A stable carbon isotope geochemistry database to reconstruct Holocene relative sea levels and paleoenvironments, Thames Estuary, UK

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ABSTRACT

We examined the use of stable carbon isotope geochemistry (δ^{13}C, TOC and C/N) of sedimentary organic matter to reconstruct former sea levels and paleoenvironments in the absence of suitable microfossil data. The modern distribution of δ^{13}C, TOC and C/N of 33 vegetation and 74 surface sediment samples collected from four coastal wetlands in the Thames Estuary and Norfolk, UK are described. The stable carbon isotope geochemistry of sediments varied in relation to the input of *in situ* vascular vegetation versus allochthonous particulate organic matter and algae, which was controlled by tidal inundation and salinity. We reviewed published and unpublished studies to produce a central and southern England database of vegetation (n = 278) and bulk sediment (n = 132) stable carbon isotope geochemistry. Statistical analyses identified four elevation-dependent environments in the stable carbon isotope geochemistry database: (1) tidal flat/low marsh (δ^{13}C: -24.9 ± 1.2 ‰; TOC: 3.6 ± 1.7 %; C/N: 9.9 ± 0.8); (2) middle marsh/high ($\delta^{13}C$: -26.2 ± 1.0 ‰; TOC: 9.8 ± 6.7 %; C/N: 12.1 ± 1.8); (3) reed swamp ($\delta^{13}C$: -27.9 ± 0.7 ‰: TOC: 36.5 ± 11.5 %; C/N: 13.9 ± 1.2); and (4) fen carr ($\delta^{13}C$: -29.0 ± 0.6 ‰; TOC: 41.6 ± 5.7 %; C/N: 17.4 ± 3.1). The stable carbon isotope geochemistry database was applied to a Holocene sediment core collected from the Thames Estuary to produce three new sea-level index points and one limiting date, illustrating the utility of $\delta^{13}C$, TOC, and C/N values to reconstruct Holocene relative sea levels.

1. INTRODUCTION

Reconstructions of Holocene relative sea level (RSL) provide important constraints for calibrating geophysical models of Earth's rheology and glacio-isostatic adjustment (GIA) (e.g., Lambeck et al., 1998; Engelhart et al., 2011; Milne and Peros, 2013). The ice sheet that formed over the British Isles at the Last Glacial Maximum (LGM) was small in global terms, but large enough for GIA to produce vastly contrasting patterns in RSL across the UK during the Holocene (e.g., Shennan, 1989; Shennan and Horton, 2002; Shennan et al., 2006; Bradley et al., 2011). For example, RSL records from Scotland, locations situated closer to the former ice sheet center, can display a mid-Holocene highstand associated with isostatic rebound (e.g., Smith et al., 2002; 2012), while RSL records in southeast England, including the Thames Estuary, show a monotonic rise throughout the Holocene associated with subsidence of the proglacial forebulge (e.g., Devoy, 1979, 1992; Long, 1992; Sidell et al., 2000).

Holocene variations in RSL in the Thames Estuary and elsewhere in the UK are derived from sea-level index points mostly obtained from lithostratigraphic changes between terrestrial and marine sediments (transgressive and regressive contacts). These changes in lithology are corroborated by microfossils (e.g., foraminifera, diatoms, pollen), which are used to delineate the initiation or removal of brackish and marine conditions and to verify that the contacts are conformable (Tooley, 1985; Shennan, 1986). However, discrepancies and data gaps in RSL records still persist that limit interpretation of the driving mechanisms of Holocene RSL dynamics in the Thames (e.g., Devoy, 1979; Shennan, 1989; Long, 1992, 1995; Haggart, 1995; Wilkinson et al., 2000; Sidell et al., 2000; Sidell, 2003) and the UK (e.g., Shennan et al., 2006; Massey et al., 2008; Gehrels, 2010). In part, this may be due to issues with preservation of identifiable microfossils in Holocene archives that are associated with microfossil life processes and post-depositional changes (e.g., Metcalfe et al., 2000; Roberts et al., 2006). Further, the application of microfossil-based transfer functions (e.g., Horton et al., 1999), which have expanded the type of sediments from which RSL estimates can be derived, have been hindered by problems associated low sample counts and/or a lack of modern analogues (e.g., Horton and Edwards, 2006). For example, of the 225 sea-level index points collected as part of the Land Ocean Interaction Study of Holocene coastal evolution of the east coast of England (Shennan and Andrews, 2000), only 52 were suitable for transfer function analyses (Horton et al., 2000).

An alternative approach to RSL reconstruction has recently been explored that utilizes the bulk stable carbon isotope geochemistry (stable carbon isotopes ($\delta^{13}C$), total organic carbon (TOC), and organic carbon to total nitrogen (C/N)) of sedimentary organic matter) (e.g., Wilson et al., 2005a, 2005b; Mackie et al., 2005, 2007; Lamb et al., 2007; Kemp et al., 2010, 2012b; Engelhart et al., 2013b). $\delta^{13}C$ and C/N are able to differentiate sources of organic matter that characteristically accumulate in coastal wetland sediments (Haines, 1977; Chmura and Aharon, 1995; Goñi and Thomas, 2000).

In particular, $\delta^{13}C$ and C/N can distinguish between freshwater and marine organic matter (e.g., Fry et al., 1977; Fogel and Cifuentes, 1993) and C_3 and C_4 vegetation (e.g., Emery et al., 1967; Malamud-Roam and Ingram, 2001). Plants that utilize the C_3 photosynthetic pathway have distinct $\delta^{13}C$ values from those that use the C_4-pathway (Smith and Epstein, 1971) due to biochemical properties of their primary CO_2-fixing enzyme (Deines, 1980). TOC measurements quantify the amount of organic matter contained within sediments (e.g., Ostrowska and Porebska, 2012). The amount of organic matter contained in sediments has traditionally been estimated using loss-on-ignition (LOI) (Ball, 1964), although this method may over- or underestimate the total organic matter and carbon content (Schumacher, 2002; Boyle, 2004). TOC values provide a direct measurement of the amount of organic carbon contained within sediments (Veres, 2002).

Studies in the UK (e.g., Andrews et al., 2000; Wilson et al., 2005a, 2005b; Lamb et al., 2007; Andrews, 2008) and the U.S. Atlantic (e.g., Kemp et al., 2010, 2012b), Gulf (e.g., DeLaune, 1986; Chmura et al., 1987) and Pacific (e.g., Engelhart et al., 2013b) coasts have demonstrated the distinct distribution of $\delta^{13}C$ and C/N values of modern tidal flat, salt marsh and freshwater environments. However, expansion upon these studies is needed to examine the boundary between salt marsh and reed swamp/fen carr environments, which is important in the interpretation of transgressive/regressive contacts in Holocene sequences of the UK. Furthermore, regional, inter-, or intra-site variability in $\delta^{13}C$ and C/N distributions is not fully understood (Wilson et al., 2005a, 2005b; Lamb et al., 2007).

Here, we examine the distribution of $\delta^{13}C$, TOC and C/N of vegetation and sedimentary organic matter within coastal wetlands of the Thames Estuary and Norfolk

Broads, UK. We compare our data to published and unpublished studies from central and southern England to produce a database of $\delta^{13}C$, TOC and C/N values. We apply the database to a Holocene sediment core collected from Swanscombe Marsh on the Thames Estuary with poor microfossil preservation to produce new sea-level data. We find the effect of post-depositional processes on $\delta^{13}C$, TOC, and C/N is not prohibitive in paleoenvironmental interpretation, thus this method can be used to reconstruct Holocene RSL in the UK and other temperate regions.

2. STUDY AREA

The modern Thames Estuary drains an area of ~16,000 km^2 of England into the North Sea (Fig. 1). The tidal portion of the estuary is approximately 110 km long, with the seaward limit extending ~80 km downstream and the tidal limit occurring approximately ~30 km upstream from the London Bridge (Mitchell et al., 2012). The estuary is macrotidal with spring tidal range varying from 5.2 m near the mouth of the estuary in Sheerness to 6.6 m at the London Bridge (Admirality Tide Tables, 2013). Salinity ranges from <1 at the tidal limit to ~32 at the estuary mouth at half-tide (time or state halfway between flood and ebb) (Juggins, 1992), although large variations occur during the tidal cycle as well as seasonally (Mitchell et al., 2012).

Undisturbed areas of coastal wetland habitat are limited in the region, because of human modifications, changes in wave and wind climate (van der Wal and Pye, 2004) and RSL rise (Woodworth et al., 2009). These anthropogenic and climate driven changes pose difficulties in locating suitable areas along the estuary to use as an analogue for Holocene salt marsh, reed swamp and fen carr paleoenvironments (Devoy, 1979). We tried to minimize these factors by confining our study sites to nature reserves or maintained marshes where well-developed successions of wetland floral zones were readily identifiable. Three sites on the Thames Estuary (Dartford Creek, Wat Tyler Country Park and Two Tree Island) and one site containing fen carr in the Norfolk Broads (Ted Ellis Nature Reserve) were chosen for study. The species composition of marsh floral zones in our study sites are representative of the low marsh (van der Wal and Pye, 2004) and high marsh (Boorman, 2003) communities that are characteristic of southeast England. With the exception of introduced C_4 *Spartina* (Ranwell, 1972), all other vegetation follows the C_3 photosynthetic pathway. Fen carr environments occur in waterlogged conditions (McVean, 1956) and commonly develop as a consequence of increasing tidal influence or elevated groundwater level associated with sea-level rise (e.g., Walker, 1970; Long and Innes, 1995; Waller et al., 2005).

The study site situated at Dartford Creek, a tributary of the Thames Estuary, is part of the Crawley marshes (Fig 1A). Porewater salinity at the site ranged from 26 to 32. One transect (A-A^1; Fig 1A) of 18 stations was established that extended through unvegetated tidal flat and low, middle, to high marsh floral zones. The low marsh was inhabited by *Puccinellia maritima, Spergularia* spp., and in localized depressions *Eleocharis* sp. The middle-high marsh was dominated by *Elymus repens* and *Festuca rubrum,* with *Spergularia* spp. present. The transition to upland vegetation was absent from this site due to levee construction.

The Wat Tyler Country Park nature reserve is located north of Canvey Island in Pitsea. One ~40 m transect (B-B^1; Fig 1B) of 15 stations was sampled that encompassed a full range of successional environments from tidal flat, low, middle to high marsh, and brackish, upland transition. Porewater salinity at the site ranged from 27 to 34. Tidal flat sediments were unvegetated. Low marsh vegetation included *Aster tripolium* and *Salicornia europaea*. The middle marsh was inhabited by *Halimione portulacoides* and *Puccinellia maritima*. The high marsh was occupied by *Festuca rubra* and *Halimione portulacoides*, and a brackish transition zone occupied by *Phragmites australis* occurred at the upper boundary of the marsh.

The final study area from the Thames Estuary is located in the marshes of Two Tree Island, east of Canvey Island, forming part of the Leigh National Nature Reserve. Porewater salinity at this site was between 34 and 37. Two transects (C-C^1; D-D^1; Fig 1C) of 11 and 6 sampling stations, respectively, were established to account for variability between low marsh environments colonized by the introduced C_4 grass *Spartina anglica*. The occurrence of this species will enable distinction among low, high and upland transition environments due to its discrete values from C3 vegetation, but the species is not represented in Holocene sedimentary archives (Long et al., 1999). Both transects extend through tidal flat, low marsh and middle marsh zones. The low to pioneer marsh hosts *Salicornia europaea* and *Spartina anglica*. The middle marsh is dominated by *Festuca rubra, Halimione portulacoides, Aster tripolium, Borrichia fructescens* and *Suaeda maritima*. Washed-in algae and seaweed (*Fucus vesiculosus)* were present throughout the marsh. Transect 2 (D-D^1) was positioned to avoid sampling sediments occupied by *Spartina*. Leveeing further inland prevented the formation of high marsh, brackish transitional and upland communities.

The Ted Ellis Nature Reserve, situated southeast of Norwich along the southern bank of the River Yare in the Norfolk Broads, contains a variety of wetland habitats. Porewater salinity at the site is < 0.5. Two transects were sampled from this site (Fig 1D).

The first transect (E-E^1) was 215 m long with 15 stations and extended from a reed swamp dominated by *Phragmites australis* and *Phalaris arundinacea* with *Carex* spp. present at the banks of the Yare to a *Salix*-dominated fen carr environment. The second transect (F-F^1) was 70 m long with 9 stations and incorporated reed swamp and *Alnus*-dominated fen carr environments.

3. METHODS

Sampling stations were positioned to maintain consistent vertical spacing (~ 3-5 cm) between each station along each transect. A total station was used to survey stations and core locations to a common reference datum (m Ordnance Datum; OD), which was determined using a Leica differential geographic positioning system with real-time kinematic capabilities. Tidal datums at all Thames Estuary sites were interpolated from the nearest tide gauge stations (Admiralty Tide Tables, 2013). Tidal datums at Ted Ellis Reserve were inferred from stream gauge readings maintained by the Environment Agency.

3.1 Modern vegetation and sediment

The vegetation cover at each sampling station was recorded (estimated percentage of total coverage) and the dominant vegetation (above- and belowground components) was sampled (n = 33) to provide context for the δ^{13}C and C/N of surface sediments (Chmura and Aharon, 1995; Malamud-Roam and Ingram, 2004). Seventy-four 10 cm^2 x 1 cm surface sample were collected for analysis of δ^{13}C, TOC, C/N at each sampling station. Salinity was measured using a calibrated refractometer at the time of sample collection. When the sample was not wet enough for the measurements, porewater was separated by centrifuge from the samples in laboratory and its salinity was measured (Horton et al., 1999; Sawai et al., 2004).

3.2 Collection of Core SW1

During a drilling campaign conducted by the British Geological Survey, a series of sediment cores from locations in the mid- and lower-estuary were collected. One core from Swanscombe Marsh (Core SW1) was selected for analysis in this study because it represented the full series of transgressive/regressive sequences recognized by Devoy (1979) in his type-site at Tilbury. A drilling rig employing a ‘wireline’ percussion tripod arrangement (also known as ‘shell and auger’) was used to retrieve core SW1. The recovered core was capped and sealed in the field and immediately refrigerated at 4 ºC. The core was described in the laboratory using the Troels-Smith (1955) method for organic-rich sediments.

3.3 Carbon and nitrogen bulk organic geochemistry of modern and core samples

Sample pretreatment for $\delta^{13}C$, TOC and C/N analysis followed Vane et al. (2013a). Plant samples were treated with 5% HCl for 2 hours, rinsed with deionized water, dried in an oven at 50°C and freezer-milled to a fine powder. Sediment samples were treated with 5% HCl overnight to remove inorganic carbon, and were subsequently rinsed with at least 1500 ml of deionized water, dried in an oven at 50°C and milled to a fine powder using a pestle and mortar. $^{13}C/^{12}C$ analyses were performed by combustion in a Costech Elemental Analyzer coupled online to an Optima dual-inlet mass spectrometer at the NERC Isotope Geosciences Laboratory, Nottingham, UK. The values were calibrated to the Vienna Pee Dee Belemnite (VPDB) scale using within-run cellulose standard Sigma Chemical C-6413 calibrated against NBS19 and NBS 22 (Vane et al., 2013b) that was included within the runs. Sample total organic C and total N were measured on the same instrument. C/N ratios were calibrated with an acetanilide standard and are given as a weight percentage (Vane et al., 2013b). Replicate analysis on well-mixed samples indicates analytical precision of <0.1 ‰. Core SW1 was analyzed for $\delta^{13}C$, TOC, and C/N at 8 cm intervals continuously throughout the core. The $\delta^{13}C$, TOC and C/N of modern vegetation and bulk sediments (including the databases), and Core SW1 data can be found in Appendices 1 and 2.

3.4 Microfossil analysis of Core SW1

Microfossil (diatom, foraminifera, pollen) analysis was undertaken on Core SW1 to support, where possible, paleoenvironmental changes inferred from $\delta^{13}C$, TOC, and C/N. We sampled for diatom and foraminiferal above and below radiocarbon-dated contacts of Core SW1; pollen counts were performed only on the sediment at dated horizons. All samples for diatom analysis under light microscopy were prepared following standard methods (Zong and Horton, 1998, 1999). Diatoms were identified and enumerated under 1000× magnification using the keys of Hartley et al. (1966), van de Werff and Huls, (1958-1966) and Patrick and Reimer (1966-1975). Classification of salinity and life form follows Denys (1991/2) and Vos and Wolf (1993). Sample preparation, identification and classification of foraminifera followed Horton and Edwards (2006). Wet counts were completed under a binocular microscope. A minimum of 200 diatom and foraminifera were counted per sample where possible. Clay-rich sediments were prepared for pollen following the technique of Riding and Kyffin-Hughes (2004) and peat samples were prepared for pollen by disaggregation with potassium hydroxide. Pollen was grouped into five broad physiognomic categories: trees, shrubs, herbs, aquatics and pteridophytes. Calculation of individual taxa is expressed as percentage of the total sum of land pollen. The microfossil data from Core SW1 can be found in Appendix 3.

3.5 Radiocarbon age determination

Radiocarbon (^{14}C) dates were selected to produce new sea-level data from Core SW1 (Table 1). Three identifiable plant macrofossils inferred to be deposited *in situ* were selected for Accelerator Mass Spectrometry (AMS) radiocarbon dating. Prior to analysis, the samples were cleaned under a binocular microscope to remove contaminating material, such as older adhered organic sediment from the matrix surrounding the macrofossil or younger ingrown rootlets (Kemp et al., 2013b). In the absence of datable macrofossil remains, one date was obtained from bulk peat substrate at -7.14 m OD. Reported radiocarbon ages were calibrated to sidereal years with a 2σ confidence interval using the IntCal13 calibration curve (Reimer et al., 2013) and a laboratory multiplier of 1. Ages are presented as calibrated years (cal yr) before present (BP), where the zero point is AD 1950 (Stuiver and Polach, 1977).

3.6 Statistical analysis

One-way Analysis of Variance (ANOVA) and Nested ANOVA was performed on the sediment database (excluding sites occupied by C_4 *Spartina*) to detect significant differences in mean $\delta^{13}C$, TOC, and C/N values, and inter-site variability in the δ13C, TOC, and C/N values of depositional environments, respectively. Analysis was completed in JMP 10.0 with “environment” as the grouping factor (Table 2). “Environment” was defined by the environmental zones present in the study areas: tidal flat/low salt marsh, middle/high marsh, reed swamp and fen carr. Data were logtransformed where necessary to meet assumptions of ANOVA (equal variance, normality). Tukey's HSD was used to identify differences among multiple means when a significant effect was found.

4. RESULTS

4.1 Characteristics of modern vegetation

Thirty-three vegetation samples from tidal flat, low, middle and high marsh, and reed swamp environments were analyzed for $\delta^{13}C$ and C/N composition. The mean $\delta^{13}C$ of all samples was -25.4 ‰, ranging from -32.1 to -13.1 ‰. The mean C/N of all samples was 38.2, spanning values of 6.3 to 122.4.

Marine and tidal flat end-member vegetation samples (n=2), including brown algae and *Fucus vesiculosis,* had a mean $\delta^{13}C$ of -26.2 ‰, which ranged from -32.1 to -20.3 ‰. The mean C/N of these samples was 10.5, with values from 6.3 to 14.6.

Vegetation end-members collected from low marsh environments (n=13), including *Aster tripolium, Borrichia fructescens, Cochleria spp., Puccinellia maritima, Salicornia europaea, Spartina anglica*, and *Sueada maritima*, had mean $\delta^{13}C$ and C/N values of -24.6 ‰ and 30.5, respectively. $\delta^{13}C$ values ranged from -30.0 (*Salicornia europaea*) to -13.1 ‰ (*Spartina anglica*), and C/N spanned values from 12.0 (*Sueada maritima*) to 61.9 (*Borrichia fructescens*).

Middle to high marsh end-member vegetation (n=14), including *Agrostis stolonifera, Elymus repens, Festuca rubra, Halimione portulacoides, Scirpus maritimus*, and *Spergularia media*, had a mean $\delta^{13}C$ of -26.0 ‰, which varied between -28.6 (*Halimione portulcoides*) and -24.1 ‰ (*Festuca rubra*). Mean C/N was 48.8, with values ranging from 15.5 (*Halimione portualcoides*) to 122.5 (*Agrostis stolonifera*).

Vegetation end-members collected from reed swamp environments (n=3), including *Phragmites australis* and *Carex* sp., had mean $\delta^{13}C$ and C/N values of -25.3 and 41.3 ‰, respectively. $\delta^{13}C$ fell between -26.5 (*Carex* sp.) and -24.6 ‰ (*Phragmites australis)*, and C/N values ranged from 30.6 (*Carex* sp.) to 61.7 (*Phragmites australis*).

4.2 Characteristics of modern sediments

Seventy-four surface sediment samples were analyzed for $\delta^{13}C$, TOC and C/N composition. The mean $\delta^{13}C$ of all samples was -26.1 ‰, ranging from -29.6 to -19.5 ‰. The mean TOC of all samples was 18.7 %, spanning values from 0.6 to 47.6 %. The mean C/N of all samples was 12.2, extending from 8.0 to 26.4.

4.2.1 Dartford Creek Transect

The Dartford Creek transect (Fig 2) covered tidal flat, low, middle and high marsh zones from an elevation of 1.63 to 3.40 m OD. The tidal flat/low marsh zone (n = 7) had $\delta^{13}C$, TOC, and C/N values of -25.9 to -25.1 ‰, 3.0 to 3.9 % and 8.8 to 9.7, respectively. $\delta^{13}C$ decreased with distance landward in the middle-high marsh zone (n = 11) from -25.9 ‰ at the boundary with the low marsh to -27.7 ‰ at the edge of the high marsh. TOC values increased from the middle to high marsh from 7.0 to 18.0 %. C/N values increased with distance along transect in the middle-high marsh with a minimum of 11.5 at ~ 12 m to a maximum of 14.1 at ~ 37 m along the transect.

4.2.2 Wat Tyler Transect

The transect at Wat Tyler (Fig 3) incorporated low, middle and high marsh and *Phragmites* brackish transition environments ranging in elevation from 1.73 to 3.22 m OD. The tidal flat/low marsh zone (n = 8) had $\delta^{13}C$ values between -26.7 to -25.2 ‰.

TOC values in this zone increased from 3.3 % to 6.9 % at 26 m along the transect in the low marsh. C/N values exhibited a similar pattern to TOC; C/N increased in the pioneer to low marsh from 10.1 to 11.4. The $\delta^{13}C$ values of the middle/high marsh zone (n = 4) are lower than the tidal flat/low marsh zone, ranging from -26.9 to -26.3 ‰. TOC values increased in the middle/high marsh from 15.5 % at 28 m to 24.0 % at 36 m along the transect. C/N values also generally increased in this zone from a minimum of 11.9 to a maximum of 14.6 at 32 m along the transect. $\delta^{13}C$ values in the *Phragmites* environment (n=3) varied between -28.0 and -26.1 ‰. TOC values increased from 28.8 % at the boundary between middle and high marsh to 33.4 % at the landward edge of the transect.

4.2.3 Two Tree Transects 1 and 2

Two Tree Transect 1 incorporates tidal flat and low and middle marsh environments (Fig 4), with undulating topography due to dissecting tidal creeks and drainage ditches. The transect extends from 2.00 to 2.80 m OD in elevation. The tidal flat/low marsh zone (n = 6) had a mean $\delta^{13}C$, TOC and C/N of -20.8, 2.6 % and 8.5, respectively. Compared to the tidal flat/low marsh zone, the middle marsh zone (n = 5) had a lower mean $\delta^{13}C$ (-23.1 ‰), higher mean TOC (3.7 %,) and and higher mean C/N (9.4).

Two Tree Transect 2 also included tidal flat, low and middle marsh environments, but lacked much of the undulating topography of Transect 1 (Fig 4). The transect ranged from 2.13 to 2.79 m OD (between MHWNT and 0.29 m below MHWST). $\delta^{13}C$ values increase with distance along transect from a minimum of -22.0 ‰ in the tidal flat/low marsh (n = 2) to a maximum of -25.1 ‰ at ~ 7 m along the transect in the middle marsh (n = 4). TOC values exhibited a similar pattern, with a minimum TOC of 1.6 % in the tidal flat/low marsh, increasing to a maximum value of 5.6 % at the landward edge of the transect in the middle marsh. C/N values also increased with distance along transect from a minimum of 9.1 in the tidal flat/low marsh to a maximum of 10.7 at the landward edge in the middle marsh.

4.2.4 Ted Ellis Transects 1 and 2

Ted Ellis Transect 1 (Fig 5) extends from the vegetated banks of the River Yare, across a reed swamp to a fen carr. Sampling stations cover elevations from 0.05 to 0.78 m OD. The reed swamp (n = 10) had a mean $\delta^{13}C$ of -28.1 ‰. The banks and river levee showed the greatest variability within the reed swamp with values between -28.7 and -27.7 ‰. Mean TOC of the reed swamp was 34.9 % with the minimum of Transect 1 of 18.3 % occurring along the riverbanks. TOC increased with distance inland, obtaining a maximum of 47.2 % at ~ 160 m along the transect. C/N values within the reed swamp had a mean of 13.3. The fen carr (n = 5) had a mean $\delta^{13}C$ of -28.8 ‰, which increased from the transect minimum of -29.5 to -28.2 ‰ at the landward edge of the fen carr. The mean TOC within the fen carr was 46.1 %, including the maximum observed on Transect 1 of 47.6 %. C/N increased within the fen carr from 13.4 to the maximum of Transect 1 of 26.4 at its landward edge.

Ted Ellis Transect 2 is located further inland from the River Yare than Transect 1 and, therefore, was found at a slightly higher elevation of 0.45 to 1.34 m OD (Fig 5). Transect 2 covered reed swamp and fen carr environments. The reed swamp (n = 6) had a mean $\delta^{13}C$ of -28.2 ‰ and a mean TOC value of 46.1. C/N values decreased with distance along transect from 16 at the beginning of the transect to 13.5 (the minimum of Transect 2) at the boundary with the fen carr. At the boundary between the fen carr (n =

3) and reed swamp, $\delta^{13}C$ was at a minimum of -29.6 ‰ and increased with distance inland to -28.8 ‰. The TOC mean was 46.6 % in the fen carr. There was an increase in C/N from values of the reed swamp with a mean of 18.3.

4.2.5 Site specific variations of modern sediments

The three sites on the Thames Estuary and one site containing fen carr in the Norfolk Broads display site-specific variations in $\delta^{13}C$, TOC and C/N values of bulk sediments from sites on the Thames Estuary (Table 2). In particular, the tidal flat/low marsh and middle/high marsh sediments of Two Tree Island differed from those of the Dartford Creek and Wat Tyler sites. We infer that these differences in $\delta^{13}C$ values are related to salinity variations among sites. Porewater salinity of sampling stations at Two Tree Island ranged from 34 to 37, while at Dartford Creek and Wat Tyler, salinity was 26 to 34. Middelburg and Herman (2007) measured the $\delta^{13}C$ of suspended organic matter in relation to a salinity gradient along the Thames Estuary and found increasing $\delta^{13}C$ with increasing salinity. Coincidently, salinity levels of > 34 corresponded to $\delta^{13}C$ values of particulate organic matter of -22 to -20 ‰, and salinity levels of 26-34 corresponded to $\delta^{13}C$ values between -26 and -24 ‰, which agrees well with the range in tidal flat/low marsh sediments at the Two Tree Island (-21.1 ± 0.9) and Dartford Creek/Wat Tyler sites (-25.4 ± 0.2 ‰ and -25.6 ± 0.5 ‰), respectively. The presence of C_4 *Spartina anglica* ($\delta^{13}C$ = -13.2 ‰) at Two Tree Island contributes to its relatively high $\delta^{13}C$ values, although it cannot entirely explain the variation between sites, because Transect 2 at the site was positioned to avoid sampling sediments colonized by *Spartina* spp., and its sediment $\delta^{13}C$ values ranged between -22.2 to -25.1 ‰. Although this range is slightly lower than sampling stations on Transect 1 occupied by *Spartina* (which ranged from -

19.5 to -23.8 ‰), it is still higher than the $\delta^{13}C$ values of > -25.0 ‰ present at the Dartford Creek and Wat Tyler sites. Likely a combination of these two factors resulted in the observed inter-site variability, although we cannot rule out that mixing of anthropogenic pollution from historical events at Two Tree Island (Scrimshaw and Lester, 1995) could also cause a shift in observed $\delta^{13}C$ values. In addition, TOC and C/N values of the middle marsh at Two Tree Island were lower than observed in the Dartford Creek and Wat Tyler sites (Table 1). This variation may be related to the lower elevation of sampling stations, and thus absence of a developed high marsh. Increased tidal flux at the Two Tree Island middle marsh prevents the accumulation of organic matter by greater export of dissolved and particulate organic matter and macro-detritus (Boorman et al., 2000).

5. DISCUSSION

5.1 $\delta^{13}C$ and C/N characteristics of vegetation from coastal environments

Understanding the range and variability in $\delta^{13}C$ and C/N of end-member vegetation are fundamental to the interpretation of stable carbon isotope geochemistry from bulk sediments (Chmura et al., 1987; Chmura and Aharon, 1995; Malamud-Roam and Ingram, 2001). We combined the measured $\delta^{13}C$ and C/N values from three sites on the Thames Estuary and one site containing fen carr in the Norfolk Broads with vegetation sampled from salt marshes of Kent (Andrews, 2008), Humber Estuary (Lamb et al., 2007) and Mersey Estuary (Wilson et al., 2005a,b), from fen carr environments in Kent, East Sussex and the Norfolk Broads (Andrews, 2008), and from particulate organic matter of the Thames Estuary (Bristow et al., 2012) to create a regional database (n = 278) from central and southern England (Appendix 1). We find distinctions in $\delta^{13}C$ and

C/N values of aquatic, C_3 salt marsh, C_4 salt marsh, and leaf and wood tissue from fen carr vegetation within the vegetation database (Fig 6A).

Algae displayed a wide range in $\delta^{13}C$ values of -19.0 ± 8.1 ‰. This wide variation in $\delta^{13}C$ values reflects the salinity (and thus pH and dissolved CO_2) of the environment in which it was formed (Benedict et al., 1980; Keeley and Sandquist, 1992). Freshwater algae is reported to range from -30 to -26 ‰, while marine algae ranges from -23 to -16 ‰ (Lamb et al., 2006). Particulate organic matter measurements from Bristow et al. (2012) ($\delta^{13}C$: -20.1 ± 4.0 ‰; C/N: 9.6 ± 1.8) were similar to algal matter measured in this study, although they estimate that algal-derived organic matter only comprised a small proportion of the particulate organic matter pool in the Thames (<15 % of particulate organic carbon and nitrogen at sampling sites where $\delta^{13}C$ values > -17 ‰; Bristow et al., 2012). Instead, Bristow et al. (2012) indicate marsh plants and seagrasses contribute significantly to the particulate organic matter pool of the Thames. Aquatic (submergent vascular) vegetation, including seaweed and macroalgae, had mean C/N values of 9.2 ± 3.3. These relatively low C/N values are similar to the range of values for this vegetation type (C/N < 10) reported in other temperate regions by Meyers (1994) and Lamb et al. (2006). Tyson (1995) indicates that the low C/N of algal matter is due to moderate amounts of structural carbohydrates and greater concentrations of N-rich protein than is present in land plant tissue.

The greatest variation in the $\delta^{13}C$ of salt marsh vegetation occurred on the basis of the photosynthetic pathway utilized by each plant; the $\delta^{13}C$ of C_4 salt marsh vegetation (*Spartina* spp.) was -13.5 ± 0.8 ‰, while the $\delta^{13}C$ of C_3 salt marsh vegetation (all other species) was -26.8 ± 1.3 ‰. These values are consistent with measurements of C_4 and C_3

salt marsh plants found in other temperate regions (e.g., Smith and Epstein, 1970; 1971; Jackson et al., 1986; Chmura and Aharon, 1995). C_4 plants typically range in $\delta^{13}C$ from -17 ‰ to -9 ‰ (Chmura and Aharon, 1995) and have mutually exclusive values from C_3 plants (Smith and Epstein, 1971), which typically range from -32 ‰ to -21 ‰ (Deines, 1980). There was greater variability in the C/N of C_3 salt marsh vegetation (34.6 ± 20.7) in comparison to C_4 plants (27.4 ± 7.7), although this difference may be an artifact of the greater number of analyses of C_3 (n = 136) versus C_4 (n = 20) vegetation types. No consistent variations in $\delta^{13}C$ or C/N values of different plant species were found among vegetation types, and as Lamb et al. (2007) observed, no difference in $\delta^{13}C$ or C/N values existed between above- and belowground components of herbaceous C_3 or C_4 marsh vegetation in the combined dataset, which enables herbaceous vegetation to be characterized by one grouping (Fig 6A).

In contrast to salt marsh vegetation, C_3 freshwater vegetation showed variation between plant components. Leaf (16.3 ± 3.5) and wood (57.5 ± 15.3) components had distinct C/N values. This variation is related to the much greater proportion of N-devoid lignin in wood compared to leaves (Hedges et al., 1986; Tyson, 1995; Vane et al., 2013a). The $\delta^{13}C$ values of leaf (-31.2 ± 1.3 ‰) and wood (-30.2 ± 1.5 ‰) components, however, were relatively similar due to greater content of ^{13}C-depleted lipids in leaves and lignin in wood (Vane et al., 2013a). These values are in agreement with those found by Hedges et al. (1986), Muller and Mathesius (1999), Muller and Voss (1999) and Mackie et al. (2005). Freshwater vegetation had lower $\delta^{13}C$ values than C_3 salt marsh vegetation, which may be related to stress imposed on salt marsh vegetation from relatively greater ambient salinity (van Groenigen and van Kessel, 2002). Decreased stomatal conductance (the ‘openness’ of the stomatal aperture; Schlesinger, 1997), due to increased salinity stress causes more CO_2 inside the leaf to react with CO_2-fixing enzymes and less fractionation of isotopes to occur (Guy et al., 1980), causing plant $\delta^{13}C$ to increase (Farquhar et al., 1982; Guy and Reid, 1986). This variation in $\delta^{13}C$ may be of great importance in distinguishing C_3 plant types accumulating under saline and freshwater conditions.

5.2 $\delta^{13}C$, TOC and C/N characteristics of bulk sediments from coastal wetlands

We combined our $\delta^{13}C$, TOC and C/N bulk sediment values with analyses from coastal wetlands of the Mersey Estuary (Wilson et al., 2005a,b), Humber Estuary (Lamb et al., 2007), and Kent, East Sussex and Norfolk (Andrews, 2008) to create a regional database (n = 132) from central and southern England (Appendix 2). Two criteria were used to determine inclusion of studies into the database: (1) all studies must utilize identical sample preparation methods prior to analysis to thus minimize bias in comparison of $\delta^{13}C$ and C/N values (Brodie et al., 2011); and (2) information regarding the environment from which the sample was collected (i.e., tidal flat, low marsh, etc. or the dominant vegetation occupying the sampling site) and/or sample elevation must be given. Tidal flat/low marsh and middle/high marsh environments were grouped together because their range of values overlapped and were indistinguishable from one another on a statistical basis (ANOVA). However, we identified statistically significant differences in bulk sediment $\delta^{13}C$, TOC, and C/N values of tidal flat/low marsh (excluding sampling stations occupied by C_4 vegetation, *Spartina* spp.), middle/high marsh, reed swamp, and fen carr floral zones of the database (Table 2).

Tidal flat and low marsh sediments had $\delta^{13}C$ values of -24.9 ± 1.2 ‰, TOC values of 3.6 ± 1.7 %, and C/N values of 9.6 ± 1.0. The relatively high $\delta^{13}C$ and low TOC and C/N values of these sediments result from minimal incorporation of *in situ* vegetation cover into sediments, greater import of allochthonous particulate organic matter and algae, and high rates of minerogenic sedimentation (Wilson et al., 2005a) (Fig 6B). In addition, *in situ* organic matter from tidal flat and low marsh environments may be exported due to tidal action (Boorman, 2000; Bristow et al., 2012) or organic matter may be altered or broken down due to high rates of microbial activity, stimulated by greater nutrient import from particulate organic matter sources (Ember et al., 1987; Lamb et al., 2006; Kemp et al., 2010). Tidal flat and low marsh $\delta^{13}C$, TOC, and C/N values in the central/southern England database were similar to those from the Pacific coast of Oregon ($\delta^{13}C$: -24.1 ± 1.7 ‰, TOC: 2.5 ± 1.8 %, and C/N values of 10.4 ± 2.7; Engelhart et al., 2013) and northwest Europe (e.g., Waarde Marsh of SW Netherlands: $\delta^{13}C$ of -22.0 ‰; TOC of 1.2 %; C/N of 17; Middelburg et al., 1997). Conversely, $\delta^{13}C$ was lower and TOC and C/N were higher than sediments from the U.S. Atlantic coast (e.g., North Carolina: $\delta^{13}C$ of -17.6 to -16.2 ‰; TOC of 4.0 to 10.7 %; C/N of 14.8 to 16.1; Kemp et al., 2010, New Jersey: $\delta^{13}C$ of -18.9 to -15.4 ‰; TOC of 7.0 to 24.0 %; C/N of 12.1 to 17.3; Kemp et al., 2012; Massachusetts: $\delta^{13}C$ of -19.5 ‰; TOC of 5.6 %; C/N of 18.3; Middelburg et al., 1997). This difference with the tidal flats and low marshes of the U.S. Atlantic coast can be explained by the dominant occurrence of C_4 grasses (predominantly *Spartina alterniflora* and *patens*) and greater incorporation of vascular vegetation into sediments and/or reduced minerogenic input (Haines, 1967; Ember et al., 1987; Chmura et al., 1987; Chmura and Aharon, 1995; Middelburg et al., 1997; Kemp et al., 2010; 2012).

Sediments from the middle/high marsh zone had $\delta^{13}C$ values of -26.2 ± 1.0 ‰, TOC values of 9.8 ± 6.7 %, and C/N values of 12.1 ± 1.8. $\delta^{13}C$ values show little alteration from their autochthonous vegetation counterparts (Fig 6B), although lower TOC and C/N values suggest a secondary contribution to sedimentary organic matter from allochthonous marine or riverine particulate organic matter sources (C/N < 10; Meyers, 1994) (Fig 6B). High minerogenic sedimentation indicates transport of allochthonous material to the marsh surface, including marine and riverine dissolved and particulate organic matter (Boorman et al., 2000). Alternatively, diagenesis where immobile nitrogen is retained during subsequent loss of carbon through oxidation (Chmura et al., 1987; Ember et al., 1987) may explain why bulk sediment C/N values fall within the lower range of vegetation. The incorporation of fungal mycelium has also been shown to increase N, with a subsequent drop in C by 10 % in degraded material (Vane et al., 2001*)*. Mid/high marsh (absent of C_4 vegetation) $\delta^{13}C$ values of central/southern England were similar to those from Oregon ($\delta^{13}C$: -27.3 ± 1.4 ‰; Engelhart et al., 2013) and North Carolina ($\delta^{13}C$: -26.3 ± 2.1 ‰; Kemp et al., 2010), although TOC and C/N values were much lower than high marsh environments of Oregon (TOC: 12.4 ± 4.0 %, C/N: 13.6 ± 1.4; Engelhart et al., 2013) and North Carolina (TOC: 16.6 ± 11.6 %, C/N: 18.4 ± 2.3; Kemp et al., 2010), which is consistent with the minerogenic and organogenic nature of UK and U.S. marshes, respectively (Allen and Pye, 1992; Middelburg et al., 1997). The organic matter content of marshes varies between regions in part because colder temperatures and the shorter growing season in the UK limits biomass productivity, making mineral matter delivered by tides a more dominant source of sediment accumulation (Allen, 1990; Allen and Pye, 1992; French and Spencer, 1993; French, 1993; Middelburg et al., 1997). However, other local factors that affect mineral sediment deposition, such as the supply of mineral matter and distance to its source, vegetation type and density, barriers to surface flows, and post-depositional reworking and erosion by waves or tides, may also account for this regional variation in δ^{13}C, TOC and C/N values.

Sediments from the reed swamp zone had δ^{13}C values of -27.9 ± 0.7 ‰, TOC values of 36.5 ± 11.5 %, and C/N values of 13.9 ± 1.2. Although *Phragmites australis*, the dominant reed swamp vegetation, has plant tissues with δ^{13}C and C/N values within the same range as C_3 salt marsh vegetation, δ^{13}C, TOC and C/N values of sediments within this floral zone vary from those of the salt marsh. This variation may be explained by the reduced tidal influence on the *Phragmites* reed swamp zone. Sediments accumulating in this zone represent *in situ* vegetation, rather than a combination of *in situ* vascular vegetation and allochthonous marine or fluvial particulate organic matter and algae. Similar to the middle/high marsh, C/N values of bulk sediment are within the lower range of vegetation, which may be related to early diagenesis. *Phragmites* TOC and C/N values from the UK are consistent with those from a brackish transitional zone occupied by *Phragmites* in New Jersey (TOC: 23.9 ± 9.7 %, C/N: 13.8 ± 0.6; Kemp et al., 2012), but δ^{13}C values of -25.1 ± 2.0 ‰ from New Jersey (Kemp et al., 2012) are slightly higher. This trend is seen in the upland border in marshes of Massachusetts, where δ^{13}C values average -24.5 ‰, perhaps due to import of adjacent C_4 vegetation or increased salinity stress on *Phragmites* vegetation itself (Farquhar et al., 1989).

Fen carr bulk sediments had $\delta^{13}C$ values of -29.0 ± 0.6 ‰, TOC of 41.6 ± 5.7 %, and C/N values of 17.4 ± 3.1. Sedimentation in this zone is dominantly organogenic, indicated by high TOC values and $\delta^{13}C$ values representative of the C_3 freshwater vegetation that occupy this zone. $\delta^{13}C$ values of sediments from the fen carr fall within the higher range of $\delta^{13}C$ values of their modern vegetation counterparts (Fig 6B), which suggests the preferential degradation of lignin by white-rot and soft-rot fungi (Hatakka, 1994; Vane et al., 2003; Vane et al., 2005; Vane et al., 2006). Lignin tends to be 4 to 7 ‰ more depleted in $\delta^{13}C$ relative to bulk plant material (Benner et al., 1987), thus its preferential decay in sediments would cause $\delta^{13}C$ values to increase. C/N values of fen carr sediment were within the range of freshwater leaf material (Fig 6B), which indicates that most sedimentary organic matter is either primarily derived from leaves or that the woody material incorporated into sediments is significantly altered to cause a large drop in its C/N content, which is also consistent with the breakdown of N-devoid lignocellulosic compounds. Fen carr $\delta^{13}C$, TOC and C/N values from the UK were similar to upland sediments from Oregon ($\delta^{13}C$: > -28.5 ‰, TOC: 30 ± 4.6 %, C/N: 20.4 ± 3.7), although UK fen carr $\delta^{13}C$ values were much lower than those from freshwater environments from the San Francisco Bay (-27.7 to -23.3 ‰; Cloern et al., 2002), upland sediments from New Jersey (-26.5 to -25.1 ‰; Kemp et al., 2012) and freshwater marshes of Louisiana (average: -27.8 ‰). These discrepancies underscore the importance of regional- and/or site-specific investigations of the modern distribution of $\delta^{13}C$, TOC, and C/N bulk sediment values before interpretation of the sedimentary record (Engelhart et al., 2013).

5.3 The use of $\delta^{13}C$, TOC and C/N to produce sea-level index points from the Thames Estuary

We assess the use of the modern distribution of δ^{13}C, TOC, and C/N values from the UK (excluding samples with influence from C_4 *Spartina*) alongside microfossil indicators to produce three sea-level index points and limiting dates from core SW1 collected from the Swanscombe marshes on the southern shore of the River Thames (Fig 7). Cores SW1 suffers from microfossil preservations problems and, therefore, can only provide supporting data.

Sea-level index points delimit the unique position of RSL over time and space. The horizontal age component of an index point is obtained from radiocarbon dating of the sample and its associated 2σ calibrated age range. The vertical component of an index point is estimated using the indicative meaning of a sample, which describes its relationship to a tidal datum (e.g., mean high water spring tide, MHWST) at the time of deposition using the mid-point (reference water level, RWL) and range over which the indicator is found in the contemporary environment (indicative range). If a sample is deposited in a terrestrial environment, it is classified as a terrestrial limiting date, providing only an upper limit on the position of RSL. Shennan (1982, 1986) and Horton et al. (2000) established the indicative meaning for litho- and biostratigraphical sequences commonly used to produce sea-level index points (Table 3). We estimated the indicative meanings of dated transgressive/regressive contacts using δ^{13}C, TOC, and C/N values of middle/high marsh (δ^{13}C: -26.2 ± 1.0 ‰; TOC: 9.8 ± 6.7 %; C/N: 12.1 ± 1.8), reed swamp (δ^{13}C: -27.9 ± 0.7 ‰: TOC: 36.5 ± 11.5 %; C/N: 13.9 ± 1.2) and fen carr (δ^{13}C: -29.0 ± 0.6 ‰; TOC: 41.6 ± 5.7 %; C/N: 17.4 ± 3.1) environments (Table 2).

The transgressive contact between a peat with unidentifiable plant macrofossils and an overlying grey mud with organics at -4.76 m OD returned a date of 4138-3896 (median: 4017) cal yr BP (Fig 7B). Across the contact, $\delta^{13}C$ increased from -28 to -26 ‰, TOC decreased from 45 to 5 % and C/N fell from 21 to 15. This shift in values is consistent with a transition from *Phragmites* reed swamp to a tidal flat/marsh environment. Foraminifera and diatoms were absent from the peat between -5.30 and -5.10 m OD. But at the transgressive contact, foraminifera switched from an agglutinated to calcareous-dominated assemblage, which is consistent with a change in environment from the upper limits of tidal influence to a middle to low marsh or tidal flat environment (Horton and Edwards, 2006). Similarly, the diatom assemblages suggest an increase in salinity preference with the number of polyhalobous and mesohalobous taxa increasing and number of oligohalobous taxa decreasing across the contact (Reference for the diatoms – perhaps Juggins, 1992). Pollen is present within the peat and is dominated by ferns with *Corylus and Pinus,* and importantly *Chenopodium* at >15% abundance, reflecting the local presence of salt marsh vegetation (ref). The geochemical and microfossil data support Devoy's (1979) paleoenvironmental interpretation, which suggested a change in depositional environment from fenwood to reed swamp with open salt marsh communities at the transgressive contact. This contact is interpreted as a *Phragmites* or monocot peat directly above a clastic saltmarsh deposit (Shennan, 1986; Horton, 2000). Therefore, the RWL is MHWST - 20 cm with an indicative range of ± 20 cm (Table 2).

A bulk monocot peat overlain by a gray mud at the regressive contact at -7.14 m OD produced an age of 6573-6412 cal yr BP (median: 6523) (Fig 7C). $\delta^{13}C$ decreased across the contact from -26 to -29 ‰, TOC increased from 5 to 50 % and C/N increased from 21 to 26. The range of TOC and C/N values within the oak fenwood peat unit (Devoy, 1979) are higher than observed ranges of comparable modern environments (Fig 7E,F), but consistent with $\delta^{13}C$, TOC, and C/N values of Holocene oak fenwood settings found in the Humber Estuary (Fig 7E,F; Andrews, 2000). The $\delta^{13}C$, TOC, and C/N suggest a transition from a middle/high salt marsh to reed swamp or fen carr environment across the regressive contact. Foraminifera were not preserved, and diatoms were sparse with too few individuals to produce quantitative counts (n = ~10), although those preserved prefer saline to brackish environment, with little change across the contact. Undifferentiated fern spores dominate the pollen assemblage. The geochemical data support the inference of Devoy (1979) who suggested the regressive contact of the peat was indicative of sedge fen/reed swamp with local salt marsh communities. Therefore, we assigned this dated contact a RWL of a *Phragmites* or monocot peat directly below clastic salt marsh deposit (Shennan, 1986; Horton et al., 2000), which is (MHWST ± HAT)/2 - 20 cm and indicative range of ± 20 cm (Table 2).

A date of 7700-7580 (median: 7640) cal yr BP was obtained from a *Phragmites* fragment at the transgressive contact between a peat and mud at -9.56 m OD (Fig 7D). Across the contact, $\delta^{13}C$ increased from -29 to -27 ‰, TOC decreased from 50 to 10 %, and C/N fell from 26 to 15. TOC values are slightly higher than the modern range of reed swamp and fen carr environments, suggesting Holocene environments accumulated greater amounts of organic matter than their modern equivalents. Foraminifera and diatoms are absent from the peat and overlying mud, although diatoms between -9.40 and -9.10 m are dominated by polyhalobous and mesohalobous taxa indicative of a tidal flat environment. Pollen within the peat are dominated by *Alnus* and *Corylus,* with Poacea grass subdominant. The change in δ^{13}C, TOC, and C/N values is consistent with a transition in paleoenvironment from reed swamp to salt marsh conditions, which is in agreement with pollen analysis from this study and Devoy (1979). Devoy (1979) suggested the depositional environment at the transgressive contact was a sedge fen/reed swamp. We interpret this contact to represent an index point with a RWL of MHWST – 20 cm and indicative range of ± 20 cm (Table 2).

A wood fragment within an alder carr peat at -9.71 m OD was dated to 7817-7620 (median: 7718) cal yr BP (Fig 7D). δ^{13}C along the date ranged from -28 to -29 ‰, TOC ranged between 30 to 50 %, and C/N increased from 20 to 30. These values are consistent with modern fen carr environments, although again, core TOC values were slightly higher. Foraminifera and diatoms were absent from the peat, which was also palynologically sparse with only *Alnus* pollen and undifferentiated fern spores preserved. The δ^{13}C, TOC and C/N values permit interpretation of this dated wood to be a freshwater limiting point, which formed above MTL (Table 2).

The utility of δ^{13}C, TOC, and C/N in the production of Holocene sea-level index points is clearly illustrated in the application to Core SW1. Poor preservation of microfossils, an issue found elsewhere throughout the Thames Estuary (Devoy, 1979) and the UK (Horton et al., 2000; Metcalfe et al., 2000; Roberts et al., 2006), inhibited interpretation of stratigraphic contacts in the core. Based on lithology and plant macrofossils, inference could have been made on transgressive/regressive contacts in the core (e.g., Shennan and Horton, 2002), but in the absence of supporting information from microfossils, uncertainties would exist in our interpretation. δ^{13}C, TOC, and C/N values provide additional confidence in the interpretation of contacts within the core that are based on an extensive modern data set. Post-depositional change may be evident in the bulk sediment TOC and C/N values, although it is not prohibitive in the interpretation of radiocarbon dated sea-level data in Core SW1.

6. CONCLUSIONS

We investigated the use of $\delta^{13}C$, TOC, and C/N values from bulk sedimentary organic matter to reconstruct RSL and paleoenvironmental change by sampling vegetation and bulk sediment from modern transects at four coastal wetlands on the Thames Estuary and Norfolk Broads, UK. We reviewed published and unpublished studies from the UK to compile a bulk sediment stable carbon isotope geochemistry database from coastal wetlands of central and southern England. Tidal flat/low marsh, mid/high marsh, reed swamp and fen carr environmental zones had statistically distinct $\delta^{13}C$, TOC, and C/N values due to the relative amounts of *in situ* vegetation and tidal-derived allochthonous particulate organic matter and algae incorporated into sediments. Intra-site variability in sediment $\delta^{13}C$ values was observed related to variations in site salinity and the presence of the C_4 species *Spartina anglica*.

$\delta^{13}C$, TOC, and C/N values of tidal flat/low marsh ($\delta^{13}C$: -24.9 ± 1.2 ‰; TOC: 3.6 ± 1.7 %; C/N: 9.9 ± 0.8), middle marsh/high ($\delta^{13}C$: -26.2 ± 1.0 ‰; TOC: 9.8 ± 6.7 %; C/N: 12.1 ± 1.8), reed swamp ($\delta^{13}C$: -27.9 ± 0.7 ‰: TOC: 36.5 ± 11.5 %; C/N: 13.9 ± 1.2) and fen carr ($\delta^{13}C$: -29.0 ± 0.6 ‰; TOC: 41.6 ± 5.7 %; C/N: 17.4 ± 3.1) environments from the bulk sediment database (removing sites occupied by *Spartina* spp.) were used to interpret sequences from a Holocene sediment core with poor microfossil preservation collected from Swanscombe marshes on the Thames Estuary.

$\delta^{13}C$, TOC, and C/N were consistent with interpretations based on microfossils, where preserved. Holocene environments appeared to accumulate greater amounts of organic matter than their modern equivalents. Post-depositional change of bulk sediment $\delta^{13}C$, TOC, and C/N values did not prohibit paleoenvironmental interpretation. The geochemical dataset was used to estimate the indicative meanings of radiocarbon-dated samples in the core to produce three new sea-level index points and one terrestrial limiting date. We find that $\delta^{13}C$, TOC, and C/N of bulk sedimentary organic matter can together be used as an effective tool in the paleoenvironmental interpretation of Holocene sediments in the absence of microfossil indicators.

Figure 1. Location map showing study areas in the United Kingdom and along the Yare River and Thames Estuary and location of transects (black dotted line) at study sites in Dartford Creek (A), Wat Tyler Country Park Nature Reserve (B), Two Tree Island (C), and Ted Ellis Reserve (D).

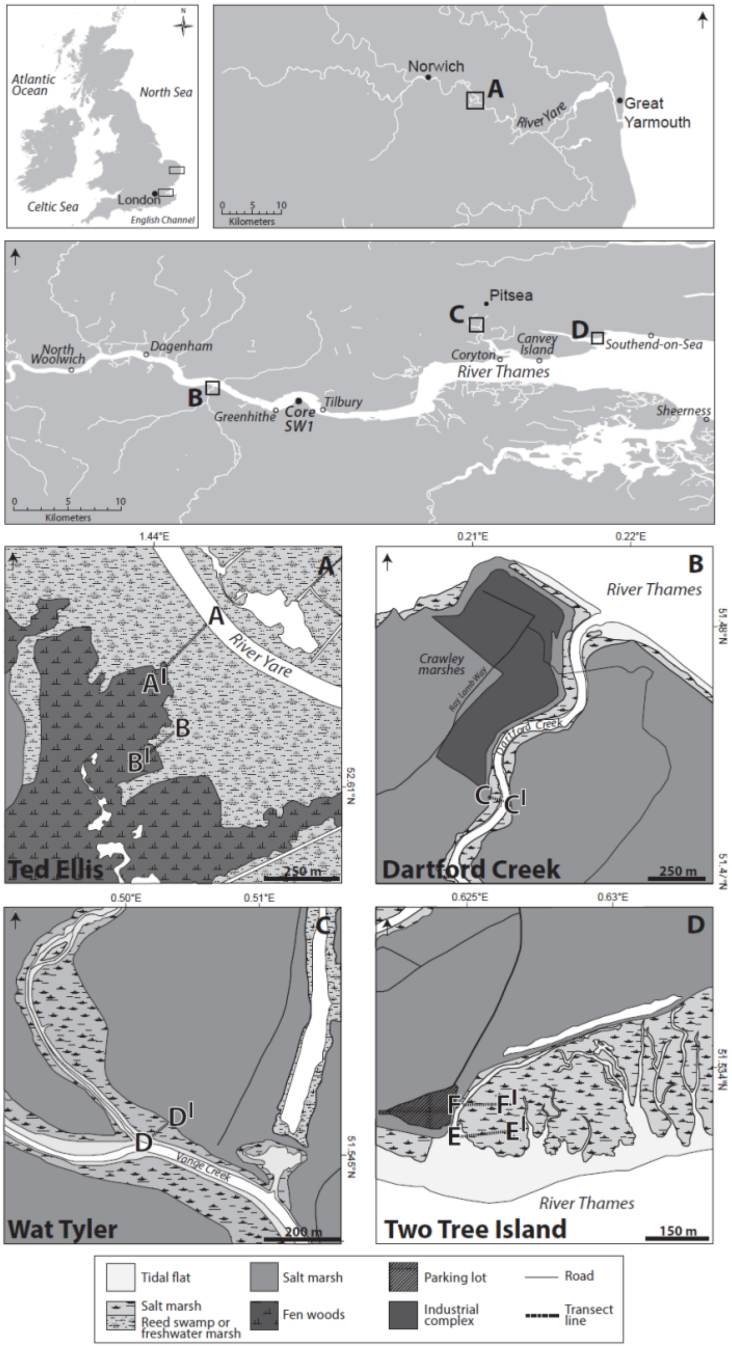


Figure 2. Transect A–A^1 at Dartford Creek. Elevation profile, floral zones, δ^{13}C values, total organic carbon (TOC) and C/N ratios are shown for bulk surface sediment samples along each transect.

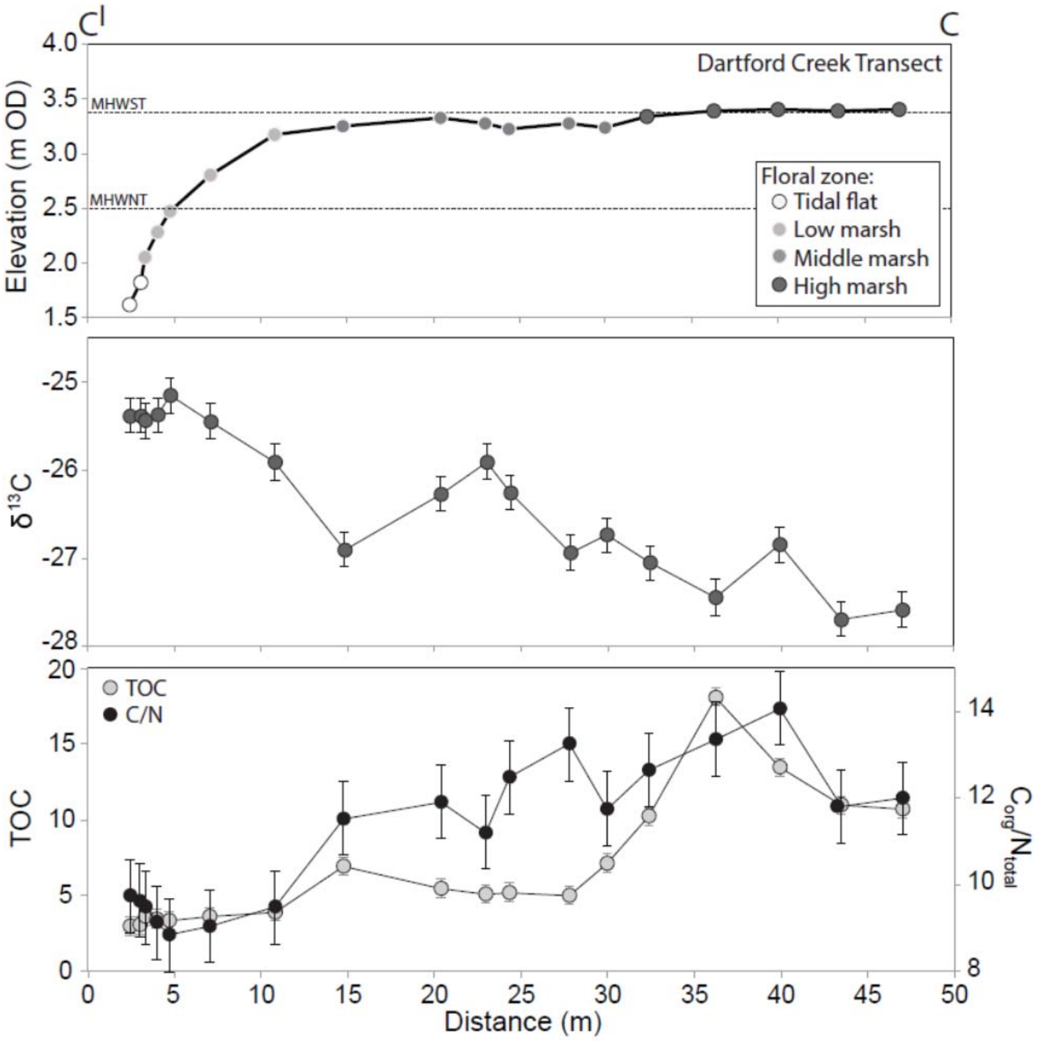


Figure 3. Transect B–B^1 at Wat Tyler Country Park nature reserve. Elevation profile, floral zones, δ^{13}C values, total organic carbon (TOC) and C/N ratios are shown for bulk surface sediment samples along each transect.

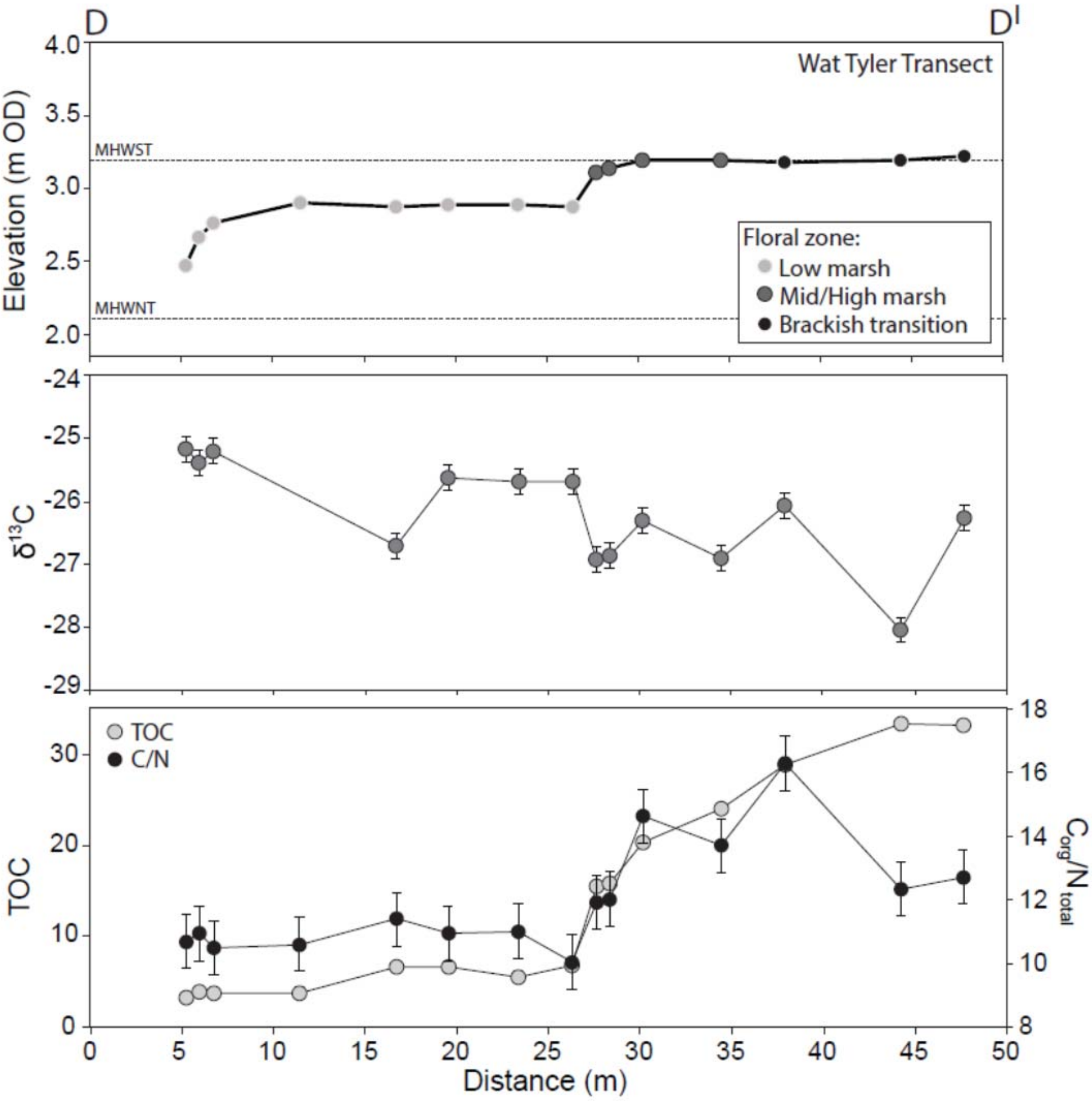


Figure 4. Transect 1 (C–C^1) and Transect 2 (D–D^1) at Two Tree Island. Elevation profile, floral zones, δ^{13}C values, total organic carbon (TOC) and C/N ratios are shown for bulk surface sediment samples along each transect.

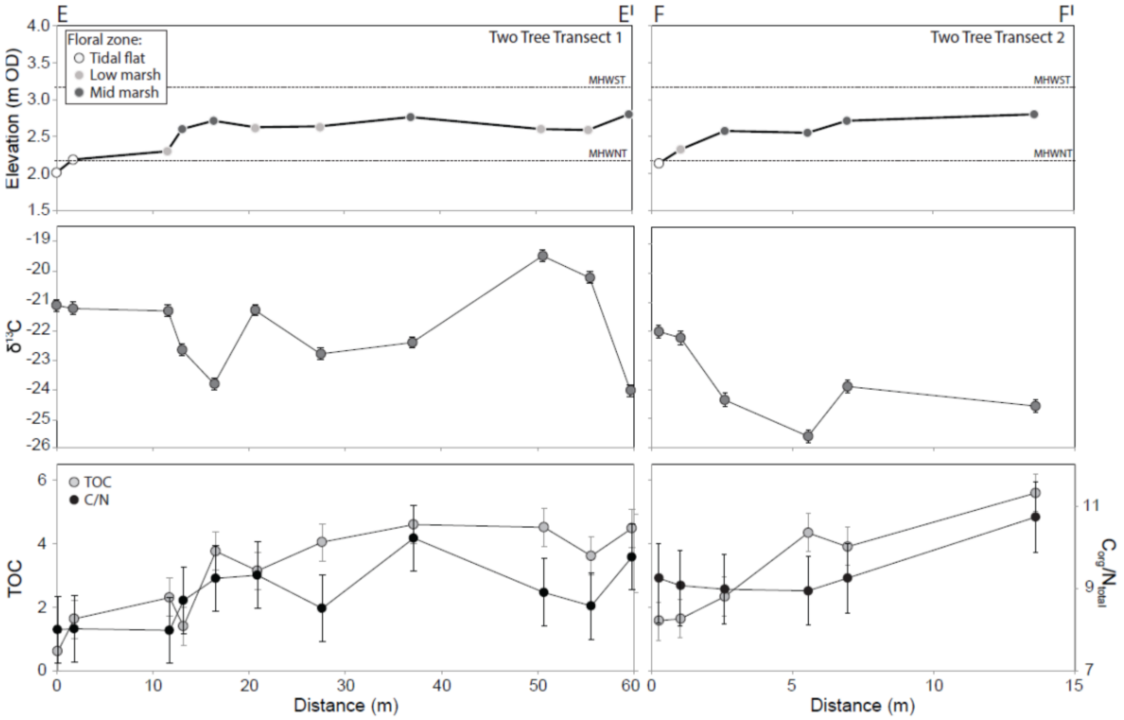


Figure 5. Transect 1 (E–E^1) and Transect 2 (F–F^1) at Ted Ellis nature reserve. Elevation profile, floral zones, δ^{13}C values, total organic carbon (TOC) and C/N ratios are shown for bulk surface sediment samples along each transect.

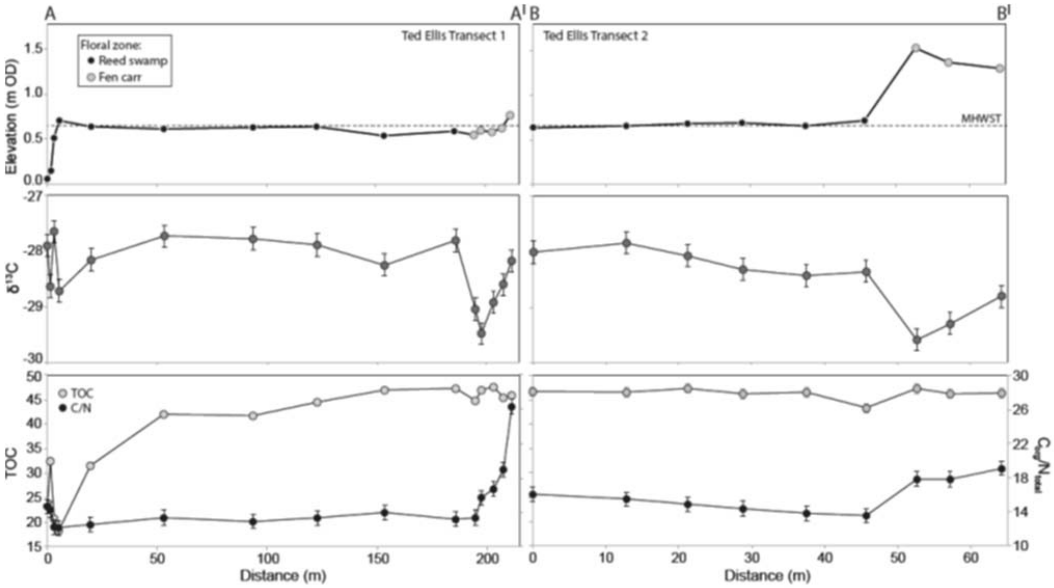


Figure 6. $\delta^{13}C$ and C/N of plants and surface sediments. (A) $\delta^{13}C$ and C/N of vegetation end-members grouped by the habitat or environment from which it was collected and the plant component analyzed. Aquatic vegetation includes brown and green algae and the genera *Fucus* and *Enteroporpha*. Salt marsh/reed swamp vegetation include the genera *Agrostis, Aster, Atriplex/Halimione, Borrichia, Cochleria, Elymus, Festuca, Limonium, Puccinellia, Phragmites, Salicornia, Scirpus, Seriphidium, Spartina, Spergularia, Suaeda,* and *Triglochlin.* Fen carr vegetation includes the genera *Alnus, Betula, Dryopteris, Rubus, Salix* and *Urtica.* Values come from this study and work by Wilson et al. (2005a,b), Lamb et al. (2007), Andrews (2009), and Bristow et al. (2012). Patterned boxes represent the mean ± 2 s.d. of each vegetation type: aquatic (light blue diagonal lines), particulate organic matter (dark blue diagonal lines), C4 salt marsh (orange diagonal lines), C_3 salt marsh (purple diagonal lines), C_3 freshwater leaves (red diagonal lines) and C_3 freshwater wood (green diagonal lines). Two samples with C/N > 100 were excluded from the plot. (B) $\delta^{13}C$ and C/N values of surface sediment from this study, grouped by depositional environment and superimposed on the ranges defined in (A). Note the change in C/N values on the x-axis.

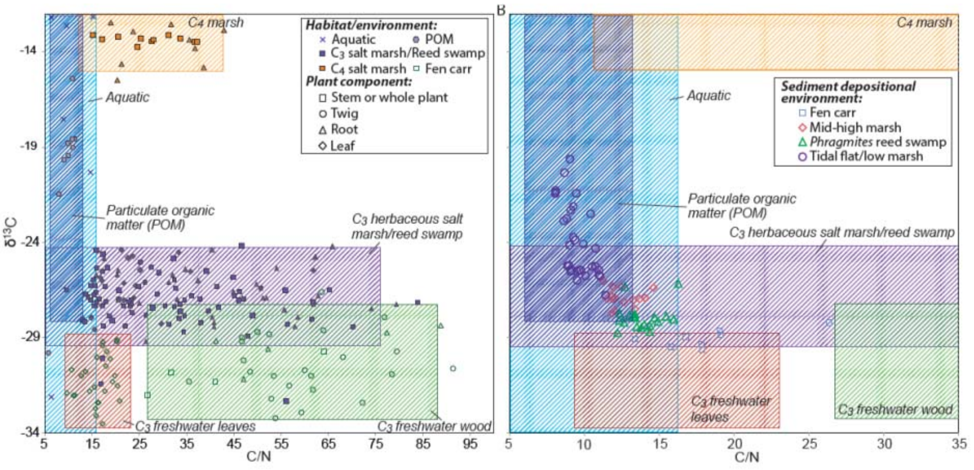
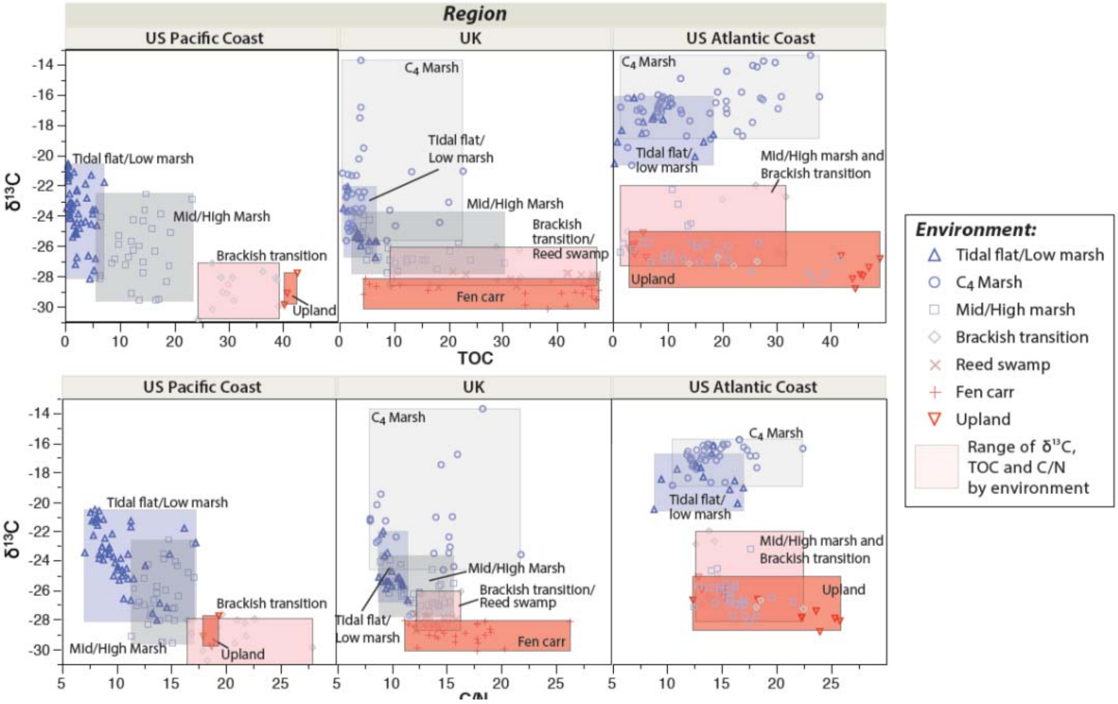
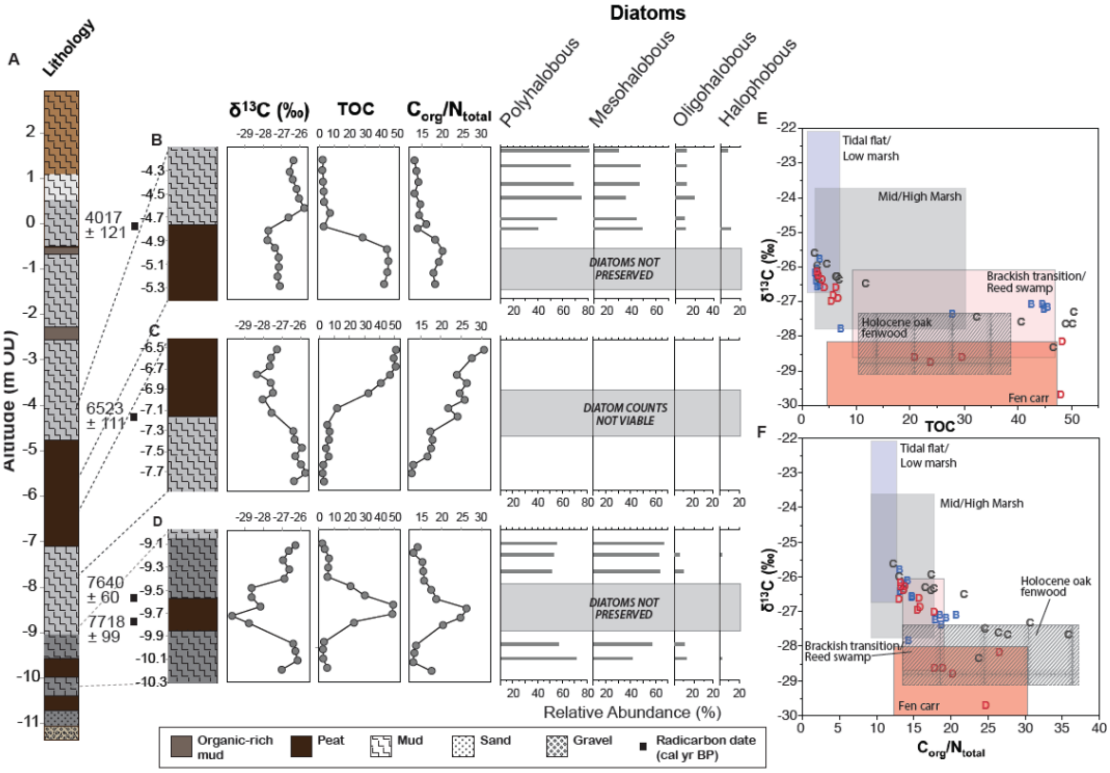


Figure 7. Derivation of sea-level index points from transgressive/regressive contacts in core SW1. A) Stratigraphy of core SW1. (B) Litho, chemo-, bio-, and chrono-stratigraphy of the transgressive contact at -4.76 m OD. (C) Litho, chemo-, bio-, and chrono-stratigraphy of the regressive contact at -7.14 m OD. (D) Litho, chemo-, bio-, and chrono-stratigraphy of the transgressive and regressive contacts at -9.56 and -9.71 m OD. (E) Comparison between modern range of bulk sediment δ^{13}C and TOC and SW1 core sediment. Shaded boxes represent full range of δ^{13}C and TOC values of each environment in the central/southern England database. (F) Comparison between modern ranges of δ^{13}C and C/N of bulk sediments and SW1 core sediment. Shaded boxes represent full range of δ^{13}C and C/N values of each environment in the central/southern England database.




A
Lithology
Altitude (m OD)
4017 ± 121
6523 ± 111
7640 ± 60
7718 ± 99
B
C
D
δ13C (‰)
TOC
Corg/Ntotal
Diatoms
Polyhalobous
Mesohalobous
Oligohalobous
Halophobous
DIATOMS NOT PRESERVED
DIATOM COUNTS NOT VIABLE
DIATOMS NOT PRESERVED
Relative Abundance (%)
Organic-rich mud
Peat
Mud
Sand
Gravel
Radicarbon date (cal yr BP)
E
Tidal flat/ Low marsh
Mid/High Marsh
Brackish transition/ Reed swamp
Holocene oak fenwood
Fen carr
TOC
F
Tidal flat/ Low marsh
Mid/High Marsh
Brackish transition/ Reed swamp
Holocene oak fenwood
Fen carr
Corg/Ntotal

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