Chapter 9
C/N ratios and Carbon Isotope Composition of Organic Matter in Estuarine Environments

Melanie J. Leng and Jonathan P. Lewis

Abstract The sediments that are preserved in estuarine environments (saltmarsh, riverine estuaries, mangrove habitats, lagoons, isolation basins and fjords) contain organic matter that allows investigation of the provenance of that material. These data can then be used specifically to investigate past sea level/land level changes and changes in freshwater flux. Where microfossils are poorly preserved or absent, C/N and $\delta^{13}C$ analyses offer an alternative method to deduce environmental histories, but they are especially useful when used in conjunction with a range of other proxies, and when local modern end-member organic variables can be measured to 'calibrate' the sedimentary C/N and $\delta^{13}C$. There are a wide range of C/N-$\delta^{13}C$ based carbon studies, here we describe examples of studies in a variety of estuarine environments.

1 Introduction

Here, an estuary is defined as a partially enclosed environment, connected to both freshwater (e.g. a river or stream) and the ocean, where sediment accumulates. Estuaries are effectively a transition zone between the terrestrial and ocean environments, are characterised by environmental gradients (particularly salinity, nutrient and geochemical), and are subjected to rapidly fluctuating conditions due to tidal cycles and periods of high river flow. This makes them extremely important as hosts to diverse

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habitats and complex ecosystems that require careful monitoring and management, and contain sediments able to record both terrestrial and marine past changes. The temporal longevity of modern estuarine records is often limited to the Holocene as most modern estuaries were formed by ice scouring during the last glacial period (high latitudes) and/or by sea level rise during the deglacial (lower latitudes). Being highly productive and receiving sediment and organic matter from catchments, they often accumulate thick sedimentary sequences providing high-resolution archives of environmental change (e.g. Jennings and Weiner 1996). Many components of estuarine deposits have been used to characterise estuary environmental change (e.g. see Chaps. 8–18 in this volume) and here we describe the carbon/nitrogen (C/N) ratios and carbon isotope composition ($\delta^{13}C$) of organic matter. One of the main justifications for investigating C/N and $\delta^{13}C$ of organic matter in estuaries relies on the fact that micro- and macrofossils (e.g. diatoms, foraminifera, plant macrophytes, pollen; Chaps. 11, 13, 17 and 18, this volume), which provide information on environmental change, can be spatially restricted to particular environments (e.g. Shennan et al. 2000); and in a dynamic environment it is not uncommon to encounter sediment deposits containing a discontinuous fossil record that may be a function of rapidly changing environments or differential preservation (e.g. Shennan et al. 1999; Wilson et al. 2005a). The C/N and $\delta^{13}C$ nature of organic matter within sediments (including estuarine) are generally presented together as they provide complementary palaeoenvironmental information. Evidence of $\delta^{13}C$ can enable reconstruction of organic matter type, habitat, in addition to productivity in some circumstances; although the signals can also be impacted by other effects such as post depositional change (Fig. 9.1). C/N data can provide information on the carbon source, in terms of both predominant type of plant and their habitat (i.e. aquatic versus terrestrial). Overall though, the use of C/N and $\delta^{13}C$ in estuarine systems has been rather limited to date, particularly in comparison to lakes and the marine environment, where the use of these geochemical proxies in environmental reconstructions are commonplace (e.g. Leng and Marshall 2004; Leng et al. 2005; Maslin and Swann 2005 and references therein).

In this chapter we outline the sources of organic matter in estuarine systems and the general method involved in obtaining C/N and $\delta^{13}C$ from bulk sediments. We consider the major controls, the limitations and problems to this approach, and discuss what palaeoenvironmental information can be obtained. The latter is largely represented via specific case studies where C/N and $\delta^{13}C$ have been used to either independently reconstruct palaeoenvironmental change or enhance multi-proxy studies. The case studies cover a range of "estuary" types, including: saltmarsh, riverine estuaries, mangroves, lagoons, isolation basins and fjords and glacial embayments.

2 Analytical Considerations

The accurate determination of C/N and $\delta^{13}C$ composition of organic matter requires the complete removal of all inorganic carbonate from the total carbon within a sample. This is usually achieved through treating the sample with an acid. There are a
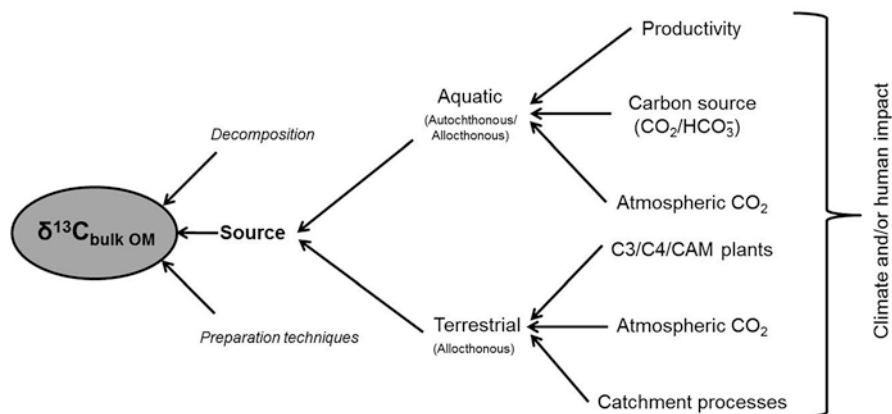
Fig. 9.1 Controls on the carbon isotope composition of organic matter in estuarine sediments. The main factor is the source of the organic matter, although decompositional processes and even analytical preparation techniques can affect $\delta^{13}C$. The main sources are aquatic and terrestrial. Aquatic plant $\delta^{13}C$ is a function of the ratio of CO_2 to HCO_3^-. Marine plants tend to utilise HCO_3^- (with higher $\delta^{13}C$) so have higher $\delta^{13}C$ values, whereas freshwater plants utilise CO_2 (with lower $\delta^{13}C$) so have lower $\delta^{13}C$ values. In the aquatic environment where nutrients can be limiting, increased productivity can lead to higher $\delta^{13}C$. The main difference in the $\delta^{13}C$ of terrestrial plants is their photosynthetic pathway; C3 plants have lower $\delta^{13}C$ than C4. However, catchment processes can have a major impact on terrestrial plant $\delta^{13}C$ including water stress, the amount of sunlight, the development of soils etc. The global carbon cycle, in particular the atmospheric CO_2 budget affects all plants as does climate and human impacts

variety of pre-analysis acid treatment methods that have been used from which it is clear there is no consensus on standard practice (see Brodie et al. 2011a). There are potentially significant non-linear biases on measured C/N and $\delta^{13}C$ values (and $\delta^{15}N$; Brodie et al. 2011b) directly associated with the pre-analysis acid treatment methods, which could undermine the environmental interpretation of the data where variations are relatively small. For example, Brodie et al. (2011a) noted C/N ranges of ~6 to 13 and $\delta^{13}C$ ranges of –27.0 to –28.4‰ for a terrestrial plant across different pre-analysis acid treatments (when compared with the raw, untreated value of C/N = 9.5; $\delta^{13}C$ = –27.4 +/– 0.1‰). These C/N values could suggest organic matter from both an aquatic source and from an admixture of aquatic and terrestrial sources. Brodie et al. (2011c) recommended that the minutiae of the bulk C/N and $\delta^{13}C$, and of organic matter, are not interpreted, but instead changes in the down-core data sets are used in addition to changes that are significantly greater than an estimate of the inaccuracy and imprecision of the data. This is often considerably greater than the standard instrument precision and may be method dependent. They finally recommended that C/N and $\delta^{13}C$ data should only be used as an indication of environmental change (non-quantifiable) and should be supported with other proxy data such as micro/macro fossil data. To date there is no consensus about how to treat samples, but what is clear from the Brodie et al. (2011c) experiments is that pre-treatment methods should be consistent within any study.

The traditional method to determine $\delta^{13}C$ of organic material within sediments is by oxidation of the carbonate-free sample off-line, via a vacuum-furnace system, to produce and collect CO_2 for isotope analysis (Boutton 1991). The CO_2 is produced by reaction of the organic matter with an oxidant, such as cupric oxide (CuO), in an evacuated sealed tube at 600–800 °C. The $^{13}C/^{12}C$ ratio of the CO_2 is measured with an isotope ratio mass spectrometer (IRMS). Although very accurate, this off-line method is slow and requires large (milligram) sample sizes (Meyers and Teranes 2001). On-line techniques now predominate, using continuous flow or dual inlet mass spectrometry. The on-line techniques require an IRMS coupled to a device that produces CO_2 from the organic matter, usually an elemental analyser, which can also be used to measure C and N concentrations simultaneously. The on-line measurement of $^{13}C/^{12}C$ allows for much reduced sample size (down to micrograms of C) and quicker/automated analysis. The reproducibility of $\delta^{13}C$ data is commonly of the order of ±0.1‰. Carbon and nitrogen weight percentages are used to calculate C/N mass ratios, which can be multiplied by 1.167 (the ratio of atomic weights of carbon and nitrogen) to provide C/N atomic ratios. Both types of values are published, but most often the weight ratios are reported. However, atomic C/N ratios are preferable because they reflect biochemical stoichiometry (Meyers and Teranes 2001).

3   Sources of Organic Matter in Estuarine Systems

Estuarine sediments receive both autochthonous (derived *in situ*, such as plants growing on the sediment surface) and allochthonous (transported to the sediment from elsewhere) organic matter. In saltmarsh sediments the dominant autochthonous component is derived from *in situ* vascular plant material. Infrequent tidal inundation allows extensive vegetation cover, and therefore highly organic-rich sediments. In contrast, the area between low and high tide, the tidal flats, are frequently inundated by marine water, thus inhibiting vascular plant vegetation, and consequently the predominant organic matter is allochthonous. Allochthonous organic matter sources include marine particulate organic carbon (POC), mainly from phytoplankton, as well as river-derived terrestrial and fluvial material.

Different sources of organic matter in the estuarine environment have (mostly) different C/N and $\delta^{13}C$ compositions. In theory this means the bulk organic C/N and $\delta^{13}C$ should reflect the relative amounts of the organic matter from the different sources (e.g. Middelburg et al. 1997), assuming the different sources have relatively uniform compositions (Fry and Sherr 1989) and preservation is similar. In environments that are not regularly flushed by fresh and/or marine water, such as lagoons or isolation basins, autochthonous sources of carbon will dominate the supply to the sediments rather than the balance between autochthonous and allochthonous components (Lamb et al. 2006). The range in C/N and $\delta^{13}C$ values for the main sources of organic matter in estuarine environments is given in Figs. 9.2 and 9.3. However, while the type of plant matter has a significant effect on C/N and $\delta^{13}C$, there are other
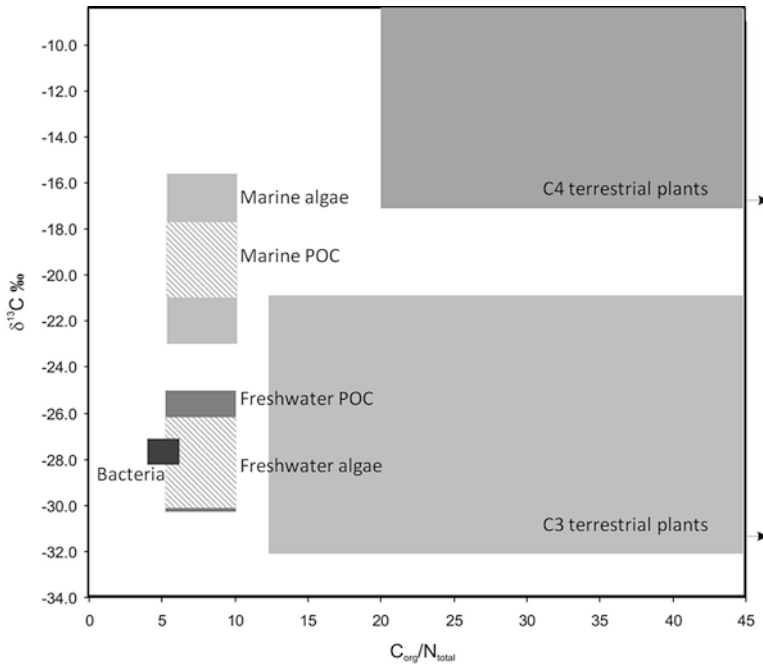
Fig. 9.2 The range in weight C/N and $\delta^{13}C$ values for the main sources of organic matter in the estuarine environment. $\delta^{13}C$ is the biggest distinguisher between freshwater and marine as well as C3 and C4 terrestrial plants, while C/N is commonly used to separate aquatic from terrestrial. The fields of data are averages and "end-member" modern values are often measured at specific sites to narrow the ranges (modified from Lamb et al. 2006)

environmental variables that have been shown to affect specific plant $\delta^{13}C$, such as drought (Farquhar et al. 1989), salinity (Seemann and Critchley 1985), vapour pressure deficit (Turney 1999) and climate (both temperature and changing isotope composition and concentrations of atmospheric CO_2; Mackie et al. 2005).

Each of the broad plant types and the undifferentiated organic matter are described in more detail below in terms of their C/N and $\delta^{13}C$ compositions.

3.1   Terrestrial Plants

Terrestrial plants use atmospheric CO_2, preferentially taking up ^{12}C, resulting in organic matter that is depleted in ^{13}C compared with the atmosphere (current atmospheric CO_2 $\delta^{13}C_{PDB}$ = −8‰; Keeling et al. 1995). Terrestrial plants are divided into three main types: C3 plants constitute about 90 % of all plants, and typically have $\delta^{13}C$ values that range between –32 and –21‰ (Deines 1980); C4 plants have $\delta^{13}C$ values of around –13‰ (range = –17 to –9‰; Deines 1980; e.g. O'Leary et al. 1992); and CAM photosynthesisers (crassulacean acid metabolism; this includes
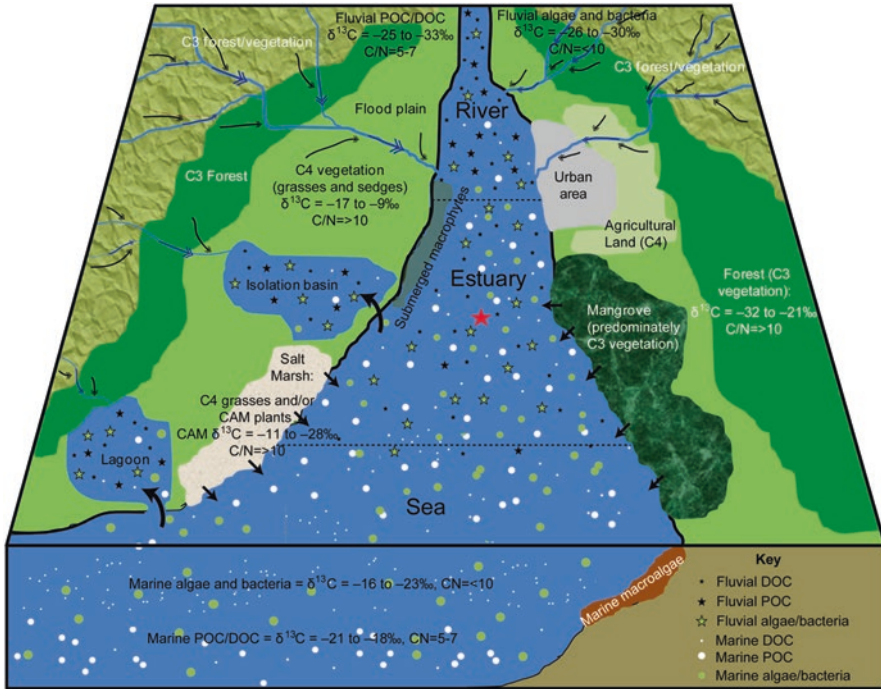
Fig. 9.3 Schematic summary diagram illustrating the major controls on bulk sediment C/N and
δ^{13}C in a C3-dominated catchment. Five of the estuarine-type habitats discussed in the text are
included: salt marsh, riverine estuary, mangrove swamp, lagoon and isolation basin. The C/N and
δ^{13}C signatures of the major components of estuarine organic matter are included: relative mixing
of these components define the C/N and δ^{13}C of estuarine organic matter, though decomposition
and/or preparation techniques might also affect values. Fjords generally act in a similar manner to
riverine estuaries, whilst C/N and δ^{13}C might fluctuate in glacial embayments due to the presence
of ice shelves, which can regulate the relative contribution of marine-sourced organic matter.
Symbols: *arrows* denote inwash. Note, δ^{13}C values are likely to be higher in a C4-dominated catch-
ment due to utilisation of dissolved organic carbon from decomposition and oxidation of C4 plants.
The *star* denotes a hypothetical core location to reconstruct long-term changes in estuarine C/N
and δ^{13}C

most succulents), use both the C3 photosynthetic pathway and a C4-like pathway,
typically resulting in a wide range of δ^{13}C values (–11 to –28‰; Schleser 1995;
Fig. 9.2). Terrestrial plants grow in estuarine environments although the type
depends on the elevation above the tidal frame (Gray 1992), but terrestrial plant
material also enters estuaries via rivers and streams. Saltmarsh species vary with
elevation within the tidal frame as a function of their salinity tolerance, but those
plants that have adapted to tolerate very saline conditions are commonly of C4 or
CAM type (Rundel et al. 1988). Terrestrial vegetation is predominantly composed
of lignin and cellulose, which are nitrogen poor (Tyson 1995) and lead to high C/N
(Prahl et al. 1980), often much greater than 10. However, data can be variable,
plants from a modern saltmarsh (both terrestrial and saltmarsh) along western

Greenland, for example, have variable C/N (10–110), while their fossil equivalents in the saltmarsh sediments have low C/N (ca. 5), although these are also likely to contain some algal material (Leng et al. 2012).

3.2   Aquatic Plants

Aquatic plants can utilise both bicarbonate (HCO_3^-) and dissolved CO_2 (Benedict et al. 1980). Dissolved CO_2 has lower $\delta^{13}C$ values (–8‰ if in equilibrium with atmospheric CO_2) than HCO_3^- (~0‰; Keeley and Sandquist 1992), and aquatic plants will preferentially take up dissolved CO_2 (Degens et al. 1968; Falkowski 1991). Because the ratio of CO_2 to HCO_3^- is a function of pH, and there is less CO_2 in the marine environment than in freshwater, marine plants have higher $\delta^{13}C$ values, and they will consequently utilise predominantly HCO_3^- (Lamb et al. 2006). Freshwater algae in C3-dominated environments tend to have lower $\delta^{13}C$ values (–26 to –30‰; Schidlowski et al. 1983; Meyers 1994) than marine algae (–16 to –23‰; Haines 1976; Meyers 1994), but algae in C4-vegetation catchments can have relatively high $\delta^{13}C$ values ($\geq$–16‰) as they also use dissolved organic carbon from decomposition and oxidation of C4 plants (Chivas et al. 2001; Fig. 9.2).

Some studies have shown that bacteria may also have an impact on the $\delta^{13}C$ (and C/N) of coastal sediments (e.g. Malamud-Roam and Ingram 2001). Peterson et al. (1980) argued that the $\delta^{13}C$ values of living *Spartina alterniflora* (−11 to −13‰) and underlying surface sediments (−18 to −24‰) are different in some saltmarshes of the eastern USA because of the presence of bacteria in the sediment. In another study, cyanobacterial blooms in San Francisco Bay (USA) saltmarsh sediments had low $\delta^{13}C$ (–26.6 to –28.0‰), suggesting that bacteria in large quantities, even in marine-influenced sediments, will cause lower $\delta^{13}C$ values (Cloern et al. 2002).

Algae and bacteria have C/N ratios of <10 (Meyers 1994; Tyson 1995) because nitrogen occurs preferentially in proteins and nucleic acids which are relatively abundant in aquatic plants (Talbot and Johannessen 1992). In particular, bacterial activity can introduce nitrogen to the sediment, and thus decrease C/N ratios (Rice and Hanson 1984). However, aquatic plants and bacteria contain a high level of labile compounds and decompose more rapidly than vascular plants (Valiela et al. 1985), and therefore become less significant to the bulk organic C/N and $\delta^{13}C$ (e.g. Andrews et al. 1998).

3.3   Particulate and Dissolved Organic Carbon

POC represents one of the main organic carbon pools in the oceans, and is mainly composed of living (phytoplankton, zooplankton and bacteria) and non-living (plant detritus and sewage) material (Lamb et al. 2006). Marine POC

typically ranges from –21 to –18‰ (Peters et al. 1978; Wada et al. 1987; Middelburg and Nieuwenhuize 1998). Fluvial POC is a function of contributions mainly from freshwater phytoplankton ($\delta^{13}C_{POC}$ values –30 to –25‰) and particulate terrestrial organic matter ($\delta^{13}C_{POC}$ values –25 to –33‰; e.g. Salomons and Mook 1981; Barth et al. 1998; Middelburg and Nieuwenhuize 1998). Therefore, mean $\delta^{13}C$ values of fluvial POC are nearly always very low. As a result of the difference between marine and fluvial POC, $\delta^{13}C_{POC}$ values commonly increase systematically towards the mouth of estuaries due to different contributions from the two end-members. POC has a large phytoplankton component and therefore C/N values tend to be low at around 5–7 (Meyers 1994; Tyson 1995; Fig. 9.2). Diatoms, a particular type of phytoplankton with a silica skeleton, are common in estuarine environments (see Chap. 11) and have particularly low C/N (ca. 5). Dissolved organic carbon (DOC) is principally derived from the decomposition of phytoplankton in the marine environment and from mixtures of terrigenous organic matter and phytoplankton in the fluvial environment (Rashid 1985). The "dissolved" fraction of organic carbon is a classification used to define compounds below 0.45 μm. Most studies of $\delta^{13}C_{DOC}$ in estuarine waters have shown that the isotope composition reflects the fluvial and/or marine source of the DOC (e.g. Peterson et al. 1994; Van Heemst et al. 2000; Goñi et al. 2003; Otero et al. 2003).

3.4 Decomposition of Plants

Organic matter decomposition can potentially have a significant influence on both the C/N and $\delta^{13}C$ composition of organic matter (Lamb et al. 2006). Early loss of labile compounds in vascular vegetation can lead to significant changes in $\delta^{13}C$ in saltmarsh organic matter, but is usually insufficient to prevent the distinction between organic matter from C3 and C4 plants on marshes (e.g. Malamud-Roam and Ingram 2004). Therefore, $\delta^{13}C$ is usually considered to remain a faithful indicator of its precursor. The loss of organic carbon in sediments as decomposition progresses can sometimes complicate the use of C/N ratios due to differential loss of one of the elements and through an increase in inorganic nitrogen relative to organic nitrogen (Sampei and Matsumoto 2001). However, the direction of change in C/N and $\delta^{13}C$, rather than absolute values, is generally more important for detecting changes in the environment. Relative changes are commonly retained in Holocene sediments, suggesting that C/N and $\delta^{13}C$ can be employed, even in the most dynamic of coastal environments. To confirm this there is often close agreement between diatom and C/N-$\delta^{13}C$ records (e.g. Mackie et al. 2005; Wilson et al. 2005b; Zong et al. 2006), despite each responding to different variables (organic source as opposed to salinity), allowing for greater confidence in palaeoenvironmental interpretations using the geochemistry of organic matter.

4   Estuarine Palaeoenvironments

4.1   Saltmarsh

The saltmarsh environment is essentially the uppermost coastal, intertidal zone between the land and the sea that is flooded regularly by tides. On saltmarshes there are both C3 and C4 plants; C4 plants have evolved to tolerate water stress and high salinity enabling them to survive on brackish/saline marshes. Such C4 grasses include those in the genus *Spartina* which can have very distinct δ^{13}C (Haines 1976; Middelburg et al. 1997; Cloern et al. 2002). In regions where both C3 and C4 plants are native to coastal marshes, the sediment δ^{13}C composition can directly relate to the ratio of C3/C4 plants, and thus is used as a proxy for changes in marine versus freshwater contributions to a saltmarsh (Fry et al. 1977; Ember et al. 1987; Middelburg et al. 1997; Johnson et al. 2007). The most successful application of the variation in C3/C4 plants is in the San Francisco Basin (Chmura and Aharon 1995; Byrne et al. 2001; Malamud-Roam and Ingram 2004). Following the rapid postglacial sea level rise culminating ~6000 ^{14}C years BP, thick sequences of estuarine marsh sediments have accumulated in the bay (Ingram et al. 1996a, b; Byrne et al. 2001). Studies have shown that the δ^{13}C composition of the surface soil organic matter on the marsh reflects the distribution of C3 and C4 plants growing in the local area (Stout et al. 1975; Chmura et al. 1987; Chmura and Aharon 1995; Malamud-Roam and Ingram 2001; Kemp et al. 2010). Therefore, it is assumed that down-core changes in δ^{13}C are a record of marsh C3 and C4 pal-aeovegetation and associated palaeosalinity (e.g. DeLaune 1986; Byrne et al. 2001; Kemp et al. 2012). δ^{13}C evidence, combined with that from other proxies such as diatoms and pollen, from the north San Francisco Bay over the last 3000 years were used to distinguish changes in salinity and human impacts (Byrne et al. 2001). Changes in the amount of freshwater discharge flowing into the bay were suggested as the key reason for changes in salinity, and thus vegetation type (C3 and C4) on the marshes, which is both a function of river discharge and sea level. All of these studies assume that the vegetation preserved in the surface organic matter has its origins in the plants growing in the local area. Studies have highlighted issues relating to different size fractions having different provenance, as well as contamination from root penetration (Lamb et al. 2006). Lamb et al. (2006) discussed issues relating to the use of simple C3/C4 mixing models. For example, some C4 plants grow on freshwater as well as saline marshes. CAM plants complicate bulk δ^{13}C mixing models as they can have intermediate δ^{13}C values, and where sediments receive a significant proportion of allochthonous material (such as tidal-derived phytoplankton), this could increase the sedimen-tary δ^{13}C values due to the contribution from marine organic matter. In addition, hypersaline environments can include edaphic algal growth and this can lead to algae forming a significant proportion of the autochthonous carbon input (Zedler 1980; Sullivan and Moncreiff 1990).
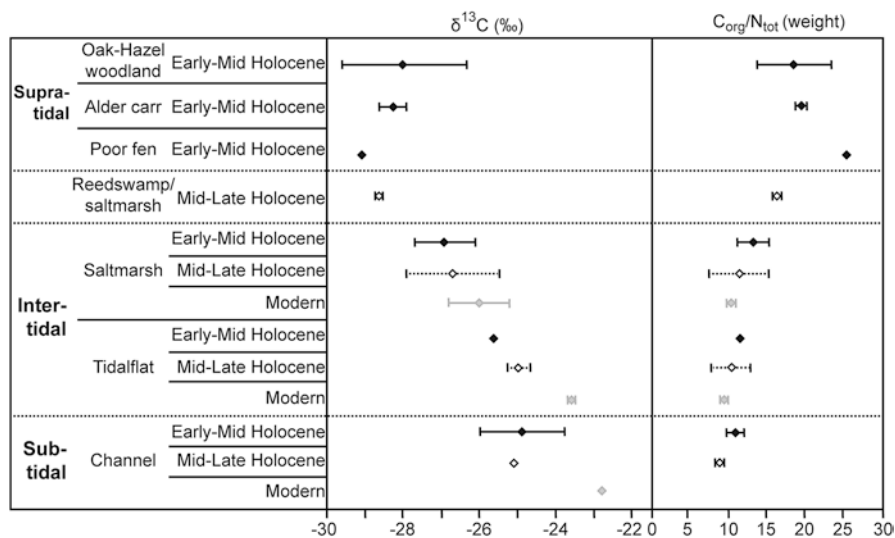
Fig. 9.4 Mean early to mid-Holocene and modern δ¹³C and C/N ratios from the various sub envi-ronments along the Mersey Estuary showing the transition from more freshwater-dominated supra-tidal to marine-dominated saltmarsh, channels and tidal flat environments (Wilson et al. 2005b)

Many mid- or high-latitude saltmarsh vegetation communities, including many saltmarshes in northern Europe, do not have native C4 plants (e.g. Preston et al. 2002). Consequently, the range in organic matter $\delta^{13}C$ values on these saltmarshes is much reduced. In the Mersey Estuary (UK), Wilson et al. (2005b) measured the C/N and $\delta^{13}C$ of the two main sources of organic carbon present, the inter-tidal sediments mainly derived from saltmarsh plants, and the sus-pended estuarine POC. It was shown that ground elevation, in relation to the tidal frame, was a key factor controlling bulk surface inter-tidal sediment C/N and $\delta^{13}C$ values. Supra-tidal and high saltmarsh sediments consisted almost entirely of organic carbon derived from the overlying C3 vegetation, and sub-tidal and tidal-flat sediments comprised mainly tidal-derived POC. The differ-ent sources of organic carbon in high saltmarsh and sub-tidal sediments resulted in differing bulk sediment $\delta^{13}C$ (–27.8‰ and –22.8‰, respectively) and C/N (11.6 and 9.3) values. This modern calibration study was then applied to a Holocene-aged sediment core taken from the Mersey Estuary. The major find-ings of the study showed that the interpretation of C/N and $\delta^{13}C$ within the Mersey Estuary agreed with other proxies and that inter-tidal and sub-tidal sur-face sediment values are preserved in the Holocene record (Fig. 9.4). However, Wilson et al. (2005b) noted that the detail of the complementary fossil analysis is often missing in the C/N and $\delta^{13}C$ data, but sea level variations can still be clearly identified. This is useful where microfossils are poorly preserved (Wilson et al. 2005b).

4.2   Riverine Estuaries

A riverine estuary is a partly enclosed coastal body of water with one or more rivers or streams flowing into it, and with a free connection to the open sea. Many studies have shown a gradient in $\delta^{13}C$ (low to high) and C/N (high to low) along the outer reaches of rivers as they approach the sea, from fluvial to marine sediments, especially in the suspended POM C/N and $\delta^{13}C$ (e.g. Lamb et al. 2006). This systematic shift in C/N and $\delta^{13}C$ is commonly preserved in the sedimentary record (Corbett et al. 2007), which also integrates seasonal fluctuations in C/N and $\delta^{13}C$. Along the Atlantic Coast of the USA, Hunt (1970) measured $\delta^{13}C$ from surface sediments in rivers and found that the river mouth sediments had $\delta^{13}C$ values of around $-20‰$, whereas several kilometres upstream, sediment $\delta^{13}C$ was around $-26‰$. In the Winyah Bay Estuary (USA), Goñi et al. (2003) showed that upstream POM had a C/N of 13 and $\delta^{13}C$ of $-26.3‰$, whereas in the lower reaches, C/N was around 6 and $\delta^{13}C$ $-22.7‰$. Similar patterns in C/N and $\delta^{13}C$ from suspended and deposited organic matter have been observed in numerous estuaries across the world (e.g. Sackett and Thompson 1963; Salomons and Mook 1981; Thornton and McManus 1994; Ruttenberg and Goñi 1997; Andrews et al. 1998; Middelburg and Nieuwenhuize 1998; Zong et al. 2006; Yu et al. 2010). The gradient in C/N and $\delta^{13}C$ commonly breaks down in the lower reaches of rivers/estuaries due to efficient sediment mixing and homogenisation (Lamb et al. 2006).

The existence of a gradient in sediment C/N and $\delta^{13}C$ along the axis of many poorly mixed riverine estuaries can be used as a palaeoenvironmental tool for investigating changes in sea level and palaeoriver discharge. In the Pearl River Estuary (southern China), analysis of C/N and $\delta^{13}C$ in surface sediments showed the gradual transition from fully marine conditions at the margins of the South China Sea to fully freshwater conditions in the inner estuary (Zong et al. 2006; Yu et al. 2010). This relationship was confirmed by diatom species analysis (Zong et al. 2006). Based on this relationship between modern diatom flora, C/N, $\delta^{13}C$, and converting diatom flora data to inferred salinity, Zong et al. (2006) were able to reconstruct the Holocene palaeodischarge history of the Pearl River Estuary from estuarine sediment cores. They showed increasing freshwater flux during the early Holocene reaching a peak at ca. 7500–6000 cal. years BP. From 6000 years BP, a reduction in freshwater flux was interpreted as being due to a weakening of the summer monsoon (Fig. 9.5).

C/N and $\delta^{13}C$ (commonly with $\delta^{15}N$) data can also be indicative of nutrient enrichment, eutrophication and anoxia (oxygen depletion), especially in riverine estuaries due to increased productivity and progressive alteration of ecosystem structure, and subsequent changes in the predominant source of organic matter supply to the sediment (e.g. Cifuentes et al. 1988; Eadie et al. 1994; Voss et al. 2000; Zimmerman and Canuel 2002; Bratton et al. 2003; Church et al. 2006; Thibodeau et al. 2006; Ellegaard et al. 2006; Rosenbauer et al. 2009). For example, a classic symptom of eutrophication in coastal systems is increased abundance of planktonic algae (Nixon 1995; Anderson et al. 2002), particularly diatoms and dinoflagellates, which has been
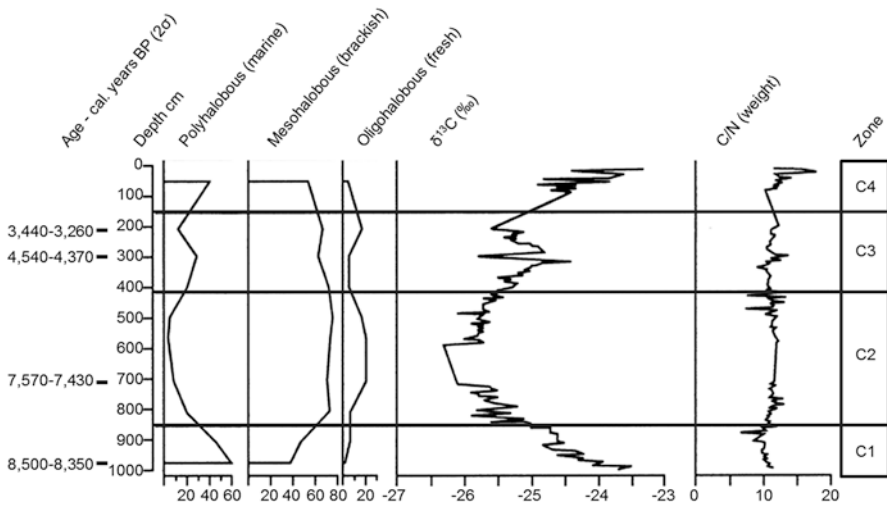
Fig. 9.5 Reconstruction of the Holocene river palaeodischarge history of the Pearl River Estuary from sediment cores taken in the Pearl River Estuary, southern China (Zong et al. 2006). C/N and $\delta^{13}C$ were first calibrated from modern surface sediments which showed a transition from fully marine conditions at the margins of the South China Sea to fully freshwater conditions in the inner estuary. Diatom flora, C/N and $\delta^{13}C$ were used as proxies for salinity and showed a significant increase in freshwater flux from 8500 cal. years BP resulting from the enhanced summer monsoon regime in the early Holocene. The strength of freshwater flux peaked between 7500 and 6000 cal. years BP. In the last 6000 years, freshwater flux decreased towards present, reflecting a gradual weakening of the summer monsoon (Zong et al. 2006)

shown to substantially shift C/N and $\delta^{13}C$ in some estuarine systems, largely through dilution of the other sources of organic matter (e.g. Ellegaard et al. 2006; Zimmerman and Canuel 2002). This is particularly well demonstrated in the eutrophic Mariager Fjord in Denmark over the last ca. 100 years, where nutrient loading has resulted in an approximately 4‰ increase in $\delta^{13}C$ and a decrease of up to 2 in C/N, concurrent with increased $\delta^{15}N$, diatom-inferred total nitrogen, sedimentary pigment abundances and a shift to a nutrient-rich dinoflagellate flora (Ellegaard et al. 2006).

Chesapeake Bay, the largest riverine estuary in the USA (situated between the states of Maryland and Virginia), is a classic example of a eutrophic estuary. It has received much attention over the past few decades due to increasing nutrient concentrations impacting the natural estuarine ecosystem (Seliger et al. 1985; Cooper and Brush 1991; Cornwell et al. 1996; Bratton et al. 2003; Brush 2009). Numerous multi-proxy palaeoenvironmental studies have been undertaken to reconstruct and monitor the extent, scale, longevity and long-term trends in nutrient concentrations (see Brush 2009 and references therein), and to study ecological responses, including the use of sedimentary C/N and $\delta^{13}C$ (Zimmerman and Canuel 2002; Bratton et al. 2003).

Zimmerman and Canuel (2002) used sediment geochemical analyses to reconstruct eutrophic progression over the past five centuries in cores collected from Chesapeake Bay. They found that $\delta^{13}C$ (and $\delta^{15}N$) began to increase in the mid-late eighteenth century, concurrent with significant land clearance (Fig. 9.6). Accompanied by increases in the flux of TOC, and plankton and bacterial biomarker
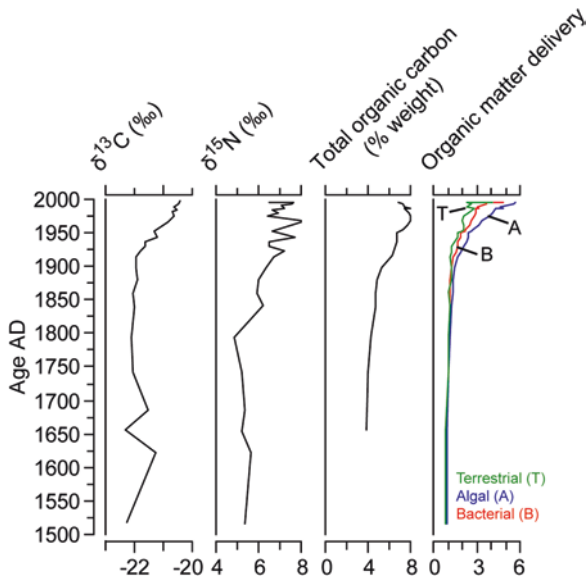
Fig. 9.6 $\delta^{13}C_{org}$, $\delta^{15}N_{org}$, total organic carbon (TOC) and biomarker evidence for organic matter source (i.e. algal, terrestrial or bacterial) from core M3 (Zimmerman and Canuel, 2002) for the last ~500 years. Increases in algal- (and bacterial-) derived OM, relative to terrestrial matter is clearly shown in the biomarker record. Similar results are evident in the two other cores (Cores RD and RR; Zimmerman and Canuel, 2002)

abundances (Fig. 9.6), this pattern generally continues up until the present day, but with increased intensity in the late 1800s and 1900s, reaching an advanced state of eutrophication in the 1950s, likely due to increased rates of land clearance following the introduction of dynamite for blasting of stumps (in the 1880s), "superphosphates", and later mechanisation (i.e. since the 1920s). The increase in $\delta^{13}C$ (of 0.5–2‰) is attributed to increasing marine primary productivity in the surface waters, carbon limitation (which uses the lighter carbon more quickly) and/or increasing phytoplankton-derived organic matter supply to the sediments. There was little change in the supply of terrestrial organic matter over this period, suggesting that this is not significantly affecting C/N or $\delta^{13}C$.

Importantly, human impact on the Chesapeake Bay watershed (beginning in the seventeenth century) pre-dates estuarine response, suggesting human impact did not trigger eutrophication and anoxia in the basin. Zimmerman and Canuel (2002) suggested climatic forcing caused the onset of eutrophication due to increased freshwater input (c.f. Stahle et al. 1998; Cronin et al. 2000) bringing more nutrients. Since the mid-late eighteenth century eutrophication occurs, even in normal rainfall years, due to the high levels of nutrients present within the watershed.

In a longer term record (ca. 2700 years) from Chesapeake Bay, Bratton et al. (2003) analysed TOC, C/N, $\delta^{13}C$ and $\delta^{15}N$ and showed that the $\delta^{13}C$ signal of the estuary reflects the relative mixing of terrestrial and marine carbon (end-members ~–26‰ and –20‰, respectively) with a trend towards increasing $\delta^{13}C$

values moving in the seaward direction from the head of the estuary. In Chesapeake Bay, marine POC is mostly produced by algae, whereas fluvial POC is isotopically lower ($\leq 25‰$). However, C/N ratios are more ambiguous possibly due to diagenesis (Bratton et al. 2003). They concluded that $\delta^{13}C$ reflects a greater input of terrestrial material, which occurs under wetter conditions, so it was possible to use $\delta^{13}C$ as a long-term proxy of wetness/dryness. They described wet-dry cycles identifiable over the last ca. 2700 years, and correlated them with environmental data from tree rings (Stahle et al. 1998), foraminifera (Cronin et al. 2000) and known historical wet/dry periods (e.g. droughts of the 1950s and 1960s).

4.3 Mangrove Habitats

Mangroves (tropical and temperate trees, shrubs and associated vegetation) live at the land-sea interface and their presence-absence are indicators of sea level change (e.g. Woodroffe et al. 1985; Woodroffe 1990; Schaeffer-Novelli et al. 2002; McKee et al. 2007). The mangrove biome (or mangle) consists of tidal swamps, common in coastal tropics and subtropics, where fine-grained sediments accumulate, and salinity can range from brackish to hypersaline conditions (e.g. Chapman 1976; Benfer et al. 2007; Krauss et al. 2008). The C/N and $\delta^{13}C$ values (and $\delta^{15}N$) of mangrove peat sediments (usually leaf fragments) are used mainly as a proxy of mangrove physiology and stand structure, i.e. the presence of tall versus dwarf plants at a particular site (Wooller et al. 2003a, b; Monacci et al. 2009). The tall/dwarf isotope differentiation is thought to be a function of nutrient limitation ($\delta^{15}N$) to the dwarf trees due to the more limited availability of nutrient-rich seawater, whereas differences in $\delta^{13}C$ are more likely a function of position/shading of the leaves on the plant. There are obvious difficulties with this interpretation, especially where visible leaf fragments are analysed, as leaf $\delta^{13}C$ will also vary up through the plant and be dependent on the amount of shading. However, the use of $\delta^{13}C$ (and $\delta^{15}N$) of mangle leaf fragments through time has been demonstrated over the last 8000 years from Twin Cays in Belize, where isotope variations are interpreted as indicative of changes between dwarf (mean $\delta^{13}C = -24.6‰$, $\delta^{15}N = -10‰$), transition and tall mangle (mean $\delta^{13}C = -28.3‰$, $\delta^{15}N = 0‰$). The interpretation is supported by $\delta^{18}O$ (of mangrove leaf fragments) as an indicator of sea level (seawater versus freshwater) (Wooller et al. 2007). While the isotope composition of mangrove plants can infer mangrove ecosystem and sea level variation, it is also obvious that local variation can lead to changes in sedimentation rate, deposition versus erosion, and fresh versus sea water availability. Monacci et al. (2009) showed that there can be significant local responses in a mangrove habitat and that regional environmental change can be manifested very differently between sites.

Mangrove sediments can be used in a similar way to estuarine sediments, allowing for physiology and stand structure variation. Peat cores from the mangrove belt of the Brazilian Amazon region, for example, have been used over the Holocene (with other proxies) to identify incidences of marine influence (Cohen et al. 2012). The authors showed enhanced variations in tidal water salinity during the early and

middle Holocene (mangrove habitats), which they took to infer increased aridity (less freshwater flux). The later Holocene showed an increase in fluvial influence that resulted in fragmentation of the mangrove belt as mangrove peat was replaced by sediments containing organic matter of a freshwater origin.

4.4   Lagoons

Lagoons are typically shallow water bodies partially separated from the sea by a physical barrier (e.g. sandbanks, shingle bars) and most are highly sensitive to sea level changes. Organic C/N and $\delta^{13}C$ analyses have been successfully applied to lagoon sequences to infer freshwater and seawater fluctuations (Müller and Mathesius 1999; Müller and Voss 1999; Yamamuro 2000). Most lagoons receive freshwater via surface inflow and seawater through narrow inlets or overbanking. Lagoons are not continuously flushed by fresh or marine water and, therefore, contain a significant portion of autochthonous organic matter, including plankton and macrophytes, but also can contain some allochthonous marginal terrestrial plant matter. Lagoons can be strongly influenced by human activities, especially the amount and flux of freshwater, which effects the types of autochthonous organic matter (Jia et al. 2012). Yamamuro (2000) examined a series of surface sediments from two large, connected, brackish lagoons in southwestern Japan using isotopes as well as carbon, nitrogen and phosphorous concentrations: the recent eutrophic sediments have C/N ratios of 8.7 to 11.4; suggesting that they contain a high proportion of plankton (either marine or freshwater) relative to terrestrial plant organic matter. The $\delta^{13}C$ values decreased with increasing distance from the seawater inlet into the lagoon, from –21.7‰ at 2.4 km from the inlet to –23.9‰ at 32.1 km, suggesting a decrease in marine organic matter which correlates with salinity. Since C/N ratios were unaffected by changes in salinity, there is no correlation between the C/N and $\delta^{13}C$ of the organic matter.

Lagoonal sediments can in places contain high amounts of inorganic nitrogen associated with clays. The amount of inorganic nitrogen becomes significant (when compared with %C) in sediments that contain very low concentrations of organic matter. In a study from Nakaumi Lagoon, southwest Japan, Sampei and Matsumoto (2001) investigated C/N ratios over the last ca. 8000 ^{14}C years BP. Their data showed two peaks in bulk C/N of >15 which could be interpreted as increases in terrestrial input, although this did not agree with the interpretation from other organic proxies. It was thought that high levels of inorganic nitrogen, throughout the core (~0.04 wt%) had the effect of lowering the C/N ratio where %C was less than 1 %. This study also highlighted the fact that high levels of phytoplankton can lead to problems when using C/N as a simple two end-member proxy. Sampei and Matsumoto (2001) modelled the relationship between the relative proportions of terrestrial and planktonic organic matter and C/N ratios, and demonstrated that the relationship was non-linear. C/N is therefore not just a function of the balance between the two end-member inputs.

In a Holocene study of coastal lagoons in the southern Baltic Sea region, Müller and Mathesius (1999) and Müller and Voss (1999), compared the C/N and δ^{13}C of modern plants and sediments to investigate sea level variation. The lagoons are currently separated from the Baltic Sea by low barrier islands, which have developed since the mid Holocene. C/N values were generally >12, with low δ^{13}C between –25 and –30‰, suggesting mainly freshwater-derived organic material (Müller and Voss 1999) with some terrestrial material (Müller and Mathesius 1999), although they also identified intermediary values of autochthonous macrophytes and plankton which complicated the interpretation. From a sediment core, the organic matter in the late Holocene had low C/N values, which was interpreted as less macrophyte and increasingly more phytoplankton input due to eutrophication (Müller and Mathesius 1999). Within the sediment core, the authors also distinguished (based on geochemistry and sedimentology) lacustrine phases (δ^{13}C = –29.1‰), sandy shallow lake environments with some aquatic macrophyte input (δ^{13}C –24.8‰, C/N > 12), as well as the more typical lagoonal phases following sand spit formation. Cores from different lagoons showed similar patterns (Müller 2002), although changes were not entirely synchronous suggesting the use of lagoonal sediments to decipher regional, as opposed to local, sea level change is not infallible.

4.5   Isolation Basins

Isolation basins are natural rock depressions that have been separated from the sea due to falls in relative sea level. They are extremely important as they provide long, high-resolution records of sea level change reaching back to the Late Glacial period (e.g. Shennan et al. 1999). Environmental data from isolation basins are extensively used to contribute to glacial-isostatic adjustment models. In a similar way to lagoons, isolation basins may be connected to the sea intermittently over a period of time depending on their height relative to sea level. The ability of C/N and δ^{13}C to record changes in the source of organic matter in C3 dominated systems has resulted in their use in isolation basin sediments as a proxy for shoreline displacement during the late Quaternary (e.g. Chivas et al. 2001; Westman and Hedenström 2002; Mackie et al. 2005; Mills et al. 2009). As UK isolation basins (common on the west coast of Scotland) are naturally C3-vegetated environments, Holocene sea level studies have traditionally relied on microfossil-based palaeoenvironmental reconstructions (e.g. Shennan et al. 2000; Berglund et al. 2005).

Mackie et al. (2005) measured a range of plants and surface sediment samples from around marine and freshwater contemporary isolation basins in western Scotland to characterise end-member values for C/N and δ^{13}C. They found that the surface sediment C/N and δ^{13}C reflected a mixture of the end-members from the range of modern inputs and thus concluded that, as with other "types" of estuaries, the dominant controlling variable on C/N and δ^{13}C of surface sediment was the source of the organic matter (terrestrial, marine). In isolation basins, C/N and δ^{13}C should therefore be a reliable proxy for past changes in basin salinity and sea

level. In a Holocene study of C/N and $\delta^{13}C$ profiles from bulk organics from Upper Loch nan Eala (Scotland), Mackie et al. (2005) described a variety of conditions in the basin from fully marine, through to transitional/brackish and freshwater (Fig. 9.7). These palaeoenvironmental changes, inferred from the core C/N and $\delta^{13}C$ data, coincide well with the diatom-inferred environments and with previously interpreted changes in sea level (Shennan et al. 2000). However, the relationship breaks down around 6000 cal. years BP when diatoms indicate fully marine conditions, whereas C/N and $\delta^{13}C$ are more indicative of freshwater. Several possible explanations were discussed including varying amounts of marine plankton or a change in temperature or CO_2 concentration that might affect the fractionation of $\delta^{13}C$. This discrepancy between the diatom salinity reconstruction and geochemical proxies suggests that although the technique appears to work, it is important to use a multi-proxy approach as factors other than organic matter source can influence the interpretation of C/N and $\delta^{13}C$. Philippsen et al.
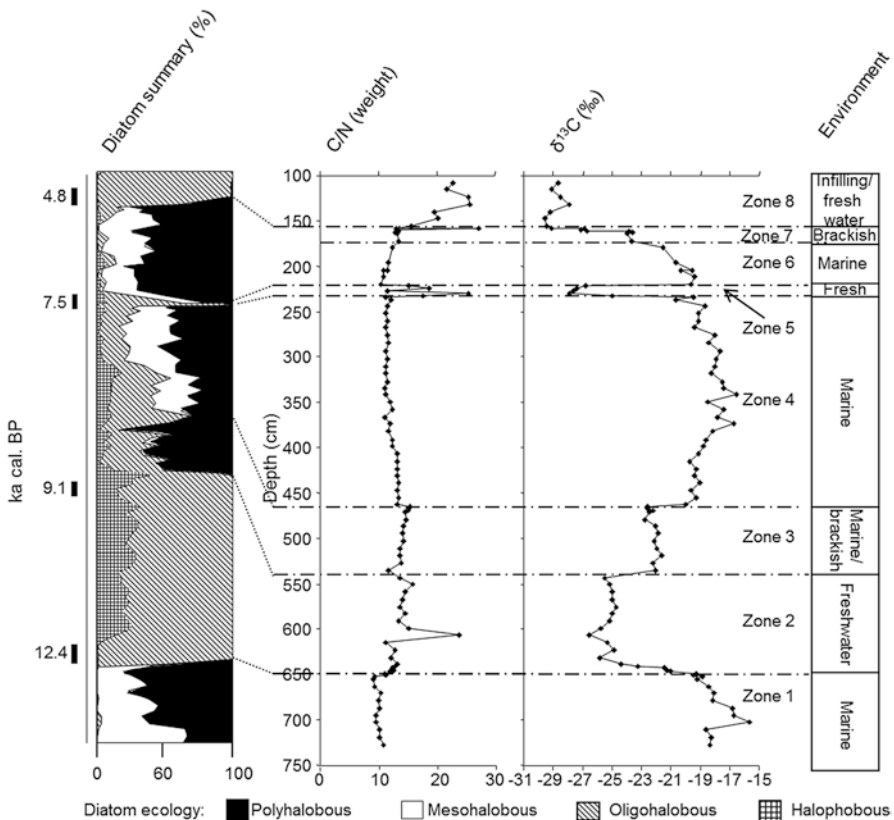

Fig. 9.7 Upper Loch nan Eala sediment core showing the qualitative diatom palaeosalinity reconstruction, C/N, and $\delta^{13}C$. The sequence is divided into seven zones based on changes in the $\delta^{13}C$ and C/N data. These zones closely correlate with changes in the diatom flora, suggesting a strong salinity control on the type of the organic material entering the basin

(2013) also demonstrated a strong relationship between diatom-inferred salinity and bulk organic $\delta^{13}C$ from a small estuary (Kilen) opening into the Danish Limfjord (a shallow sound subject to changing exposure to, and occasional isolation from, the North Sea and Skagerrak), which was further supported by mollusc, foraminifera and plant macrofossil data (Lewis et al. 2013).

The Gulf of Carpentaria (between Australia and New Guinea) has periodically been cut off from the Indian and Pacific Oceans during the Late Quaternary, forming Lake Carpentaria (Chivas et al. 2001). During periods of low sea level the lake forms an isolation basin with an outlet channel into the Arafura Sea. A multi-proxy study of sediment cores from the lake (going back to 130,000 ^{14}C years BP) showed periods of open ocean, estuarine and lacustrine conditions, as well as sub-aerial exposure. C/N and $\delta^{13}C$ from 9700 ^{14}C years BP showed that C/N was predominantly higher in the non-marine facies, while $\delta^{13}C$ values showed differences between the non-marine (–14 to –15‰) and marine (–19 to –21‰) phases. The non-marine $\delta^{13}C$ values, with high C/N of 10–30 were thought to reflect the abundance of C4 grasses growing around Lake Carpentaria during periods of low sea level (Chivas et al. 2001).

4.6   Fjords and Glacial Embayments

Fjords are deep, submerged, long and narrow inlet valleys formed by glacial activity. Mixing occurs between the freshwater-terrestrial inflow of plant material and marine POM. Due to the depth of many fjords, tidally derived water can also enter a fjord through deep-water inflows that can reach as far as the fjord head. There are relatively few examples where C/N and $\delta^{13}C$ have been applied to fjord sediments. In general though, we expect the distribution between marine and terrestrial-freshwater organic matter to change along the fjord much as it does in a river estuary. $\delta^{13}C$ values increase towards the marine environment whereas C/N decreases (St-Onge and Hillaire-Marcel 2001; Sepúlveda et al. 2011). Similar to fjords are polar embayments formed by indentations in the shoreline. These are often ice dammed, creating semi-enclosed bays which contain a lid of freshwater. One such embayment occurs along the Antarctic Peninsula and Alexander Island where $\delta^{13}C$ has been used to investigate past phases of collapse in the George VI Ice Shelf (Bentley et al. 2005). Lakes forming behind the ice shelf have freshwater lids but retain a deep marine connection under the ice shelf. Bentley et al. (2005) used both the presence of marine-dominated organisms and bulk organic $\delta^{13}C$ to prove the presence/absence of the ice shelves through the Holocene. Specifically, where the organic matter in the sediments had a high $\delta^{13}C$ (between –23 and –22‰), there was more marine organic matter, suggesting the absence of ice shelves at that time (and no freshwater lid). When the sediments contained organic matter with low $\delta^{13}C$ (around –26‰), then there was likely to be a lid of freshwater and the shelves were more likely to have been present (Fig. 9.8).
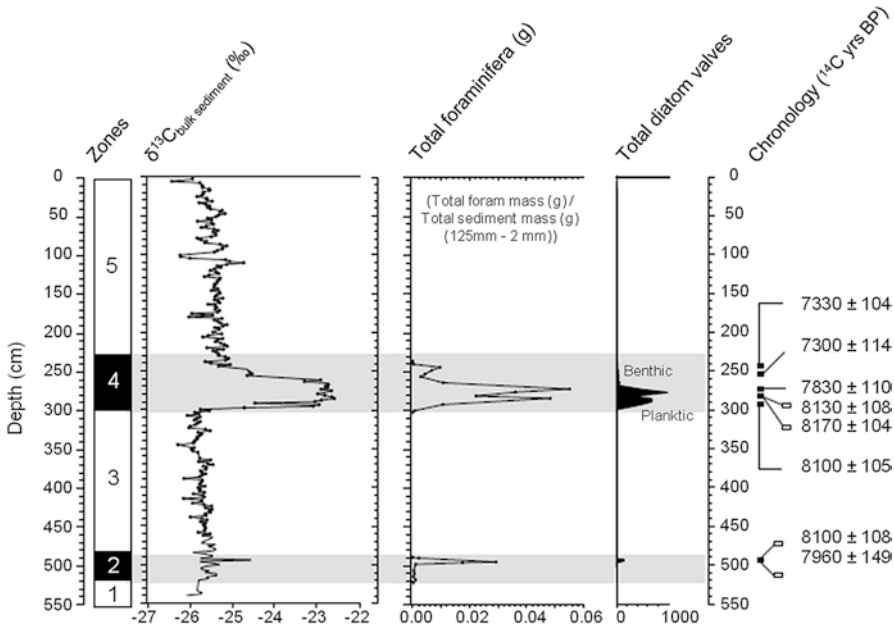
Fig. 9.8 Multi-proxy analysis of sediments from Moutonnee Lake on the Antarctic Peninsula. Proxies include $\delta^{13}C$ of organic matter in bulk sediment, and foraminiferal and diatom concentrations. The bulk organic $\delta^{13}C$ as well as the presence of marine-dominated organisms were used to prove the presence/absence of the ice shelves through the Holocene. Specifically, where the organic matter in the sediments has a high $\delta^{13}C$ then there is more marine organic matter suggesting the absence of the ice shelves. When the sediments contain organic matter with low $\delta^{13}C$ then there was likely to be a lid of freshwater and the shelves are more likely to have been present (from Bentley et al. 2005)

5   Summary

The sediments that are preserved in estuarine environments (saltmarsh, riverine estuaries, mangrove habitats, lagoons, isolation basins and fjords) contain organic matter that allows investigation of the provenance of that material. These data can then be used specifically to investigate past sea level/land level changes and changes in freshwater flux. Where microfossils are poorly preserved or absent, C/N and $\delta^{13}C$ analyses offer an alternative method to deduce environmental histories, especially when used in conjunction with a range of other proxies, and when local modern end-member organic variables can be measured to 'calibrate' the sedimentary C/N and $\delta^{13}C$. There are a wide range of C/N-$\delta^{13}C$ based carbon budget studies, providing a database of examples of different coastal conditions that can be used for end-member composition for C/N and $\delta^{13}C$.

The most successful studies are probably those that have utilised a known relationship between C3 and C4 plant distribution and salinity in coastal environments, and have then applied this relationship back through the Holocene. In particular, the

pioneering work in the San Francisco Basin demonstrated that the relative proportions of C3 and C4 plants growing in an area were preserved in the $\delta^{13}C$ composition of the underlying surface sediment, and thus past changes in salinity could be interpreted by observing sedimentary changes in $\delta^{13}C$. Where there are no native C4 plants, $\delta^{13}C$ and C/N have also been successfully used as palaeoenvironmental indicators, as bulk inter-tidal sedimentary $\delta^{13}C$ and C/N can reflect elevation within the tidal frame. Supra-tidal and high saltmarsh sediments consist almost entirely of organic carbon derived from the overlying C3 vegetation, and sub-tidal and tidal-flat sediments of tidal-derived POM.

In riverine estuaries the use of C/N and $\delta^{13}C$ works because of the systematic shift of the provenance of organic matter along the estuary. Several examples can be found all over the world, but in particular along the Pearl River Estuary (China) and Chesapeake Bay (USA), although in the latter case sea level indicators are overprinted by anthropogenic effects in the more recent sediments. The use of C/N and $\delta^{13}C$ to provenance organic matter has also been used to varying degrees of success in mangrove habitats and lagoons, although other environmental effects, like tree stands, sediment dispersal and eutrophication, can over print the primary signal. In isolation basins, C/N and $\delta^{13}C$ work particularly well because the change from marine to non-marine conditions can be abrupt, as the isolation is due to a physical barrier. This has been proven particularly well in northwest Scotland. C/N and $\delta^{13}C$ in fjords and glacial embayments are used in a similar way to riverine estuaries in that the distribution of freshwater/terrestrial and marine organic matter, as a result of variations in sea level, freshwater flux, and in the case of glacial embayments the presence/absence of ice shelves, may be determined.

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