp and fen carr environments) in temperate NW Europe is compiled, and procedures implemented to correct for the ^{13}C Suess effect on contemporary $\delta^{13}C$ are detailed. Partitioning around medoids analysis identifies two distinctive geochemical groups in the NW European dataset, with tidal flat / saltmarsh and reedswamp / fen carr environments exhibiting characteristically different sediment $\delta^{13}C$, C/N and TOC values. A logistic regression model is developed from the NW European dataset in order to objectively identify in the sediment record geochemical groups and, more importantly, group transitions, thus allowing the altitude of reference water levels to be determined. The application of this method in RSL research is demonstrated using the Holocene sediments of the Mersey Estuary (UK), in which $\delta^{13}C$, C/N and TOC variability is typical of that encountered in Holocene sediments from C_3 coastal wetlands in NW Europe. Group membership was predicted with high probability in the depositional contexts studied and the accuracy of group prediction is verified by microfossil evidence. The method presented facilitates the application of $\delta^{13}C$, C/N and TOC analysis in RSL reconstruction studies in C_3 vegetated wetlands throughout temperate NW Europe.

Abbreviations

C/N, carbon/nitrogen; HAT, highest astronomical spring tide, MHWS, mean high water of spring tide; OD, Ordnance Datum; PAM, partitioning around medoids; POC, particulate organic carbon; POM, particulate organic matter; RSL, relative sea-level; RWL, reference water level; SLI, sea-level index point; TOC, total organic carbon.

1. Introduction

A detailed knowledge of relative sea-level (RSL) change is necessary to understand coastal evolution and coastline response to processes operating over a range of spatial and temporal scales. Additionally, RSL records contribute to a better understanding of viscoelastic earth structure, ice sheet configuration and melt history through their use in glacial isostatic adjustment models (e.g. Bradley et al., 2011), which in turn has societal relevance for the effective projection of, and planning for, future sea-level change (Shennan et al., 2009). Sediments accumulating in low energy tidal-dominated coastal wetlands can provide a natural archive of RSL change (Edwards, 2013). In temperate regions, minerogenic tidal flats occupying lower-intertidal areas are replaced by vegetated saltmarshes at higher elevations, and (where intact) ultimately by organogenic reedswamp and wet woodland (e.g. fen carr) environments in upper inter-tidal and supra-tidal zones respectively (Waller et al., 1999). This vertical zonation reflects the reducing frequency and duration of tidal flooding with increasing ground elevation within the tidal frame. Changes in RSL, whether driven by external factors (e.g. vertical changes in ocean level (Fairbanks, 1989), or land level (Bradley et al., 2011)), or by internal factors (e.g. through the promotion of sediment accumulation on inter-tidal vegetated surfaces (e.g. Kirwan and Murray, 2007), or due to sediment compaction (e.g. Brain et al., 2012)) result in the displacement of zones and, typically, the accumulation of intercalated minerogenic and organogenic deposits over Holocene time-scales (Allen, 2003). RSL records generated from unconsolidated coastal sediment deposits comprise a series of sea-level index points (SLIs) – dated sediment horizons with a known altitude (relative to a local datum) and relationship (indicative meaning) to a reference water level (RWL) (Edwards, 2013). The indicative meaning of coastal depositional environments is determined from contemporary observation (Shennan, 1982). SLIs are often derived from transgressive (organogenic to minerogenic) or regressive (minerogenic to organogenic) lithostratigraphic overlaps in intercalated coastal sediment sequences (Tooley, 1982). The indicative range (the possible altitudinal envelope of inferred RWLs) at lithostratigraphic overlaps is minimal (typically ± 20cm, depending on tidal range) and the availability of organic material enables lithostratigraphic overlaps to be placed in a chronological framework, thus permitting the reconstruction of RSL time-altitude changes with defined temporal and vertical errors.

The indicative meaning at lithostratigraphic overlaps is usually determined by the characteristics of the preserved microfossil assemblages (van de Plassche, 1986), particularly the composition of diatoms (e.g. Zong, 1997), foraminifera (e.g. Edwards and Horton, 2000) and pollen (e.g. Bernhardt and Willard, 2015), as informed by contemporary surveys. Microfossil analysis is necessary to determine the sedimentary environments (e.g. tidal flat, saltmarsh, reedswamp, wet woodland) represented in depositional sequences, and to ensure a conformable facies sequence at lithostratigraphic overlaps. The application of microfossils as sea-level indicators has several limitations, however. These include: (i) an assumption of unchanged optima and tolerance of biota in relation to a RWL (Gehrels, 2002); (ii) the vertical range restriction of different biological indicators within the tidal frame (Gehrels et al., 2001); (iii) the susceptibility to chemical and mechanical damage in the journey from biocoenose to thanatocoenose, and in the final fossil stage (e.g. Birks and Birks, 1980; Kato et al., 2003). The use of microfossils to quantitatively estimate past RWLs using transfer functions may suffer additional drawbacks, including the absence of equivalent modern analogues (e.g. Wilson and Lamb, 2012), problems of spatial autocorrelation (e.g. Telford and Birks, 2005) and a large amount of unexplained variability in contemporary training sets (e.g. Zong and Horton, 1999).

Bulk organic δ^{13}C, C/N and TOC as sea-level indicators

The application of stable carbon isotope analysis (δ^{13}C analysis), used in conjunction with supporting geochemistry (particularly the ratio of organic carbon to total nitrogen (C_{org}/N_{tot}) and total organic carbon content (TOC)) is gaining traction as a viable sea-level indicator (Khan et al., 2015a). When used in combination with microfossil indicators, an increase in the precision of inferred palaeotidal levels has been achieved (e.g. Kemp et al., 2013; Cahill et al., 2016). Used in isolation, these geochemical techniques prove to be effective alternative sea-level indicators and can prevent redundancy of potential SLIs at lithostratigraphic overlaps in the event of poor microfossil preservation (Goslin et al., 2015; Khan et al., 2015b). In North America, the application of δ^{13}C and C/N analysis in palaeosea-level research (Kemp et al., 2010; Kemp et al., 2012; 2013; Milker et al., 2015; Cahill et al., 2016), and in palaeoseismology (Engelhart et al., 2013) has proved particularly effective due to the common existence of isotopically distinctive vegetated coastal marshes. For example, on the southern Atlantic coast of New Jersey, saltmarshes are typically colonized by plants which utilize the C_4 photosynthetic pathway (e.g. *Spartina patens*: δ^{13}C between –14.0‰ and –13.8‰ (Kemp et al., 2012)), whilst plants utilizing the C_3 photosynthetic pathway are frequent in more upland brackish and freshwater marshes (e.g. *Phragmites australis*: δ^{13}C between –25.2‰ and –24.6‰ (Kemp et al., 2012)). This can facilitate the identification of saltmarsh and upland brackish / freshwater marsh deposits in the sediment record using $\delta^{13}C$ because sediment $\delta^{13}C$ values faithfully reflect the relative contributions of organic carbon from C_3 and C_4 plants at the time of formation (Stout et al., 1975; Chmura et al., 1987). The presence or absence of agglutinated foraminifera can further distinguish between brackish and freshwater marsh deposits respectively and used together with bulk organic $\delta^{13}C$ measurements have been shown to provide a precise indication of past RSL (Kemp et al., 2012).

Since the exploration and development of $\delta^{13}C$ and C/N analysis of marsh deposits specifically for application in sea-level research (e.g. Wilson et al., 2004; 2005a), the uptake and application of this method in European sea-level research is, by comparison, more limited (Lamb et al., 2007; Goslin et al., 2015; Khan et al., 2015b). In northern Europe, C_4 saltmarsh vegetation has either been recently introduced or is relatively rare (Preston et al., 2002). In this context (i.e. in the absence of C_4 vegetated coastal marshes), the purpose of bulk organic sediment $\delta^{13}C$ and C/N analysis is principally to distinguish between organic carbon derived from C_3 vascular vegetation and tidal-derived C_3 particulate organic carbon (POC) (Wilson et al., 2005a). The $\delta^{13}C$ value of organic carbon from C_3 vascular vegetation typically ranges between –32‰ and –21‰; tidal-derived particulate organic carbon $\delta^{13}C$ ($\delta^{13}C_{POC}$) values range between –33‰ to –18‰ (Deines, 1980). $\delta^{13}C_{POC}$ mainly reflects the $\delta^{13}C$ values of phytoplankton, but can also be influenced by terrigenous material and, to a lesser extent, zooplankton (Lamb et al., 2006). Because the $\delta^{13}C$ range of these two end-members (C_3 vascular vegetation and C_3 POC) overlap, C/N analysis is required alongside $\delta^{13}C$ analysis in C_3 estuaries to distinguish between organic carbon from vascular vegetation (C/N typically >12) and phytoplankton (C/N typically <10) sources (Tyson, 1995). The progressive transition from tidal-derived POC dominance in sub-tidal and lower inter-tidal areas, to C_3 vascular vegetation dominance in high inter-tidal and supra-tidal areas is reflected in falling surface sediment bulk organic $\delta^{13}C$ and rising C/N values (Wilson et al., 2005b). The relationship between bulk organic $\delta^{13}C$ and C/N values and ground elevation within the tidal frame is retained in Holocene sediment deposits (Wilson et al., 2005a). Therefore, within-core trends in $\delta^{13}C$ and C/N can be used qualitatively to identify changing RSL.

An alternative approach is to identify distinctive elevation-dependent environments in the sediment record based on 'signature' $\delta^{13}C$ and C/N values. However, post-depositional organic matter degradation resulting in the selective preservation of ^{13}C-depleted refractory material may compromise the use of bulk organic $\delta^{13}C$ values in this way (Wilson et al., 2005a). A further problem is that upper inter-tidal and supra-tidal zones are often absent due to human activity and so the full range of $\delta^{13}C$ and C/N values are unknown. The lack of modern environmental analogues and their associated bulk sediment $\delta^{13}C$ and C/N values can prevent confident identification of Holocene depositional environments using $\delta^{13}C$ and C/N data. In an innovative study to address this issue, Khan et al. (2015b) compiled a regional dataset consisting of published contemporary bulk sediment $\delta^{13}C$, C/N and TOC observations from coastal sites in northern and southern England, and new observations from the Thames Estuary and Norfolk (Khan et al., 2015b). The measurement of TOC alongside $\delta^{13}C$ and C/N is important because large changes in sediment organic content occur in response to the vertical changes in vegetation density within the tidal frame (Plater et al., 2015). Khan et al. (2015b) were able to distinguish between tidal flat/low saltmarsh, mid/high saltmarsh, reedswamp and fen carr environments based on contemporary sediment $\delta^{13}C$, C/N and TOC values, and applied the dataset to identify RWLs at lithostratigraphic overlaps in the sediment sequences of the Thames Estuary, UK.

The study presented here seeks to explore and develop further the regional $\delta^{13}C$, C/N and TOC dataset approach developed by Khan et al. (2015b) for use in palaeosea-level research by:

(i) including all additional appropriate surface sediment $\delta^{13}C$, C/N and TOC measurements from C_3 tidal-dominated wetland sediments in NW Europe. This will increase the range of modern analogues for $\delta^{13}C$, C/N and TOC values in Holocene coastal deposits, and capture the local variability in contemporary $\delta^{13}C$, C/N and TOC values from specific coastal environments;

(ii) implementing a procedure to correct contemporary bulk sediment $\delta^{13}C$ values for the ^{13}C Suess effect to enable their use as appropriate analogues for pre-industrial $\delta^{13}C$ values;

(iii) using partitioning around medoids (PAM) cluster analysis to objectively explore whether specific coastal depositional environments can be robustly distinguished in the NW European contemporary geochemical dataset;

(iv) applying logistic regression to generate probabilistic estimates of the origin of Holocene coastal sediment deposits based on the similarity between deposited and contemporary bulk organic sediment $\delta^{13}C$, C/N and TOC values.

The utility of a regional dataset approach is evaluated and the application of these measurements to distinguish depositional environments and RWLs at lithostratigraphic overlaps in C_3 estuarine deposits is demonstrated in Holocene sediment sequences from the Mersey Estuary, UK.

2. Methods

2.1. NW European C_3 coastal wetland sediment $\delta^{13}C$, C/N and TOC dataset

The compiled NW European contemporary bulk organic sediment $\delta^{13}C$, C/N and TOC dataset is based on 142 samples collated from C_3 coastal wetlands (comprising tidal flats, saltmarshes, reedswamps and fen carr environments) in the UK (Mersey Estuary: Wilson et al., 2005a, b; Humber Estuary: Lamb et al., 2007; East Sussex and Norfolk: Andrews, 2008; Thames Estuary: Khan et al., 2015b), Ireland (Shannon Estuary: Craven et al., 2013) and France (Tresseny Marsh and Mousterlin Marsh, Brittany: Goslin et al., 2015) (Figure 1). In addition, observations of deposits along the axis of estuaries allows the variability in $\delta^{13}C$, C/N and TOC to be captured between riverine and marine end-members, thereby providing a range of possible values for tidal-derived POC. However, in NW Europe such data are limited (e.g. Schelde Estuary (Netherlands / Belgium) (Middelburg and Nieuwenhuize, 1998); Tay Estuary (Scotland) (Thornton and McManus, 1994). The eutrophic Schelde Estuary is highly polluted (Abril et al., 2002) and so has been excluded from the dataset. Only Tay estuary bulk organic sediment $\delta^{13}C$, C/N and TOC data, taken at low tide along its axis, is included (Thornton and McManus, 1994). The Firth of Tay, a long coastal embayment, drains a 6500 km^2 catchment and receives c. 1.6 million tonnes of terrigenous sediment input per year (Al-Jabbari et al., 1980). Because the estuary is macro-tidal, marine organic material is also an important carbon source (Thornton and McManus, 1994). Therefore, the influence of both terrigenous and marine organic matter inputs on estuarine tidal flat sediment $\delta^{13}C$, C/N and TOC values are well-represented. Samples located in close proximity to sewage outfalls were excluded from the dataset. Additionally, samples and sites dominated by C_4 vascular vegetation (e.g. Waarde marsh, Netherlands: (Middelburg et al., 1997)), which are non-native to NW European saltmarshes, were also excluded from the dataset, although there are developing methods to correct surface sediment $\delta^{13}C$ values for C_4 plant invasion (Craven et al., 2017). Each of the included samples in the regional dataset has been prepared for isotopic and geochemical analysis using the same standard technique of acid rinsing. This pre-treatment method to remove inorganic carbon does not result in any significant distortion in inter-tidal or supra-tidal bulk organic $\delta^{13}C$ or C/N values (Craven et al., 2013). The dataset collated contains the entirety of published appropriate bulk organic surface sediment $\delta^{13}C$, C/N and TOC measurements from tidal-dominated C_3 wetlands in NW Europe to-date and represent a range of physiographic conditions commonly encountered in coastal wetland Holocene sediment sequences.

FIGURE 1 HERE

2.2. Correction for the ^{13}C Suess effect

It is necessary to correct for the ^{13}C Suess effect (Keeling et al., 1979) before absolute 'characteristic' $\delta^{13}C$ values of coastal wetland environments can be used as contemporary analogues to infer the depositional environments of coastal sediment deposits based on their pre-industrial $\delta^{13}C$ values. Due to fossil fuel burning and deforestation, the introduction of ^{12}C–enriched CO_2 into the atmosphere has resulted in a decrease in atmospheric $\delta^{13}CO_2$ values from −6.4‰ in 1845 (Francey et al., 1999) to more recent values of approximately –8.3‰ (mean 2014 Antarctic air sample value: http://www.esrl.noaa.gov/). Air-water CO_2 gas exchange has resulted in an associated decrease in $\delta^{13}C$ values of aqueous CO_2 (CO_{2aq}) in the ocean mixed layer. For example, surface ocean global mean $\delta^{13}C$ values fell by 0.16‰ ± 0.02‰ per decade between the 1970s and 1990s (Quay et al., 2003), although the oceanic ^{13}C Suess effect is spatially variable (e.g. Quay et al., 1992; 2003; Kortzinger et al., 2003; Eide et al., 2017). Because isotopic fractionation is additive (O'Leary et al., 1992), this reduction in inorganic carbon source $\delta^{13}C$ values is expressed in the $\delta^{13}C$ values of terrestrial and aquatic photosynthetic autotrophs (e.g. Schelske and Hodell, 1995; Zimmerman and Canuel, 2002; McCarroll and Loader, 2004; Verburg, 2007; McMahon et al., 2015). Consequently, contemporary wetland bulk organic sediment $\delta^{13}C$ values will be up to c.2‰ lower (based on the date of measurement – see Supplementary file 1) than pre-industrial equivalent samples. Correction for the ^{13}C Suess effect has been achieved by adjusting contemporary bulk sediment $\delta^{13}C$ values in the NW European dataset (termed $\delta^{13}C_{adjusted}$) to account for the difference between the atmospheric $\delta^{13}CO_2$ at the time of sample collection (as observed from modern air samples or Antarctic ice core records (Francey et al., 1999)) and a pre-industrial standard value of –6.4‰ (McCarroll and Loader, 2004). All of the statistical analyses of the contemporary dataset in this paper use the standardized $\delta^{13}C_{adjusted}$ co-variate (see Section 2.4). All of the core $\delta^{13}C$ values are pre-industrial and therefore do not require adjustment.

In addition to the ^{13}C Suess effect, some additional change in $\delta^{13}C$ of terrestrial vegetation (Schubert and Jahren, 2012) and phytoplankton (Laws et al., 1995; Cullen et al., 2001) may occur in response to an accompanying increase in the concentration of atmospheric CO_2 and CO_{2aq} in oceans and freshwaters. Such changes in vegetation are environment- and species-specific (McCarroll et al., 2009), and appear spatially variable in phytoplankton owing to differences in water biogeochemistry. Although this effect is acknowledged, no corrections are attempted. This is because correction methods are an area of ongoing research (e.g. McCarroll et al., 2009), and the specific provenance of organic carbon (i.e. to species level) in bulk organic samples is unknown, and will often comprise a mixture of organic carbon sources (e.g. terrestrial vascular vegetation, freshwater and marine phytoplankton, bacteria).

2.3. *Mersey Estuary sediment cores*

Two long (>6m) unconsolidated sediment cores from the intercalated organogenic and minerogenic deposits of the Mersey Estuary (Figure 1) are used to illustrate and evaluate the application of the NW European geochemical dataset for reconstructing Holocene RSL. Cores Ince 2 (I-2) from Ince Marshes and Ince 4 (I-4) from Helsby Marsh, which are proximal (<0.5km) and distal (>1km) to the Mersey Estuary respectively, capture a wide range of coastal palaeoenvironments and represent an effective test for the contemporary dataset. Diatom and pollen evidence from the same sequences are used to assess the performance of the database approach. A full $\delta^{13}C$, C/N, diatom and pollen record of both cores is detailed in Wilson et al. (2005a) and Wilson and Lamb (2012), along with specific details of core lithology and chronology.

2.4. *Statistical analysis*

PAM analysis (Kaufman and Rousseeuw, 1990) is employed to determine the number of distinctive depositional groups in the *NW European C_3 coastal wetland dataset* based on the combined measurements of $\delta^{13}C$, C/N and TOC. PAM analysis has been used effectively to objectively distinguish groups, or clusters, in contemporary ecological and geochemical datasets (e.g. Kemp et al., 2012; Goslin et al., 2015). This cluster method is more robust because it is based on the minimization of sums of dissimilarities rather than on the sums of squares of dissimilarities. The latter approach, used in some other clustering techniques, is extremely sensitive to the effect of one or more outliers (Kaufman and Rousseeuw, 1990). PAM analysis partitions samples into groups based on their measured dissimilarity to the group centrotype, or medoid. The medoid is the sample (i.e. the sample $\delta^{13}C$, C/N and TOC values) of a group of samples for which the average dissimilarity to all the samples of the group is minimal. PAM analysis generates Silhouette plots that indicate how securely a sample is allocated to a given group (Rousseeuw, 1987). Sample silhouette widths approaching +1 indicate a sample which is well classified to its group (i.e. average within group dissimilarity is much smaller than between group dissimilarity). Sample widths approaching –1 indicate misclassification of the sample to its group, whilst widths of around 0 indicate samples which lie between groups and are thus poorly classified. PAM analysis was completed using the '*cluster*' package in *R* (Maechler et al., 2005). To account for the differences in unit measurements of the three variables, PAM analysis was performed on standardized data (z-scores).

Based on the contemporary group $\delta^{13}C$, C/N and TOC characteristic values identified in PAM analysis, multivariate logistic regression is used to objectively identify the probable origin (group membership) of Mersey Estuary sediment deposits. The advantage of using logistic regression is that it offers a probabilistic estimate of a core sample being assigned to a specific group. Logistic regression was preferred over other classification techniques, such as discriminant analysis, because the TOC sample distribution is bi-modal and thus deviates from a normal distribution. Unlike discriminant analysis, logistic regression makes no assumptions about the distribution of the datasets (Pohar et al., 2004). The sediment core geochemical values were standardized, with z-scores of sediment core $\delta^{13}C$, C/N and TOC values calculated using the mean and standard deviation of $\delta^{13}C$, C/N and TOC in the contemporary dataset to allow meaningful comparison between the two datasets (Supplementary file 2). Poorly or incorrectly-grouped contemporary samples identified by silhouette widths of <0.25 were not included in the training set. The covariates in the logistic regression model (Section 3.2) result in separation of the outcome groups. Consequently, it was necessary to run Firth's bias reduced logistic regression (Firth, 1993) to produce valid parameter estimates using penalized likelihood. This analysis was conducted in *R* using the '*logistf*' package (Heinz and Ploner, 2016).

3. Results

3.1. *NW European C_3 coastal wetland sediment $\delta^{13}C$, C/N and TOC dataset*

Contemporary $\delta^{13}C$ (unadjusted), C/N and TOC values from NW European C_3 coastal wetland sediments are shown in Figure 2 (see also Supplementary file 1). Following Khan et al (2015b), samples have been sub-divided into tidal flat / low saltmarsh (n=49), mid / high saltmarsh (n=54), reedswamp (n=20) and fen carr (n=19) for the purposes of illustration. $\delta^{13}C$ values range from –30.1‰ to –21.7‰, C/N 2.3 to 26.4 and TOC 0.4% to 47.6%. There are clear relationships between all three variables: $\delta^{13}C$ is inversely correlated with C/N (r = –0.68, p=0.00) and TOC (r = –0.71, p=0.00); C/N and TOC are positively correlated (r = 0.70, p=0.00). There are also some obvious patterns in the geochemistry of the different coastal environments. Reedswamp and fen carr samples mostly have $\delta^{13}C$ values < –27‰ and C/N >12 (Figure 2). TOC values are more variable, but typically >25%. Tidal flat / low saltmarsh samples tend to have low TOC (<10%), whereas TOC content of mid / high saltmarsh samples can extend to 30% (Figure 2). Tidal flat / low saltmarsh and mid / high saltmarsh $\delta^{13}C$ and C/N values overlap considerably, although there are more observations of mid / high saltmarsh samples with C/N ratios >13 (Figure 2).

FIGURE 2 HERE

The group average silhouette widths generated by PAM analysis provides an indication of how 'tight' and distinctive the group is clustered, and thus can be used to identify weak clusters or groups. The average silhouette width of all of the groups is used to identify the most appropriate number of groups within the dataset. Based on the highest average silhouette width of 0.54, PAM analysis distinguishes two major geochemical ($\delta^{13}C_{adjusted}$, C/N, TOC) groups in the NW European dataset (Figure 3). Group 0 has $\delta^{13}C_{adjusted}$, C/N and TOC medoid values of –24.4‰, 10.8 and 4.8% respectively. Group 1 has $\delta^{13}C_{adjusted}$, C/N and TOC medoid values of –27.5‰, 15.8 and 40.7% respectively. Group 0 (n=103, mean silhouette width of 0.55) is populated by samples mostly from tidal flat / low saltmarsh and mid / high saltmarsh environments. In addition, one supra-tidal sample from Ringmoylan (Ireland) and two reedswamp samples from Norfolk and the Thames (England) also appear in this group, but these samples have very low silhouette widths (0.16, 0.07 and –0.01, respectively) and are poorly grouped on account of their elevated TOC, C/N and/or lower $\delta^{13}C_{adjusted}$ values compared with other group samples. Group 1 (n=39, mean silhouette width of 0.54) is dominated by samples from reedswamp and fen carr environments (n=36). This group also contains three mid / high saltmarsh samples from the

Humber Estuary (England), Tressény and Mousterlin marshes (France), respectively (silhouette widths of 0.32, 0.26, 0.26), each of which have much higher TOC values compared with samples drawn from similar locations. The Group 0–1 midpoint $\delta^{13}C_{adjusted}$, C/N and TOC values (i.e. the average of the Group 0 and Group 1 medoid values) are –26.0‰ (c. –27.5‰ unadjusted), 13.3 and 22.8% respectively. These values generally separate spatially adjacent mid / high saltmarsh and reedswamp samples in the contemporary dataset (Figure 2). The transition between saltmarsh and reedswamp deposition (Group 0–1 transition) is meaningful in RSL reconstruction. In temperate macro-tidal systems the RWL for a *Phragmites* or monocotyledonous peat deposited conformably above clastic saltmarsh sediments is M^1–20cm ± c.20cm (where M^1 is the average of mean high water of spring tide height (MHWS) and highest astronomical tide height (HAT) (M^1 = 0.5 x (MHWS + HAT)), or MHWS–20cm ± c.20cm for *Phragmites* or monocotyledonous peat deposits located conformably below clastic saltmarsh sediments (Shennan, 1982). Therefore, locating the elevation of the Group 0–1 transition in the sediment column permits the allocation of a RWL. In Section 3.2. below, the NW European geochemical dataset is applied to the Holocene coastal sediment deposits of the macro-tidal Mersey Estuary to determine the group membership of core samples and to locate Group 0–Group 1 transitions (and associated RWLs) in the sediment column.

FIGURE 3 HERE

3.2. Dataset application: Mersey Estuary Holocene sediments

The binary logistic regression model (Equation 1) successfully predicts the group membership of each sample in the contemporary dataset (Supplementary file 1). The results of the model application to predict the group membership of the Holocene sediments in cores I-2 and I-4 are detailed below. The logistic regression model yields a $\hat{p}$ value for each core sample $\delta^{13}C$, C/N and TOC (combined) measurement (Supplementary file 2). A calculated $\hat{p}$ value of ≥ 0.5 indicates that Group 1 membership (reedswamp / fen carr deposition) is more likely. Conversely, a $\hat{p}$ value <0.5 indicates that Group 1 membership is unlikely and therefore samples are allocated to Group 0 (tidal flat / saltmarsh deposition). Group predictions are compared with existing microfossil records from each core. Core I-2 and I-4 microfossil and geochemical data are summarized in Figures 4 – 9.

$$\hat{p} = \frac{e^{\beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3}}{1+e^{\beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3}} \quad \text{Equation 1}$$

where β_0 = −2.904385, β_1 is the $\delta^{13}C_{adjusted}$ z-score coefficient of −2.006975; β_2 is the C/N z-score coefficient of 1.666785; β_3 is the TOC z-score coefficient of 2.986418. x_1, x_2 and x_3 denote core sample $\delta^{13}C$, C/N and TOC z-score values, respectively. The mean and standard deviation of the $\delta^{13}C_{adjusted}$, C/N and TOC values in the NW Europe training set, which are used to calculate core sample z-scores, are as follows: $\delta^{13}C_{adjusted}$ μ = −24.91‰, σ = 1.72; C/N μ = 12.22, σ = 3.30; %TOC μ = 15.59%, σ = 16.04.

Helsby Marsh core Ince 4

The replacement of a basal peat deposit by organic clay at –0.61m OD (6,800 ± 50 ^{14}C yr BP) followed by clay deposition from –0.37m OD is the first transgressive overlap recorded at Helsby Marsh (Figures 4 and 5). $\delta^{13}C$ values remain generally low throughout the basal peat (c. –29.1‰ to –27.2‰) with C/N ratios ranging from 18.5–28.5. Organic carbon, derived primarily from C_3 vascular vegetation, is present in concentrations of 33%–52%. Logistic regression analysis indicates continued Group 1 membership throughout the basal peat. Sediment TOC falls from 42% in the peat unit at –0.65m OD to ≤3% in the clay unit at –0.35m OD. A fall in C/N from 25.4 to 15.0 accompanies the change in lithology from peat to organic clay deposition. C/N values continue to fall to around 11 in the overlying clay. Little change is apparent in $\delta^{13}C$ between the peat and the organic clay, but a rise in $\delta^{13}C$ from –29.6‰ to –27.7‰ occurs in the organic clay unit, and this rise continues to –26.7‰ into the overlying clay. Taken together, this indicates that C/N initially responds to an increase in the freshwater table, followed by a change in $\delta^{13}C$ in response to more direct marine influences. Logistic regression analysis indicates a switch from Group 1 membership at –0.39m OD ($\hat{p}$ of Group 1 = 0.75) to Group 0 membership at –0.35m OD ($\hat{p}$ of Group 1 = 0.02). The Group 1–Group 0 transition, placed at the midpoint between these two elevations, is –0.37m OD. This elevation marks the transition between reedswamp and saltmarsh environments according to the contemporary NW European geochemical dataset, and can be assigned a RWL of MHWST–20cm ± 20cm (Shennan, 1982). The geochemical-based reconstruction is consistent with the independent, multi-proxy, microfossil record. In the geochemical-inferred Group 1 deposits, the pollen assemblages (Figure 4) indicate the presence of poor fen (–1.06m OD), alder carr (–1.01 to –0.79m OD) and oak-hazel woodland

(–0.60 to –0.56m OD). Freshwater diatoms, particularly the freshwater epiphyte *Gomphonema angustatum* (Kützing) Rabenhorst, dominate between –1.07 and –1.03 m OD, but are sparse in the overlying occasional wood-containing peat deposits (Figure 5). A single sediment sample dominated by marine diatoms at –0.61m OD indicates an episode of increased coastal exposure, perhaps from a storm surge event. Leading up to the transition to Group 0 membership, brackish-freshwater species, particularly the tychoplankton *Staurosirella pinnata* (Ehrenberg) D.M. Williams & Round*,* occur in high frequencies, indicating standing water / waterlogged conditions (Vos and De Wolf, 1993). The transition to Group 0 membership coincides with the onset of clay from –0.37m OD and is supported by a pollen assemblage consistent with saltmarsh conditions.

FIGURE 4 HERE

A thick (c. 2.6m) minerogenic deposit overlies the organic clay unit at –0.37m OD. Higher $\delta^{13}C$ values, typically between –26‰ and –25‰, and C/N values typically of <10 in the lower sections of this unit reveal tidal-derived organic carbon. TOC values are very low, mostly ≤ 1%. Logistic regression analysis indicates continued Group 0 membership between –0.35m OD and +2.09m OD, although in three samples with low $\delta^{13}C$ values there is uncertainty in group membership. This deposit is dominated by the marine species *Paralia sulcata* (Ehrenberg) Cleve, *Thalassiosira eccentrica* (Ehrenberg) Cleve, *Cymatosira belgica* Grunow and *Delphineis surirella* (Ehrenberg) G.W. Andrews (Figure 5). The appearance of occasional *Phragmites* remains from +1.67m OD in the upper minerogenic deposits coincides with a shift to dominance of marine-brackish taxa, particularly *Tryblionella navicularis* (Brébisson) Ralfs and *Navicula peregrena* (Ehrenberg) Kützing. The onset of peat deposition, containing occasional wood fragments, occurs at +2.18m OD (5,940 $\pm$ 40 ^{14}C yr BP). Diatoms are absent in the sediments deposited immediately before peat development. Nevertheless, Poaceae pollen frequencies of >20% (Figure 4) at +2.15m OD and the presence of occasional *Phragmites* macrofossils indicate reedswamp conditions immediately prior to the regressive overlap, with the proximity of marine conditions suggested by the presence of pollen from saltmarsh taxa. *Quercus* and *Ulmus* pollen frequencies increase as peat deposition commences, with *Alnus*, *Corylus* and Poaceae remaining important components of the pollen assemblage. This suggests fen woodland conditions, perhaps with nearby oak-hazel woodland. The sediment TOC content increases across the regressive overlap from 2% at +2.09m OD to >40% from +2.19m OD. The fall in $\delta^{13}C$ from –25.6‰ to –29.3‰ associated with the change from clay to peat deposition, and the accompanying rise in C/N from 11.4 to 22, demonstrates a progressive change in organic carbon source from tidal-derived POC to C_3 vascular vegetation. Logistic regression analysis indicates a switch from Group 0 membership at +2.09m OD ($\hat{p}$ of Group 1 = 0.01) to Group 1 membership at +2.19m OD ($\hat{p}$ of Group 1 = 1.00). The midpoint between Group 0–Group 1 membership is +2.14m OD. This elevation marks the transition between saltmarsh and reedswamp environments according to the contemporary NW European geochemical dataset, and can be assigned a RWL of M^1–20cm ± 20cm (Shennan, 1982).

FIGURE 5 HERE

The replacement of peat at +2.91m OD (3,220 $\pm$ 40 ^{14}C yr BP) with interlaminated peat and clay forms the second transgressive overlap recorded at Helsby Marsh (Figures 6 and 7). A decrease in C/N from 21.7 at +2.79m OD to 16.2 at +2.90m OD is apparent in the upper levels of the peat unit, and C/N continues to fall from 15.6 at 2.95m OD to 5.9 at 3.34m OD in the successive peat and clay and the mottled clay units. Sediment TOC values progressively fall from >50% in the upper levels of the peat, to 1% in the mottled clay unit. $\delta^{13}C$ values of between –29.1‰ to –28.3‰ are recorded in the upper peat, and the overlying interlaminated peat and clay. A marked increase in $\delta^{13}C$ occurs in the mottled clay unit, which replaces the interlaminated peat and clay at +2.99m OD, where values rise from –28.4‰ at +3.01m OD and reach –24.6‰ at +3.26m OD. The C/N data again indicates an initial rise in the freshwater table prior to the registration of direct marine conditions by $\delta^{13}C$. Logistic regression analysis predicts Group 1 membership between +2.31m OD and +2.95m OD. Pollen was poorly preserved in the sections investigated at +2.83m and +2.86m OD, but the pollen assemblages between +2.91 and +2.95m OD in the peat and clay unit corroborate the geochemical data and indicate reedswamp conditions (Figure 6). The presence of marine plankton and tychoplankton species alongside marine-brackish and brackish-freshwater epipelons (Figure 7), together with the presence of pollen from saltmarsh taxa in the peat and clay deposit, suggests proximal saltmarsh conditions and some degree of coastal exposure. A mottled clay unit overlies the peat and clay at +2.99m OD and the geochemistry indicates a switch to Group 0 membership at +3.01m OD. In the assemblages investigated at +3.06 and +3.10m OD, marine-brackish and brackish-freshwater diatoms, particularly the saltmarsh species *N. peregrina* and *Cosmioneis pusilla* (W. Smith)

D.G. Mann & A.J. Stickle (Zong, 1997) dominate, and therefore support deposition in a Group 0 environment. The midpoint between Group 1 membership at +2.95m OD ($\hat{p}$ of Group 1 = 0.83) and Group 0 membership at +3.01m OD ($\hat{p}$ of Group 1 = 0.38) is +2.98m OD. This elevation marks the transition between reedswamp and saltmarsh environments according to the contemporary NW European geochemical dataset, and can be assigned a RWL of MHWST–20cm ± 20cm (Shennan, 1982).

FIGURE 6 HERE

Peat accumulation between +3.59 and +3.63m OD (800 ± 40 ^{14}C yr BP) marks a brief return of semi-terrestrial conditions (Figures 6 and 7). Diatoms are absent in much of the mottled clay deposits underlying the peat unit. However, in these mottled clay deposits, δ^{13}C values fall from –24.6‰ to –27.8‰, and C/N values rise from 5.9 to 11.5 between +3.26 and +3.56m OD, indicating a progressive increase in organic carbon from vascular vegetation in the sediments leading up to peat deposition. δ^{13}C, C/N and TOC values of up to –28.9‰, 12.2 and 7.7% are recorded in the peat deposits. δ^{13}C values rise to –24.1‰ and C/N and TOC values fall to 9.1 and 0.3% respectively, indicating an increase in tidal-derived POC in the overlying clay and silt with fine sand deposits. Logistic regression analysis predicts continued Group 0 membership, although $\hat{p}$ values of 0.49 between +3.59 and +3.61m OD suggest uncertainty in group allocation due to the elevated values of C/N, TOC and the low values of δ^{13}C. Continued inter-tidal deposition is supported by the microfossil data. Immediately prior to peat deposition at +3.46m OD, high frequencies of the marine-brackish epipelon *N. peregrina* and the marine-brackish aerophilous *Diploneis interrupta* (Kützing) Cleve are present (Figure 7), species common to low saltmarshes (e.g. Zong & Horton, 1998). The almost complete absence of marine plankton and tychoplankton species, however, may suggest deposition higher in the inter-tidal zone. In the assemblages at +3.58m OD and in the peat unit at +3.60 m OD, an increase in brackish-freshwater aerophilous (e.g. *C. pusilla* and *Pinnularia viridis* (Nitzsch) Ehrenberg) and in the freshwater *Pinnularia rupestris* Hantzsch suggest high saltmarsh conditions. The existence of saltmarshes is supported by the high frequency of *Plantago maritima* type and increasing Chenopodiaceae (Figure 6). A transition to lower saltmarsh conditions at +3.62m OD is suggested by high frequencies of marine-brackish aerophilous (e.g. *Nitzschia vitrea* G. Norman) and marine-brackish epipelons (e.g. *N. peregrina*). The pollen assemblages also indicate saltmarsh conditions between +3.60m OD and in the overlying dark grey clay at +3.64m OD, with high frequencies of Poaceae, *Plantago maritima* type and Chenopodiaceae. The change in lithology from clay to interlaminated sandy silt and silty clay at +3.68m OD, and the prominence of marine tychoplanktons, together with the presence of marine-brackish epipsammons (e.g. *Planothidium delicatulum* (Kützing) Round & Bukhtiyarova) indicates the replacement of low saltmarshes by tidal flats. The presence of the freshwater epipelon *P. rupestris* may signify some freshwater input, although this species is equally likely to be allochthonous.

FIGURE 7 HERE

Ince Marshes core Ince 2

The organic clay unit between –1.08 and –1.15m OD (6,410 ± 50 ^{14}C yr BP) marks a brief period of semi-terrestrial conditions at Ince Marshes (Figure 8 and 9). The absence of a chronostratigraphical sequence prevents verification beyond relative dating (via comparison of local and regional arboreal pollen) and so this radiocarbon date must be treated with appropriate caution. Diatom preservation is poor in the silt unit beneath the organic clay deposit (Figure 8). Nevertheless, the change in lithology from sandy silt (–2.21 to –1.53m OD), to silt with organic fragments (–1.15 to –1.53m OD) and ultimately to organic clay, corresponds with a fall in δ^{13}C from –24.9‰ to –27.3‰, a rise in C/N from 9.3 to 14.1, and a rise in TOC from 0.19% to 12.9%, suggesting a progressive removal of tidal-derived POC in the underlying silt unit and the dominance of organic carbon derived from vascular vegetation and freshwater plankton in the organic peat unit. Logistic regression analysis indicates continued Group 0 membership in the sandy silt and silt units and inter-tidal deposition is supported by the microfossil data, with marine diatoms, particularly *P. sulcata and D. surirella*, dominating assemblages between –2.22 and –1.60 m OD. Logistic regression suggests almost continued Group 0 membership in the organic clay deposit. Some uncertainty of a single sample origin is suggested at –1.09m OD, where the probability of Group 1 membership is very marginal ($\hat{p}$ = 0.58). Indeed, *N. peregrina* dominance, and the presence of Chenopodiaceae and Poaceae in the organic clay unit (Figure 9), indicate continued saltmarsh deposition. Given this uncertainty, a RWL cannot be verified. A change to higher δ^{13}C (up to –23.9‰) and lower C/N and TOC values (reaching 9.9 and 0.29%) in the overlying silt and clay unit (–1.00 to –0.42m OD) demonstrate an increase in tidal-derived

POC. Logistic regression analysis predicts Group 0 membership and this is again supported by the diatom data, which suggest that saltmarsh conditions are replaced by lower inter-tidal / sub-tidal channel conditions as indicated by high frequencies of marine planktons (*P. sulcata*, *Podosira stelligera* (J.W. Bailey) A. Mann, *T. eccentrica*) and marine tychoplanktons (*C. belgica*, *D. surirella*, *Rhaphoneis amphiceros* (Ehrenberg) Ehrenberg).

FIGURE 8 HERE

FIGURE 9 HERE

4. Discussion

4.1. NW European C_3 coastal wetland sediment $\delta^{13}C$, C/N and TOC dataset

PAM analysis distinguishes two major geochemical ($\delta^{13}C_{adjusted}$, C/N, TOC) groups in the NW European dataset: tidal flat / saltmarsh (Group 0) and reedswamp / fen carr (Group 1). By comparison, in the English $\delta^{13}C$, C/N and TOC dataset of Khan et al. (2015b), four statistically distinct zones were recognized using analysis of variance: fen carr, reedswamp, mid / high saltmarsh and tidal flat / low saltmarsh. As in the NW European dataset, application of PAM cluster analysis identifies an optimal group of two in the English dataset (not shown here); clustering values into four groups resulted in a lower overall silhouette width in both the English and in the NW European datasets. This difference in statistical tolerance when calculating group identity using PAM cluster analysis results in fewer groups, but with greater group value ranges. Furthermore, the binary division of samples in both the English and in the NW European datasets suggests that there is no significant change in the variability of $\delta^{13}C$, C/N and TOC between these two spatial scales.

$\delta^{13}C$ values are more variable in Group 0 (sediment $\delta^{13}C_{adjusted}$ standard deviation = 1.36) than in Group 1 (sediment $\delta^{13}C_{adjusted}$ standard deviation = 0.79), based on samples classified with silhouette widths >0.25. This reflects the receipt by tidal flat and saltmarsh sediments of allochthonous tidal-derived POC, which can be highly variable (unadjusted values c. –30‰ to –18‰: Lamb et al., 2006), in addition to autochthonous organic carbon from vascular vegetation. The range in $\delta^{13}C_{POC}$ values arise because of the difference in $\delta^{13}C$ of the inorganic carbon sources (HCO_3^- and dissolved CO_2) utilized by freshwater and marine autotrophs, with dissolved $\delta^{13}C_{CO_2}$ values typically several per mil lower than $\delta^{13}C_{HCO_3^-}$ (Keeley and Sandquist, 1992). Because the ratio of CO_2 to HCO_3^- is a function of ambient pH, marine plankton typically have higher $\delta^{13}C$ values, as HCO_3^- is predominantly utilized as the inorganic carbon source. In addition, phytoplankton $\delta^{13}C$ may also vary between species (Wong and Sackett, 1978) and as a result of temperature and the availability and partial pressure of CO_2 (Fontugne and Duplessy, 1981; Bentaleb et al., 1996). Coastal marshes proximal (distal) to a freshwater source, or situated in estuaries with a large (small) riverine input, will receive POC with lower (higher) $\delta^{13}C$ values (Lamb et al., 2006). In the dataset, sites from the Tay Estuary both proximal and distal to a freshwater source, as well as sites in estuaries of varying river input are represented. This is important because the relative influence of marine and riverine sources will be dynamic over Holocene timescales. Reedswamp and fen carr environments (Group 1) receive organic carbon principally from autochthonous vascular vegetation, and thus variability in surface sediment $\delta^{13}C$ is more conservative. The lower $\delta^{13}C_{adjusted}$ medoid value of Group 0 (–24.4‰) therefore reflects the greater overall proportional input of tidal-derived POC in tidal flat and saltmarsh sediments compared with reedswamp and fen carr sediments ($\delta^{13}C_{adjusted}$ medoid value of Group 1 = –27.5‰).

The C/N and TOC medoid values of Group 0 (10.8 and 4.8% respectively) are lower than Group 1 medoid values (15.8 and 40.7% respectively), and these values in both groups are similarly variable (Group 0 standard deviations: C/N = 2.24, TOC = 3.37; Group 1 standard deviations: C/N = 2.81, TOC = 7.84), based on samples classified with silhouette widths >0.25. The lower overall C/N values in Group 0 reflect the receipt by tidal flat and saltmarsh sediments of tidal-derived POC because phytoplankton typically have C/N values of <10 (Tyson, 1995). This reflects the high protein content of phytoplankton (up to 34%), which is relatively rich in nitrogen (15% to 19% on average: Bordovskiy, 1965). The reedswamp and fen carr sediments in the dataset are consistently >12 (Figure 2), reflecting the importance of inputs of carbon-rich vascular vegetation (Prahl et al., 1980). Organogenic reedswamp / fen carr sediments represented by Group 1 and minerogenic tidal flat / saltmarsh sediments represented by Group 0 are clearly distinguished by TOC. In European saltmarshes, closed vegetation cover occurs relatively high in the inter-tidal zone, usually well above mean high water of neap tides (MHWN) (Beefink, 1977). The detritus of much of the organic matter produced in high inter-tidal and supra-tidal zone environments is allowed to accumulate *in situ* (Bouchard et al., 1998; Bouchard and Lefeuvre, 2000) resulting in organic-rich sediments. This is due to the relatively small consumption by herbivores (Teal, 1962), indirect or limited direct tidal influence, and the presence of anaerobic conditions under an elevated water table which allow the accumulation of refractory organic matter, which may lead to peat accumulation (Valiela, 1995). The variability within the groups is largely confined to end-members with shorter silhouette widths (e.g. Group 0 samples from some higher high saltmarsh areas exposed to infrequent tidal inundation, and thus accumulating proportionally more autochthonous organic carbon).

Of the three variables, C/N values overlap the most between the two groups. This is largely due to changes in the relative concentrations of carbon and nitrogen in decaying plant litter (see Section 4.2), which can result in C/N ratios of bulk surface organic sediments being lower than the C/N ratios of *in situ* source vegetation (e.g. Wilson et al., 2005b). In contrast, C/N ratios of particulate organic matter (POM) tends to increase as degradation proceeds (Cifuentes, 1991; Middelburg and Nieuwenhuize, 1998). Therefore, degradation of organic matter leads to some convergence, and thus overlap, of C/N ratios. Nevertheless, because freshwater POM is indistinguishable from C_3 vascular vegetation based on $\delta^{13}C$ alone, the measurement of C/N is necessary to distinguish between these two sources in estuarine saltmarsh sediments (e.g. Thornton and McManus, 1994).

4.2. Inferring depositional environments using the NW European $\delta^{13}C$, C/N and TOC dataset

Using a contemporary dataset approach assumes that the $\delta^{13}C$, C/N and TOC values of the modern and the deposited (core) geochemical groups are comparable and that post-depositional decomposition has an insignificant effect on bulk organic sediment geochemical values. Post depositional changes in bulk organic sediment $\delta^{13}C$ and C/N is a potential limitation in the use of absolute geochemical values to infer distinct coastal depositional environments. Hemi-cellulose, cellulose and lignin together account for up to 90% of plant material. Cellulose and hemi-cellulose are enriched in ^{13}C by 1‰ and 2‰ relative to the whole plant (Benner et al., 1987), whilst lignin, found only in vascular plants, is depleted in ^{13}C by between 2‰ and 6‰ relative to the whole plant and between 4‰ and 7‰ relative to cellulose (Benner et al., 1987). Lignin extracted from saltmarsh vegetation in the Mersey Estuary was depleted in ^{13}C by up to 3.9‰ relative to the whole plant (Wilson et al., 2005b). Changes in the relative abundance of these plant compounds during decomposition of organic-rich high inter-tidal and supra-tidal sediments will therefore lead to post-depositional shifts in bulk organic $\delta^{13}C$ values. Field saltmarsh studies and laboratory incubation experiments demonstrate the preferential decay of hemi-cellulose and cellulose (Maccubbin and Hodson, 1980, Wilson, 1985; Fogel et al., 1989; Melillo et al., 1989; Benner et al., 1991), with lignified macrophyte detritus the most refractory particulate organic component of sediments (Tyson, 1995). The early loss of labile organic matter during decomposition and the selective preservation of ^{13}C-depleted refractory lignin in sediments can result in a decrease in bulk sediment $\delta^{13}C$ by several per mil (DeLaune 1986; Benner et al., 1987; 1991; Fogel et al., 1989; Wilson et al., 2005a). Similarly, in phytoplankton, the preferential degradation of ^{13}C-enriched compounds such as carbohydrates and proteins, and the subsequent increasing concentration of the more refractory ^{12}C-enriched lipid fraction (Deines, 1980) can also result in a decrease in lower inter-tidal bulk organic sediment $\delta^{13}C$ (Wilson et al., 2005a).

Marked changes in C/N typically occur during the early stages of decomposition (Valiela et al., 1985). Organic matter in estuarine sub-tidal and lower inter-tidal sediments (tidal flats and European lower saltmarshes) is mostly derived from riverine and marine suspended POM (Lamb et al., 2006). Much of the terrigenous component of riverine POM may have already been extensively degraded on land or further upstream and should be relatively resistant to further degradation (Hedges and Keil, 1995). Phytoplankton undergoes considerable degradation in the water column, with C/N ratios of POM tending to increase as degradation proceeds as a result of the breakdown of nitrogen-rich compounds of plankton (Lamb et al., 2006). In vegetated inter-tidal and supra-tidal areas, the relative concentrations of carbon and nitrogen in decaying plant litter alters during three phases of decomposition (Valiela et al., 1985), although not all of these phases may be seen in practice (e.g. Haynes,1986). Initial leaching of soluble compounds can lead to a loss of mass in vascular plant detritus within days, which can result in an increase in C/N as nitrogen is lost more rapidly than carbon (e.g. Rice and Tenore, 1981; White and Howes, 1994; Benner et al., 1991). A fall in C/N may follow during microbial degradation of organic matter (principally by bacteria (Benner et al., 1984)), due to fixation of external nitrogen sources (Glenn, 1976; Rice, 1982; Benner et al., 1991) alongside continued carbon loss through respiration, leaching, or particulate transport. This phase can last up to a year (Valiela et al., 1985). In the final phase, the rates of decomposition slow as only relatively refractory material, such as lignin, remains (Melillo et al. 1989; White and Howes, 1994). Although degradation can lead to marked differences in bulk surface sediment C/N values compared to that of the principal organic source material (i.e. overlying vascular vegetation (Wang et al., 2003; Wilson et al., 2005b) or phytoplankton (Cifuentes, 1991; Middelburg and Nieuwenhuize, 1998), C/N values tend to stabilise in the refractory phase, as carbon and nitrogen is lost at approximately the same rate (Melillo et al. 1989; White and Howes, 1994). This results in relatively unchanged bulk sediment C/N ratios in recent coastal wetland sediment deposits (Wang et al 2003; Arzayus and Canuel, 2004), although conservative shifts in C/N (<3) over millennial timescales may result from further decomposition of organic matter and the concentration of carbon-rich refractory organic compounds (Wilson et al., 2005a).

Post-depositional changes in bulk organic sediment properties does not affect the integrity of using bulk organic $\delta^{13}C$ or C/N qualitatively to detect the onset or removal of marine conditions across lithostratigraphic contacts (Wilson et al., 2005a). This is because within-core trends in $\delta^{13}C$ and C/N, rather than absolute values, are the focus. The ability to identify precise coastal depositional environments in sedimentary records based on absolute values of $\delta^{13}C$ and C/N may be compromised by the post-depositional alteration of bulk organic $\delta^{13}C$ in particular. However, the difference between Group 0 and Group 1 medoid $\delta^{13}C$ and C/N values of 2.9‰ and 5.3 respectively is greater than observed average post-depositional changes in bulk organic $\delta^{13}C$ and C/N in Mersey Estuary deposits (Wilson et al., 2005a). Furthermore, with the inclusion of the additional parameters of C/N and TOC, the application of absolute $\delta^{13}C$, C/N and TOC values to distinguish between tidal flat / saltmarsh and reedswamp / fen carr deposits in Holocene sediments is possible, despite the influence of decomposition on bulk organic sediments. Indeed, any uncertainty in the group assignment of Holocene deposits, which may arise as a result of post depositional alteration in $\delta^{13}C$, for example, will be reflected in a lower predicted probability of group membership.

Group membership of Mersey Estuary Holocene sediment samples, based on combined $\delta^{13}C$, C/N and TOC values, were predicted with high probability in the majority of samples analysed. The veracity of prediction is confirmed by the correspondence between predicted group membership and independent microfossil evidence. The few instances of predicted group membership with low probability are mainly associated with two brief episodes of semi-terrestrial deposition (the organic clay unit between –1.08 and –1.15m OD in core I-2 ($\hat{p}$ of Group 1 = 0.58 at –1.09m OD) and the peat unit between +3.59 and +3.63m OD in core I-4 ($\hat{p}$ of Group 1 = 0.49 at +3.61 and +3.59m OD)). The microfossil assemblages in both deposits suggests continued deposition high in the inter-tidal zone. In the examples from core I-2, uncertainty in group allocation is mainly caused by an isolated peak in TOC. Similarly, in the example from core I-4, very low $\delta^{13}C$ values mainly account for the uncertainty in group allocation. This illustrates the sensitivity of the logistic regression model to changes in individual co-variate values, but also the robustness of the model in assigning group membership with high probability only when all of the co-variates are in agreement.

4.3. Application of the NW European dataset in RSL studies from C_3 vegetated estuaries

Group 0–1 mid-point $\delta^{13}C_{adjusted}$, C/N and TOC values of –26.0‰, 13.3 and 22.8%, respectively, generally separate spatially adjacent mid / high saltmarsh and reedswamp samples in the contemporary NW European dataset (Figure 2). $\delta^{13}C$ measurements have been corrected for the ^{13}C Suess effect as a first step to allow comparison of contemporary and pre-industrial $\delta^{13}C$ values, thus permitting the use of contemporary $\delta^{13}C$ values as analogues for Holocene deposits. By comparison, Khan et al., (2015b) calculated $\delta^{13}C$, C/N and TOC threshold values of –27‰, 14 and 18% respectively to distinguish between mid / high saltmarsh and reedswamp environments in the English database, and applied these threshold values to assign RWLs at lithostratigraphic overlaps in Thames Estuary Holocene deposits. Their use of $\delta^{13}C$ values uncorrected for the ^{13}C Suess effect mostly accounts for the observed difference in the $\delta^{13}C$ threshold value between mid / high saltmarsh and reedswamp environments (an uncorrected threshold value of approximately –27.5‰ was found to separate these environments in the contemporary NW European geochemical dataset). Saltmarsh and reedswamps are part of the natural coastal vegetation zonation of temperate NW Europe, with each zone typically containing common characteristic taxa (Beeftink, 1977). As such, the saltmarsh and reedswamp transition will often form part of a conformable lithostratigraphy in temperate NW European coastal wetland deposits. RWLs at saltmarsh and reedswamp transitions are established for temperate macro-tidal systems

(Shennan, 1982). Nevertheless, local conditions can influence the relationship between tidal parameters and vegetation succession, particularly in estuaries with varying river input. Additionally, the indicative range at lithostratigraphic overlaps will vary with tidal range. Therefore, the contemporary association between tidal regime and the elevation of the saltmarsh–reedswamp transition should be verified at each study site wherever possible.

In the study presented here, the identification of saltmarsh and reedswamp transitions and associated RWLs have been identified objectively in sediment sequences using binary logistic regression. Crucially, transitions between depositional group membership in sediment sequences should be accompanied by a demonstrable progressive increase or removal of marine conditions; this can be qualitatively inferred by trends in $\delta^{13}C$, C/N and TOC. This demonstrates the transition between spatially adjacent environments (and the absence of erosive contacts) in core samples, thereby narrowing the altitudinal envelope of the indicative meaning of the sample and allowing a more confident distinction of RWLs. Where present, Group 0–Group 1 transitions are only apparent at lithostratigraphic overlaps in the Mersey Estuary deposits. This suggests that targeted geochemical measurements of sediments across transgressive and regressive overlaps will offer a more efficient (less labour intensive) method of identifying RWLs compared with microfossil analysis. The logistic regression model is equally useful in highlighting instances of uncertainty in the depositional group membership allocation of samples. For example, when $\hat{p}$ values are equivocal in assigning group membership, this should deter further analysis (e.g. radiocarbon dating) of facies changes as potential SLIs.

The division of contemporary C_3 coastal wetland sediments into two distinctive geochemical groups by PAM analysis, as identified in the NW European $\delta^{13}C$, C/N and TOC dataset, is also seen elsewhere. PAM analysis of contemporary bulk organic sediment $\delta^{13}C$ and C/N values of coastal C_3 wetlands fringing the White Sea (Russia) also identified two geochemical groups: clastic dominated tidal flat and saltmarsh environments below mean higher high water (MHHW) and organic rich *Phragmites* wetland and Taiga forest environments above MHHW (Kemp et al., 2017). The vertical range of the two geochemical groups recognised in the NW European and White Sea datasets are broad (sub-tidal to inter-tidal and inter-tidal to supra-tidal, respectively). As demonstrated in this study, this appears to necessarily restrict to group transitions (and thus lithostratigraphic overlaps) the application of $\delta^{13}C$, C/N and TOC to infer RWLs. The use of additional geochemical parameters (e.g. $\delta^{15}N$) in PAM analysis may be necessary to identify multiple geochemical groups in C_3 vegetated estuaries (e.g. Goslin et al., 2015).

The method introduced here to identify RWLs in the sediment deposits of C_3 vegetated coastal wetlands in temperate NW Europe is robust because (i) the difference in medoid $\delta^{13}C$ and C/N values between contemporary depositional groups is greater than the typical post-depositional shift in bulk $\delta^{13}C$ and C/N resulting from the selective degradation of organic compounds; (ii) coastal depositional environments are identified in sediment records based on a probabilistic measure of correspondence with the contemporary geochemical dataset, thus uncertainty introduced as a result of an unusual combination of values will yield a lower probability of group allocation; (iii) agreement between all co-variates is required to achieve a high probability of group membership. Therefore, without a corresponding change in C/N and TOC, any shift in $\delta^{13}C$ due to selective organic matter degradation, for example, should not lead to a change in group allocation of core samples - a fall in the probability of group allocation is more likely. In addition, the qualitative use of $\delta^{13}C$, C/N and TOC can demonstrate the progressive arrival or removal of marine conditions, therefore confirming the integrity of lithostratigraphic overlaps and preventing their redundancy in the event of poor microfossil preservation. Using the geochemical method detailed here, RWLs have been successfully identified in the deposits of the Mersey Estuary (Section 3.2). The variability in Mersey Estuary core values of $\delta^{13}C$ (μ = –26.6‰, σ = 1.5), C/N (μ = 13.5, σ = 4.9) and TOC (μ = 10.4, σ = 17.5), which is typical of the variability encountered in Holocene sediment sequences from temperate C_3 coastal wetlands (e.g. Lamb et al., 2007; Goslin et al., 2015; Khan et al., 2015b), is sufficiently represented in the NW European geochemical dataset. This method, which will be particularly valuable for studies in which the collection of local contemporary geochemical datasets is restricted or prohibitive, should therefore be applicable to Holocene sediment sequences from C_3-vegetated coastal wetlands throughout temperate NW Europe.

5. Conclusions

Statistical analysis of a compiled geochemical (bulk organic sediment $\delta^{13}C$, C/N and TOC) dataset, drawn from published studies of contemporary C_3-vegetated NW European coastal wetlands and corrected for the ^{13}C Suess effect, distinguish two major geochemical groups: tidal flat / saltmarsh (Group 0) and reedswamp / fen carr environments (Group 1). The transition between saltmarsh and reedswamp environments (Group 0–1 transition) can be related to a reference water level and so its distinction in the sediment record allows the altitude of past tidal levels to be inferred. The application of the NW European $\delta^{13}C$, C/N and TOC dataset in relative sea-level reconstruction studies is exemplified using the Holocene sediment deposits of the Mersey Estuary, UK. Group membership of sediment deposits was predicted using binary logistic regression, which models the correspondence between sediment core $\delta^{13}C$, C/N and TOC values and the contemporary NW European training set.

Group membership was predicted with high probability in the various depositional contexts studied and the accuracy of group prediction is verified by microfossil evidence. Group 0–1 transitions coincide with changes in litho- and bio-stratigraphy, and the presence of transitions between saltmarsh and reedswamp environments is demonstrated by systematic changes in $\delta^{13}C$, CN and TOC reflecting the progressive arrival or removal of marine conditions. The variability in core $\delta^{13}C$, C/N and TOC values of the Mersey Estuary is typical of the variability encountered in Holocene sediment sequences from temperate C_3 coastal wetlands and is sufficiently represented in the NW European geochemical dataset. The geochemical-based relative sea-level reconstruction method introduced here should therefore be applicable to Holocene sediment sequences from C_3 coastal wetlands throughout temperate NW Europe.

Acknowledgements

Nicole Khan, Angela Lamb, Kieran Craven, Jérôme Goslin, Antony Long and Steve Thornton kindly provided their datasets for use in this work. The British Geological Survey granted access to the Mersey Estuary cores and isotope analysis was carried out by Carol Arrowsmith, Hilary Sloane and Joanne Green at the UK NERC Isotope Geosciences Laboratory, Nottingham (NIGFSC grant (no. IP/708/0901). Nicole Khan and two other anonymous reviewers are thanked for providing thoughtful and constructive reviews which have improved the manuscript.

References

Abril G., Nogueira M., Etcheber H., Cabecadas G., Lemaire E. and Brogueira M.J. (2002) Behaviour of organic carbon in nine contrasting European estuaries. *Estuar. Coast Shelf S.* **54**, 241-262.

Al-Jabbari M.H., McManus J. and Al-Ansari N.A. (1980) Sediment and solute discharge into the Tay Estuary from the River Sytem. *P. Roy. Soc. Edinb. B* **78**, 15-32.

Allen J.R.L. (2003) An eclectic morphostratigraphic model for the sedimentary response to Holocene sea-level rise in northwest Europe. *Sediment. Geol.* **161**, 31-54.

Andrews J.B. (2008) Use of carbon isotope and C/N geochemistry in reconstructing vegetation communities: a mid- to late- Holocene palaeoenvironmental investigation from Romney Marsh, Kent, UK. Masters thesis, Durham Univ., UK.

Arzayus K.M. and Canuel E.A. (2004) Organic matter degradation in sediments of the York River Estuary: effects of biological vs. physical mixing. *Geochim. Cosmochim. Acta* 69, 455-463.

Beeftink W.G. (1977) The coastal salt marshes of western and northern Europe: an ecological and phytosociological approach. In *Ecosystems of the World I: Wet Coastal Ecosystems* (ed. V.J. Chapman). Elsevier, Amsterdam. pp. 109-155.

Benner R., Fogel M.L., Sprague E.K. and Hodson R.E. (1987) Depletion of ^{13}C in lignin and its implications for stable carbon isotope studies. *Nature* **329**, 708-710.

Benner R., Fogel M.L., Sprague E.K. and Hodson R.E. (1984) Relative contributions of bacteria and fungi to rates of degradation of lignocellulosic detritus in salt-marsh sediments. Appl. *Environ. Microb.* **48**, 36-40.

Benner R., Fogel M.L. and Sprague E.K. (1991) Diagenesis of below ground biomass of *Spartina alterniflora* in salt-marsh sediments. *Limnol. Oceanogr.* **36**, 1358-1374.

Bentaleb I., Fontugne M., Descolas-Gros C., Girardin C., Mariotti A., Pierre C., Brunet C. and Poisson A. (1996) Organic carbon isotopic composition of phytoplankton and sea-surface pCO_2 reconstructions in the Southern Indian Ocean during the last 50,000 yr. *Org. Geochem.* **24**, 399-401.

Bernhardt C.E. and Willard D.A. (2015). Pollen and spores of terrestrial plants. In *Handbook of Sea-Level Research* (eds. I. Shennan, A.J. Long and B.P. Horton). Wiley, Sussex. pp. 218-232.

Birks H.J.B. and Birks H.H. (1980) *Quaternary Palaeoecology*. University Park Press, Baltimore.

Bordovskiy O.K. (1965). Accumulation of organic matter in bottom sediments. *Mar. Geol.* **3**, 33-82.

Bouchard V., Creach V., Lefeuvre J.C., Bertru G. and Mariotti A. (1998) Fate of plant detritus in a European salt marsh dominated by *Atriplex portulacoides* (L.) Aellen. *Hydrobiologia* **374**, 75-87.

Bouchard V. and Lefeuvre J.C. (2000) Primary production and macro-detritus dynamics in a European salt marsh: carbon and nitrogen budgets. *Aquat. Bot.* **67**, 23-42.

Bradley S.L., Milne G.A., Shennan I. and Edwards R. (2011) An improved Glacial Isostatic Adjustment model for the British Isles. *J. Quaternary Sci.* **26**, 541-552.

Brain M.J., Long A.J., Woodroffe S.A., Petley D.N., Milledge D.G. and Parnell A.C. (2012) Modelling the effects of sediment compaction on saltmarsh reconstructions of recent sea-level rise. *Earth Planet. Sc. Lett.* **345-348**, 180-193.

Cahill N., Kemp A.C., Horton B.P. and Parnell A.C. (2016) A Bayesian hierarchical model for reconstructing relative sea level: from raw data to rates of change. *Clim. Past* **12**, 525-542.

Chmura G.L., Aharon P., Socki R.A. and Abernethy R. (1987) An inventory of ^{13}C abundances in coastal wetlands of Louisiana, USA: vegetation and sediments. *Oecologia* **74**, 264-271.

Cifuentes L.A. (1991) Spatial and temporal variations in terrestrially-derived organic-matter from sediments of the Delaware estuary. *Estuaries* **14**, 414-429.

Craven K.F., Edwards R.J. and Flood R.P. (2017) Source organic matter analysis of saltmarsh sediments using SIAR and its application in relative sea-level studies in regions of C_4 plant invasion. Boreas

Craven K.F., Edwards R.J., Goodhue R. and Rocha C. (2013) Evaluating the influence of selected acid pre-treatment methods on C/N and $\delta^{13}C$ of temperate inter-tidal sediments for relative sea level reconstruction. *Irish J. Earth Sci.* **31**, 25-42.

Cullen J.T., Rosenthal Y. and Falkowski P.G. (2001) The effect of anthropogenic CO_2 on the carbon isotope composition of marine phytoplankton. *Limnol. Oceanogr.* **46**, 996-998.

Deines P. (1980) The isotopic composition of reduced organic carbon. In *Handbook of Environmental Isotope Geochemistry. The Terrestrial Environment, Vol. 1. A.* (eds. P. Fritz and J.C. Fontes). Elsevier, Amsterdam. pp. 329-406.

DeLaune R.D. (1986) The use of $\delta^{13}C$ signature of C3 and C4 plants in determining past depositional environments in rapidly accreting marshes of the Mississippi River deltaic plain, Louisiana, U.S.A. *Chem. Geol*. **59**, 315-320.

Edwards R.J. (2013) Sedimentary Indicators of Relative Sea-Level Changes - Low Energy. In *The Encyclopedia of Quaternary Science (2nd Edition) vol.* 4 (ed. S.A. Elias). Elsevier, Netherlands. pp. 396-408.

Edwards R.J. and Horton B.P. (2000) Reconstructing relative sea-level change using UK salt-marsh foraminifera. *Mar. Geol.* **169**, 41-56.

Eide M., Olsen A., Ninnemann U.S. and Eldevik T. (2017) A global estimate of the full oceanic ^{13}C Suess effect since the preindustrial. *Global Biogeochem Cy*. **31**, 492-514.

Engelhart S.E., Horton B.P., Vane C.H., Nelson A.R., Witter R.C., Brody S.R. and Hawkes A.D. (2013) Modern foraminifera, δ^{13}C, and bulk geochemistry of central Oregon tidal marshes and their application in paleoseismology. *Palaeogeogr. Palaeocl.* **377**, 13-27.

Fairbanks R.G. (1989) A 17,000-year glacio-eustatic sea level record: Influence of glacial melting rates on the Younger Dryas event and deep-ocean circulation. *Nature* **342**, 637-642.

Firth D. (1993) Bias reduction of maximum likelihood estimates. *Biometrika* 80, 27–38.

Fogel M.L., Sprague K.E., Gize A.P. and Frey R.W. (1989) Diagenesis of organic matter in Georgia salt marshes. *Estuar. Coast Shelf S.* **28**, 211-230.

Fontugne M.R. and Duplessy J.C. (1981) Organic-carbon isotopic fractionation by marine plankton in the temperature-range -1 to 31 ^{o}C. *Oceanol. Acta* **4**, 85-90.

Francey R.J., Allison C.E., Etheridge D.M., Trudinger C.M., Enting I.G., Leuenberger M., Langenfelds R.L., Michel E. and Steele L.P. (1999) A 1000-year high precision record of delta δ^{13}C in atmospheric CO_2. *Tellus B* **51**, 170-193.

Gehrels W.R. (2002) Intertidal foraminifera as palaeoenvironmental indicators. In *Quaternary Environmental Micropaleontology* (ed. S.K. Haseltt). Arnold, London. pp. 91-114.

Gehrels W.R., Roe H.M. and Charman D.J. (2001) Foraminifera, testate amoebae and diatoms as sea-level indicators in UK saltmarshes: a quantitative multiproxy approach. *J. Quaternary Sci.* **16**, 201-220.

Glenn A.R. (1976) Production of extracellular protein by bacteria. *Annu. Rev. Microbiol.* **30**, 41-62.

Goslin J., Lanoe B.V.V., Spada G., Bradley S., Tarasov L., Neill S. and Suanez S. (2015) A new Holocene relative sea-level curve for western Brittany (France): Insights on isostatic dynamics along the Atlantic coasts of north-western Europe. *Quaternary Sci. Rev.* **129**, 341-365.

Hedges J.I. and Keil R.H. (1995) Sedimentary organic matter preservation: an assessment and speculative synthesis. *Mar. Chem.* **49**, 81-115.

Heinz G. and Ploner M. (2016) *logistf: Firth's bias-reduced logistic regression*. R package version 1.22, URL https://rdrr.io/cran/logistf/

Kato M., Tanimura Y., Matsuoka K. and Fukusawa H. (2003) Plankton diatoms from sediment traps in Omura Bay, western Japan with implications for ecological and taphonomic studies of coastal marine environments. *Quatern. Int.* **105**, 25-31.

Kaufman L., Rousseeuw P.J. (1990) *Finding Groups in Data: An Introduction to Cluster Analysis*. Wiley-Interscience, New Jersey.

Keeley J.E. and Sandquist D.R. (1992) Carbon: freshwater plants. *Plant Cell Environ.* **15**, 1021-1035.

Keeling C.D., Mook W.G. and Tans P.P. (1979). Recent trends in the $^{13}C/^{12}C$ ratio of atmospheric carbon dioxide. *Nature* **277**, 121-123.

Kemp A.C., Vane C.H., Horton B.P. and Culver S.J. (2010) Stable carbon isotopes as potential sea-level indicators in salt marshes, North Carolina, USA. *Holocene* **20**, 623-636.

Kemp A.C., Vane C.H., Horton B.P., Engelhart S.E. and Nikitina D. (2012) Application of stable carbon isotopes for reconstructing salt-marsh floral zones and relative sea level, New Jersey, USA. *J. Quaternary Sci.* **27**, 404-414.

Kemp A.C., Horton B.P., Vane C.H., Bernhardt C.E., Reide Corbett D., Engelhart S.E., Ainsfield S.C., Parnell A.C. and Cahill N. (2013) Sea-level change during the last 2500 years in New Jersey, USA. *Quaternary Sci. Rev.* **81**, 90-104.

Kemp A.C., Horton B.P., Nikitina D., Vance C.H., Potapova M., Weber-Bruya, E., Culver S.J., Repkina T. and Hill D.F. (2017) Th distribution and utility of sea-level indicators in Eurasian sub-Arctic salt marshes (White Sea, Russia). Boreas

Khan N.S., Vane C.H. and Horton, B.P. (2015a) Stable carbon isotope and C/N geochemistry of coastal wetland sediments as a sea-level indicator. In *Handbook of Sea-Level Research* (eds. I. Shennan, A.J. Long and B.P. Horton). Wiley, Sussex. pp. 295-311.

Khan N.S., Vane C.H., Horton B.P., Hillier C., Riding J.B. and Kendrick C.P. (2015b) The application of $\delta^{13}C$, TOC and C/N geochemistry to reconstruct Holocene relative sea levels and paleoenvironments in the Thames Estuary, UK. *J. Quaternary Sci.* **30**, 417-433.

Kirwan M.L. and Murray A.B. (2007) A coupled geomorphic and ecological model of tidal marsh evolution. *P. Natl. Acad. Sci. USA* **104**, 6118-6122.

Kortzinger A., Quay P.D. and Sonnerup R.E. (2003) Relationship between anthropogenic CO_2 and the C-13 suess effect in the North Atlantic Ocean. *Global Biogeochem. Cy.* **17**.

Lamb A.L., Wilson G.P. and Leng M.J. (2006) A review of coastal palaeoclimate and relative sea-level reconstructions using delta $\delta^{13}C$ and C/N ratios in organic material. *Earth-Sci. Rev.* **75**, 29-57.

Lamb A.L., Vane C.H., Wilson G.P., Rees J.G. and Moss-Hayes V.L. (2007) Assessing $\delta^{13}C$ and C/N ratios from organic material in archived cores as Holocene sea level and palaeoenvironmental indicators in the Humber Estuary, UK. *Mar. Geol.* **244**, 109-128.

Laws E.A., Popp B.N., Bidigare R.R., Kennicutt M.C. and Macko S.A. (1995) Dependence of phytoplankton carbon isotopic composition on growth-rate and CO_2 (aq) - theoretical considerations and experimental results. *Geochim. Cosmochim. Acta* **59**, 1131-1138.

Maccubbin A.E. and Hodson R.E. (1980) Mineralization of detrital lignocelluloses by salt marsh sediment microflora. *Appl. Environ. Microb.* **40**, 735-740.

Maechler M., Rousseeuw P., Struyf A. and Hubert M. (2005) *Cluster Analysis Basics and Extensions*.

McCarroll D. and Loader N.J. (2004) Stable isotopes in tree rings. *Quaternary Sci. Rev.* **23**, 771-801.

McCarroll D., Gagen M.H., Loader N.J., Robertson I., Anchukaitis K.J., Los S., Young G.H.F., Jalkanen R., Kirchhefer A. and Waterhouse J.S. (2009) Correction of tree ring stable carbon isotope chronologies for changes in the carbon dioxide content of the atmosphere. *Geochim. Cosmochim. Acta* **73**, 1539-1547.

McMahon K.W., McCarthy M.D., Sherwood O.A., Larsen T. and Guilderson T.P. (2015) Millennial-scale plankton regime shifts in the subtropical North Pacific Ocean. *Science* **350**, 1530-1533.

Melillo J.M., Aber J.D., Linkins A.E., Ricca A., Fry B. and Nadelhoffer K.J. (1989) Carbon and nitrogen dynamics along the decay continuum: plant litter to soil organic matter. *Plant Soil* **115**, 189-198.

Middelburg J.J. and Nieuwenhuize J. (1998) Carbon and nitrogen stable isotopes in suspended matter and sediments from the Schelde Estuary. *Mar. Chem* **60**, 217-225.

Middelburg J.J., Nieuwenhuize J., Lubberts R.K. and van de Plassche O. (1997) Organic carbon isotope systematics of coastal marshes. *Estuar. Coast Shelf S.* **45**, 681-687.

Milker Y., Horton B.P., Vane C.H., Engelhart S.E., Nelson A.R., Witter R.C., Khan N.S. and Bridgeland W.T. (2015) Annual and seasonal distribution of intertidal foraminifera and stable carbon isotope geochemistry, Bandon marsh, Oregon, USA. *J. Foramin. Res.* **45**, 146-166.

O'Leary M.H., Madhavan S. and Paneth P. (1992) Physical and chemical basis of carbon isotope fractionation in plants. *Plant Cell Environ.* **15**, 1099-1104.

Plater A.J., Kirby J.R., Boyle J.F., Shaw T. and Mills H. (2015) Loss on ignition and organic content. In *Handbook of Sea-Level Research* (eds. I. Shennan, A.J. Long and B.P. Horton). Wiley, Sussex. pp. 312-330.

Pohar M., Blas M. and Turk S. (2004) Comparison of Logistic Regression and Linear Discriminant Analysis: A Simulation Study. *Metodološki zvezki* **1**, 143-161.

Prahl F.G., Bennett J.T. and Carpenter R. (1980) The early diagenesis of aliphatic hydrocarbons and organic matter in sedimentary particulates from Dabob Bay, Washington. *Geochim. Cosmochim. Acta* **44**, 1967-1976.

Preston C.D., Pearman D.A. and Dines T.D. (2002) *New Atlas of the British and Irish Flora*. Oxford University Press, Oxford.

Quay P.D., Tilbrook, B. and Wong, C.S. (1992) Oceanic uptake of fossil-fuel CO_2: Carbon-13 evidence. *Science* **256**, 74-79.

Quay P., Sonnerup R., Westby T., Stutsman J. and McNichol A. (2003) Changes in the C-13/C-12 of dissolved inorganic carbon in the ocean as a tracer of anthropogenic CO_2 uptake. *Global Biogeochem. Cy.* **17**.

Rice D.L. (1982) The detritus nitrogen problem. New observations and perspectives from organic geochemistry. *Mar. Ecol.-Prog. Ser.* **9**, 153-162.

Rice D.L. and Tenore K.R. (1981) Dynamics of carbon and nitrogen during the decomposition of detritus derived from estuarine macrophytes. *Estuar. Coast Shelf S.* **13**, 681-690.

Rousseeuw P. (1987) Silhouettes: a graphical aid to the interpretation and validation of cluster techniques. *J. Comput. App. Math.* **20**, 53-65.

Schelske C.L. and Hodell D.A. (1995) Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. *Limnol. Oceanogr.* **40**, 918-929.

Schubert B.A. and Jahren A.H. (2012) The effect of atmospheric CO_2 concentration on carbon isotope fractionation in C-3 land plants. *Geochim. Cosmochim. Acta* **96**, 29-43.

Shennan I. (1982) Interpretation of Flandrian sea-level data from the Fenland, England. *P. Geologist. Assoc.* **83**, 53-63.

Shennan I., Milne G. and Bradley S. (2009) Late Holocene relative land- and sea-level changes: Providing information for stakeholders. *GSA Today* **19**, 52-53.

Stout J.D., Rafter T.A. and Troughton J.H. (1975) The possible significance of isotopes ratios in palaeoecology. *B. Roy. S. NZ* **13**, 279-286.

Teal J.M. (1962) Energy flow in the salt marsh ecosystem of Georgia. *Ecology* **43**, 614-624.

Telford R.J. and Birks H.J.B. (2005) The secret assumption of transfer functions: problems with spatial autocorrelation in evaluating model performance. *Quaternary Sci. Rev.* **24**, 2173-2179.

Thornton S.F. and Mcmanus J. (1994) Application of organic-carbon and nitrogen stable-isotope and C/N ratios as source indicators of organic-matter provenance in estuarine systems - evidence from the Tay Estuary, Scotland. *Estuar. Coast Shelf S.* **38**, 219-233.

Tooley M.J. (1982) Sea-level changes in northern England. *P. Geologist. Assoc.* **93**, 43-51.

Tyson R.V. (1995) *Sedimentary Organic Matter: Organic Facies and Palynofacies*. Chapman and Hall, London.

Valiela I. (1995) *Marine Ecological Processes*. Springer-Verlag, New York.

Valiela I., Teal J.M. and Allen S.D. (1985) Decomposition in salt marsh ecosystems: the phases and major factors affecting disappearance of above-ground organic matter. *J. Exp. Mar. Biol. Ecol.* **89**, 29-54.

Van de Plassche O. (1986) *Sea-level Research: A Manual for the Collection and Evaluation of Data*. Geo Books, Norwich.

Verburg P. (2007) The need to correct for the Suess effect in the application of δ13C in sediment of autotrophic Lake Tanganyika, a sa productivity proxy in the Anthropocene. *J Palaeoelimnol.* **37**, 591-602.

Vos, P.C. and De Wolf H. (1993) Diatoms as a tool for reconstructing sedimentary environments in coastal wetlands; methodological aspects. *Hydrobiologia* **269/270**, 285-296.

Waller M.P., Long A.J., Long D. and Innes, J.B. (1999) Patterns and processes in the development of coastal mire vegetation: Multi-site investigations from Walland Marsh, Southeast England. *Quaternary Sci. Rev.* **18**, 1419-1444.

Wang X.-C., Chen R.F. and Berry A. (2003) Sources and preservation of organic matter in Plum Island salt marsh sediments (MA, USA); long-chain *n*-alkanes and stable carbon isotope compositions. *Estuar. Coast Shelf S.* **58**, 917-928.

White D.S. and Howes B.L. (1994) Nitrogen incorporation into decomposing litter of *Spartina alterniflora*. *Limnol. Oceanogr.* **39**, 133-140.

Wilson J.O. (1985) Decomposition of [^{14}C] lignocelluloses of *Spartina alterniflora* and a comparison with field experiments. *Appl. Environ. Microb.* **49**, 478-484.

Wilson G.P. and Lamb A.L. (2012) An assessment of the utility of regional diatom-based tidal-level transfer functions. *J. Quaternary Sci.* **27**, 360-370.

Wilson G.P., Lamb A.L., Leng M.J., Gonzalez S. and Huddart D. (2004) The potential of carbon isotope ratios as indicators of coastal palaeoenvironmental change: preliminary results from the Mersey Estuary, North West England. In *The Quaternary of the Isle of Man and and North West England: Field Guide* (eds. R.C. Chiverrell, A.J. Plater and G.S.P. Thomas). Quaternary Research Association, London. pp. 217-225.

Wilson G.P., Lamb A.L., Leng M.J., Gonzalez S. and Huddart D. (2005a) δ^{13}C and C/N as potential coastal palaeoenvironmental indicators in the Mersey Estuary, UK. *Quaternary Sci. Rev.* **24**, 2015-2029.

Wilson G.P., Lamb A.L., Leng M.J., Gonzalez S. and Huddart D. (2005b) Variability of organic δ^{13}C and C/N in the Mersey Estuary, UK and its implications for sea-level reconstruction studies. *Estuar. Coast Shelf S.* **64**, 685-698.

Wong W.W. and Sackett W.M. (1978) Fractionation of stable carbon isotopes by marine phytoplankton. *Geochim. Cosmochim. Acta* **42**, 1809-1815.

Zimmerman A.R. and Canuel, E.A. (2002) Sediment geochemical records of eutrophication in the mesohaline Chesapeake Bay. *Limnol. Oceanogr.* **47**, 1084-1093.

Zong Y. (1997) Mid- and late-Holocene sea-level changes in Roundsea Marsh, northwest England: a diatom biostratigraphical investigation. *Holocene* **7**, 311-323.

Zong Y.Q. and Horton B.P. (1998) Diatom zones across intertidal flats and coastal saltmarshes in Britain. *Diatom Res.* **13**, 375-394.

Zong Y.Q. and Horton B.P. (1999) Diatom-based tidal-level transfer functions as an aid in reconstructing Quaternary history of sea-level movements in the UK. *J. Quaternary Sci.* **14**, 153-167.

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Figure 1. A: Location map of the study sites included in the geochemical database. B: Holocene sediment core site Ince 2 (I–2) and Ince 4 (I–4), inner Mersey Estuary, England.

Figure 2. Bi-plots of contemporary bulk organic sediment $\delta^{13}C$, C/N and TOC samples from the C_3 estuaries and coastal wetlands used in the NW European dataset (Supplementary file 1). Values are drawn from published studies (Thornton and McManus, 1994; Wilson et al., 2005; Lamb et al., 2007; Andrews, 2008; Craven et al., 2013; Goslin et al., 2015; Khan et al., 2015). $\delta^{13}C$ values in this figure are unadjusted for the ^{13}C Suess effect.

Figure 3. Partitioning Around Medoids (PAM) analysis identifies two distinctive groups in the NW European geochemical dataset, as illustrated in the overall optimal average silhouette width of 0.54. Groups of 3–8 were also considered, but yielded lower average silhouette widths: 3 Groups = 0.42; 4 Groups = 0.33; 5 Groups = 0.35; 6 Groups = 0.35; 7 Groups = 0.29; 8 Groups = 0.30). $\delta^{13}C$ values are adjusted for the Suess effect. PAM analysis was conducted on standardized $\delta^{13}C_{adjusted}$, C/N and TOC values (unstandardized values are shown in this figure). Samples are numbered 1–142 (corresponding locations are detailed in Supplementary file 1).

Figure 4. Core Ince 4 pollen assemblages at stratigraphic overlaps, together with $\delta^{13}C$ (inverted axis), C/N, TOC sample values and group classification (–0.98 to +2.42m Ordnance Datum (OD, Newlyn)). Logistic regression predicts the probability of Group 1 membership. $\hat{p}$ values ≥ 0.5 indicate Group 1 membership is more likely; $\hat{p}$ values <0.5 indicate Group 1

membership is unlikely and therefore samples are allocated to Group 0. Core lithostratigraphy and chronology are also shown (1 = 7,350 ± 60 ^{14}C yr BP; 2 = 6,800 ± 50 ^{14}C yr BP; 3 = 5,940 ± 40 ^{14}C yr BP).

Figure 5. Core Ince 4 diatom assemblages together with δ^{13}C (inverted axis), C/N, TOC sample values and group classification (–0.98 to +2.42m OD). Core lithostratigraphy and chronology are also shown (1 = 7,350 ± 60 ^{14}C yr BP; 2 = 6,800 ± 50 ^{14}C yr BP; 3 = 5,940 ± 40 ^{14}C yr BP). See Figure 3 for the lithology key.

Figure 6. Core Ince 4 pollen assemblages at stratigraphic overlaps, together with δ^{13}C (inverted axis), C/N, TOC sample values and group classification (+2.62 to +3.82m OD). Core lithostratigraphy and chronology are also shown (4 = 3,220 ± 40 ^{14}C yr BP; 5 = 800 ± 40 ^{14}C yr BP). See Figure 3 for the lithology key.

Figure 7. Core Ince 4 diatom assemblages together with δ^{13}C (inverted axis), C/N, TOC sample values and group classification (+2.62 to +3.82m OD). Core lithostratigraphy and chronology are also shown (4 = 3,220 ± 40 ^{14}C yr BP; 5 = 800 ± 40 ^{14}C yr BP). See Figure 3 for the lithology key.

Figure 8. Core Ince 2 diatom assemblages together with δ^{13}C (inverted axis), C/N, TOC sample values and group classification (–2.22 to –0.42m OD). Core lithostratigraphy and chronology are also shown (6 = 6,410 ± 50 ^{14}C yr BP). See Figure 3 for the lithology key.

Figure 9. Core Ince 2 pollen assemblages at stratigraphic overlaps, together with $\delta^{13}C$ (inverted axis), C/N, TOC sample values and group classification (–2.22 to –0.42m OD). Core lithostratigraphy and chronology are also shown (5 = 6,410 ± 50 ^{14}C yr BP). See Figure 3 for the lithology key.

Supplementary Files

Supplementary file 1: Contemporary bulk organic sediment $\delta^{13}C$, C/N and TOC dataset drawn from published studies on C_3 coastal wetland and estuarine sediments in temperate NW Europe. Suess effect correction procedures, standardized (z-score) values, and Partitioning Around Medoids (PAM) results are also provided.

Supplementary file 2: Mersey Estuary (UK) sediment core $\delta^{13}C$, C/N and TOC values, with predicted group membership base on logistic regression analysis of the NW Europe dataset. Details of the procedure to calculate $\hat{p}$ using the logistic regression model are provided.

Figure 1

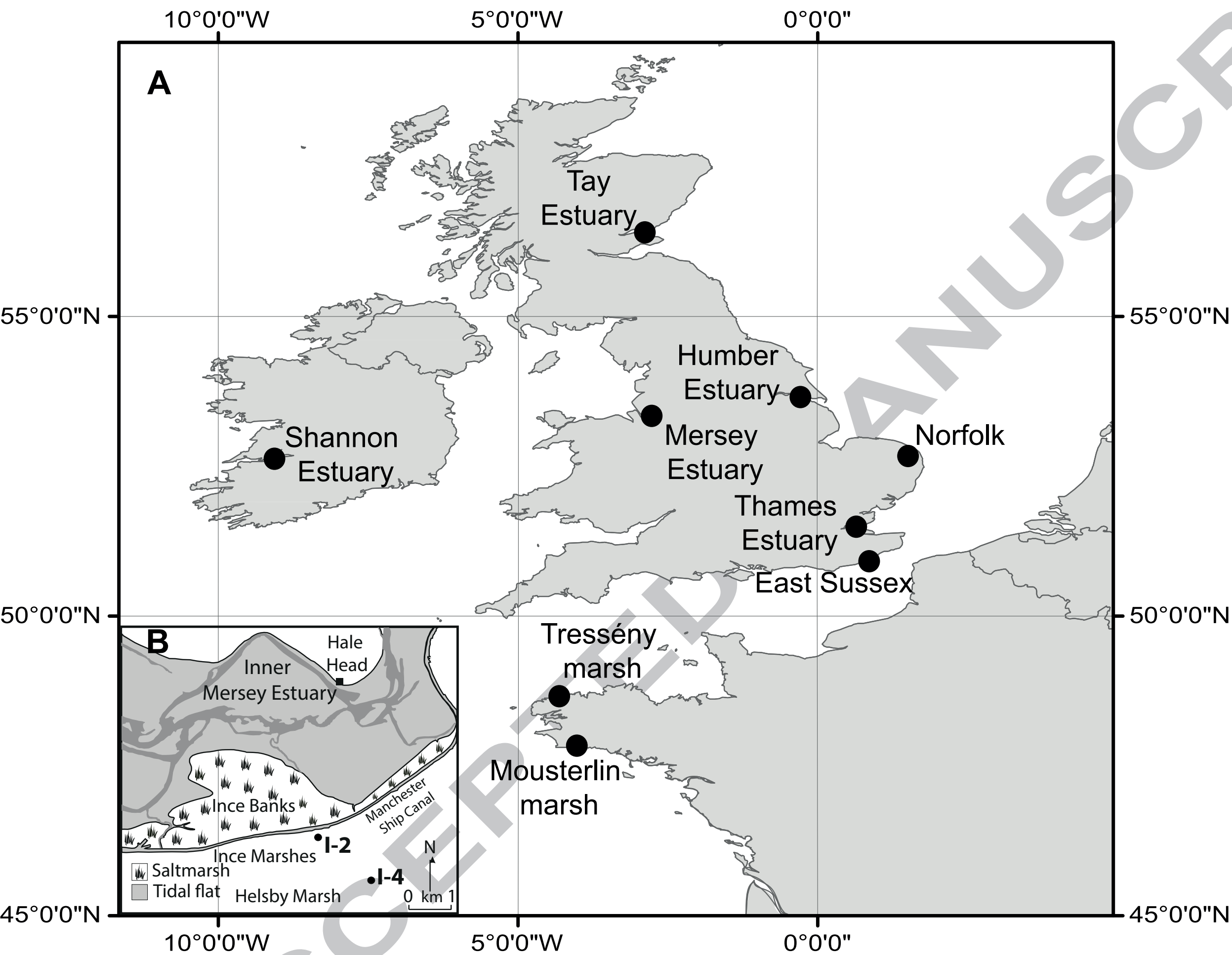
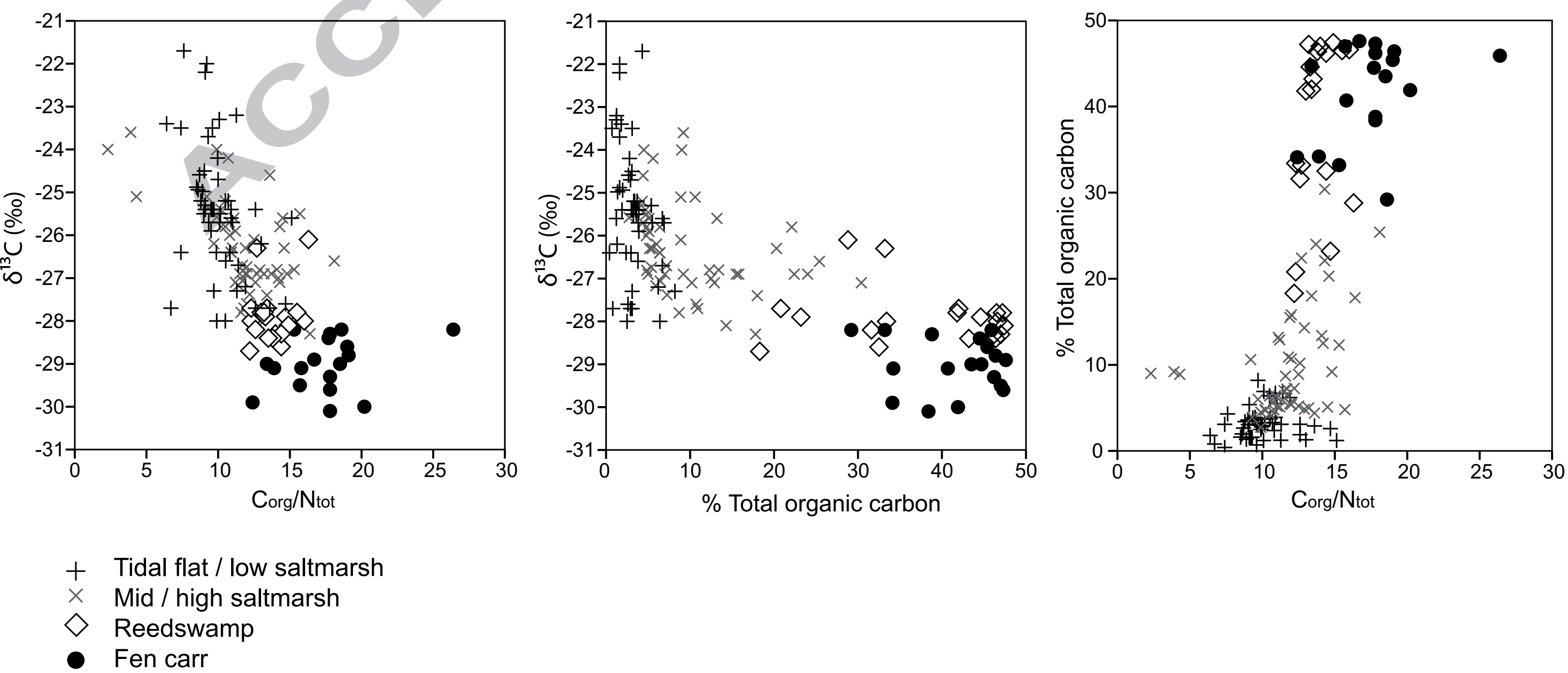
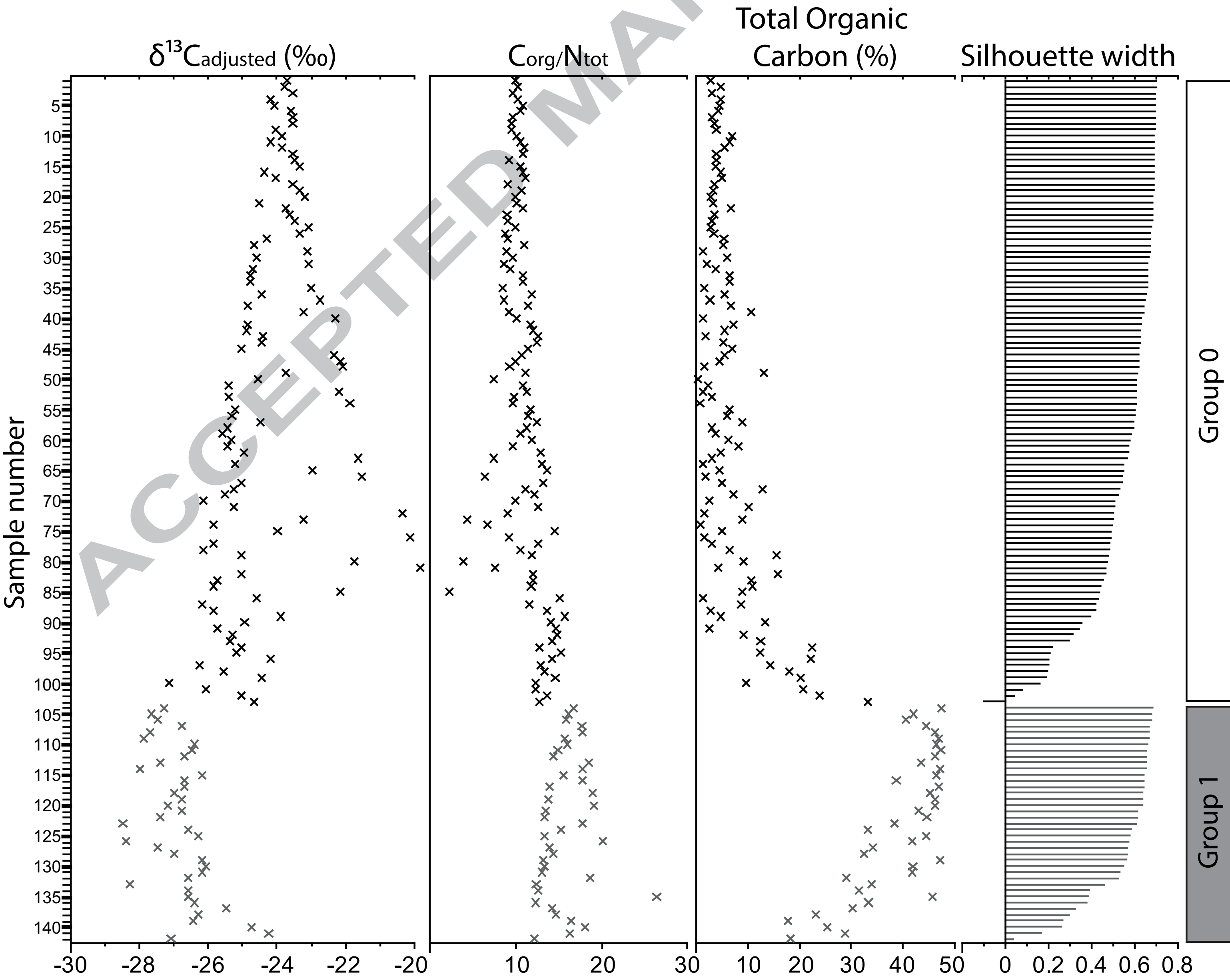

10°0'0"W
5°0'0"W
0°0'0"
55°0'0"N
50°0'0"N
45°0'0"N
A
Tay Estuary
Humber Estuary
Mersey Estuary
Shannon Estuary
Norfolk
Thames Estuary
East Sussex
Tressény marsh
Mousterlin marsh
B
Hale Head
Inner Mersey Estuary
Ince Banks
Manchester Ship Canal
Ince Marshes
I-2
I-4
Helsby Marsh
Saltmarsh
Tidal flat
N
0 km 1

Figure 2



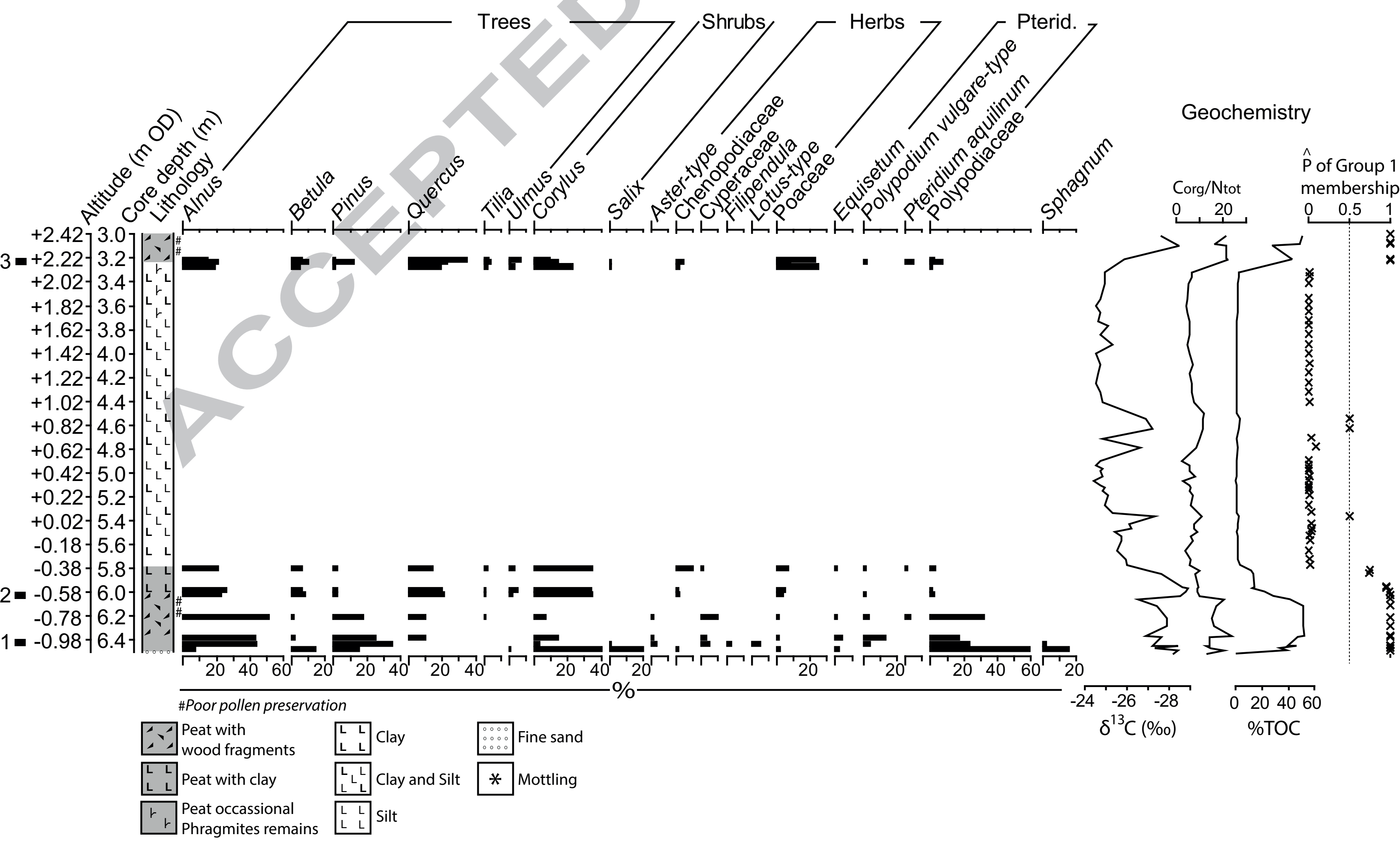
δ13C (‰)
Corg/Ntot
% Total organic carbon
% Total organic carbon
Corg/Ntot
Tidal flat / low saltmarsh
Mid / high saltmarsh
Reedswamp
Fen carr

Figure 3



$\delta^{13}C_{adjusted}$ (‰)
C_{org}/N_{tot}
Total Organic Carbon (%)
Silhouette width
Sample number
Group 0
Group 1
-30
-28
-26
-24
-22
-20
10
20
30
40
50
0
0.2
0.4
0.6
0.8
5
15
25
35
45
55
65
75
85
95
105
115
125
135
100
110
120
130
140

Figure 4



Trees
Shrubs
Herbs
Pterid.
Altitude (m OD)
Core depth (m)
Lithology
Alnus
Betula
Pinus
Quercus
Tilia
Ulmus
Corylus
Salix
Aster-type
Chenopodiaceae
Cyperaceae
Filipendula
Lotus-type
Poaceae
Equisetum
Polypodium vulgare-type
Pteridium aquilinum
Polypodiaceae
Sphagnum
Geochemistry
Corg/Ntot
P̂ of Group 1 membership
δ13C (‰)
%TOC
%
#Poor pollen preservation
Peat with wood fragments
Peat with clay
Peat occassional Phragmites remains
Clay
Clay and Silt
Silt
Fine sand
Mottling

Figure 5

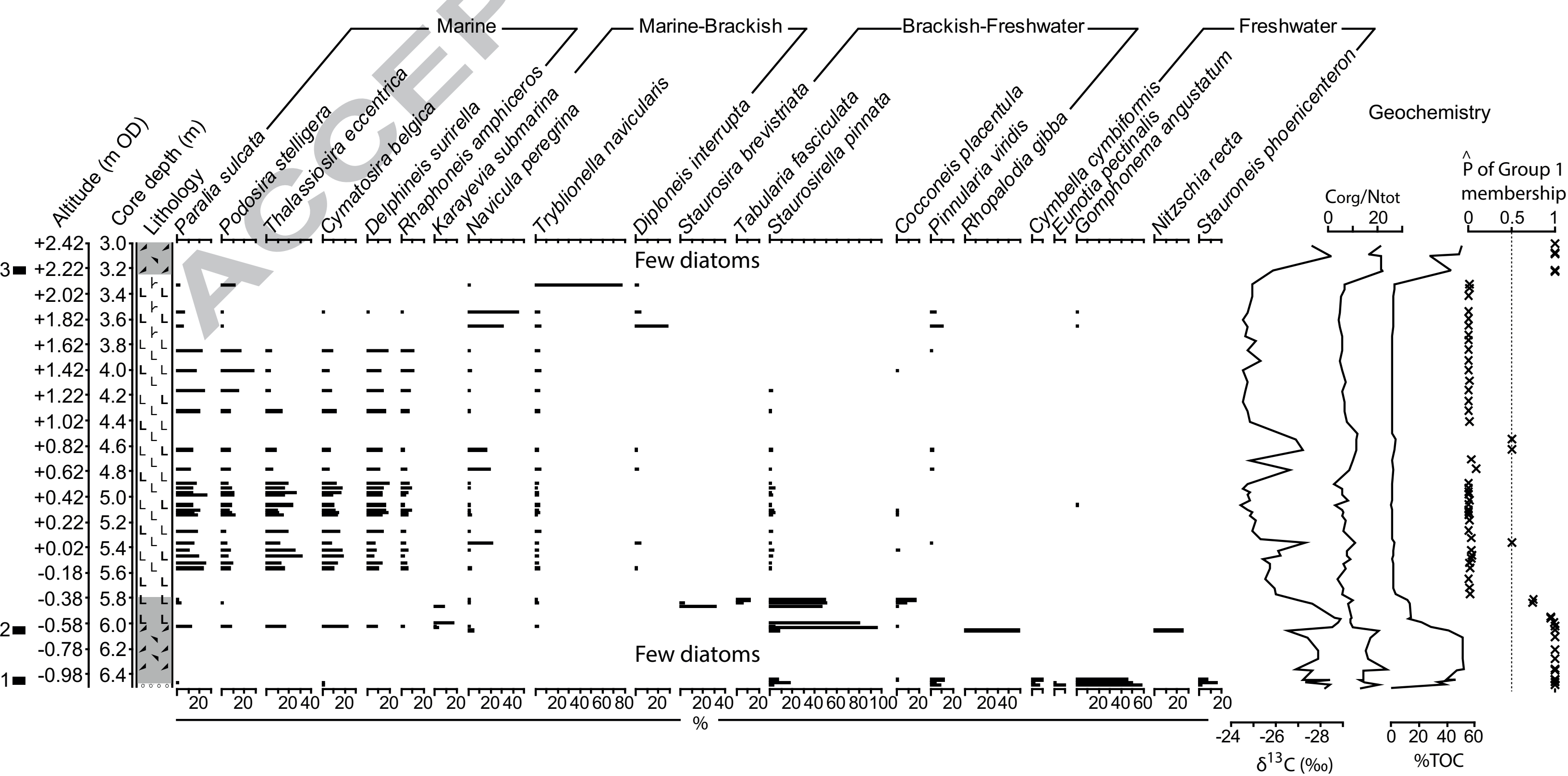
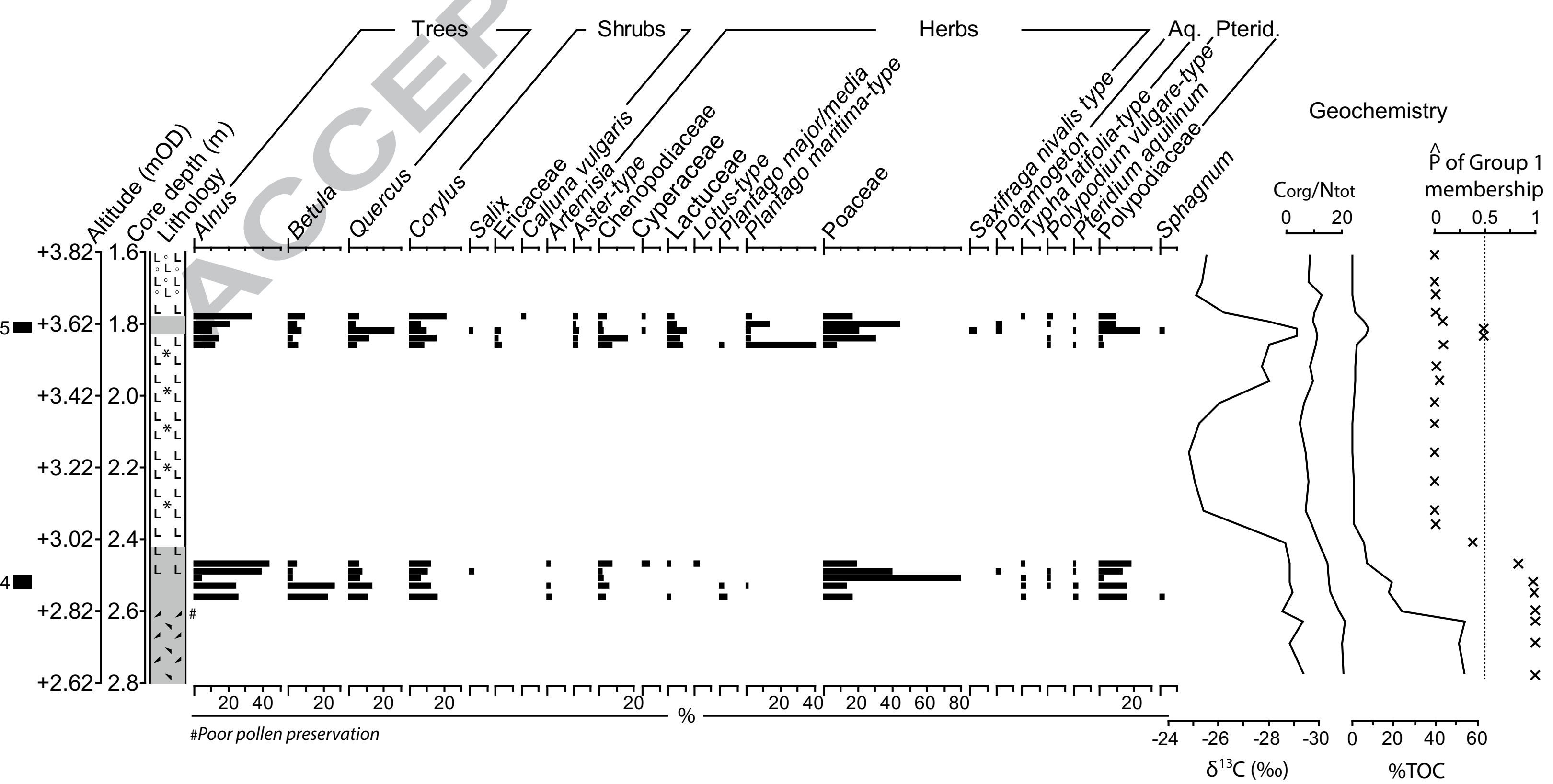
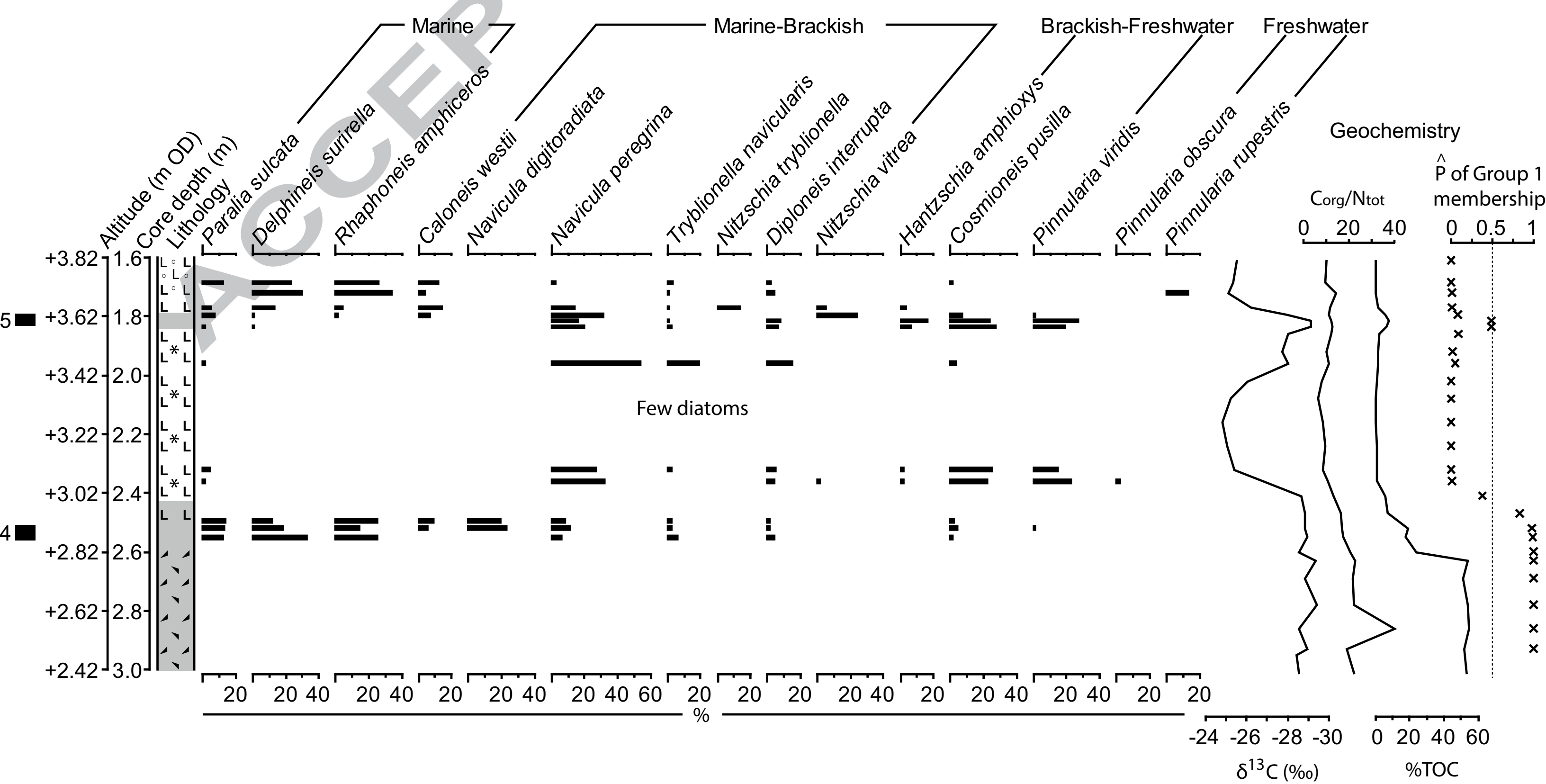

Marine
Marine-Brackish
Brackish-Freshwater
Freshwater
Altitude (m OD)
Core depth (m)
Lithology
Paralia sulcata
Podosira stelligera
Thalassiosira eccentrica
Cymatosira belgica
Delphineis surirella
Rhaphoneis amphiceros
Karayevia submarina
Navicula peregrina
Tryblionella navicularis
Diploneis interrupta
Staurosira brevistriata
Tabularia fasciculata
Staurosirella pinnata
Cocconeis placentula
Pinnularia viridis
Rhopalodia gibba
Cymbella cymbiformis
Eunotia pectinalis
Gomphonema angustatum
Nitzschia recta
Stauroneis phoenicenteron
Geochemistry
Corg/Ntot
$\hat{P}$ of Group 1 membership
Few diatoms
Few diatoms
%
δ13C (‰)
%TOC
3
2
1
+2.42 3.0
+2.22 3.2
+2.02 3.4
+1.82 3.6
+1.62 3.8
+1.42 4.0
+1.22 4.2
+1.02 4.4
+0.82 4.6
+0.62 4.8
+0.42 5.0
+0.22 5.2
+0.02 5.4
-0.18 5.6
-0.38 5.8
-0.58 6.0
-0.78 6.2
-0.98 6.4
-24 -26 -28
0 20 40 60
0 20
0 0.5 1

Figure 6



Trees
Shrubs
Herbs
Aq.
Pterid.
Geochemistry
Altitude (mOD)
Core depth (m)
Lithology
Alnus
Betula
Quercus
Corylus
Salix
Ericaceae
Calluna vulgaris
Artemisia
Aster-type
Chenopodiaceae
Cyperaceae
Lactuceae
Lotus-type
Plantago major/media
Plantago maritima-type
Poaceae
Saxifraga nivalis type
Potamogeton
Typha latifolia-type
Polypodium vulgare-type
Pteridium aquilinum
Polypodiaceae
Sphagnum
Corg/Ntot
P̂ of Group 1 membership
+3.82 1.6
+3.62 1.8
+3.42 2.0
+3.22 2.2
+3.02 2.4
+2.82 2.6
+2.62 2.8
5
4
%
#Poor pollen preservation
δ13C (‰)
%TOC

Figure 7



Marine
Marine-Brackish
Brackish-Freshwater
Freshwater
Altitude (m OD)
Core depth (m)
Lithology
Paralia sulcata
Delphineis surirella
Rhaphoneis amphiceros
Caloneis westii
Navicula digitoradiata
Navicula peregrina
Tryblionella navicularis
Nitzschia tryblionella
Diploneis interrupta
Nitzschia vitrea
Hantzschia amphioxys
Cosmioneis pusilla
Pinnularia viridis
Pinnularia obscura
Pinnularia rupestris
Geochemistry
Corg/Ntot
P̂ of Group 1 membership
Few diatoms
%
δ13C (‰)
%TOC
+3.82
+3.62
+3.42
+3.22
+3.02
+2.82
+2.62
+2.42
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
5
4

Figure 8

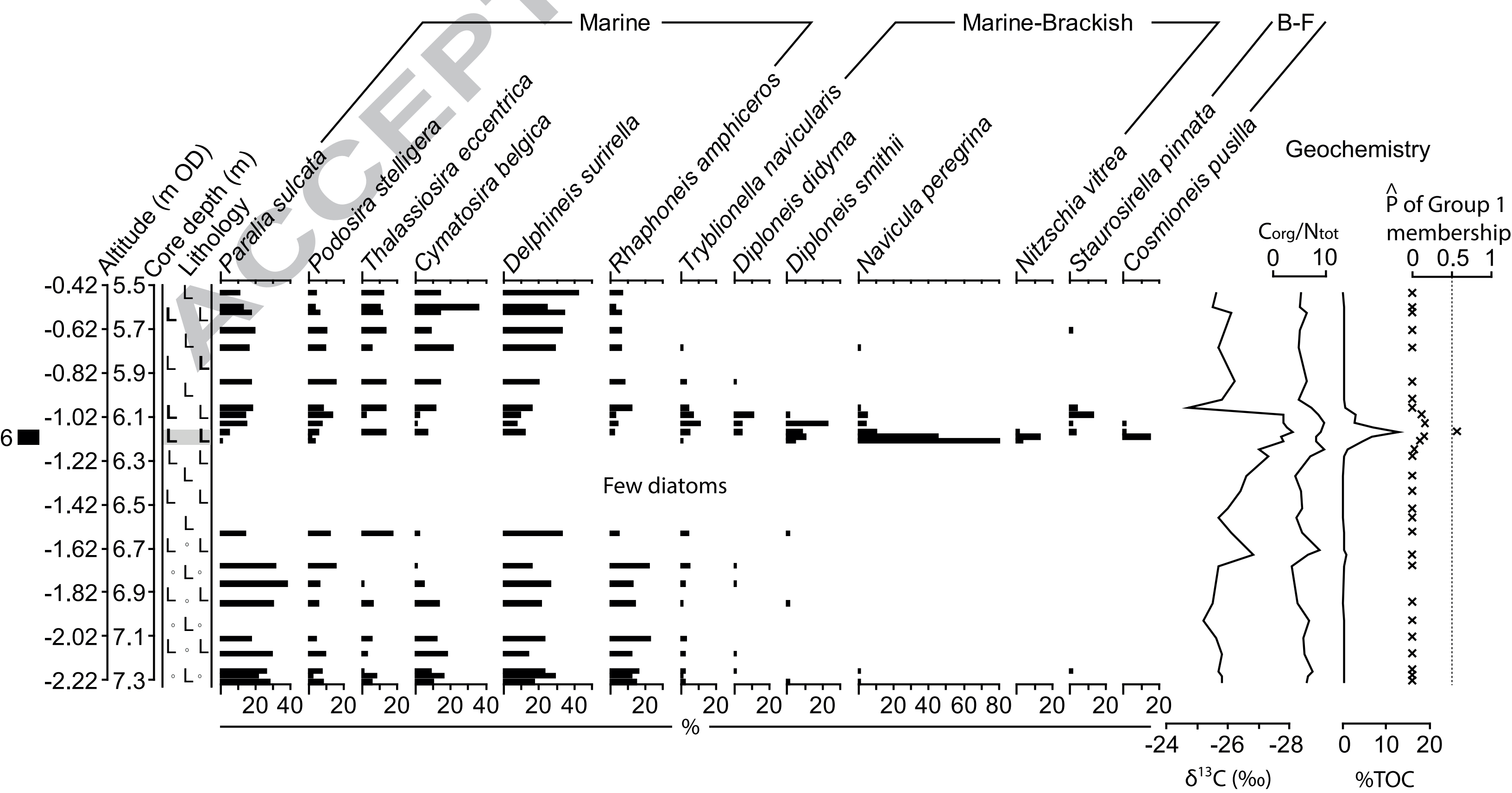
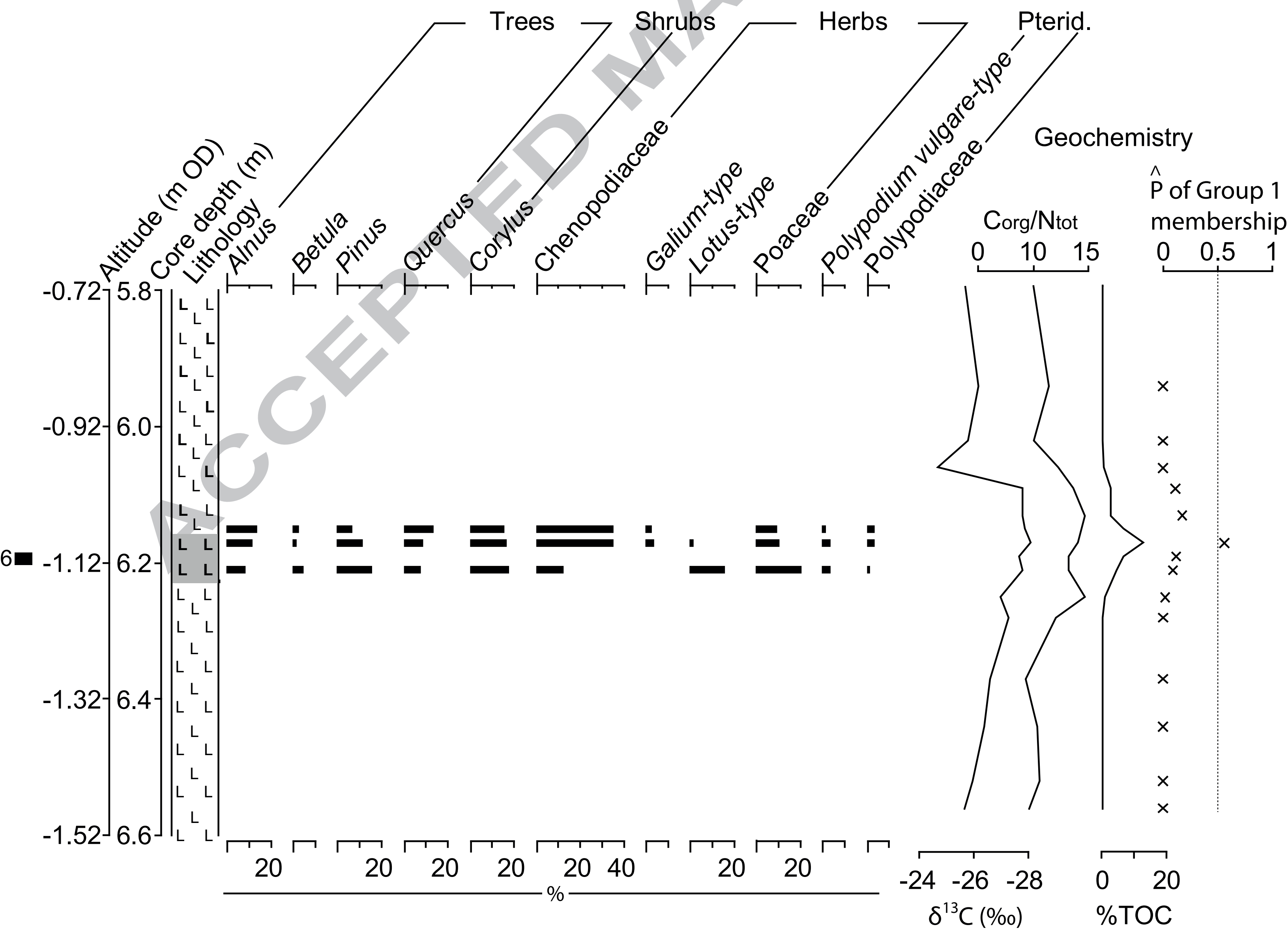

Marine
Marine-Brackish
B-F
Altitude (m OD)
Core depth (m)
Lithology
Paralia sulcata
Podosira stelligera
Thalassiosira eccentrica
Cymatosira belgica
Delphineis surirella
Rhaphoneis amphiceros
Tryblionella navicularis
Diploneis didyma
Diploneis smithii
Navicula peregrina
Nitzschia vitrea
Staurosirella pinnata
Cosmioneis pusilla
Geochemistry
Corg/Ntot
P̂ of Group 1 membership
Few diatoms
%
δ13C (‰)
%TOC
-0.42 5.5
-0.62 5.7
-0.82 5.9
-1.02 6.1
-1.22 6.3
-1.42 6.5
-1.62 6.7
-1.82 6.9
-2.02 7.1
-2.22 7.3
6

Figure 9



Trees
Shrubs
Herbs
Pterid.
Altitude (m OD)
Core depth (m)
Lithology
Alnus
Betula
Pinus
Quercus
Corylus
Chenopodiaceae
Galium-type
Lotus-type
Poaceae
Polypodium vulgare-type
Polypodiaceae
Geochemistry
Corg/Ntot
0 10 15
P̂ of Group 1 membership
0 0.5 1
-0.72 5.8
-0.92 6.0
6 -1.12 6.2
-1.32 6.4
-1.52 6.6
20 20 20 20 20 40 20 20
%
-24 -26 -28
δ13C (‰)
0 20
%TOC

Highlights

- $\delta^{13}C$, C/N & TOC measurements are increasingly used in Holocene sea-level research
- A compiled NW Europe coastal sediment $\delta^{13}C$, C/N & TOC database is presented
- NW Europe coastal wetland sediment $\delta^{13}C$, C/N & TOC values cluster into two groups
- Database used to distinguish past tidal levels in C3-vegetated estuary deposits
- Methodology permits $\delta^{13}C$, C/N & TOC use in sea-level research in temperate NW Europe