

## Allocation of particulate organic carbon from different sources in two contrasting estuaries of southeastern U.S.A.

*Ernesto Otero*

Department of Marine Science, University of Puerto Rico, Isla Magueyes Laboratories, P.O. Box 908, Lajas, Puerto Rico 00681

*Randolph Culp and John E. Noakes*

Center for Applied Isotopes Study, University of Georgia, 120 Riverbend Road, Athens, Georgia 30602-4702

*Robert E. Hodson*

School of Marine Programs, Marine Sciences Building Room 212, University of Georgia, Athens, GA 30602-3636

### *Abstract*

Particulate organic carbon (POC) is an important component in the carbon cycle of estuarine systems. Many studies have utilized carbon isotopic composition ( $\delta^{13}\text{C}$ -POC) to estimate the origin of POC. Most of the early studies were restricted to areas of minimum terrestrial inputs of POC, whereas later studies used multiple stable isotope analysis. In our study, we assess the proportion of POC from  $\text{C}_3$  and  $\text{C}_4$  plants and microalgae in two terrestrially affected, contrasting estuaries of the southeastern U.S.A.: the Altamaha (Piedmont) and the Satilla (blackwater) Rivers. Our analysis was based on a mass balance equation, taking into consideration the estimated amounts of microalgae and  $\text{C}_3$  and  $\text{C}_4$  plant material. Analysis of  $\delta^{13}\text{C}$  of extracted chlorophyll *a* (Chl *a*) was used to estimate the isotopic signature of microalgae to constrain the three endmember mass balance. The maximum concentration of POC fluctuated between 9 and 11 mg C L<sup>-1</sup>, coinciding with the period of maximum riverine flow. The POC represented 50–70% of the total organic carbon. However, large fluctuations were observed, suggesting important tidal- and wind-driven resuspension. The  $\delta^{13}\text{C}$ -POC ranged from  $-21$  to  $-28\text{‰}$ , being more depleted at lower salinities. This indicates rapid dilution of terrestrially derived material with estuarine- or marine-derived material. The Chl *a* concentration was maximal during summer in upstream stations of the Altamaha estuary, while the Satilla generally showed a midestuary maximum. The  $\delta^{13}\text{C}$  of Chl *a* ranged from  $-20.7$  to  $-31.43\text{‰}$ , indicating isotopically depleted inputs of microalgal-derived material (MaDM). Our results suggest that MaDM is the dominant component of POC in the Altamaha River during summer, whereas the  $\text{C}_3$  component is dominant during periods of lower productivity and high flushing. Although MaDM is significant in the Satilla estuary, most of the POC consists of material derived from  $\text{C}_3$  and  $\text{C}_4$  plants.

Particulate organic matter (POM) in estuarine systems is derived from a multitude of sources. Darnell (1967) divided these into autochthonous and allochthonous inputs. The former includes phytoplankton, submerged vegetation, benthic diatoms and cyanobacteria, and periphyton living on stems of emergent plants, whereas the latter consists of marginal marsh and swamp vegetation; marine- or river-borne phytoplankton and detritus; and beach, shoreline, and wind-blown material. In estuaries of the eastern United States, this complex mix of POM can be classified as upriver salt marsh and microalgal derived. Upriver POM is dominated by  $\text{C}_3$  plant material, whereas  $\text{C}_4$  plant material (*Spartina* sp.) dominates salt marsh-derived POM. These two types of POM can be differentiated based on their stable carbon isotope

signature ( $\delta^{13}\text{C}$ ). Typical  $\delta^{13}\text{C}$  values for  $\text{C}_3$  plants range from  $-23$  to  $-34$ , with an average of  $-27\text{‰}$ , whereas  $\text{C}_4$  plants range from  $-6$  to  $-23$ , with an average of  $-12$  to  $-14\text{‰}$ , respectively (Shidlowksi et al. 1983). Although microalgae fix carbon via the  $\text{C}_3$  pathway, the range of microalgal  $\delta^{13}\text{C}$  signatures encompass those of  $\text{C}_3$  and  $\text{C}_4$  plants (Shidlowksi et al. 1983). This is due to changes in the type of inorganic carbon ( $\text{CO}_2$  or  $\text{HCO}_3^{-1}$ ) available for assimilation and photosynthetic rates (Laws et al. 1995; Fry 1996).

The *outwelling hypothesis* (Odum 1968) triggered numerous studies assessing the importance of different sources on the composition of POM in estuarine environments. Early  $\delta^{13}\text{C}$  analysis of suspended particulate organic matter (SPOM) indicated that the  $\delta^{13}\text{C}$  of detritus was similar to that of *Spartina*, only in tidal creek sediments (Haines 1976; Sherr 1982). The limited stable isotope evidence of *Spartina* detritus in estuarine SPOM is explained by the net deposition of particles within salt marshes (Chalmers et al. 1985). However, studies using multiple stable isotopes to trace the origins of particles (Peterson et al. 1985; Peterson and Howarth 1987; Fogel et al. 1989; Currin et al. 1995) indicate that *Spartina* is a significant component of SPOM and an important nutritional supplement for consumers in salt marsh estuarine systems. Similarly, Benner et al. (1987) indicated

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a depletion of the  $\delta^{13}\text{C}$  of *Spartina* material, suggesting that salt marsh material export could have been underestimated.

Estuaries with significant inputs of terrestrial material are expected to contain more depleted  $\delta^{13}\text{C}$ -POM. Sherr (1982) found POM  $\delta^{13}\text{C}$  of about  $-28\text{‰}$  at the head of the Altamaha River estuary with a rapid change to  $-23\text{‰}$  downstream, indicating fast dilution of terrestrial material with POM from microalgae or salt marshes. In contrast, Cifuentes (1991) observed a range of  $\delta^{13}\text{C}$ -POM of  $-24.1$  to  $-18.1\text{‰}$  in the Delaware estuary similar to the range found by Gearing et al. (1984) in Narragansett Bay, Rhode Island. The higher minimum  $\delta^{13}\text{C}$  of POM in these systems, relative to that found by Sherr (1982) in the Altamaha estuary, suggests that the proportion of terrestrial material in the POM mix is less in the Delaware and Narragansett estuaries than in the Altamaha. Cifuentes et al. (1988) found geographical and temporal increments in the  $\delta^{13}\text{C}$  of POM concomitant with the increase in primary productivity in the Delaware estuary. These results suggest that phytoplankton supplies a large portion of the SPOM in these estuaries, controlling the observed intra-annual variability.

The identification of the major sources of organic matter in estuarine systems using only  $\delta^{13}\text{C}$  analysis of bulk material is difficult to interpret because of the complex mixture of sources mentioned above. Elemental analyses have been utilized in estuarine and coastal systems to assess potential sources of POM. A decline in the C/N ratio of POM from 15 to  $\sim 6$  has been associated with higher proportions of phytoplankton products in the sedimentary organic pool in the Delaware and Narragansett Bays (Oviatt and Nixon 1975; Cifuentes 1991). Mishima et al. (1999) found C/N ratios in Osaka Bay sediments ranging from 8 to 21, with higher values closer to sources of riverine (terrestrial) inputs of organic matter. However, diagenetic or biological alteration of organic matter diminishes the capacity of C/N ratio analysis to distinguish the original source of POM (Thornton and McManus 1994). More detailed information about the origins of POM in estuaries can be derived from chemical marker analysis. Vascular plant-derived material can be detected, and proportions from  $\text{C}_3$  and  $\text{C}_4$  plants can be assessed by examining lignin oxidation products (LOPs) coupled with  $\delta^{13}\text{C}$  analysis (Goñi and Eglington 1996). The content and  $\delta^{13}\text{C}$  analysis of lipid biomarkers have been used to study potential sources of POM and the effect of the source on the organic matter isotopic signature observed in surficial sediments of estuaries. Canuel et al. (1997) found a profound effect on the total organic carbon  $\delta^{13}\text{C}$  signature due to annual fluctuations in microbially derived matter.

It is important to determine the stable carbon composition of microalgae when studying the proportion of materials from different sources in estuaries. Microalgae are a potentially significant component of the SPOM and their  $\delta^{13}\text{C}$  may overlap that of  $\text{C}_4$  and  $\text{C}_3$  plants, causing the  $\delta^{13}\text{C}$  analysis of bulk POM to be insufficient for distinguishing the main sources of organic matter in estuarine systems (Matson and Brinson 1990). For this reason, different approaches have been taken to produce location-specific estimates of phytoplankton biomass. Phytoplankton  $\delta^{13}\text{C}$  have been estimated mainly by analysis of SPOM trapped on filters (Boutton 1991), but the presence of other sources of POM in estuaries

and rivers makes this approach prone to errors because of contamination by nonphytoplankton-derived SPOM. To diminish contamination problems, the  $\delta^{13}\text{C}$  of microalgae have been estimated analyzing material from algal mats (Haines 1976), cells that have migrated through fine nettings (Currin et al. 1995), and alga-rich material obtained by centrifugation with colloidal silica (Hamilton and Lewis 1992). The determination of  $\delta^{13}\text{C}$  of pigments extracted from SPOM is another approach to estimate the isotopic signature of microalgae. Bidigare et al. (1991) found that the  $\delta^{13}\text{C}$  of bulk plant material versus that of its Chl *a* covaried linearly, with an  $r^2$  of 0.93. Using the Chl *a*  $\delta^{13}\text{C}$  signatures, Qian et al. (1996) estimated that fixation of  $^{13}\text{C}$ -depleted  $\text{CO}_2$  from local decomposition of organic matter or freshwater inputs was responsible for the low  $\delta^{13}\text{C}$  values of SPOM in Corpus Christi Bay, Texas. Considering the above, we examined the seasonal and spatial changes in the distribution, concentration, and carbon stable isotope composition of SPOM in two contrasting coastal systems, the Altamaha and Satilla River estuaries (piedmont and blackwater rivers) in the southeastern United States. We estimated the contribution made by upriver ( $\text{C}_3$ -dominated forests), adjacent marsh ( $\text{C}_4$ -dominated wetlands), and microalgal material to the complex SPOM mix. For the first time, the SPOM  $\delta^{13}\text{C}$  data was complemented with microalgal-derived material data (Chl *a* concentration and  $\delta^{13}\text{C}$  signature) and used in a mass balance approach.

## Methods

**Study area**—The study was conducted in the estuaries of the Altamaha and Satilla Rivers adjacent to the South Atlantic Bight, southern Georgia coast (Fig. 1). The Altamaha and Satilla Rivers are representative of the two types of estuarine systems found in the region. The Satilla is a blackwater river that receives most of its runoff from the adjacent coastal plain region. Its waters have high concentrations of dissolved organic carbon (DOC of  $\sim 30$ – $40 \text{ mg C L}^{-1}$ ), are slightly acidic (pH 6–7), and have residence times up to 3 months (Wiegert et al. unpubl.). In contrast, a large proportion of the runoff transported to the Altamaha estuary is derived from the upland Piedmont region. The headwaters of the Altamaha River are characterized by a higher clay content, lower DOC concentration ( $\sim 5 \text{ mg C L}^{-1}$ ), and neutral pH. The water residence time in the Altamaha estuary is on the order of a few days to a few weeks (Wiegert et al. unpubl.). Marked differences between both estuarine systems are also observed when considering fluctuations in river discharge (Table 1). The Satilla River is characterized by a more uniform, lower discharge throughout the year, whereas the Altamaha discharge increases significantly during spring. Salinity measurements during our samplings in stations at the mouth of these estuaries show a pattern corresponding to the expected discharge rate (Table 1).

**Sample collection**—Surface water samples were collected from three to five stations at salinities from 0‰ (upstream) to the maximum salinity at or near the river mouth on board the RV *BlueFin* or RV *El Mar* from April 1995 to July 1996.

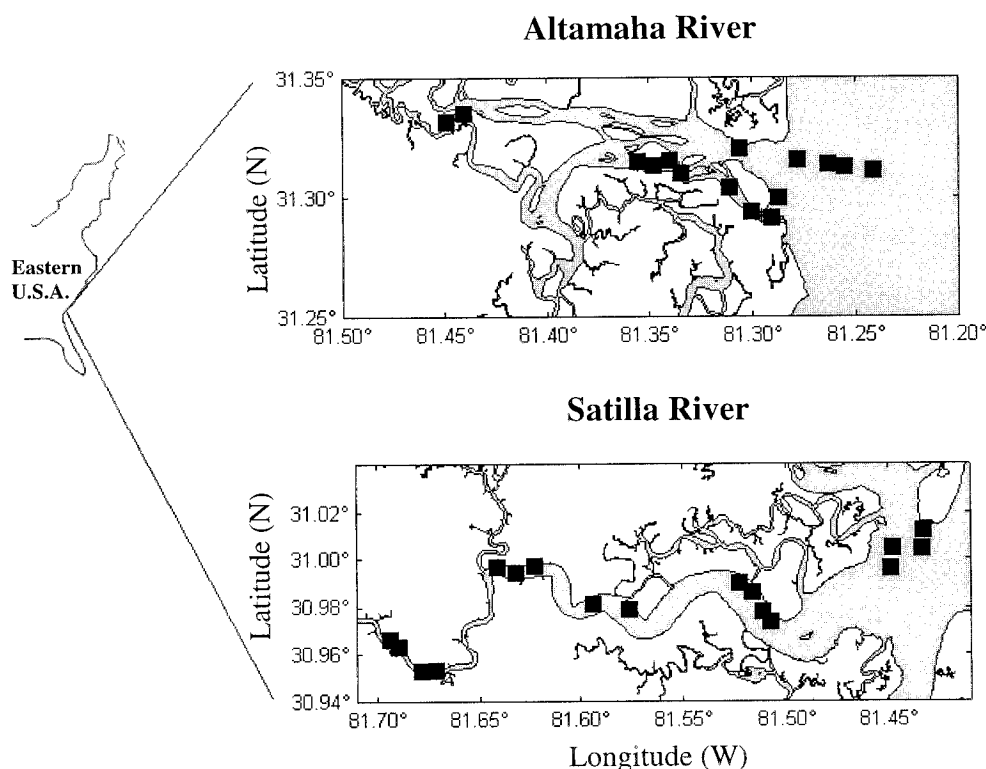


Fig. 1. Collection of sampling stations from April 1995 through July 1996 in the Altamaha and Satilla River estuaries.

Sampling station position was determined using a shipboard differential GPS system (Magellan).

**Particulate organic carbon**—Particulate organic carbon (POC) was estimated based on the difference between total organic carbon (TOC) content of unfiltered water samples and DOC of filtered (Whatman GF/F) water samples. Samples for TOC and DOC were collected either in 50-ml polypropylene centrifuge tubes (Corning) or in Teflon-capped glass vials and were stored at 5°C. Analysis of TOC and DOC was conducted using high-temperature catalytic com-

bustion on a TOC 5000 analyzer (Shimadzu) within 5 d of collection. Prior to analysis for DOC, samples were acidified with 20  $\mu$ l phosphoric acid. Purging was set to 15 min, and TOC samples were vortexed every 15 min to insure proper mixing.

**Chl *a* concentration**—Chl *a* concentration was determined by direct water extractions of 3-ml water samples in 100% acetone (Phinney and Yentsch 1985) with 0.1 g  $MgCO_3$  cooled to  $-20^\circ C$  for a maximum of a week. Chl *a* was estimated through the change in fluorescence of samples before and after acidification to compensate for the presence of pheopigments. Measurements were made on a Model 650-40 Fluorescence Spectrofluorometer (Perkin-Elmer) set at an excitation of 436 nm and an emission of 670 nm with a slit width of 10 nm. This excitation and emission combination was chosen to provide better discrimination between Chl *a* and pheophytin *a* (Welschmeyer 1994). Blanks for each station were determined to correct for the potential interference of high concentrations of DOC when analyzing GF/F-filtered water samples (Vyhnalek 1995). Calibrations were conducted using a Chl *a* standard from *Anacystis nidulans* (Sigma) during each batch of samples.

Table 1. Seasonal variation of river discharge (RD), salinity (S) at or close to the mouth of the river, and particulate organic carbon (POC) for the Altamaha and Satilla Rivers. River discharge is taken from Dai and Wiegert (unpubl. data). Salinity determinations were made from discrete water samples by refractometry or using a shipboard salinometer on board the RV *BlueFin*. Values for POC represent the average (1 SE) of samples collected throughout each estuary.

	Altamaha			Satilla		
	RD ( $m^3 s^{-1}$ )	S (‰)	POC ( $mg C L^{-1}$ )	RD ( $m^3 s^{-1}$ )	S (‰)	POC ( $mg C L^{-1}$ )
March	838	0	5.5 (1.4)	134	27	7.1 (1.2)
April	747	14	1.3 (0.35)	108	29	n.d.
July	219	30	1.5 (0.73)	42	31	1.2 (0.74)
October	172	22	1.0 (0.67)	32	26	0.76 (n.d.)*

\* Only data for the upper estuary station were available. n.d., not done.

**Carbon stable isotope determinations**—POC was collected by filtration on QMA quartz filters (Whatman) precombusted overnight at  $800^\circ C$ . Samples on filters were frozen in precombusted aluminum foil. Once back in the laboratory, filters were thawed and exposed to HCl vapors for 3 h (tests

with CaCO<sub>3</sub> indicated the absence of carbonates after exposure to HCl vapors). Afterward, samples were dried at 55°C, pulverized in pre-ashed Vycor tubes, and sealed with CuO and Cu under vacuum (Boutton 1991).

Twenty-liter water samples were collected in plastic buckets either directly from the surface or from the specimen pump on board the *BlueFin* (2 m deep) for the determination of δ<sup>13</sup>C of Chl *a*. Samples were passed through 293-mm GF/F filters with peristaltic pumps using silicone tubing. Afterward, filters were folded and frozen at -20°C until further treatment. Once back in the laboratory, Chl *a* samples were extracted overnight with 90% acetone saturated with MgCO<sub>3</sub> at -20°C in amber glass bottles. The following day, crude extracts were sonicated until reaching room temperature and filtered through GF/F filters, and the extracts were saved at -70°C until the next step. Crude extracts were further concentrated by serial addition of 1/20 volumes of chloroform and 1/2 volume of deionized water to the acetone crude extract in 500-ml polypropylene centrifuge bottles. (Care should be taken to add solvents in the above order; otherwise, Chl *a* degrades rapidly.) Samples were centrifuged 10 min at 8,000 × g, and the lower phase was pipetted out into 40-ml pre-ashed amber bottles with Teflon-lined septa. Solvent was evaporated under a stream of N<sub>2</sub> in a water bath at 30°C.

Chlorophyll *a* was purified from the above crude extract mix by high-performance liquid chromatography (HPLC). The dried crude extracts were diluted in 1 ml of prefiltered 90% acetone (MgCO<sub>3</sub> saturated) just before the injection of aliquots (0.05–1 ml) into a Waters HPLC system (Millipore) fitted with a 5 × 100 mm NOVA PAK C18 Radial-Pak (Millipore) reversed-phase cartridge and C18-guard column. Detection of pigment peaks was achieved by simultaneously monitoring from 400–650 nm using a Waters 900 PAD detector (Millipore). Solvent mixing and pumping rates were controlled using a Model 680 Automated Gradient Controller (Waters-Millipore) to which two Waters 501 pumps were connected. To elute extracted pigments, the column was initially equilibrated with methanol at 2 ml min<sup>-1</sup>. The initial conditions were changed to 72:28 (v/v) methanol:acetone at 1.5 ml min<sup>-1</sup> using gradient controller program 10, 2 min after injection of the sample. (Program 10 is characterized by an initial slow change in solvent conditions with a higher rate of change at the end of the time interval.) Afterward, the solvent was gradually changed to 100% acetone at 2 ml min<sup>-1</sup> during the next 8 min, as in the previous step. These conditions were held for 5 min for column washing followed by a stepwise change to 100% methanol at 2 ml min<sup>-1</sup> for 13 min. In this way, the system was readied for another injection. The retention time of Chl *a* under these conditions was determined using *Anacystis nidulans* Chl *a* standard (Sigma). Preliminary trials to determine pigment separation conditions were conducted using spinach and *Ulva* sp. 90% acetone extracts.

The Chl *a* fraction was collected from the detector outflow in pre-ashed Pyrex glass vials in which it was dried under a N<sub>2</sub> flow. Samples were rediluted in 1 ml of 100% acetone, mixed with 50 μL of 10% HCl, transferred to pre-ashed Vycor tubing, dried under a stream of N<sub>2</sub> at 60°C, and sealed under vacuum. In order to evaluate our protocol, we examined the relationship of δ<sup>13</sup>C from bulk plant material and Chl *a*

extracted as described above. Plant material included tomato and corn leaves, microalgae from mixed algal enrichments (Guillard's f/2 medium), and microalgal cultures (Guillard's f/2 medium) supplemented with 99% NaH<sup>13</sup>CO<sub>3</sub> (Isotec).

*Stable C isotope analysis*—The sealed Vycor tubes containing the POC and Chl *a* samples were combusted as described by Boutton (1991). The δ<sup>13</sup>C of cryogenically distilled CO<sub>2</sub> was determined on a MAT 252 or MAT 251 isotope ratio mass spectrometer (IRMS). The latter was equipped with a CO<sub>2</sub> microvolume cold finger for online sample concentration in autofreeze mode to analyze samples containing <1 μmol C. Results were reported per mil (‰) relative to a Cretaceous belemnite standard, *Bellemnitella americana*, of the Pee Dee formation (PDB), where δ<sup>13</sup>C<sub>PDB</sub> = (R<sub>SA</sub> - R<sub>ST</sub>)/R<sub>ST</sub> · 1,000‰ and R<sub>SA</sub> and R<sub>ST</sub> are the <sup>13</sup>C/<sup>12</sup>C ratios of the sample and the PDB standard, respectively (~0.0112372). Typical standard errors for δ<sup>13</sup>C of POC and Chl *a* were less than 0.1 and 0.4‰, respectively. Chl *a* from mixed microalgal cultures was isolated, re-concentrated, and HPLC-treated to assess isotopic shifts. The δ<sup>13</sup>C of Chl *a* after one and two purification steps was -17.5 ± 0.5 (average ± SE) and -16.6 ± 0.3‰, respectively (not significantly different; *t*-test *P* = 0.15, 4 df).

*Proportions of C<sub>3</sub>, C<sub>4</sub>, and MaDM*—The percentage of MaDM POC was estimated using a C:Chl *a* of 30:1, which is close to that found by Hamilton and Lewis (1992). Occasionally this estimate was higher than that of the total POC, in which case it was set to 100%. The percent MaDM was then incorporated into the mass balance equation

$$\delta_t\%_t = \delta_4\%_4 + \delta_{\text{MaDM}}\%_{\text{MaDM}} + \delta_3\%_3,$$

where δ is the δ<sup>13</sup>C of the total POC mix (t), of C<sub>4</sub> (4), C<sub>3</sub> (3), and microalgal (MaDM) origin, and % is the proportion of the total mix of each of these sources. The δ<sub>MaDM</sub> was calculated based on a comparison between the δ<sup>13</sup>C signatures of known plant material and that of their Chl *a*. Assuming these three sources represent the total amount of POC in these estuaries, solving the above equation for %<sub>4</sub> yields

$$\%_4 = [\delta_t - \delta_{\text{MaDM}}\%_{\text{MaDM}} + \delta_3(1 - \%_{\text{MaDM}})]/(\delta_4 - \delta_3),$$

where δ<sub>4</sub> and δ<sub>3</sub> were taken as -18 and -28‰, respectively. We used -18‰ as the δ<sup>13</sup>C for C<sub>4</sub> plants (mainly *Spartina*-derived material) to account for the effects of bacterial mineralization on lignocellulose (Benner et al. 1987). Using -18 instead of the -14‰ δ<sup>13</sup>C value maximizes the contribution of C<sub>4</sub> plants to the SPOM as calculated with the above equation. Finally, we chose a value of -28‰ as representative of C<sub>3</sub> plant material based on Sherr (1982) and Hedges et al. (1986), who found similar δ<sup>13</sup>C for detrital material in the Altamaha estuary and the Amazon River, respectively.

## Results and discussion

*Particulate organic carbon*—The concentration of POC in the Altamaha and Satilla River estuaries during the sampling period fluctuated from undetectable levels to 9 and 11 mg C L<sup>-1</sup>, respectively (Table 1). Pomeroy and Imberger

(1981) studied transport of materials in the Duplin River (a tidal river near our study area) and determined an average POC concentration of  $3.8 \text{ mg C L}^{-1}$ . In comparison, Hamilton and Lewis (1992) reported lower concentrations for the Orinoco floodplain ( $0.9\text{--}1.2 \text{ mg C L}^{-1}$ ). The maximal annual POC concentration was observed during March 1996 in the Altamaha River, which coincides with the season of highest expected river discharge (Table 1). Evidence for a high discharge rate during March 1996 was the low surface salinity at the mouth of the Altamaha. There was no evidence of high freshwater discharge observed in the Satilla River, indicated by high salinities at the river mouth during all samplings, to explain the increase in SPOM during the same sampling period. Other factors, such as tidal and wind stress on bottom sediments, would allow for higher concentrations of POC (Oviatt and Nixon 1975). Alexander et al. (unpubl.) observed that the concentration of SPOM is 2–10 times higher during neap tides in both the Altamaha and Satilla Rivers and that the bulk of the material during peak ebb and flood currents is of a coarse size and, therefore, settles rapidly. It has been estimated that the transport of this coarse fraction has a net inland flux; however, the flux of the finer fraction has still to be calculated (Blanton et al. unpubl.). The interaction of bottom resuspension and changes in the flushing rate throughout the time of sampling result in a complex pattern of POC distribution in these estuaries. This makes it difficult to arrive at a conclusion with respect to POC transport to the sea and may explain the high variability and large proportion of POC within the organic carbon pool (Fig. 2), which is 50 and 70% of the TOC in the Altamaha and Satilla, respectively.

There was a marked seasonal variation in  $\delta^{13}\text{C}$ -POC in the Altamaha, but not in the Satilla, estuary. The range of  $\delta^{13}\text{C}$ -POC during the entire sampling period in the Altamaha and Satilla River estuaries was  $-21$  to  $-28\text{‰}$  (Fig. 3). Excluding samples taken outside the main channel, the range and average  $\delta^{13}\text{C}$ -POC values were minimum during the months of March and April in the Altamaha estuary, whereas a wider range of  $\delta^{13}\text{C}$  values were observed the rest of the sampling period. In contrast, the Satilla estuary showed a similar dispersion of  $\delta^{13}\text{C}$ -POC during each sampling (Fig. 3). The contrasts in the  $\delta^{13}\text{C}$ -POC patterns observed between both estuaries could be induced by differences in the flushing (or replacement) times of water between estuaries. The Altamaha River exhibits significant intra-annual changes in river discharge (Table 1), increasing the transport of terrestrially derived material during periods of high discharge and causing an overall decrease in the  $\delta^{13}\text{C}$ -POC. During periods of low discharge, the flux of terrestrial material through the Altamaha estuary diminishes, and other sources of POM are reflected in the isotopic signature of SPOM. In contrast, the Satilla River discharge is lower than that of the Altamaha throughout the year; therefore, other processes, such as wind- and tide-driven movement of SPOM, are predominant in this system throughout the year. Similar fluctuations in the  $\delta^{13}\text{C}$ -POC caused by changes in river discharge have been observed in the St. Lawrence River, Canada (Tan 1987) and by Bird et al. (1998) in the Sanaga River system, Cameroon. Annual changes in average flushing time could explain the results of the correlation analysis of  $\delta^{13}\text{C}$ -POC versus salin-

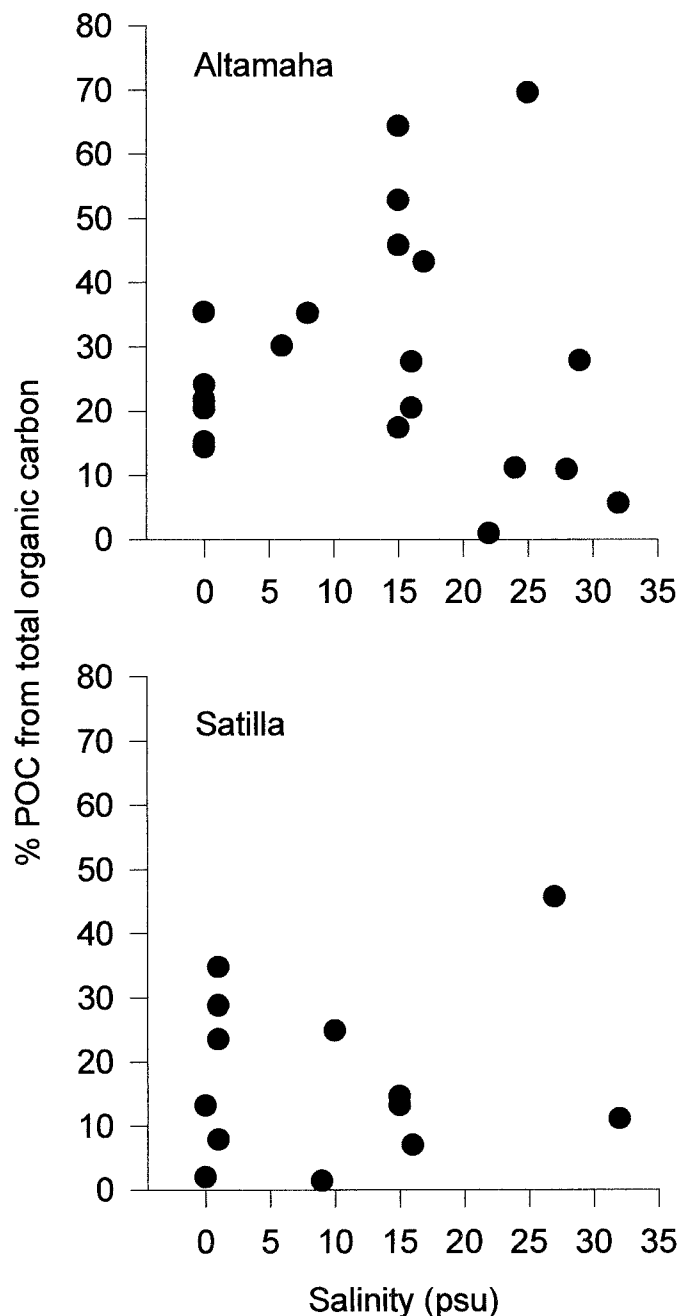


Fig. 2. Distribution of percent POC from total organic carbon along the salinity gradient of the Altamaha and Satilla River estuaries. Data is a summary of all samples collected during the sampling period.

ity for the Altamaha and Satilla Rivers (Fig. 4), with  $r^2$  values of 0.70 and 0.35, respectively.

The distribution of POC-isotopic signatures indicates the input of significant amounts of depleted terrestrial material mixing with POC from estuarine sources. Samples at the head of the Altamaha and Satilla estuaries (Fig. 5) are consistent with the isotopic signatures found in the mainstem of the Amazon River, where Hedges et al. (1986) found a similar range ( $-28$  to  $-27\text{‰}$ ). Increases in the isotopic

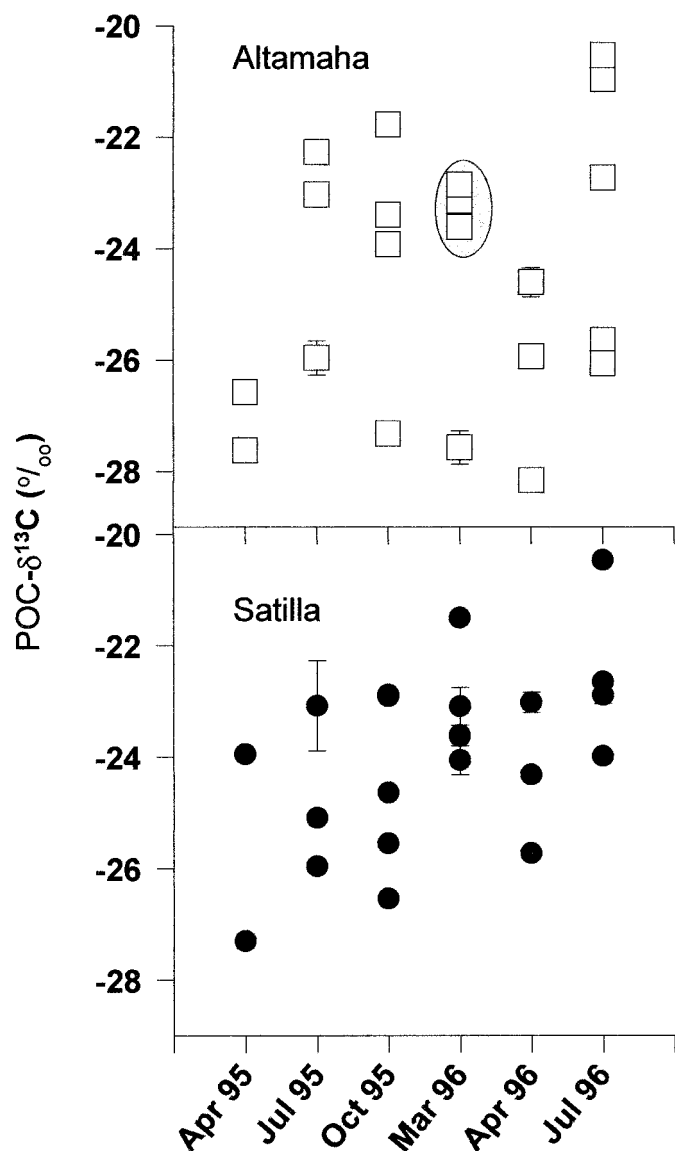


Fig. 3. Average  $\delta^{13}\text{C}$ -POC in the Altamaha and Satilla River estuaries throughout the sampling period. Error bars are included and represent 1 SE. Samples collected outside the main estuary path are indicated within shaded area.

signature of POC within the Altamaha and Satilla estuaries are controlled by the mix with salt marsh- or microalga-derived material. Studies in southeastern U.S. estuarine systems have indicated *Spartina* or microalgal material dominates in these types of systems (Haines 1977; Haines and Montague 1979). Stable carbon isotopic signatures from fauna collected in Sippewissett and Sapelo Island salt marshes (Peterson et al. 1985; Peterson and Howarth 1987; Currin et al. 1995) also suggest salt marsh-derived particles are dominant in tidally dominated systems. Stable carbon isotopic signatures similar to those in nearby tidal-river estuarine communities were observed toward higher salinities in the present study, suggesting the dilution of terrestrial material by a large background of estuarine POC. Our data confirm the findings of Sherr (1982) from samples at sim-

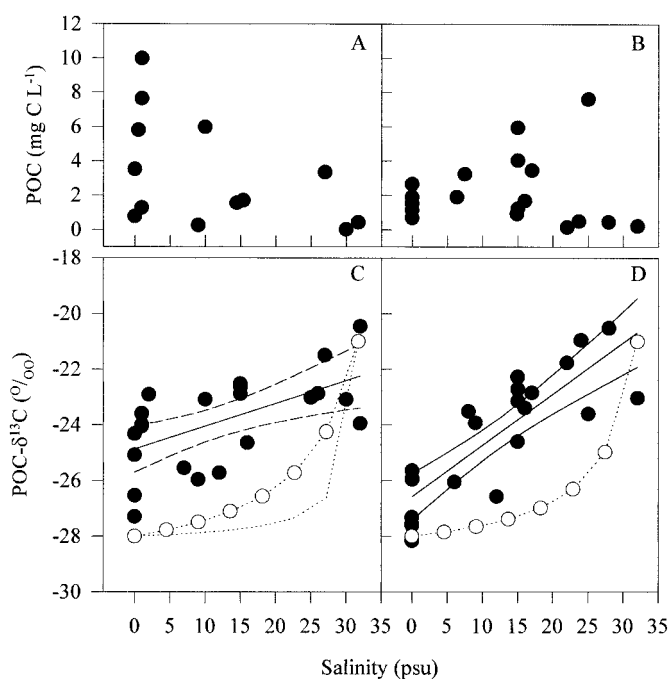


Fig. 4. Distribution of POC parameters in the Satilla and Altamaha River estuaries during the sampling period. Concentration of POC with salinity in the (A) Satilla and (B) Altamaha estuaries show fluctuations indicative of high turbulent conditions and autochthonous sources of POC. The  $\delta^{13}\text{C}$ -POC distribution with salinity (black circles) shows linear trends for both the (C) Satilla and (D) Altamaha estuaries. The straight and flanking dashed lines are the resulting  $\delta^{13}\text{C}$ -POC versus salinity linear regression and 95% confidence interval, respectively. The  $r^2$  for the Satilla and Altamaha estuaries are 0.35 and 0.70, respectively. For comparison, the expected  $\delta^{13}\text{C}$ -POC due to conservative mixing is included for each river (white circles with dashed lines). Recalculation of  $\delta^{13}\text{C}$ -POC versus salinity due to conservative mixing using the highest POC concentration observed (C; dashed concave line) shows evident differences only for the Satilla estuary.

ilar locations in the Altamaha, who indicated for the first time the dominance of terrestrial materials in part of Georgia estuaries with fast dilution by POC from other sources. We calculated the expected distribution of  $\delta^{13}\text{C}$ -POC based on Spiker (1980), using the same endpoints of  $-28$  and  $-21$ ‰ for upriver and marine  $\delta^{13}\text{C}$ -POC in the Altamaha and Satilla estuaries and compared it to the observed isotopic distribution (Fig. 4). The overall distribution of POC in both estuaries shows large fluctuations, probably because of the turbulent mixing and river discharge patterns inherent to both estuaries (Fig. 4A,B). In comparison to the expected  $\delta^{13}\text{C}$ -POC distribution, the observed  $\delta^{13}\text{C}$ -POC covaried linearly with salinity, indicating an excess of  $^{13}\text{C}$ -rich POC throughout the length of both estuaries (Fig. 4C,D). However, the  $\delta^{13}\text{C}$ -POC values in the Altamaha estuary at salinity = 0‰ were closer to the expected value than those in the Satilla, probably because of differences in water transport rate. The significant departure from the expected isotopic distribution strongly suggests the modification of the bulk POM mixtures by biological processes autochthonous to the estuary. The effect of changes in the concen-

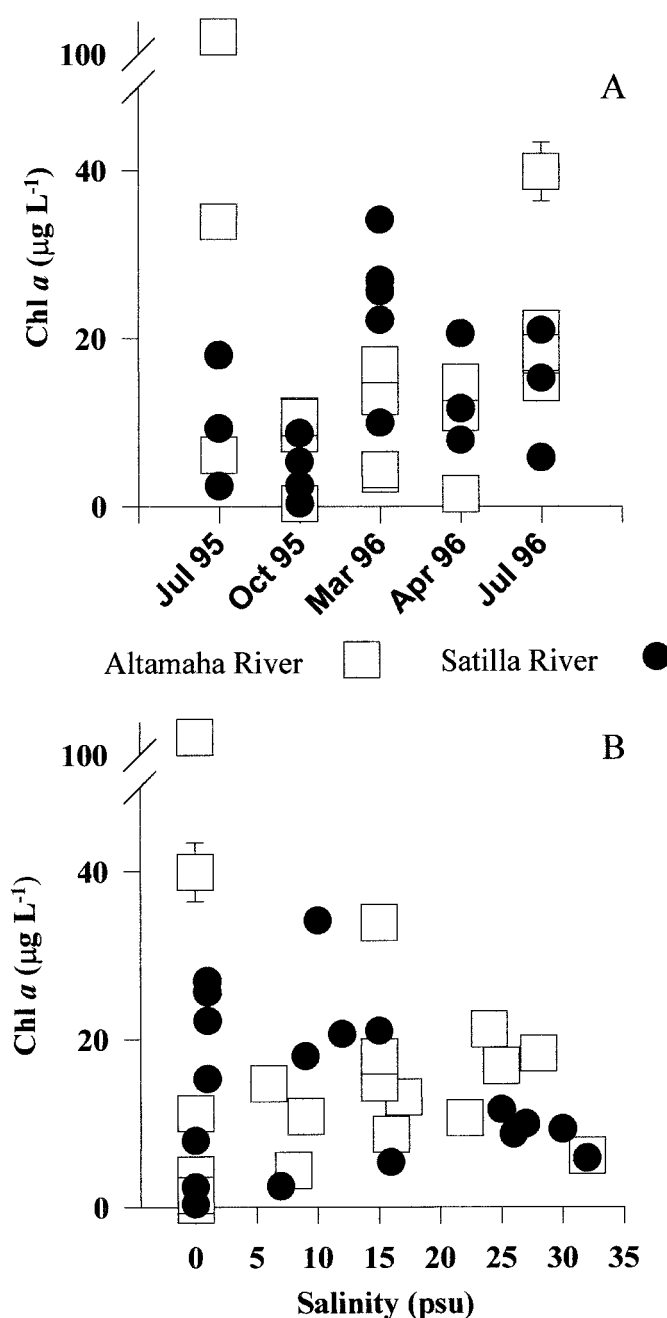


Fig. 5. (A) Concentration of Chl *a* in the Altamaha and Satilla River estuaries during the sampling dates and (B) its distribution with salinity. Included are 1 SE bars, which usually are smaller than the symbols.

tration of POC used for the calculations was taken under consideration. Increasing the concentration of POC to the maximum observed forced a more concave distribution in the Satilla estuary (Fig. 4C), increasing the difference between the expected and the observed values. The same computation was done with POC concentrations at the mouth of the estuaries. However, the expected distribution was insensitive to these permutations because of the limited range in the POC concentrations (Fig. 4A,B).

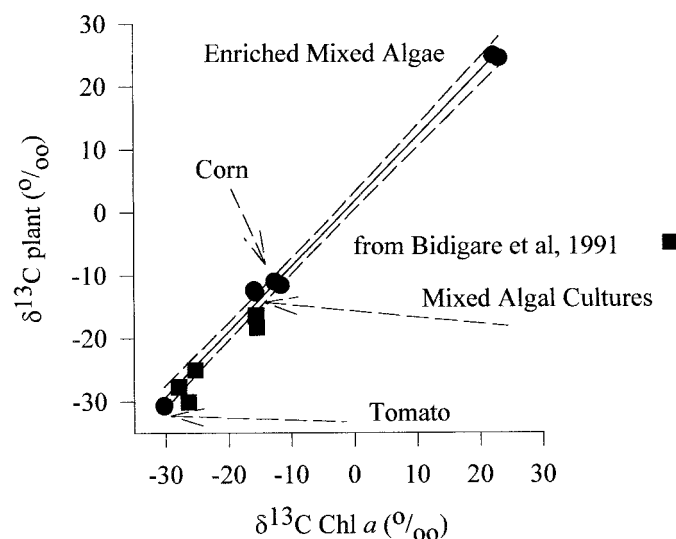


Fig. 6. Results of regression analysis of  $\delta^{13}\text{C}$  of whole-plant material and extracted Chl *a* (circles). Dashed lines represent 95% confidence intervals. Results from Bidigare et al. (1991) are included for comparison (squares).

Other estuarine systems show similar range and changes in  $\delta^{13}\text{C}$ -POC along the salinity gradient (Amazon, Brazil; Girard, France; Mook and Tan 1991 and references therein), whereas others contain a more enriched range of  $\delta^{13}\text{C}$ -POC. In Narragansett Bay, Gearing et al. (1984) found values of  $\delta^{13}\text{C}$ -POC from  $-24.5$  to  $-20.6$ , whereas in Delaware Bay, Cifuentes (1991) found a range of isotopic signatures of suspended POC from  $-24.2$  to  $-18.1$ ‰. Although both of these systems have significant upriver freshwater inputs, their seston is dominated by phytoplankton-derived material, which usually has  $\delta^{13}\text{C}$  values within the range observed by the investigators (Fry and Sherr 1984).

*Chlorophyll a*—Estimates of the expected MaDM  $\delta^{13}\text{C}$  were derived from  $\delta^{13}\text{C}$ -Chl *a* based on a regression derived from known materials (Fig. 6). Our results indicate good agreement between  $\delta^{13}\text{C}$ -Chl *a* with that of the whole-plant tissue ( $r^2 = 0.995$ ). However, because our extraction procedures were different from those of previous work, we were concerned with the potential introduction of bias. The data of Bidigare et al. (1991) were plotted against our data to determine the similarity of the results from both studies (Fig. 6). Laws et al. (1995) also found a similar regression line ( $\delta^{13}\text{C}$ -plants =  $1.09\delta^{13}\text{C}$ -Chl *a* + 2.74), indicating that our extraction procedures did not introduced significant deviations from the expected results. Using the regression formula from our results, the calculated MaDM  $\delta^{13}\text{C}$  for the Altamaha and Satilla estuaries ranged from  $-30.6$  to  $-19.6$  and from  $-28$  to  $-20.9$ ‰, respectively. The more depleted values of MaDM were found in samples collected at salinities of 0 and  $<10$ ‰ in the Altamaha and Satilla estuaries, respectively. These values fall within the range of plankton found in river water (Boutton 1991), although even lower values ( $-37$ ) have been reported (Hamilton and Lewis 1992). Recently, Laws et al. (1995) described how fractionation of fixed carbon by *Phaedactylum tricorutum* (Bacil-

lariaceae) is related to the ratio of growth rate to  $\text{CO}_2$  concentration, where the fractionation increases as the ratio decreases. In the upper estuary of the Altamaha and Satilla Rivers, the environmental conditions that would maximize fractionation by the microalgal community are present. Cai and Wang (1998) found supersaturation of  $\text{CO}_2$  in Satilla waters with salinities of less than 5‰, which is explained by production of  $\text{CO}_2$  by benthic respiratory processes. These conditions are ideal for the fixation of depleted algal material because  $\text{CO}_2$  would be already depleted and the ratio of growth rate to  $\text{CO}_2$  concentration would be minimal. Therefore, it is feasible to find these low MaDM  $\delta^{13}\text{C}$  in the upper estuarine reaches of our study area.

*Proportion of  $\text{C}_3$ ,  $\text{C}_4$ , and microalgal material in the mixture of POC*—A potentially significant source of POC in our study area is MaDM. In comparison to other estuarine systems, the amount of Chl *a* found in our system ranges from moderate to high. This suggests that the isotopic signature of microalgae could be reflected in that of the bulk POC. In order to examine this possibility, we conducted regression analyses of  $\delta^{13}\text{C}$ -POC versus  $\delta^{13}\text{C}$ -Chl *a* for both the Altamaha and Satilla samples. The results (Fig. 7) indicate a tight relationship in the Altamaha River, suggesting that the contribution of MaDM to the SPOM is substantial. Although the relationship is also significant for the Satilla River, this system shows evidence of a higher contribution of POC from other sources.

Certain assumptions were made for the estimation of the proportions of MaDM,  $\text{C}_3$ , and  $\text{C}_4$  plant material within the POC mixture. These assumptions include using 30 as the proportion of C to Chl *a* in microalgae within these systems and  $-18\text{‰}$  as the  $\delta^{13}\text{C}$  of *Spartina*-derived material. Both of these values were used to derive conservative estimates of the amount of MaDM and *Spartina* detritus present in the systems. An average of C/Chl *a* (wt/wt) equal to 42 with a range of 22–79 (Valiela 1995) has been observed. Similar values have been found for mixed phytoplankton communities in the North Sea, where in spring the C/Chl *a* ratio was 20, and in summer the ratio increased to 100 (Kirk 1983). In the Orinoco River floodplain, Hamilton and Lewis (1992) found a range of C/Chl *a* of 29–57. Lower ratios have been measured ( $\sim 10$ ), but these have been for cultures of *Chlorella* and *Euglena* (Kirk 1983). We decided to utilize 30 as a conservative estimate of the average C/Chl *a* ratio for our estimates of MaDM concentration because maximal concentrations of Chl *a* were found in the freshwater endpoint of the Altamaha, which suggests that upriver inputs of MaDM are significant. Also, this C/Chl *a* ratio is close to the minimum ratio found in the Orinoco River floodplain by Hamilton and Lewis (1992).

The utilization of  $-18\text{‰}$  as the *Spartina*-derived material  $\delta^{13}\text{C}$  isotopic signature is the maximum deviation from fresh material because of enrichment of the lignin moiety of lignocellulose (Benner et al. 1987). Using this value overestimates the proportion of the  $\text{C}_4$  detritus by approximately 5–10% relative to a  $\delta^{13}\text{C}$  value of  $-16\text{‰}$ . A loss of 98% of the original *Spartina* material, or about 10 yr of below-ground decomposition are needed for *Spartina* detritus to achieve a  $-17.2\text{‰}$  isotopic signature. Thus, the percentage

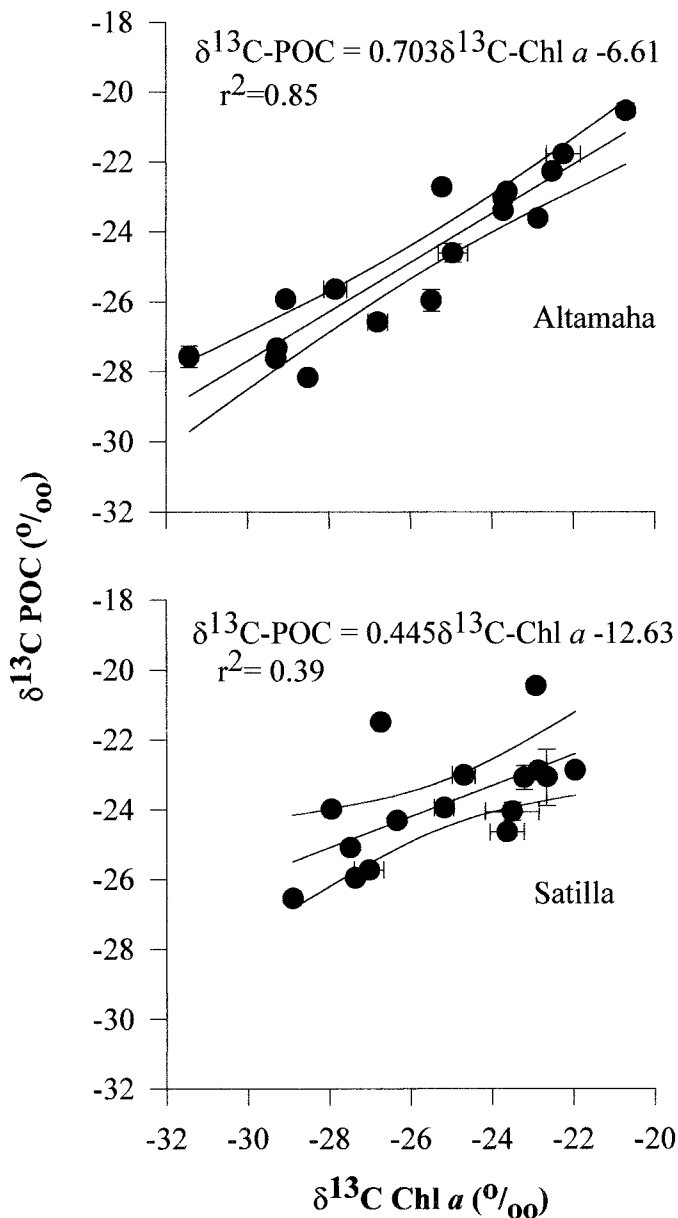


Fig. 7. Regression of  $\delta^{13}\text{C}$  of POC and Chl *a* in samples collected in the Altamaha and Satilla River estuaries. Curved lines represent the 95% confidence intervals of the regression. Included are 1 SE bars for both variables.

of *Spartina*-derived material presented here approaches the maximum limit.

Estimates of the proportion of POC from different sources in the estuarine systems in our study showed marked differences (Fig. 8). There was a greater contribution to POC from MaDM in the Altamaha estuary. On average, the supply of  $\text{C}_3$ -derived material for both systems was approximately 40% of the total. However, the MaDM contribution was 40 and 20% in the Altamaha and Satilla Rivers, respectively. The Altamaha River showed a tendency for an increased supplement of POC by microalgae during the month of July when the calculated microalgal material accounted for more

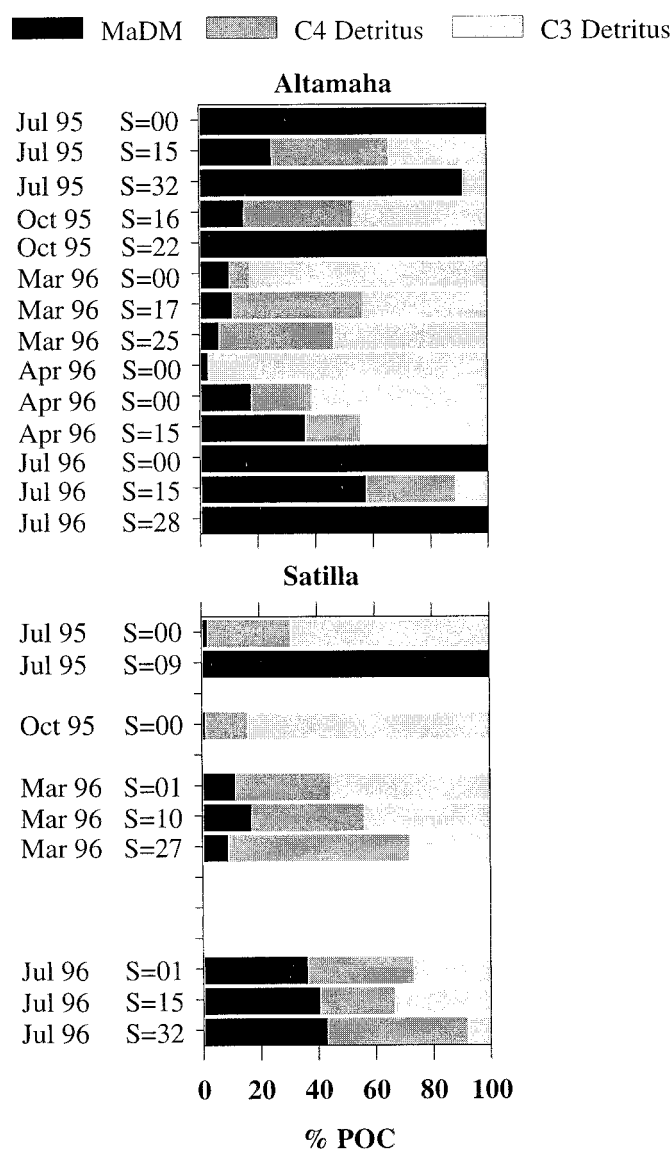


Fig. 8. Predicted proportion of MaDM, C<sub>4</sub>, and C<sub>3</sub> detritus in samples collected in the Altamaha and Satilla estuaries. Blank spaces represent missing or uncollected samples.

than 9 % of the POC concentration. In contrast, there was a marked dominance of C<sub>3</sub>-derived material during late winter–early spring. The dataset for the Satilla estuary is not as complete as that for the Altamaha; however, it is evident that MaDM is not as dominant in the Satilla. These results suggest a fundamental difference between both estuarine systems. We evaluated the sensitivity of the proportion of POC from the different sources to shifts in the C/Chl *a* ratio of MaDM. As observed previously, this ratio experienced fluctuations because of the rapid loss of Chl *a* from senescent or dead MaDM. A value of C/Chl *a* of 90 was used to maximize the presence of MaDM in POC, resulting in a 20 ± 5 and 29 ± 9 (average percent ± SE) increase in MaDM in the Altamaha and Satilla Rivers, respectively. The increase in MaDM composition was reflected mainly in an

average %C<sub>3</sub> decrease of 20% for both rivers, whereas %C<sub>4</sub> was mainly unchanged.

Different studies have calculated the proportion of different sources of POC in the suspended and bottom fractions of diverse coastal and estuarine environments using a stable carbon isotope balance approach. For example, bottom sediments have been reported to contain from 25 to 100% C<sub>3</sub> plant-derived material in the upper estuarine region of the Tay estuary, Scotland, with a sudden decrease to <2% toward the mouth of the estuary (Thornton and McManus 1994). This suggests that either terrestrial POC transported downstream is concentrated in the upper estuarine region or that the isotopic signature of terrestrially derived POC is hidden by the incoming marine-derived material. Rezende et al. (1990) studied the tidal transport of SPOM related to coastal mangrove systems in Sepetiba Bay, Brazil. The authors established that there were differences in the composition of mangrove-derived material according to the tidal regime. During spring tide, the percent POC contributed by mangrove varied from 2–100%, and during neap tides, the contribution fluctuated from 16 to 48%, during ebb and flood stages, respectively. This indicates that terrestrial material transport into coastal areas is episodic in nature because of the daily tidal cycle, where the magnitude of the pulse is controlled by the tidal range.

In contrast to the above studies, our study area receives POC from three primary sources, as indicated by the Chl *a* concentration and the range of δ<sup>13</sup>C values. We utilized the same mass balance approach as the above studies. However, by estimating the portion of the POC derived from microalgae and approximating the isotopic signature from the δ<sup>13</sup>C of Chl *a*, we determined the contribution of one of the main sources of POC in these two estuarine systems. Mathematically, inclusion of the isotopic and concentration estimates of MaDM allows for the simplification of the three-component into a two-component equation, which may then be solved using only δ<sup>13</sup>C-POC estimates.

The estuarine systems we studied here are subject to significant annual variations, especially the Altamaha River because of its higher fluctuations in discharge. The increased proportion of MaDM in the Altamaha estuary during the months of July may be due to increased productivity during this time of year accentuated by decreased river flow, which permits the establishment of significant levels of microalgal biomass. In contrast, during late winter–early spring, the biomass of microalgae was minimal, concomitant to high water replacement rates. This pattern is not evident in the Satilla River, in which microalgal biomass was minimal even at low discharge. There is no clear explanation for the difference between the Altamaha and Satilla estuaries in terms of the MaDM contribution to overall POC concentration. Although it appears that light is rapidly attenuated in the Satilla estuary because of more colored organic matter, light attenuation in the Altamaha is also significant because of large amounts of suspended solids (Alexander et al. unpubl.). The most dominant POC component is that derived from C<sub>3</sub> plants, which averages about 40% in both estuaries. Although we expected to find a significant amount of C<sub>3</sub> material in both systems, we expected its proportion to vary among estuaries, in part because of differences in river discharge. The proportion of

C<sub>4</sub> detritus in the SPOM (up to 40% of the total) was smaller than that presented by Fogel et al. (1989) and with a tendency to be higher in the Satilla system because of the increased extension of marsh area relative to the riverine flux.

**Conclusion**—Although the Altamaha and Satilla Rivers differ in several aspects, such as DOC and river discharge, overall the content and annual fluctuation of POC are similar even when the headwaters are derived from different environmental settings. The  $\delta^{13}\text{C}$  signature of POC in these estuaries suggests nonconservative mixing. Considering the annual fluctuations in POC concentration at the upriver stations, an increase in nonconservative mixing of POC was revealed in the Satilla River. This is due to the large fluctuations in POC concentrations that are only observed in the Satilla estuary. It is possible that conservative transport of POC occurs, but only during high discharge periods, especially in the Altamaha River. In fact, we found evidence for a strong annual fluctuation in  $\delta^{13}\text{C}$  in the Altamaha suggesting significant transport of terrestrially derived material related to the annual peak in river discharge.

We used the  $\delta^{13}\text{C}$  of Chl *a* to calculate the isotopic signature of MaDM. Although  $\delta^{13}\text{C}$ –Chl *a* values have been used to establish the isotopic predominance of microalgae in several coastal systems, this is the first time it has been incorporated in a mass balance approach in an attempt to quantify the proportion contributed by microalgae to the bulk POC in complex estuarine systems. Our results show depleted values in the freshwater areas of both estuaries. The  $\delta^{13}\text{C}$ –Chl *a* correlates strongly with the  $\delta^{13}\text{C}$  in the Altamaha estuary. The correlation indicates that although this system is turbid because of bottom sediment resuspension, there is a significant contribution of POC from microalgae, especially during lower flows. In contrast, MaDM is less dominant in the Satilla River estuary probably due to the higher concentration of dissolved organic matter derived from its drainage area. Significant amounts of C<sub>4</sub> (*Spartina*)-derived material were found in these estuaries, though; in contrast with other works, it was found to contribute only 20 to 40% of the POC. These values are less than those expected from areas where salt marshes are ubiquitous, as in the lower reaches of these estuaries. These contrasting results are probably due to differences in the type of areas sampled, as most previous studies investigated areas with nonsignificant riverine inputs.

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