Chemical Geology 255 (2008) 114–119

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Influence of *Spartina* and *Juncus* on saltmarsh sediments. III. Organic geochemistry

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ARTICLE INFO

Article history:
Received 17 January 2008
Received in revised form 10 June 2008
Accepted 15 June 2008

Editor: D. Rickard

Keywords:
Saltmarsh
Juncus roemarianus
Spartina alterniflora
Organic matter
Carbon stable isotopes
Bioturbation

ABSTRACT

Total organic carbon, C/N ratios of sediment organic matter and $\delta^{13}C$ of sediment organic matter ($\delta^{13}C_{org}$) were measured as a function of depth at four sites in a saltmarsh on Sapelo Island, GA during summer 2006. The goal of this study is to assess the sources of sediment organic matter at each site and to investigate the influence of macrophytes and macrofauna on the observed carbon isotopic signatures and C/N ratios at each site. The four sites include two adjacent creekside sites, one densely vegetated by tall-form *Spartina alterniflora* and the other mostly unvegetated, together with two adjacent sites higher in the marsh, including a site with sparse short-form *Spartina* and a neighboring site densely vegetated with *Juncus roemarianus*. Total organic carbon in the sediments of these sites varies between 2.1 and 6.4%, with the highest values observed at shallow depths at the unvegetated creek bank and the lowest at the short *Spartina* site. C/N ratios of the sediment organic matter vary between 10.6 and 17.3, with higher values at the short *Spartina* site compared to the other three sites. $\delta^{13}C_{org}$ varies little with depth, averaging −20.1 ± 0.2‰ at the *Juncus*, tall *Spartina* and adjacent unvegetated sites, and −17.8 ± 0.6‰ at the short *Spartina* site. Mixing calculations completed with the depth-averaged C/N and $\delta^{13}C_{org}$ for each site, assuming three endmember organic matter sources (C_3 plants, C_4 plants, phytoplankton), suggest that up to 75% of the organic matter at all four sites is derived from phytoplankton. Surprisingly, the average $\delta^{13}C_{org}$ and C/N values, and therefore the calculated contributions of the three endmember organic matter sources to the total sediment organic matter, are very similar at the *Juncus*, tall *Spartina* and unvegetated creekbank sites. The greater $\delta^{13}C_{org}$ and C/N of the short *Spartina* sediments is consistent with little or no inclusion of C_3-derived organic matter in the sediments at this site, in spite of the close proximity to the densely-vegetated *Juncus* site, and with less degradation of the organic matter compared to the other three sites.

1. Introduction

Carbon cycling in saltmarsh sediments has received considerable attention, because saltmarshes have long been recognized as ecosystems with very high rates of primary productivity (Schubauer and Hopkinson, 1984; Dame and Kenny, 1986; Dai and Wiegert, 1996). There is an increasing interest in quantifying carbon accumulation, processing and export from these important coastal ecosystems (e.g., Chmura et al., 2003; Choi and Wang, 2004; Borges, 2005; Duarte et al., 2005; Wang et al., 2005). Carbon stable isotopes have been used as a tracer of the sources of accumulated organic carbon in saltmarsh sediments (e.g., Haines, 1976a,b; Ember et al., 1987; Peterson and Howarth, 1987; Fogel et al., 1989; Gardner, 1990; Benner et al., 1991; Currin et al., 1995; Middelburg et al., 1997; Boschker et al., 1999; Goni and Thomas, 2000; Dai et al., 2005). Potential organic carbon sources in Georgia coastal marshes include: (1) organic matter derived from the C_4 macrophyte *Spartina alterniflora*, (2) material derived from C_3 macrophytes within the saltmarsh, such as *Juncus roemarianus*, together with allochthonous contributions from terrestrial upland C_3 plants and (3) organic matter derived from phytoplankton.

C_4 and C_3 sources are readily distinguished by their distinctive $\delta^{13}C$ values. Live *Spartina alterniflora* (C_4 plant) has been reported to have $\delta^{13}C$ signatures ranging from −12.2 to −13.6‰ (Haines, 1976a; Peterson and Howarth, 1987; Currin et al., 1995; Middelburg et al., 1997; Boschker et al., 1999; Goni and Thomas, 2000; Cheng et al., 2006), while senescent stems and leaves have $\delta^{13}C$ values between −12.8 and −12.9‰ (Currin et al., 1995; Middelburg et al., 1997). Although Currin et al. (1995) report no change in the $\delta^{13}C$ of *Spartina* during aerial decomposition, Ember et al. (1987) observed a shift from −13.6‰ (fresh *Spartina*) to between −15 and −16‰ after burial in marsh sediments for approximately one year. Benner et al. (1991) similarly observed a decrease in *Spartina* $\delta^{13}C$ after 18 months of decomposition, which they attributed to preferential loss of isotopically heavy polysaccharides during degradation of the organic matter. C_3-derived organic matter is considerably lighter than either fresh or degraded *Spartina*, with $\delta^{13}C$ typically ranging from −22.8 to −29.3‰ (Haines, 1976a; Peterson and Howarth, 1987; Goni and Thomas, 2000). The $\delta^{13}C$ of *Juncus roemarinus*, for example, has been reported to range between −22.8 and −26‰ (Haines, 1976a; Hughes and Sherr, 1983; Goni and Thomas, 2000), with little difference observed between living and dead tissue. Distinguishing between C_3 and C_4 source material in saltmarsh sediments is complicated, however, by the

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doi:10.1016/j.chemgeo.2008.06.015

potential contributions of phytoplankton, which have intermediate $\delta^{13}C$ values. For example, Haines (1976a) reports $\delta^{13}C$ between −16.2 and −17.9‰ for benthic diatoms collected in a Georgia coastal saltmarsh, while Currin et al. (1995) report values between −13 and −17.6‰, depending on season, for microalgae from a saltmarsh located in North Carolina. Dai et al. (2005) report $\delta^{13}C$ of −20.16 for fresh marine diatoms collected in Maine, and −19.47‰ for degraded diatoms, similar to values of −22.1 to −22.7‰ reported by Haines and Montague (1979) for diatoms collected in Georgia.

Previous studies of *Spartina*-vegetated saltmarsh sites have consistently observed more ^{13}C-depleted bulk sediment organic carbon than would be expected if *Spartina*, either fresh or degraded, was the primary source of sediment organic carbon (Haines 1976a; Ember et al., 1987; Peterson and Howarth, 1987; Fogel et al., 1989; Middelburg et al., 1997; Goni and Thomas, 2000; Dai and Sun, 2007). This has been attributed primarily to mixing with more ^{13}C-depleted organic carbon, either derived from phytoplankton or upland C_3 plants. In contrast, studies of *Juncus*-vegetated marsh sites have shown that $\delta^{13}C_{org}$ in the bulk sediment is more ^{13}C-enriched than the *Juncus*, again suggesting dilution, but with more ^{13}C-enriched organic matter sources, such as C_4 detritus or phytoplankton.

C/N ratios can also be useful for distinguishing organic source material in saltmarsh sediments, because phytoplankton, C_3 and C_4 plants have distinctive C/N ratios (e.g., Dai and Sun, 2007). However, C/N ratios change significantly with degradation of organic matter, probably because nitrogen-rich refractory compounds are preferentially retained in the partially decomposed organic matter (Benner et al., 1991; Goni and Thomas, 2000). For example, Middelburg et al. (1997) report C/N for living *Spartina* of 74.2 (above ground) and 69.8 (below ground) compared to 55.3 for senescent stems and 37.3 for *Spartina* litter. Dai et al. (2005) report a decrease from 8.2 to 6.9 for the C/N ratio of fresh compared to degraded marine diatoms and a decrease from 16.5 to 14.2 for fresh compared to degraded C_3 land grass (*Festuca arundinacea*). However, Dai et al. (2005) report relatively little change in the C/N of fresh *Spartina* (34.0) compared to the same material after experimental degradation (33.5). Goni and Thomas (2000) report high C/N values in the tissues of living *Juncus* (48) and *Spartina* (62), with lower C/N in sediment macro-organic material and even lower C/N in sediment humus, again consistent with preferential retention of nitrogen-rich compounds as organic matter degradation proceeds.

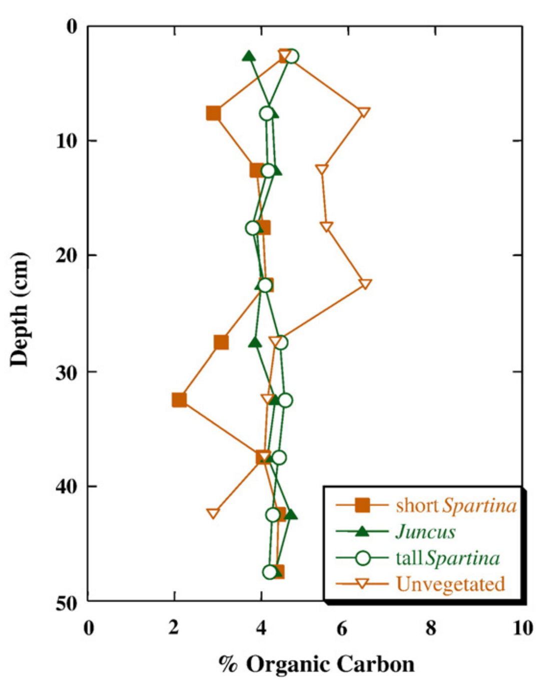

Fig. 1. Percent organic carbon as a function of depth at the short *Spartina* (filled squares), *Juncus* (filled triangles), tall *Spartina* (open circles), and unvegetated creekbank (open triangles) sites.

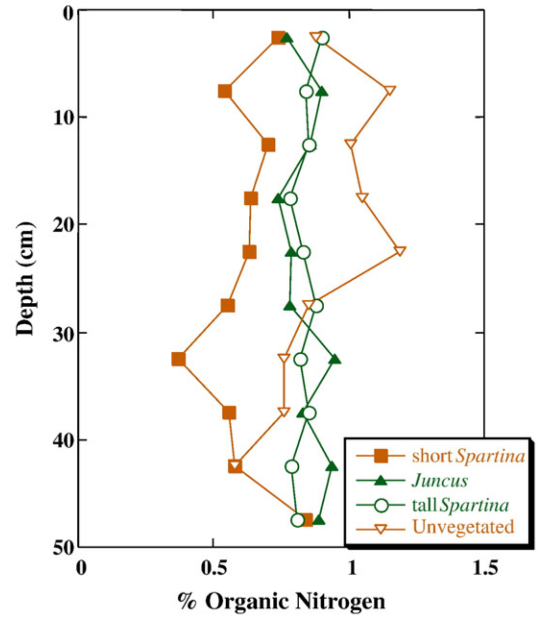

Fig. 2. Percent organic nitrogen as a function of depth at the short *Spartina* (filled squares), *Juncus* (filled triangles), tall *Spartina* (open circles), and unvegetated creekbank (open triangles) sites.

In this study, the percent organic carbon and C/N and $\delta^{13}C$ of sediment organic matter are assessed as a function of depth (at 5 cm intervals to 50 cm depth) at two pairs of saltmarsh sites. The first pair of sites, located near a tidal creek, includes an unvegetated creekbank and an adjacent site with dense, tall-form *Spartina alterniflora*. The second pair of sites, higher in the marsh, includes a site with very sparse short-form *Spartina* and a neighboring site with dense *Juncus roemarinus*. The goal of the present study is to assess the contribution of various carbon sources (C_3-, C_4- and phytoplankton-derived organic matter) to the sedimentary organic matter at each site and to determine the influence of site location within the marsh, together with macrophyte and macrofaunal activity, on the carbon isotopic signatures and C/N ratios. The pore water geochemistry, including major elements, redox-sensitive species and nutrients at these sites are reported elsewhere (Koretsky et al., 2008a), and operationally-defined sequential extractions have been used to assess the partitioning of trace elements in the same cores used in this study (Koretsky et al., 2008b).

2. Field sites

The field sites are discussed in more detail in a companion study (Koretsky et al., 2008a). Briefly, the four sites are in a saltmarsh near the University of Georgia Marine Institute at Sapelo Island, GA. One site, mostly unvegetated is located near a large tidal creek. A second creekside site, located <1 m away, is in an area of dense tall-form *Spartina alterniflora*. Two other sites are located at ~70 m distance, higher in the marsh. One of these sites is sparsely vegetated by short-form *Spartina alterniflora*, and the other, ~1 m away, is in an area densely vegetated by *Juncus roemarianus*. Sampling was completed during July 2006, with one core retrieved and processed each day during a 4-day sampling period. Each core was extracted within 50 cm of the pore water sampling site.

3. Materials and methods

Cores were extracted using a stainless steel Russian peat corer (Aquatic Research Instruments) to minimize compaction, and divided into 4–5 cm sections in the field using a plastic spatula, under ambient