1 # A stable carbon isotope geochemistry database to reconstruct

2 # Holocene relative sea levels and paleoenvironments, Thames

3 # Estuary, UK

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12 **ABSTRACT**

13 We examined the use of stable carbon isotope geochemistry (δ^{13}C, TOC and C/N)

14 of sedimentary organic matter to reconstruct former sea levels and paleoenvironments in

15 the absence of suitable microfossil data. The modern distribution of δ^{13}C, TOC and C/N

16 of 33 vegetation and 74 surface sediment samples collected from four coastal wetlands in

17 the Thames Estuary and Norfolk, UK are described. The stable carbon isotope

18 geochemistry of sediments varied in relation to the input of *in situ* vascular vegetation

19 versus allochthonous particulate organic matter and algae, which was controlled by tidal

20 inundation and salinity. We reviewed published and unpublished studies to produce a

21 central and southern England database of vegetation (n = 278) and bulk sediment (n =

22 132) stable carbon isotope geochemistry. Statistical analyses identified four elevation-

23 dependent environments in the stable carbon isotope geochemistry database: (1) tidal

24 flat/low marsh (δ^{13}C: -24.9 ± 1.2 ‰; TOC: 3.6 ± 1.7 %; C/N: 9.9 ± 0.8); (2) middle

25 marsh/high ($\delta^{13}C$: -26.2 ± 1.0 ‰; TOC: 9.8 ± 6.7 %; C/N: 12.1 ± 1.8); (3) reed swamp

26 ($\delta^{13}C$: -27.9 ± 0.7 ‰: TOC: 36.5 ± 11.5 %; C/N: 13.9 ± 1.2); and (4) fen carr ($\delta^{13}C$: -29.0

27 ± 0.6 ‰; TOC: 41.6 ± 5.7 %; C/N: 17.4 ± 3.1). The stable carbon isotope geochemistry

28 database was applied to a Holocene sediment core collected from the Thames Estuary to

29 produce three new sea-level index points and one limiting date, illustrating the utility of

30 $\delta^{13}C$, TOC, and C/N values to reconstruct Holocene relative sea levels.

31 **1. INTRODUCTION**

32 Reconstructions of Holocene relative sea level (RSL) provide important

33 constraints for calibrating geophysical models of Earth's rheology and glacio-isostatic

34 adjustment (GIA) (e.g., Lambeck et al., 1998; Engelhart et al., 2011; Milne and Peros,

35 2013). The ice sheet that formed over the British Isles at the Last Glacial Maximum

36 (LGM) was small in global terms, but large enough for GIA to produce vastly contrasting

37 patterns in RSL across the UK during the Holocene (e.g., Shennan, 1989; Shennan and

38 Horton, 2002; Shennan et al., 2006; Bradley et al., 2011). For example, RSL records from

39 Scotland, locations situated closer to the former ice sheet center, can display a mid-

40 Holocene highstand associated with isostatic rebound (e.g., Smith et al., 2002; 2012),

41 while RSL records in southeast England, including the Thames Estuary, show a

42 monotonic rise throughout the Holocene associated with subsidence of the proglacial

43 forebulge (e.g., Devoy, 1979, 1992; Long, 1992; Sidell et al., 2000).

44 Holocene variations in RSL in the Thames Estuary and elsewhere in the UK are

45 derived from sea-level index points mostly obtained from lithostratigraphic changes

46 between terrestrial and marine sediments (transgressive and regressive contacts). These

47 changes in lithology are corroborated by microfossils (e.g., foraminifera, diatoms,

48 pollen), which are used to delineate the initiation or removal of brackish and marine

49 conditions and to verify that the contacts are conformable (Tooley, 1985; Shennan,

50 1986). However, discrepancies and data gaps in RSL records still persist that limit

51 interpretation of the driving mechanisms of Holocene RSL dynamics in the Thames (e.g.,

52 Devoy, 1979; Shennan, 1989; Long, 1992, 1995; Haggart, 1995; Wilkinson et al., 2000;

53 Sidell et al., 2000; Sidell, 2003) and the UK (e.g., Shennan et al., 2006; Massey et al.,

54 2008; Gehrels, 2010). In part, this may be due to issues with preservation of identifiable

55 microfossils in Holocene archives that are associated with microfossil life processes and

56 post-depositional changes (e.g., Metcalfe et al., 2000; Roberts et al., 2006). Further, the

57 application of microfossil-based transfer functions (e.g., Horton et al., 1999), which have

58 expanded the type of sediments from which RSL estimates can be derived, have been

59 hindered by problems associated low sample counts and/or a lack of modern analogues

60 (e.g., Horton and Edwards, 2006). For example, of the 225 sea-level index points

61 collected as part of the Land Ocean Interaction Study of Holocene coastal evolution of

62 the east coast of England (Shennan and Andrews, 2000), only 52 were suitable for

63 transfer function analyses (Horton et al., 2000).

64   An alternative approach to RSL reconstruction has recently been explored that

65 utilizes the bulk stable carbon isotope geochemistry (stable carbon isotopes (δ^{13}C), total

66 organic carbon (TOC), and organic carbon to total nitrogen (C/N)) of sedimentary

67 organic matter) (e.g., Wilson et al., 2005a, 2005b; Mackie et al., 2005, 2007; Lamb et al.,

68 2007; Kemp et al., 2010, 2012b; Engelhart et al., 2013b). δ^{13}C and C/N are able to

69 differentiate sources of organic matter that characteristically accumulate in coastal

70 wetland sediments (Haines, 1977; Chmura and Aharon, 1995; Goñi and Thomas, 2000).

71   In particular, δ^{13}C and C/N can distinguish between freshwater and marine organic matter

72   (e.g., Fry et al., 1977; Fogel and Cifuentes, 1993) and C_3 and C_4 vegetation (e.g., Emery

73   et al., 1967; Malamud-Roam and Ingram, 2001). Plants that utilize the C_3 photosynthetic

74   pathway have distinct δ^{13}C values from those that use the C_4-pathway (Smith and Epstein,

75   1971) due to biochemical properties of their primary CO_2-fixing enzyme (Deines, 1980).

76   TOC measurements quantify the amount of organic matter contained within sediments

77   (e.g., Ostrowska and Porebska, 2012). The amount of organic matter contained in

78   sediments has traditionally been estimated using loss-on-ignition (LOI) (Ball, 1964),

79   although this method may over- or underestimate the total organic matter and carbon

80   content (Schumacher, 2002; Boyle, 2004). TOC values provide a direct measurement of

81   the amount of organic carbon contained within sediments (Veres, 2002).

82   Studies in the UK (e.g., Andrews et al., 2000; Wilson et al., 2005a, 2005b; Lamb

83   et al., 2007; Andrews, 2008) and the U.S. Atlantic (e.g., Kemp et al., 2010, 2012b), Gulf

84   (e.g., DeLaune, 1986; Chmura et al., 1987) and Pacific (e.g., Engelhart et al., 2013b)

85   coasts have demonstrated the distinct distribution of δ^{13}C and C/N values of modern tidal

86   flat, salt marsh and freshwater environments. However, expansion upon these studies is

87   needed to examine the boundary between salt marsh and reed swamp/fen carr

88   environments, which is important in the interpretation of transgressive/regressive contacts

89   in Holocene sequences of the UK. Furthermore, regional, inter-, or intra-site variability in

90   δ^{13}C and C/N distributions is not fully understood (Wilson et al., 2005a, 2005b; Lamb et

91   al., 2007).

92   Here, we examine the distribution of δ^{13}C, TOC and C/N of vegetation and

93   sedimentary organic matter within coastal wetlands of the Thames Estuary and Norfolk

94   Broads, UK. We compare our data to published and unpublished studies from central and

95   southern England to produce a database of $\delta^{13}C$, TOC and C/N values. We apply the

96   database to a Holocene sediment core collected from Swanscombe Marsh on the Thames

97   Estuary with poor microfossil preservation to produce new sea-level data. We find the

98   effect of post-depositional processes on $\delta^{13}C$, TOC, and C/N is not prohibitive in

99   paleoenvironmental interpretation, thus this method can be used to reconstruct Holocene

100   RSL in the UK and other temperate regions.

101   **2. STUDY AREA**

102   The modern Thames Estuary drains an area of ~16,000 km^2 of England into the

103   North Sea (Fig. 1). The tidal portion of the estuary is approximately 110 km long, with

104   the seaward limit extending ~80 km downstream and the tidal limit occurring

105   approximately ~30 km upstream from the London Bridge (Mitchell et al., 2012). The

106   estuary is macrotidal with spring tidal range varying from 5.2 m near the mouth of the

107   estuary in Sheerness to 6.6 m at the London Bridge (Admirality Tide Tables, 2013).

108   Salinity ranges from <1 at the tidal limit to ~32 at the estuary mouth at half-tide (time or

109   state halfway between flood and ebb) (Juggins, 1992), although large variations occur

110   during the tidal cycle as well as seasonally (Mitchell et al., 2012).

111   Undisturbed areas of coastal wetland habitat are limited in the region, because of

112   human modifications, changes in wave and wind climate (van der Wal and Pye, 2004)

113   and RSL rise (Woodworth et al., 2009). These anthropogenic and climate driven changes

114   pose difficulties in locating suitable areas along the estuary to use as an analogue for

115   Holocene salt marsh, reed swamp and fen carr paleoenvironments (Devoy, 1979). We

116   tried to minimize these factors by confining our study sites to nature reserves or

117   maintained marshes where well-developed successions of wetland floral zones were

118   readily identifiable. Three sites on the Thames Estuary (Dartford Creek, Wat Tyler

119   Country Park and Two Tree Island) and one site containing fen carr in the Norfolk

120   Broads (Ted Ellis Nature Reserve) were chosen for study. The species composition of

121   marsh floral zones in our study sites are representative of the low marsh (van der Wal and

122   Pye, 2004) and high marsh (Boorman, 2003) communities that are characteristic of

123   southeast England. With the exception of introduced C_4 *Spartina* (Ranwell, 1972), all

124   other vegetation follows the C_3 photosynthetic pathway. Fen carr environments occur in

125   waterlogged conditions (McVean, 1956) and commonly develop as a consequence of

126   increasing tidal influence or elevated groundwater level associated with sea-level rise

127   (e.g., Walker, 1970; Long and Innes, 1995; Waller et al., 2005).

128   The study site situated at Dartford Creek, a tributary of the Thames Estuary, is

129   part of the Crawley marshes (Fig 1A). Porewater salinity at the site ranged from 26 to 32.

130   One transect (A-A[1]; Fig 1A) of 18 stations was established that extended through

131   unvegetated tidal flat and low, middle, to high marsh floral zones. The low marsh was

132   inhabited by *Puccinellia maritima, Spergularia* spp., and in localized depressions

133   *Eleocharis* sp. The middle-high marsh was dominated by *Elymus repens* and *Festuca*

134   *rubrum,* with *Spergularia* spp. present. The transition to upland vegetation was absent

135   from this site due to levee construction.

136   The Wat Tyler Country Park nature reserve is located north of Canvey Island in

137   Pitsea. One ~40 m transect (B-B[1]; Fig 1B) of 15 stations was sampled that encompassed a

138   full range of successional environments from tidal flat, low, middle to high marsh, and

139   brackish, upland transition. Porewater salinity at the site ranged from 27 to 34. Tidal flat

140 sediments were unvegetated. Low marsh vegetation included *Aster tripolium* and

141 *Salicornia europaea.* The middle marsh was inhabited by *Halimione portulacoides* and

142 *Puccinellia maritima.* The high marsh was occupied by *Festuca rubra* and *Halimione*

143 *portulacoides*, and a brackish transition zone occupied by *Phragmites australis* occurred

144 at the upper boundary of the marsh.

145   The final study area from the Thames Estuary is located in the marshes of Two

146 Tree Island, east of Canvey Island, forming part of the Leigh National Nature Reserve.

147 Porewater salinity at this site was between 34 and 37. Two transects (C-C[1]; D-D[1]; Fig

148 1C) of 11 and 6 sampling stations, respectively, were established to account for

149 variability between low marsh environments colonized by the introduced C_4 grass

150 *Spartina anglica.* The occurrence of this species will enable distinction among low, high

151 and upland transition environments due to its discrete values from C3 vegetation, but the

152 species is not represented in Holocene sedimentary archives (Long et al., 1999). Both

153 transects extend through tidal flat, low marsh and middle marsh zones. The low to

154 pioneer marsh hosts *Salicornia europaea* and *Spartina anglica.* The middle marsh is

155 dominated by *Festuca rubra, Halimione portulacoides, Aster tripolium, Borrichia*

156 *fructescens* and *Suaeda maritima.* Washed-in algae and seaweed (*Fucus vesiculosus)*

157 were present throughout the marsh. Transect 2 (D-D[1]) was positioned to avoid sampling

158 sediments occupied by *Spartina*. Leveeing further inland prevented the formation of high

159 marsh, brackish transitional and upland communities.

160   The Ted Ellis Nature Reserve, situated southeast of Norwich along the southern

161 bank of the River Yare in the Norfolk Broads, contains a variety of wetland habitats.

162 Porewater salinity at the site is < 0.5. Two transects were sampled from this site (Fig 1D).

163   The first transect (E-E[1]) was 215 m long with 15 stations and extended from a reed

164   swamp dominated by *Phragmites australis* and *Phalaris arundinacea* with *Carex* spp.

165   present at the banks of the Yare to a *Salix*-dominated fen carr environment. The second

166   transect (F-F[1]) was 70 m long with 9 stations and incorporated reed swamp and *Alnus*-

167   dominated fen carr environments.

168   **3. METHODS**

169   Sampling stations were positioned to maintain consistent vertical spacing (~ 3-5

170   cm) between each station along each transect. A total station was used to survey stations

171   and core locations to a common reference datum (m Ordnance Datum; OD), which was

172   determined using a Leica differential geographic positioning system with real-time

173   kinematic capabilities. Tidal datums at all Thames Estuary sites were interpolated from

174   the nearest tide gauge stations (Admiralty Tide Tables, 2013). Tidal datums at Ted Ellis

175   Reserve were inferred from stream gauge readings maintained by the Environment

176   Agency.

177   *3.1 Modern vegetation and sediment*

178   The vegetation cover at each sampling station was recorded (estimated percentage

179   of total coverage) and the dominant vegetation (above- and belowground components)

180   was sampled (n = 33) to provide context for the $\delta^{13}C$ and C/N of surface sediments

181   (Chmura and Aharon, 1995; Malamud-Roam and Ingram, 2004). Seventy-four 10 cm^2 x

182   1 cm surface sample were collected for analysis of $\delta^{13}C$, TOC, C/N at each sampling

183   station. Salinity was measured using a calibrated refractometer at the time of sample

184   collection. When the sample was not wet enough for the measurements, porewater was

185   separated by centrifuge from the samples in laboratory and its salinity was measured

186   (Horton et al., 1999; Sawai et al., 2004).

187   ***3.2 Collection of Core SW1***

188   During a drilling campaign conducted by the British Geological Survey, a series

189   of sediment cores from locations in the mid- and lower-estuary were collected. One core

190   from Swanscombe Marsh (Core SW1) was selected for analysis in this study because it

191   represented the full series of transgressive/regressive sequences recognized by Devoy

192   (1979) in his type-site at Tilbury. A drilling rig employing a 'wireline' percussion tripod

193   arrangement (also known as 'shell and auger') was used to retrieve core SW1. The

194   recovered core was capped and sealed in the field and immediately refrigerated at 4 ºC.

195   The core was described in the laboratory using the Troels-Smith (1955) method for

196   organic-rich sediments.

197   ***3.3 Carbon and nitrogen bulk organic geochemistry of modern and core samples***

198   Sample pretreatment for $\delta^{13}C$, TOC and C/N analysis followed Vane et al.

199   (2013a). Plant samples were treated with 5% HCl for 2 hours, rinsed with deionized

200   water, dried in an oven at 50°C and freezer-milled to a fine powder. Sediment samples

201   were treated with 5% HCl overnight to remove inorganic carbon, and were subsequently

202   rinsed with at least 1500 ml of deionized water, dried in an oven at 50°C and milled to a

203   fine powder using a pestle and mortar. $^{13}C/^{12}C$ analyses were performed by combustion in

204   a Costech Elemental Analyzer coupled online to an Optima dual-inlet mass spectrometer

205   at the NERC Isotope Geosciences Laboratory, Nottingham, UK. The values were

206   calibrated to the Vienna Pee Dee Belemnite (VPDB) scale using within-run cellulose

207   standard Sigma Chemical C-6413 calibrated against NBS19 and NBS 22 (Vane et al.,

208   2013b) that was included within the runs. Sample total organic C and total N were

209   measured on the same instrument. C/N ratios were calibrated with an acetanilide standard

210   and are given as a weight percentage (Vane et al., 2013b). Replicate analysis on well-

211   mixed samples indicates analytical precision of <0.1 ‰. Core SW1 was analyzed for

212    $\delta^{13}C$, TOC, and C/N at 8 cm intervals continuously throughout the core. The $\delta^{13}C$, TOC

213   and C/N of modern vegetation and bulk sediments (including the databases), and Core

214   SW1 data can be found in Appendices 1 and 2.

215   *3.4 Microfossil analysis of Core SW1*

216   Microfossil (diatom, foraminifera, pollen) analysis was undertaken on Core SW1

217   to support, where possible, paleoenvironmental changes inferred from $\delta^{13}C$, TOC, and

218   C/N. We sampled for diatom and foraminiferal above and below radiocarbon-dated

219   contacts of Core SW1; pollen counts were performed only on the sediment at dated

220   horizons. All samples for diatom analysis under light microscopy were prepared

221   following standard methods (Zong and Horton, 1998, 1999). Diatoms were identified and

222   enumerated under 1000× magnification using the keys of Hartley et al. (1966), van de

223   Werff and Huls, (1958-1966) and Patrick and Reimer (1966-1975). Classification of

224   salinity and life form follows Denys (1991/2) and Vos and Wolf (1993). Sample

225   preparation, identification and classification of foraminifera followed Horton and

226   Edwards (2006). Wet counts were completed under a binocular microscope. A minimum

227   of 200 diatom and foraminifera were counted per sample where possible. Clay-rich

228   sediments were prepared for pollen following the technique of Riding and Kyffin-Hughes

229   (2004) and peat samples were prepared for pollen by disaggregation with potassium

230   hydroxide. Pollen was grouped into five broad physiognomic categories: trees, shrubs,

231 herbs, aquatics and pteridophytes. Calculation of individual taxa is expressed as

232 percentage of the total sum of land pollen. The microfossil data from Core SW1 can be

233 found in Appendix 3.

234 *3.5 Radiocarbon age determination*

235 Radiocarbon (^{14}C) dates were selected to produce new sea-level data from Core

236 SW1 (Table 1). Three identifiable plant macrofossils inferred to be deposited *in situ* were

237 selected for Accelerator Mass Spectrometry (AMS) radiocarbon dating. Prior to analysis,

238 the samples were cleaned under a binocular microscope to remove contaminating

239 material, such as older adhered organic sediment from the matrix surrounding the

240 macrofossil or younger ingrown rootlets (Kemp et al., 2013b). In the absence of datable

241 macrofossil remains, one date was obtained from bulk peat substrate at -7.14 m OD.

242 Reported radiocarbon ages were calibrated to sidereal years with a 2σ confidence interval

243 using the IntCal13 calibration curve (Reimer et al., 2013) and a laboratory multiplier of 1.

244 Ages are presented as calibrated years (cal yr) before present (BP), where the zero point

245 is AD 1950 (Stuiver and Polach, 1977).

246 *3.6 Statistical analysis*

247 One-way Analysis of Variance (ANOVA) and Nested ANOVA was performed on

248 the sediment database (excluding sites occupied by C$_4$ *Spartina*) to detect significant

249 differences in mean δ^{13}C, TOC, and C/N values, and inter-site variability in the δ13C,

250 TOC, and C/N values of depositional environments, respectively. Analysis was

251 completed in JMP 10.0 with "environment" as the grouping factor (Table 2).

252 "Environment" was defined by the environmental zones present in the study areas: tidal

253 flat/low salt marsh, middle/high marsh, reed swamp and fen carr. Data were log-

254 transformed where necessary to meet assumptions of ANOVA (equal variance,

255 normality). Tukey's HSD was used to identify differences among multiple means when a

256 significant effect was found.

257 **4. RESULTS**

258 *4.1 Characteristics of modern vegetation*

259   Thirty-three vegetation samples from tidal flat, low, middle and high marsh, and

260 reed swamp environments were analyzed for δ^{13}C and C/N composition. The mean δ^{13}C

261 of all samples was -25.4 ‰, ranging from -32.1 to -13.1 ‰. The mean C/N of all samples

262 was 38.2, spanning values of 6.3 to 122.4.

263   Marine and tidal flat end-member vegetation samples (n=2), including brown

264 algae and *Fucus vesiculosis,* had a mean δ^{13}C of -26.2 ‰, which ranged from -32.1 to -

265 20.3 ‰. The mean C/N of these samples was 10.5, with values from 6.3 to 14.6.

266   Vegetation end-members collected from low marsh environments (n=13),

267 including *Aster tripolium, Borrichia fructescens, Cochleria spp., Puccinellia maritima,*

268 *Salicornia europaea, Spartina anglica*, and *Sueada maritima*, had mean δ^{13}C and C/N

269 values of -24.6 ‰ and 30.5, respectively. δ^{13}C values ranged from -30.0 (*Salicornia*

270 *europaea*) to -13.1 ‰ (*Spartina anglica*), and C/N spanned values from 12.0 (*Sueada*

271 *maritima*) to 61.9 (*Borrichia fructescens*).

272   Middle to high marsh end-member vegetation (n=14), including *Agrostis*

273 *stolonifera, Elymus repens, Festuca rubra, Halimione portulacoides, Scirpus maritimus*,

274 and *Spergularia media*, had a mean δ^{13}C of -26.0 ‰, which varied between -28.6

275 (*Halimione portulcoides*) and -24.1 ‰ (*Festuca rubra*). Mean C/N was 48.8, with values

276 ranging from 15.5 (*Halimione portualcoides*) to 122.5 (*Agrostis stolonifera*).

277   Vegetation end-members collected from reed swamp environments (n=3),

278   including *Phragmites australis* and *Carex* sp., had mean $\delta^{13}C$ and C/N values of -25.3

279   and 41.3 ‰, respectively. $\delta^{13}C$ fell between -26.5 (*Carex* sp.) and -24.6 ‰ (*Phragmites*

280   *australis)*, and C/N values ranged from 30.6 (*Carex* sp.) to 61.7 (*Phragmites australis*).

281   ***4.2 Characteristics of modern sediments***

282   Seventy-four surface sediment samples were analyzed for $\delta^{13}C$, TOC and C/N

283   composition. The mean $\delta^{13}C$ of all samples was -26.1 ‰, ranging from -29.6 to -19.5 ‰.

284   The mean TOC of all samples was 18.7 %, spanning values from 0.6 to 47.6 %. The

285   mean C/N of all samples was 12.2, extending from 8.0 to 26.4.

286   *4.2.1 Dartford Creek Transect*

287   The Dartford Creek transect (Fig 2) covered tidal flat, low, middle and high marsh

288   zones from an elevation of 1.63 to 3.40 m OD. The tidal flat/low marsh zone (n = 7) had

289     $\delta^{13}C$, TOC, and C/N values of -25.9 to -25.1 ‰, 3.0 to 3.9 % and 8.8 to 9.7, respectively.

290     $\delta^{13}C$ decreased with distance landward in the middle-high marsh zone (n = 11) from -25.9

291   ‰ at the boundary with the low marsh to -27.7 ‰ at the edge of the high marsh. TOC

292   values increased from the middle to high marsh from 7.0 to 18.0 %. C/N values increased

293   with distance along transect in the middle-high marsh with a minimum of 11.5 at ~ 12 m

294   to a maximum of 14.1 at ~ 37 m along the transect.

295   *4.2.2 Wat Tyler Transect*

296   The transect at Wat Tyler (Fig 3) incorporated low, middle and high marsh and

297   *Phragmites* brackish transition environments ranging in elevation from 1.73 to 3.22 m

298   OD. The tidal flat/low marsh zone (n = 8) had $\delta^{13}C$ values between -26.7 to -25.2 ‰.

299   TOC values in this zone increased from 3.3 % to 6.9 % at 26 m along the transect in the

300   low marsh. C/N values exhibited a similar pattern to TOC; C/N increased in the pioneer

301   to low marsh from 10.1 to 11.4. The δ^{13}C values of the middle/high marsh zone (n = 4)

302   are lower than the tidal flat/low marsh zone, ranging from -26.9 to -26.3 ‰. TOC values

303   increased in the middle/high marsh from 15.5 % at 28 m to 24.0 % at 36 m along the

304   transect. C/N values also generally increased in this zone from a minimum of 11.9 to a

305   maximum of 14.6 at 32 m along the transect. δ^{13}C values in the *Phragmites* environment

306   (n=3) varied between -28.0 and -26.1 ‰. TOC values increased from 28.8 % at the

307   boundary between middle and high marsh to 33.4 % at the landward edge of the transect.

308   *4.2.3 Two Tree Transects 1 and 2*

309   Two Tree Transect 1 incorporates tidal flat and low and middle marsh

310   environments (Fig 4), with undulating topography due to dissecting tidal creeks and

311   drainage ditches. The transect extends from 2.00 to 2.80 m OD in elevation. The tidal

312   flat/low marsh zone (n = 6) had a mean δ^{13}C, TOC and C/N of -20.8, 2.6 % and 8.5,

313   respectively. Compared to the tidal flat/low marsh zone, the middle marsh zone (n = 5)

314   had a lower mean δ^{13}C (-23.1 ‰), higher mean TOC (3.7 %,) and and higher mean C/N

315   (9.4).

316   Two Tree Transect 2 also included tidal flat, low and middle marsh environments,

317   but lacked much of the undulating topography of Transect 1 (Fig 4). The transect ranged

318   from 2.13 to 2.79 m OD (between MHWNT and 0.29 m below MHWST). δ^{13}C values

319   increase with distance along transect from a minimum of -22.0 ‰ in the tidal flat/low

320   marsh (n = 2) to a maximum of -25.1 ‰ at ~ 7 m along the transect in the middle marsh

321   (n = 4). TOC values exhibited a similar pattern, with a minimum TOC of 1.6 % in the

322 tidal flat/low marsh, increasing to a maximum value of 5.6 % at the landward edge of the

323 transect in the middle marsh. C/N values also increased with distance along transect from

324 a minimum of 9.1 in the tidal flat/low marsh to a maximum of 10.7 at the landward edge

325 in the middle marsh.

326 *4.2.4 Ted Ellis Transects 1 and 2*

327 Ted Ellis Transect 1 (Fig 5) extends from the vegetated banks of the River Yare,

328 across a reed swamp to a fen carr. Sampling stations cover elevations from 0.05 to 0.78 m

329 OD. The reed swamp (n = 10) had a mean $\delta^{13}C$ of -28.1 ‰. The banks and river levee

330 showed the greatest variability within the reed swamp with values between -28.7 and -

331 27.7 ‰. Mean TOC of the reed swamp was 34.9 % with the minimum of Transect 1 of

332 18.3 % occurring along the riverbanks. TOC increased with distance inland, obtaining a

333 maximum of 47.2 % at ~ 160 m along the transect. C/N values within the reed swamp

334 had a mean of 13.3. The fen carr (n = 5) had a mean $\delta^{13}C$ of -28.8 ‰, which increased

335 from the transect minimum of -29.5 to -28.2 ‰ at the landward edge of the fen carr. The

336 mean TOC within the fen carr was 46.1 %, including the maximum observed on Transect

337 1 of 47.6 %. C/N increased within the fen carr from 13.4 to the maximum of Transect 1

338 of 26.4 at its landward edge.

339 Ted Ellis Transect 2 is located further inland from the River Yare than Transect 1

340 and, therefore, was found at a slightly higher elevation of 0.45 to 1.34 m OD (Fig 5).

341 Transect 2 covered reed swamp and fen carr environments. The reed swamp (n = 6) had a

342 mean $\delta^{13}C$ of -28.2 ‰ and a mean TOC value of 46.1. C/N values decreased with

343 distance along transect from 16 at the beginning of the transect to 13.5 (the minimum of

344 Transect 2) at the boundary with the fen carr. At the boundary between the fen carr (n =

345   3) and reed swamp, δ^{13}C was at a minimum of -29.6 ‰ and increased with distance

346   inland to -28.8 ‰. The TOC mean was 46.6 % in the fen carr. There was an increase in

347   C/N from values of the reed swamp with a mean of 18.3.

348   *4.2.5 Site specific variations of modern sediments*

349   The three sites on the Thames Estuary and one site containing fen carr in the

350   Norfolk Broads display site-specific variations in δ^{13}C, TOC and C/N values of bulk

351   sediments from sites on the Thames Estuary (Table 2). In particular, the tidal flat/low

352   marsh and middle/high marsh sediments of Two Tree Island differed from those of the

353   Dartford Creek and Wat Tyler sites. We infer that these differences in δ^{13}C values are

354   related to salinity variations among sites. Porewater salinity of sampling stations at Two

355   Tree Island ranged from 34 to 37, while at Dartford Creek and Wat Tyler, salinity was 26

356   to 34. Middelburg and Herman (2007) measured the δ^{13}C of suspended organic matter in

357   relation to a salinity gradient along the Thames Estuary and found increasing δ^{13}C with

358   increasing salinity. Coincidently, salinity levels of > 34 corresponded to δ^{13}C values of

359   particulate organic matter of -22 to -20 ‰, and salinity levels of 26-34 corresponded to

360   δ^{13}C values between -26 and -24 ‰, which agrees well with the range in tidal flat/low

361   marsh sediments at the Two Tree Island (-21.1 ± 0.9) and Dartford Creek/Wat Tyler sites

362   (-25.4 ± 0.2 ‰ and -25.6 ± 0.5 ‰), respectively. The presence of C_4 *Spartina anglica*

363   (δ^{13}C = -13.2 ‰) at Two Tree Island contributes to its relatively high δ^{13}C values,

364   although it cannot entirely explain the variation between sites, because Transect 2 at the

365   site was positioned to avoid sampling sediments colonized by *Spartina* spp., and its

366   sediment δ^{13}C values ranged between -22.2 to -25.1 ‰. Although this range is slightly

367   lower than sampling stations on Transect 1 occupied by *Spartina* (which ranged from -

368   19.5 to -23.8 ‰), it is still higher than the $\delta^{13}C$ values of > -25.0 ‰ present at the

369   Dartford Creek and Wat Tyler sites. Likely a combination of these two factors resulted in

370   the observed inter-site variability, although we cannot rule out that mixing of

371   anthropogenic pollution from historical events at Two Tree Island (Scrimshaw and Lester,

372   1995) could also cause a shift in observed $\delta^{13}C$ values. In addition, TOC and C/N values

373   of the middle marsh at Two Tree Island were lower than observed in the Dartford Creek

374   and Wat Tyler sites (Table 1). This variation may be related to the lower elevation of

375   sampling stations, and thus absence of a developed high marsh. Increased tidal flux at the

376   Two Tree Island middle marsh prevents the accumulation of organic matter by greater

377   export of dissolved and particulate organic matter and macro-detritus (Boorman et al.,

378   2000).

379   **5. DISCUSSION**

380   ***5.1 $\delta^{13}C$ and C/N characteristics of vegetation from coastal environments***

381   Understanding the range and variability in $\delta^{13}C$ and C/N of end-member

382   vegetation are fundamental to the interpretation of stable carbon isotope geochemistry

383   from bulk sediments (Chmura et al., 1987; Chmura and Aharon, 1995; Malamud-Roam

384   and Ingram, 2001). We combined the measured $\delta^{13}C$ and C/N values from three sites on

385   the Thames Estuary and one site containing fen carr in the Norfolk Broads with

386   vegetation sampled from salt marshes of Kent (Andrews, 2008), Humber Estuary (Lamb

387   et al., 2007) and Mersey Estuary (Wilson et al., 2005a,b), from fen carr environments in

388   Kent, East Sussex and the Norfolk Broads (Andrews, 2008), and from particulate organic

389   matter of the Thames Estuary (Bristow et al., 2012) to create a regional database (n =

390   278) from central and southern England (Appendix 1). We find distinctions in $\delta^{13}C$ and

391   C/N values of aquatic, C_3 salt marsh, C_4 salt marsh, and leaf and wood tissue from fen

392   carr vegetation within the vegetation database (Fig 6A).

393   Algae displayed a wide range in $\delta^{13}C$ values of -19.0 ± 8.1 ‰. This wide variation

394   in $\delta^{13}C$ values reflects the salinity (and thus pH and dissolved CO_2) of the environment in

395   which it was formed (Benedict et al., 1980; Keeley and Sandquist, 1992). Freshwater

396   algae is reported to range from -30 to -26 ‰, while marine algae ranges from -23 to -16

397   ‰ (Lamb et al., 2006). Particulate organic matter measurements from Bristow et al.

398   (2012) ($\delta^{13}C$: -20.1 ± 4.0 ‰; C/N: 9.6 ± 1.8) were similar to algal matter measured in this

399   study, although they estimate that algal-derived organic matter only comprised a small

400   proportion of the particulate organic matter pool in the Thames (<15 % of particulate

401   organic carbon and nitrogen at sampling sites where $\delta^{13}C$ values > -17 ‰; Bristow et al.,

402   2012). Instead, Bristow et al. (2012) indicate marsh plants and seagrasses contribute

403   significantly to the particulate organic matter pool of the Thames. Aquatic (submergent

404   vascular) vegetation, including seaweed and macroalgae, had mean C/N values of 9.2 ±

405   3.3. These relatively low C/N values are similar to the range of values for this vegetation

406   type (C/N < 10) reported in other temperate regions by Meyers (1994) and Lamb et al.

407   (2006). Tyson (1995) indicates that the low C/N of algal matter is due to moderate

408   amounts of structural carbohydrates and greater concentrations of N-rich protein than is

409   present in land plant tissue.

410   The greatest variation in the $\delta^{13}C$ of salt marsh vegetation occurred on the basis of

411   the photosynthetic pathway utilized by each plant; the $\delta^{13}C$ of C_4 salt marsh vegetation

412   (*Spartina* spp.) was -13.5 ± 0.8 ‰, while the $\delta^{13}C$ of C_3 salt marsh vegetation (all other

413   species) was -26.8 ± 1.3 ‰. These values are consistent with measurements of C_4 and C_3

414 salt marsh plants found in other temperate regions (e.g., Smith and Epstein, 1970; 1971;

415 Jackson et al., 1986; Chmura and Aharon, 1995). C_4 plants typically range in $\delta^{13}C$ from -

416 17 ‰ to -9 ‰ (Chmura and Aharon, 1995) and have mutually exclusive values from C_3

417 plants (Smith and Epstein, 1971), which typically range from -32 ‰ to -21 ‰ (Deines,

418 1980). There was greater variability in the C/N of C_3 salt marsh vegetation (34.6 ± 20.7)

419 in comparison to C_4 plants (27.4 ± 7.7), although this difference may be an artifact of the

420 greater number of analyses of C_3 (n = 136) versus C_4 (n = 20) vegetation types. No

421 consistent variations in $\delta^{13}C$ or C/N values of different plant species were found among

422 vegetation types, and as Lamb et al. (2007) observed, no difference in $\delta^{13}C$ or C/N values

423 existed between above- and belowground components of herbaceous C_3 or C_4 marsh

424 vegetation in the combined dataset, which enables herbaceous vegetation to be

425 characterized by one grouping (Fig 6A).

426   In contrast to salt marsh vegetation, C_3 freshwater vegetation showed variation

427 between plant components. Leaf (16.3 ± 3.5) and wood (57.5 ± 15.3) components had

428 distinct C/N values. This variation is related to the much greater proportion of N-devoid

429 lignin in wood compared to leaves (Hedges et al., 1986; Tyson, 1995; Vane et al., 2013a).

430 The $\delta^{13}C$ values of leaf (-31.2 ± 1.3 ‰) and wood (-30.2 ± 1.5 ‰) components, however,

431 were relatively similar due to greater content of ^{13}C-depleted lipids in leaves and lignin in

432 wood (Vane et al., 2013a). These values are in agreement with those found by Hedges et

433 al. (1986), Muller and Mathesius (1999), Muller and Voss (1999) and Mackie et al.

434 (2005). Freshwater vegetation had lower $\delta^{13}C$ values than C_3 salt marsh vegetation,

435 which may be related to stress imposed on salt marsh vegetation from relatively greater

436 ambient salinity (van Groenigen and van Kessel, 2002). Decreased stomatal conductance

437   (the 'openness' of the stomatal aperture; Schlesinger, 1997), due to increased salinity

438   stress causes more CO_2 inside the leaf to react with CO_2-fixing enzymes and less

439   fractionation of isotopes to occur (Guy et al., 1980), causing plant $\delta^{13}C$ to increase

440   (Farquhar et al., 1982; Guy and Reid, 1986). This variation in $\delta^{13}C$ may be of great

441   importance in distinguishing C_3 plant types accumulating under saline and freshwater

442   conditions.

443   ***5.2 $\delta^{13}C$, TOC and C/N characteristics of bulk sediments from coastal wetlands***

444   We combined our $\delta^{13}C$, TOC and C/N bulk sediment values with analyses from

445   coastal wetlands of the Mersey Estuary (Wilson et al., 2005a,b), Humber Estuary (Lamb

446   et al., 2007), and Kent, East Sussex and Norfolk (Andrews, 2008) to create a regional

447   database (n = 132) from central and southern England (Appendix 2). Two criteria were

448   used to determine inclusion of studies into the database: (1) all studies must utilize

449   identical sample preparation methods prior to analysis to thus minimize bias in

450   comparison of $\delta^{13}C$ and C/N values (Brodie et al., 2011); and (2) information regarding

451   the environment from which the sample was collected (i.e., tidal flat, low marsh, etc. or

452   the dominant vegetation occupying the sampling site) and/or sample elevation must be

453   given. Tidal flat/low marsh and middle/high marsh environments were grouped together

454   because their range of values overlapped and were indistinguishable from one another on

455   a statistical basis (ANOVA). However, we identified statistically significant differences

456   in bulk sediment $\delta^{13}C$, TOC, and C/N values of tidal flat/low marsh (excluding sampling

457   stations occupied by C_4 vegetation, *Spartina* spp.), middle/high marsh, reed swamp, and

458   fen carr floral zones of the database (Table 2).

459   Tidal flat and low marsh sediments had $\delta^{13}C$ values of -24.9 ± 1.2 ‰, TOC values

460   of 3.6 ± 1.7 %, and C/N values of 9.6 ± 1.0. The relatively high $\delta^{13}C$ and low TOC and

461   C/N values of these sediments result from minimal incorporation of *in situ* vegetation

462   cover into sediments, greater import of allochthonous particulate organic matter and

463   algae, and high rates of minerogenic sedimentation (Wilson et al., 2005a) (Fig 6B). In

464   addition, *in situ* organic matter from tidal flat and low marsh environments may be

465   exported due to tidal action (Boorman, 2000; Bristow et al., 2012) or organic matter may

466   be altered or broken down due to high rates of microbial activity, stimulated by greater

467   nutrient import from particulate organic matter sources (Ember et al., 1987; Lamb et al.,

468   2006; Kemp et al., 2010). Tidal flat and low marsh $\delta^{13}C$, TOC, and C/N values in the

469   central/southern England database were similar to those from the Pacific coast of Oregon

470   ($\delta^{13}C$: -24.1 ± 1.7 ‰, TOC: 2.5 ± 1.8 %, and C/N values of 10.4 ± 2.7; Engelhart et al.,

471   2013) and northwest Europe (e.g., Waarde Marsh of SW Netherlands: $\delta^{13}C$ of -22.0 ‰;

472   TOC of 1.2 %; C/N of 17; Middelburg et al., 1997). Conversely, $\delta^{13}C$ was lower and

473   TOC and C/N were higher than sediments from the U.S. Atlantic coast (e.g., North

474   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

475   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

476   17.3; Kemp et al., 2012; Massachusetts: $\delta^{13}C$ of -19.5 ‰; TOC of 5.6 %; C/N of 18.3;

477   Middelburg et al., 1997). This difference with the tidal flats and low marshes of the U.S.

478   Atlantic coast can be explained by the dominant occurrence of C_4 grasses (predominantly

479   *Spartina alterniflora* and *patens*) and greater incorporation of vascular vegetation into

480   sediments and/or reduced minerogenic input (Haines, 1967; Ember et al., 1987; Chmura

481 et al., 1987; Chmura and Aharon, 1995; Middelburg et al., 1997; Kemp et al., 2010;

482 2012).

483   Sediments from the middle/high marsh zone had $\delta^{13}C$ values of -26.2 ± 1.0 ‰,

484 TOC values of 9.8 ± 6.7 %, and C/N values of 12.1 ± 1.8. $\delta^{13}C$ values show little

485 alteration from their autochthonous vegetation counterparts (Fig 6B), although lower

486 TOC and C/N values suggest a secondary contribution to sedimentary organic matter

487 from allochthonous marine or riverine particulate organic matter sources (C/N < 10;

488 Meyers, 1994) (Fig 6B). High minerogenic sedimentation indicates transport of

489 allochthonous material to the marsh surface, including marine and riverine dissolved and

490 particulate organic matter (Boorman et al., 2000). Alternatively, diagenesis where

491 immobile nitrogen is retained during subsequent loss of carbon through oxidation

492 (Chmura et al., 1987; Ember et al., 1987) may explain why bulk sediment C/N values fall

493 within the lower range of vegetation. The incorporation of fungal mycelium has also been

494 shown to increase N, with a subsequent drop in C by 10 % in degraded material (Vane et

495 al., 2001). Mid/high marsh (absent of C_4 vegetation) $\delta^{13}C$ values of central/southern

496 England were similar to those from Oregon ($\delta^{13}C$: -27.3 ± 1.4 ‰; Engelhart et al., 2013)

497 and North Carolina ($\delta^{13}C$: -26.3 ± 2.1 ‰; Kemp et al., 2010), although TOC and C/N

498 values were much lower than high marsh environments of Oregon (TOC: 12.4 ± 4.0 %,

499 C/N: 13.6 ± 1.4; Engelhart et al., 2013) and North Carolina (TOC: 16.6 ± 11.6 %, C/N:

500 18.4 ± 2.3; Kemp et al., 2010), which is consistent with the minerogenic and organogenic

501 nature of UK and U.S. marshes, respectively (Allen and Pye, 1992; Middelburg et al.,

502 1997). The organic matter content of marshes varies between regions in part because

503 colder temperatures and the shorter growing season in the UK limits biomass

504   productivity, making mineral matter delivered by tides a more dominant source of

505   sediment accumulation (Allen, 1990; Allen and Pye, 1992; French and Spencer, 1993;

506   French, 1993; Middelburg et al., 1997). However, other local factors that affect mineral

507   sediment deposition, such as the supply of mineral matter and distance to its source,

508   vegetation type and density, barriers to surface flows, and post-depositional reworking

509   and erosion by waves or tides, may also account for this regional variation in $\delta^{13}C$, TOC

510   and C/N values.

511   Sediments from the reed swamp zone had $\delta^{13}C$ values of -27.9 ± 0.7 ‰, TOC

512   values of 36.5 ± 11.5 %, and C/N values of 13.9 ± 1.2. Although *Phragmites australis*,

513   the dominant reed swamp vegetation, has plant tissues with $\delta^{13}C$ and C/N values within

514   the same range as C_3 salt marsh vegetation, $\delta^{13}C$, TOC and C/N values of sediments

515   within this floral zone vary from those of the salt marsh. This variation may be explained

516   by the reduced tidal influence on the *Phragmites* reed swamp zone. Sediments

517   accumulating in this zone represent *in situ* vegetation, rather than a combination of *in situ*

518   vascular vegetation and allochthonous marine or fluvial particulate organic matter and

519   algae. Similar to the middle/high marsh, C/N values of bulk sediment are within the

520   lower range of vegetation, which may be related to early diagenesis. *Phragmites* TOC

521   and C/N values from the UK are consistent with those from a brackish transitional zone

522   occupied by *Phragmites* in New Jersey (TOC: 23.9 ± 9.7 %, C/N: 13.8 ± 0.6; Kemp et

523   al., 2012), but $\delta^{13}C$ values of -25.1 ± 2.0 ‰ from New Jersey (Kemp et al., 2012) are

524   slightly higher. This trend is seen in the upland border in marshes of Massachusetts,

525   where $\delta^{13}C$ values average -24.5 ‰, perhaps due to import of adjacent C_4 vegetation or

526   increased salinity stress on *Phragmites* vegetation itself (Farquhar et al., 1989).

527   Fen carr bulk sediments had $\delta^{13}C$ values of -29.0 ± 0.6 ‰, TOC of 41.6 ± 5.7 %,

528   and C/N values of 17.4 ± 3.1. Sedimentation in this zone is dominantly organogenic,

529   indicated by high TOC values and $\delta^{13}C$ values representative of the C_3 freshwater

530   vegetation that occupy this zone. $\delta^{13}C$ values of sediments from the fen carr fall within

531   the higher range of $\delta^{13}C$ values of their modern vegetation counterparts (Fig 6B), which

532   suggests the preferential degradation of lignin by white-rot and soft-rot fungi (Hatakka,

533   1994; Vane et al., 2003; Vane et al., 2005; Vane et al., 2006). Lignin tends to be 4 to 7 ‰

534   more depleted in $\delta^{13}C$ relative to bulk plant material (Benner et al., 1987), thus its

535   preferential decay in sediments would cause $\delta^{13}C$ values to increase. C/N values of fen

536   carr sediment were within the range of freshwater leaf material (Fig 6B), which indicates

537   that most sedimentary organic matter is either primarily derived from leaves or that the

538   woody material incorporated into sediments is significantly altered to cause a large drop

539   in its C/N content, which is also consistent with the breakdown of N-devoid

540   lignocellulosic compounds. Fen carr $\delta^{13}C$, TOC and C/N values from the UK were

541   similar to upland sediments from Oregon ($\delta^{13}C$: > -28.5 ‰, TOC: 30 ± 4.6 %, C/N: 20.4

542   ± 3.7), although UK fen carr $\delta^{13}C$ values were much lower than those from freshwater

543   environments from the San Francisco Bay (-27.7 to -23.3 ‰; Cloern et al., 2002), upland

544   sediments from New Jersey (-26.5 to -25.1 ‰; Kemp et al., 2012) and freshwater

545   marshes of Louisiana (average: -27.8 ‰). These discrepancies underscore the importance

546   of regional- and/or site-specific investigations of the modern distribution of $\delta^{13}C$, TOC,

547   and C/N bulk sediment values before interpretation of the sedimentary record (Engelhart

548   et al., 2013).

549   *5.3 The use of $\delta^{13}C$, TOC and C/N to produce sea-level index points from the Thames*

550   *Estuary*

551   We assess the use of the modern distribution of $\delta^{13}C$, TOC, and C/N values from

552   the UK (excluding samples with influence from C_4 *Spartina*) alongside microfossil

553   indicators to produce three sea-level index points and limiting dates from core SW1

554   collected from the Swanscombe marshes on the southern shore of the River Thames (Fig

555   7). Cores SW1 suffers from microfossil preservations problems and, therefore, can only

556   provide supporting data.

557   Sea-level index points delimit the unique position of RSL over time and space.

558   The horizontal age component of an index point is obtained from radiocarbon dating of

559   the sample and its associated 2σ calibrated age range. The vertical component of an index

560   point is estimated using the indicative meaning of a sample, which describes its

561   relationship to a tidal datum (e.g., mean high water spring tide, MHWST) at the time of

562   deposition using the mid-point (reference water level, RWL) and range over which the

563   indicator is found in the contemporary environment (indicative range). If a sample is

564   deposited in a terrestrial environment, it is classified as a terrestrial limiting date,

565   providing only an upper limit on the position of RSL. Shennan (1982, 1986) and Horton

566   et al. (2000) established the indicative meaning for litho- and biostratigraphical sequences

567   commonly used to produce sea-level index points (Table 3). We estimated the indicative

568   meanings of dated transgressive/regressive contacts using $\delta^{13}C$, TOC, and C/N values of

569   middle/high marsh ($\delta^{13}C$: -26.2 ± 1.0 ‰; TOC: 9.8 ± 6.7 %; C/N: 12.1 ± 1.8), reed

570   swamp ($\delta^{13}C$: -27.9 ± 0.7 ‰: TOC: 36.5 ± 11.5 %; C/N: 13.9 ± 1.2) and fen carr ($\delta^{13}C$: -

571   29.0 ± 0.6 ‰; TOC: 41.6 ± 5.7 %; C/N: 17.4 ± 3.1) environments (Table 2).

572   The transgressive contact between a peat with unidentifiable plant macrofossils

573   and an overlying grey mud with organics at -4.76 m OD returned a date of 4138-3896

574   (median: 4017) cal yr BP (Fig 7B). Across the contact, $\delta^{13}C$ increased from -28 to -26 ‰,

575   TOC decreased from 45 to 5 % and C/N fell from 21 to 15. This shift in values is

576   consistent with a transition from *Phragmites* reed swamp to a tidal flat/marsh

577   environment. Foraminifera and diatoms were absent from the peat between -5.30 and -

578   5.10 m OD. But at the transgressive contact, foraminifera switched from an agglutinated

579   to calcareous-dominated assemblage, which is consistent with a change in environment

580   from the upper limits of tidal influence to a middle to low marsh or tidal flat environment

581   (Horton and Edwards, 2006). Similarly, the diatom assemblages suggest an increase in

582   salinity preference with the number of polyhalobous and mesohalobous taxa increasing

583   and number of oligohalobous taxa decreasing across the contact (Reference for the

584   diatoms – perhaps Juggins, 1992). Pollen is present within the peat and is dominated by

585   ferns with *Corylus and Pinus,* and importantly *Chenopodium* at >15% abundance,

586   reflecting the local presence of salt marsh vegetation (ref). The geochemical and

587   microfossil data support Devoy's (1979) paleoenvironmental interpretation, which

588   suggested a change in depositional environment from fenwood to reed swamp with open

589   salt marsh communities at the transgressive contact. This contact is interpreted as a

590   *Phragmites* or monocot peat directly above a clastic saltmarsh deposit (Shennan, 1986;

591   Horton, 2000). Therefore, the RWL is MHWST - 20 cm with an indicative range of ± 20

592   cm (Table 2).

593   A bulk monocot peat overlain by a gray mud at the regressive contact at -7.14 m

594   OD produced an age of 6573-6412 cal yr BP (median: 6523) (Fig 7C). $\delta^{13}C$ decreased

595   across the contact from -26 to -29 ‰, TOC increased from 5 to 50 % and C/N increased

596   from 21 to 26. The range of TOC and C/N values within the oak fenwood peat unit

597   (Devoy, 1979) are higher than observed ranges of comparable modern environments (Fig

598   7E,F), but consistent with δ^{13}C, TOC, and C/N values of Holocene oak fenwood settings

599   found in the Humber Estuary (Fig 7E,F; Andrews, 2000). The δ^{13}C, TOC, and C/N

600   suggest a transition from a middle/high salt marsh to reed swamp or fen carr environment

601   across the regressive contact. Foraminifera were not preserved, and diatoms were sparse

602   with too few individuals to produce quantitative counts (n = ~10), although those

603   preserved prefer saline to brackish environment, with little change across the contact.

604   Undifferentiated fern spores dominate the pollen assemblage. The geochemical data

605   support the inference of Devoy (1979) who suggested the regressive contact of the peat

606   was indicative of sedge fen/reed swamp with local salt marsh communities. Therefore,

607   we assigned this dated contact a RWL of a *Phragmites* or monocot peat directly below

608   clastic salt marsh deposit (Shennan, 1986; Horton et al., 2000), which is (MHWST ±

609   HAT)/2 - 20 cm and indicative range of ± 20 cm (Table 2).

610   A date of 7700-7580 (median: 7640) cal yr BP was obtained from a *Phragmites*

611   fragment at the transgressive contact between a peat and mud at -9.56 m OD (Fig 7D).

612   Across the contact, δ^{13}C increased from -29 to -27 ‰, TOC decreased from 50 to 10 %,

613   and C/N fell from 26 to 15. TOC values are slightly higher than the modern range of reed

614   swamp and fen carr environments, suggesting Holocene environments accumulated

615   greater amounts of organic matter than their modern equivalents. Foraminifera and

616   diatoms are absent from the peat and overlying mud, although diatoms between -9.40 and

617   -9.10 m are dominated by polyhalobous and mesohalobous taxa indicative of a tidal flat

618   environment. Pollen within the peat are dominated by *Alnus* and *Corylus,* with Poacea

619   grass subdominant. The change in $\delta^{13}C$, TOC, and C/N values is consistent with a

620   transition in paleoenvironment from reed swamp to salt marsh conditions, which is in

621   agreement with pollen analysis from this study and Devoy (1979). Devoy (1979)

622   suggested the depositional environment at the transgressive contact was a sedge fen/reed

623   swamp. We interpret this contact to represent an index point with a RWL of MHWST –

624   20 cm and indicative range of ± 20 cm (Table 2).

625   A wood fragment within an alder carr peat at -9.71 m OD was dated to 7817-7620

626   (median: 7718) cal yr BP (Fig 7D). $\delta^{13}C$ along the date ranged from -28 to -29 ‰, TOC

627   ranged between 30 to 50 %, and C/N increased from 20 to 30. These values are consistent

628   with modern fen carr environments, although again, core TOC values were slightly

629   higher. Foraminifera and diatoms were absent from the peat, which was also

630   palynologically sparse with only *Alnus* pollen and undifferentiated fern spores preserved.

631   The $\delta^{13}C$, TOC and C/N values permit interpretation of this dated wood to be a

632   freshwater limiting point, which formed above MTL (Table 2).

633   The utility of $\delta^{13}C$, TOC, and C/N in the production of Holocene sea-level index

634   points is clearly illustrated in the application to Core SW1. Poor preservation of

635   microfossils, an issue found elsewhere throughout the Thames Estuary (Devoy, 1979)

636   and the UK (Horton et al., 2000; Metcalfe et al., 2000; Roberts et al., 2006), inhibited

637   interpretation of stratigraphic contacts in the core. Based on lithology and plant

638   macrofossils, inference could have been made on transgressive/regressive contacts in the

639   core (e.g., Shennan and Horton, 2002), but in the absence of supporting information from

640   microfossils, uncertainties would exist in our interpretation. $\delta^{13}C$, TOC, and C/N values

641   provide additional confidence in the interpretation of contacts within the core that are

642   based on an extensive modern data set. Post-depositional change may be evident in the

643   bulk sediment TOC and C/N values, although it is not prohibitive in the interpretation of

644   radiocarbon dated sea-level data in Core SW1.

645   **6. CONCLUSIONS**

646   We investigated the use of $\delta^{13}C$, TOC, and C/N values from bulk sedimentary

647   organic matter to reconstruct RSL and paleoenvironmental change by sampling

648   vegetation and bulk sediment from modern transects at four coastal wetlands on the

649   Thames Estuary and Norfolk Broads, UK. We reviewed published and unpublished

650   studies from the UK to compile a bulk sediment stable carbon isotope geochemistry

651   database from coastal wetlands of central and southern England. Tidal flat/low marsh,

652   mid/high marsh, reed swamp and fen carr environmental zones had statistically distinct

653    $\delta^{13}C$, TOC, and C/N values due to the relative amounts of *in situ* vegetation and tidal-

654   derived allochthonous particulate organic matter and algae incorporated into sediments.

655   Intra-site variability in sediment $\delta^{13}C$ values was observed related to variations in site

656   salinity and the presence of the C_4 species *Spartina anglica*.

657          $\delta^{13}C$, TOC, and C/N values of tidal flat/low marsh ($\delta^{13}C$: -24.9 ± 1.2 ‰; TOC: 3.6

658   ± 1.7 %; C/N: 9.9 ± 0.8), middle marsh/high ($\delta^{13}C$: -26.2 ± 1.0 ‰; TOC: 9.8 ± 6.7 %;

659   C/N: 12.1 ± 1.8), reed swamp ($\delta^{13}C$: -27.9 ± 0.7 ‰: TOC: 36.5 ± 11.5 %; C/N: 13.9 ±

660   1.2) and fen carr ($\delta^{13}C$: -29.0 ± 0.6 ‰; TOC: 41.6 ± 5.7 %; C/N: 17.4 ± 3.1)

661   environments from the bulk sediment database (removing sites occupied by *Spartina*

662   spp.) were used to interpret sequences from a Holocene sediment core with poor

663   microfossil preservation collected from Swanscombe marshes on the Thames Estuary.

664 $\delta^{13}C$, TOC, and C/N were consistent with interpretations based on microfossils, where

665 preserved. Holocene environments appeared to accumulate greater amounts of organic

666 matter than their modern equivalents. Post-depositional change of bulk sediment $\delta^{13}C$,

667 TOC, and C/N values did not prohibit paleoenvironmental interpretation. The

668 geochemical dataset was used to estimate the indicative meanings of radiocarbon-dated

669 samples in the core to produce three new sea-level index points and one terrestrial

670 limiting date. We find that $\delta^{13}C$, TOC, and C/N of bulk sedimentary organic matter can

671 together be used as an effective tool in the paleoenvironmental interpretation of Holocene

672 sediments in the absence of microfossil indicators.

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691   Figure 1. Location map showing study areas in the United Kingdom and along the
692 Yare River and Thames Estuary and location of transects (black dotted line) at study sites
693 in Dartford Creek (A), Wat Tyler Country Park Nature Reserve (B), Two Tree Island (C),
694   and Ted Ellis Reserve (D).
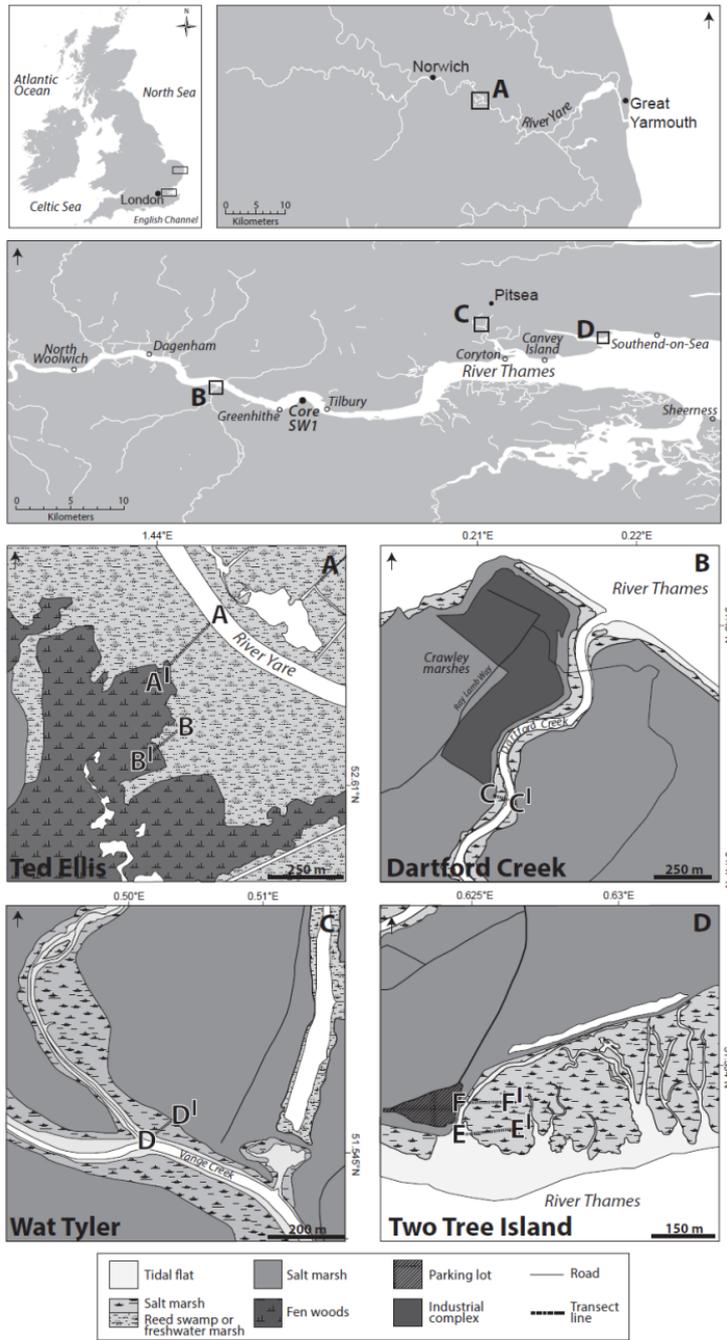
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697   Figure 2. Transect A–A[1] at Dartford Creek. Elevation profile, floral zones, $\delta^{13}C$

698   values, total organic carbon (TOC) and C/N ratios are shown for bulk surface sediment

699   samples along each transect.
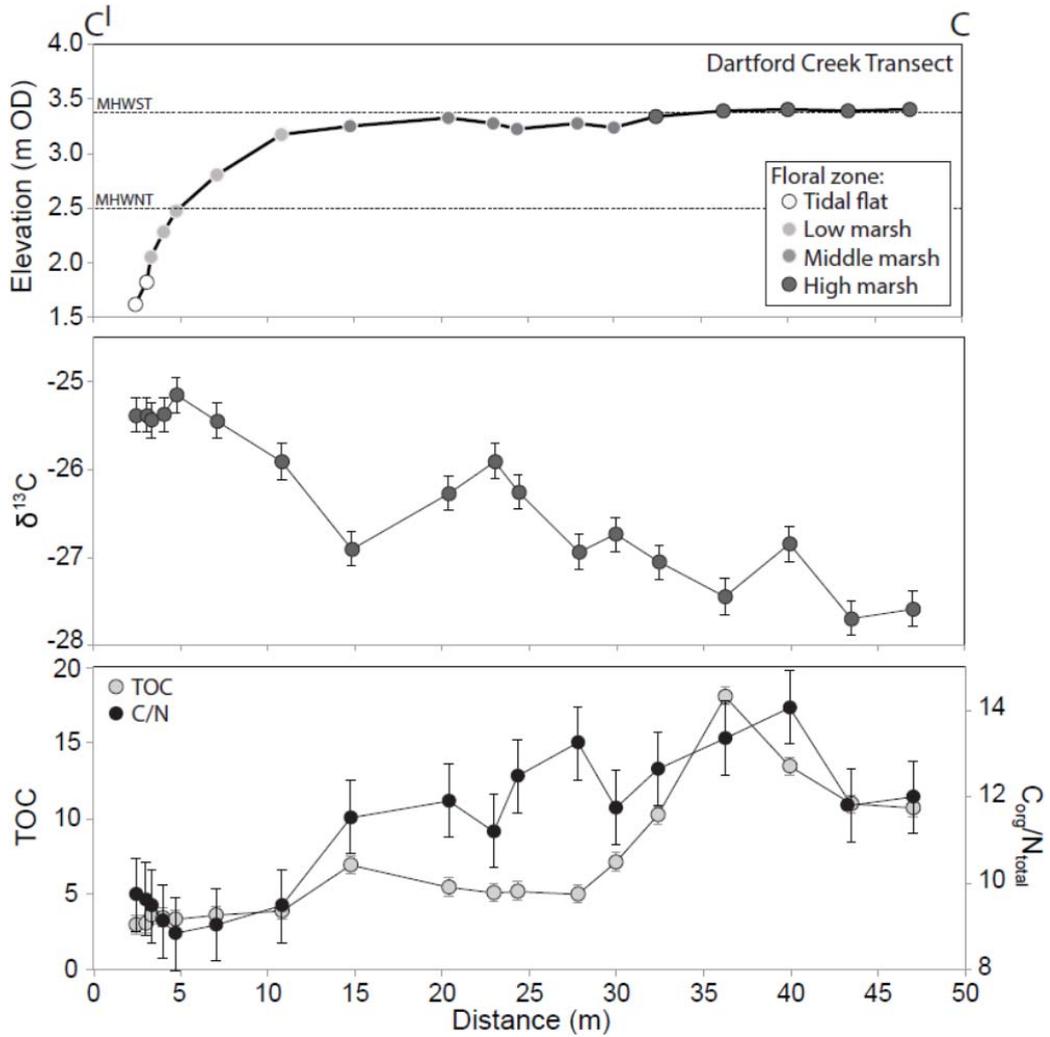
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707   Figure 3. Transect B–B[1] at Wat Tyler Country Park nature reserve. Elevation

708   profile, floral zones, $\delta^{13}C$ values, total organic carbon (TOC) and C/N ratios are shown

709   for bulk surface sediment samples along each transect.
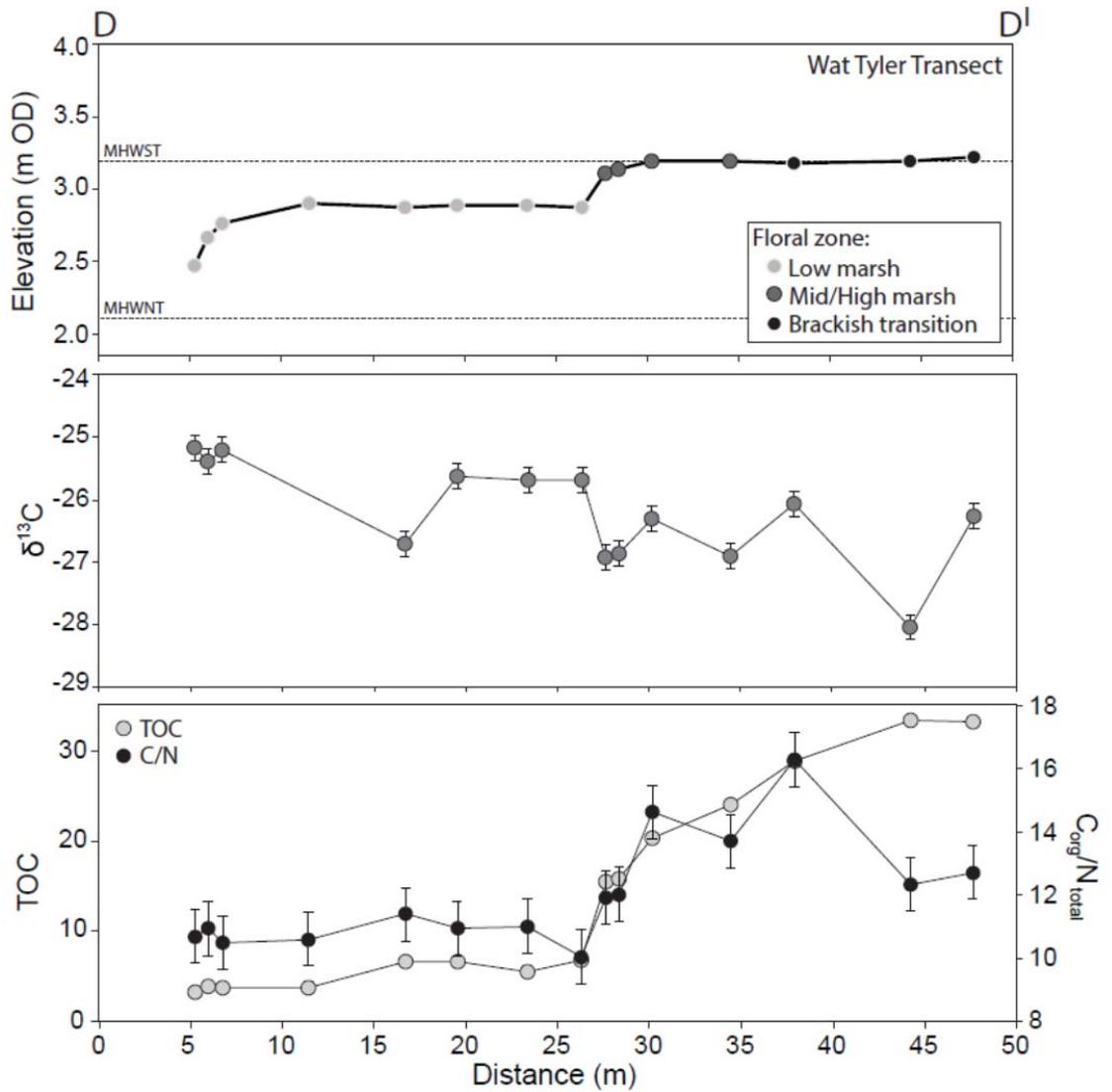
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714   Figure 4. Transect 1 (C–C^1) and Transect 2 (D–D^1) at Two Tree Island. Elevation

715   profile, floral zones, δ^{13}C values, total organic carbon (TOC) and C/N ratios are shown

716   for bulk surface sediment samples along each transect.
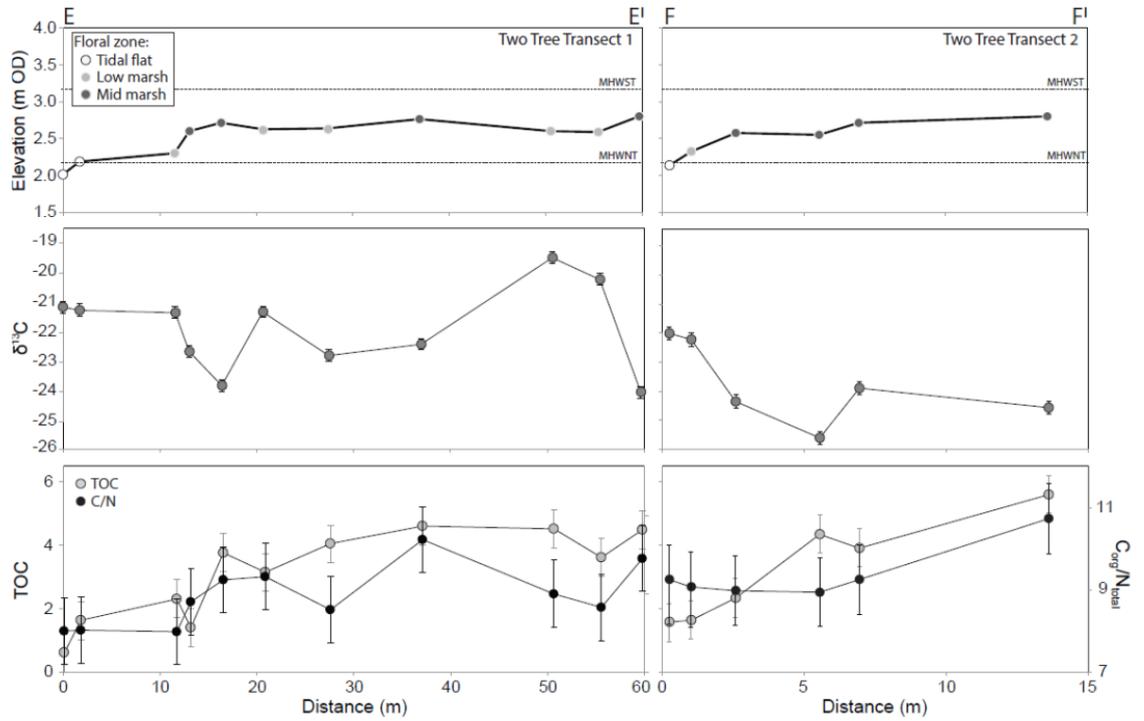
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727   Figure 5.   Transect 1 (E–E[1]) and Transect 2 (F–F[1]) at Ted Ellis nature reserve.

728   Elevation profile, floral zones, $\delta^{13}C$ values, total organic carbon (TOC) and C/N ratios

729   are shown for bulk surface sediment samples along each transect.
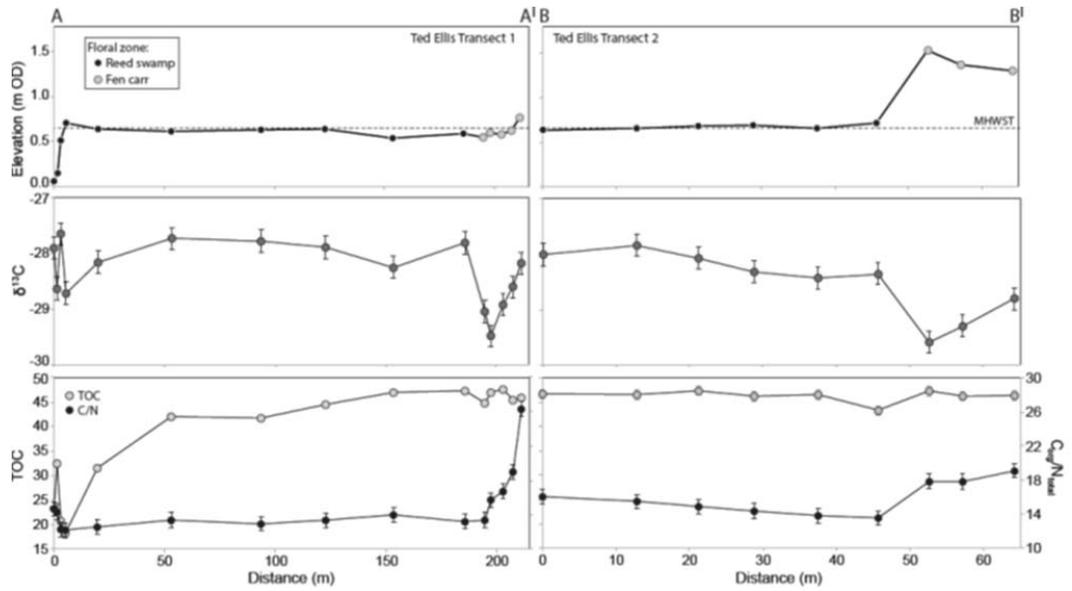
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743   Figure 6. $\delta^{13}C$ and C/N of plants and surface sediments. (A) $\delta^{13}C$ and C/N of

744   vegetation end-members grouped by the habitat or environment from which it was

745   collected and the plant component analyzed. Aquatic vegetation includes brown and

746   green algae and the genera *Fucus* and *Enteroporpha*. Salt marsh/reed swamp vegetation

747   include the genera *Agrostis, Aster, Atriplex/Halimione, Borrichia, Cochleria, Elymus,*

748   *Festuca, Limonium, Puccinellia, Phragmites, Salicornia, Scirpus, Seriphidium, Spartina,*

749   *Spergularia, Suaeda,* and *Triglochlin.* Fen carr vegetation includes the genera *Alnus,*

750   *Betula, Dryopteris, Rubus, Salix* and *Urtica.* Values come from this study and work by

751   Wilson et al. (2005a,b), Lamb et al. (2007), Andrews (2009), and Bristow et al. (2012).

752   Patterned boxes represent the mean ± 2 s.d. of each vegetation type: aquatic (light blue

753   diagonal lines), particulate organic matter (dark blue diagonal lines), C4 salt marsh

754   (orange diagonal lines), C_3 salt marsh (purple diagonal lines), C_3 freshwater leaves (red

755   diagonal lines) and C_3 freshwater wood (green diagonal lines). Two samples with C/N >

756   100 were excluded from the plot. (B) $\delta^{13}C$ and C/N values of surface sediment from this

757   study, grouped by depositional environment and superimposed on the ranges defined in

758   (A). Note the change in C/N values on the x-axis.
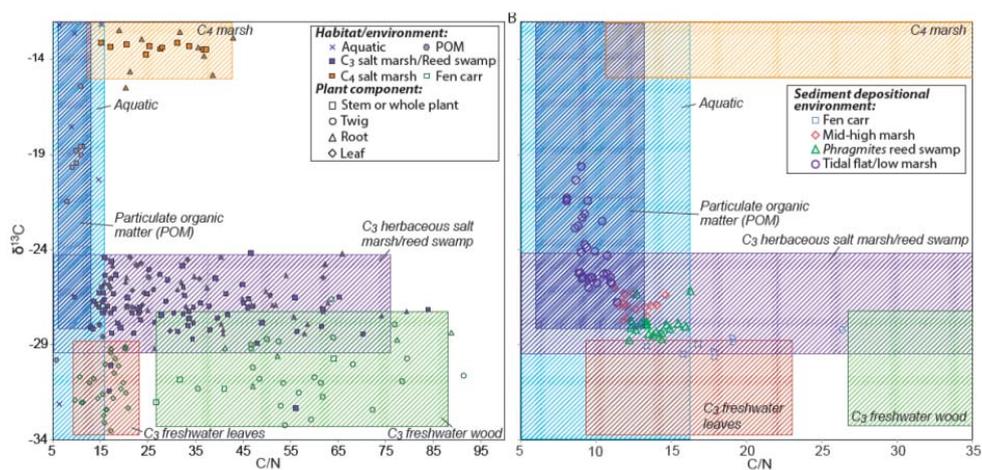
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760   Figure 7. Derivation of sea-level index points from transgressive/regressive

761   contacts in core SW1. A) Stratigraphy of core SW1. (B) Litho, chemo-, bio-, and chrono-

762   stratigraphy of the transgressive contact at -4.76 m OD. (C) Litho, chemo-, bio-, and

763   chrono-stratigraphy of the regressive contact at -7.14 m OD. (D) Litho, chemo-, bio-, and

764   chrono-stratigraphy of the transgressive and regressive contacts at -9.56 and -9.71 m OD.

765   (E) Comparison between modern range of bulk sediment δ^{13}C and TOC and SW1 core

766   sediment. Shaded boxes represent full range of δ^{13}C and TOC values of each

767   environment in the central/southern England database. (F) Comparison between modern

768   ranges of δ^{13}C and C/N of bulk sediments and SW1 core sediment. Shaded boxes

769   represent full range of δ^{13}C and C/N values of each environment in the central/southern

770   England database.

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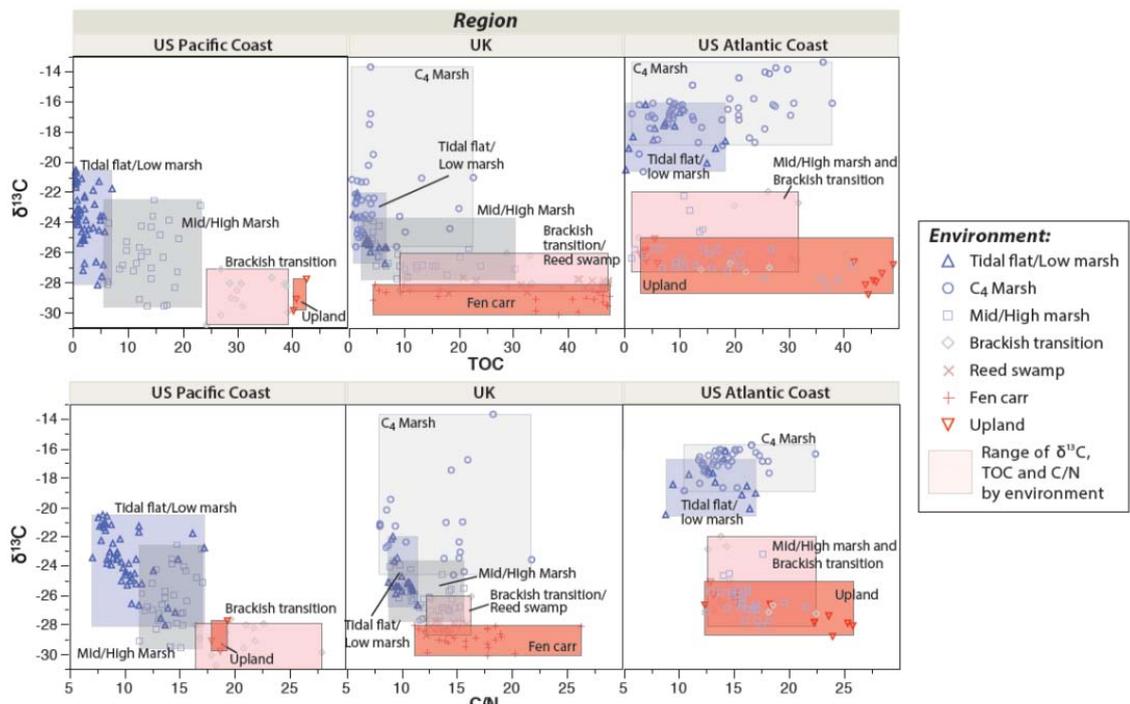
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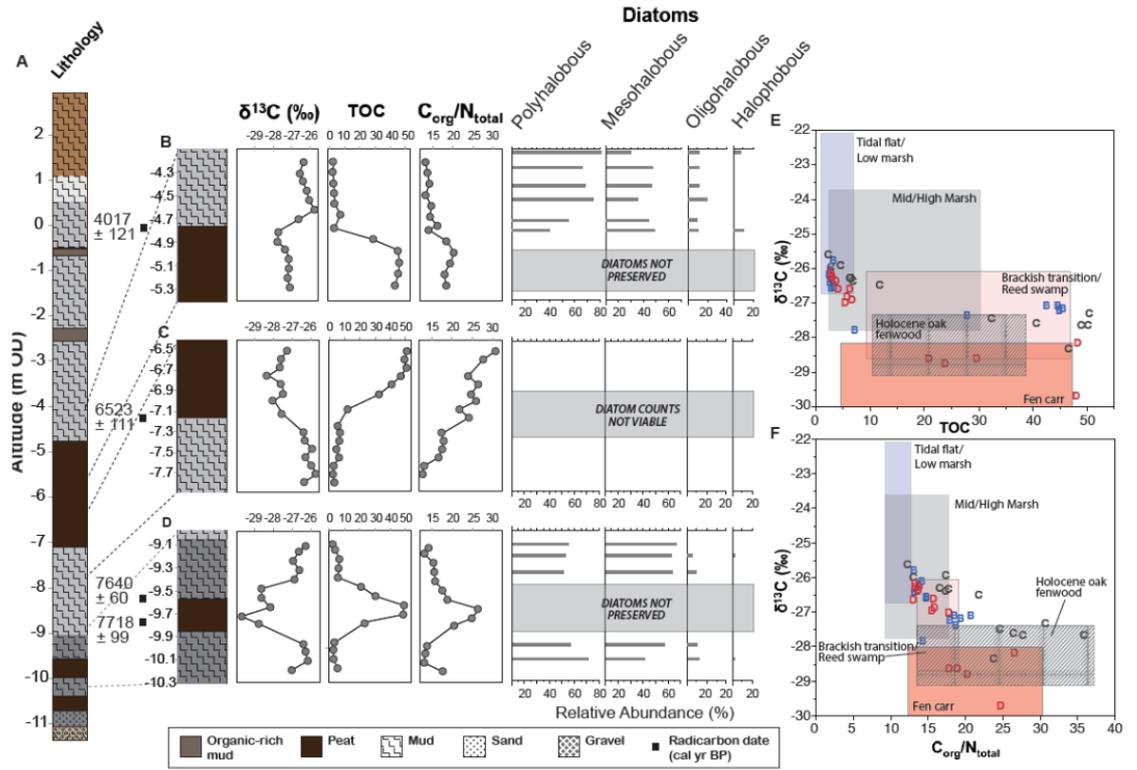
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