

PREDICTION OF ATMOSPHERIC $\delta^{13}\text{C}_{\text{CO}_2}$ USING PLANT CUTICLE ISOLATED FROM FLUVIAL SEDIMENT: TESTS ACROSS A GRADIENT IN SALT CONTENT

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ABSTRACT

In order to test the assertion that the carbon-isotopic composition of the ancient atmosphere ($\delta^{13}\text{C}_{\text{CO}_2}$) can be reconstructed from the carbon-isotopic composition of fossil terrestrial plant tissues across a variety of environments, the $\delta^{13}\text{C}$ value of land-plant tissues isolated from modern fluvial sediments was compared to that of today's atmosphere. Plant stem and leaf fragments were isolated from organic carbon-rich sediments of the Black River in Jamaica, which drains a basin containing only C3 ecosystems. Sediment was sampled at 12 sites along a dissolved salt-content gradient, from the coastal plain to near its mouth, which allowed evaluation of the effect of salt influence on the organic carbon-isotope signature. Many properties of the sediment varied systematically with salt content (e.g., mass-percentage carbonate, abundance of palynomorphs, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonate), confirming a significant and increasing marine influence closer to the mouth of the river. The $\delta^{13}\text{C}$ value of total organic carbon systematically decreased by $\sim 2\%$ with increased NaCl concentration, indicating the presence of a mixing line between marine and terrestrial organic inputs. In contrast, for leaf and stem isolates, there was no significant dependence of $\delta^{13}\text{C}$ value on NaCl concentration, suggesting that the isotopic signature of the integrated terrestrial contribution is independent of the salt content of the depositional environment. The mean values of all isolates retrieved from the sediments predicted a $\delta^{13}\text{C}_{\text{CO}_2}$ value of $-9.7 (\pm 1.0)$ for leaf material and $-8.2 (\pm 1.7)$ for stems. Both of these values are within $\sim 1\%$ of recent regional-scale measurements of atmospheric $\delta^{13}\text{C}_{\text{CO}_2}$ value.

INTRODUCTION

Paleoclimate reconstructions are facilitated by an understanding of the size and composition of active carbon reservoirs and the flux between them. Of particular interest are those reservoirs—such as the atmosphere—that vary significantly in isotopic composition ($\delta^{13}\text{C}_{\text{CO}_2}$) through time because these reservoirs closely reflect the dynamic nature of the carbon cycle. Flux changes among reservoirs can be linked to carbon sources and sinks by their isotopic composition (e.g., Dickens, 2003); this is especially true when normal carbon cycling is disrupted (e.g., Dickens et al., 1995). In addition, an accurate reconstruction of atmospheric $\delta^{13}\text{C}_{\text{CO}_2}$ is useful for determinations of paleo- pCO_2 using soil carbonate (e.g., Ekart et al., 1999). Therefore, a quantitative estimate of the isotopic composition of atmospheric CO_2 would greatly facilitate efforts to describe and model carbon cycling through geologic time. Because land plants sample the atmosphere directly during photosynthesis, organic carbon derived from C3 plants can be used as an isotopic proxy for $\delta^{13}\text{C}_{\text{CO}_2}$ of the atmosphere (Arens et al., 2000; Jahren et al., 2008). It has long been recognized that the $\delta^{13}\text{C}_{\text{CO}_2}$ of the atmosphere assigns

the $\delta^{13}\text{C}$ of plant tissue, since the atmosphere is the only important source of carbon for plant growth (Park and Epstein, 1960, 1961).

In calculating the $\delta^{13}\text{C}_{\text{CO}_2}$ of the atmosphere from the $\delta^{13}\text{C}$ of plant tissue, the following relationship for C3 plants is used (Farquhar et al., 1989):

$$\delta^{13}\text{C}_p = \delta^{13}\text{C}_a - a - (b - a) \times (c_i/c_a) \quad (1)$$

where $\delta^{13}\text{C}_a$ and $\delta^{13}\text{C}_p$ represent atmospheric CO_2 and CO_2 of the resulting plant tissue, respectively; a and b result from gaseous diffusion and enzymatic carboxylation, respectively; and (c_i/c_a) reflects the difference in the partial pressure of CO_2 within the stomatal chamber (c_i) and that of CO_2 in the external atmosphere (c_a ; see Farquhar et al., 1989). Because a and b emerge from diffusion and enzyme activity, they vary little. Published estimates of (c_i/c_a) , however, range from 0.38 to 0.89 (Arens and Jahren, 2000) and reflect a time-averaged integration of moment-to-moment stomatal regulation of gas exchange in a constantly changing environment. Elsewhere it has been shown that for plants growing across a very large range of pCO_2 values (one to three times current levels), a consistent correlation exists between $\delta^{13}\text{C}_a$ and $\delta^{13}\text{C}_p$ ($p < 0.001$; see Jahren et al., 2008).

Because opening and closing the stomata is the plant's main mechanism for responding to environmental variation, a wide variety of environmental factors (e.g., light, temperature, nitrogen status, and water availability; see the review in Dawson et al., 2002) have been linked to variability in the ratio of the partial pressure of CO_2 within the stomatal chamber and that in the external atmosphere (c_i/c_a). Since these factors can fluctuate significantly in time and space, the best reconstructions of $\delta^{13}\text{C}_{\text{CO}_2}$ should use a substrate that reflects the input of (at least) tens to hundreds of individuals, from a variety of species, in different ecological conditions (Arens et al., 2000). Previously, cuticle and stem (xylem) tissues isolated from bulk terrestrial organic matter have been used to estimate the $\delta^{13}\text{C}_{\text{CO}_2}$ at several moments in geological history (e.g., Arens and Jahren, 2000, 2002; Jahren et al., 2001, 2005; Jahren, 2002; Retallack and Jahren, 2008).

In these examples, plant material used to reconstruct $\delta^{13}\text{C}_{\text{CO}_2}$ came primarily from fluviodeltaic, floodplain, and coastal plain deposits. In addition to being the most common terrestrial depositional environments, these facies provide ideal environments for the preservation of plant material and its original carbon isotopic signature. Such distal fluvial environments are commonly rich in clay minerals. The power of clays to preserve organic tissues otherwise vulnerable to decomposition and isotopic alteration has been proposed for both marine settings (Butterfield, 1990; Orr et al., 1998; Petrovich, 2001; Mapstone and McIlroy, 2006; Schwimmer and Montante, 2007) and terrestrial sediments (Benner et al., 1987; Briggs et al., 2000). Clay apparently preserves organic material by retarding microbial decay (Butterfield, 1990; Mapstone and McIlroy, 2006); therefore clay-rich sedimentary environments should preserve plant material in its most pristine form.

Distal fluvial facies prized for clay-rich deposits may be consistently or periodically brackish. Because ocean water has inherently high salt content ($\text{NaCl} = 30 \text{ g}\cdot\text{l}^{-1}$), while rainwater has very low salt content

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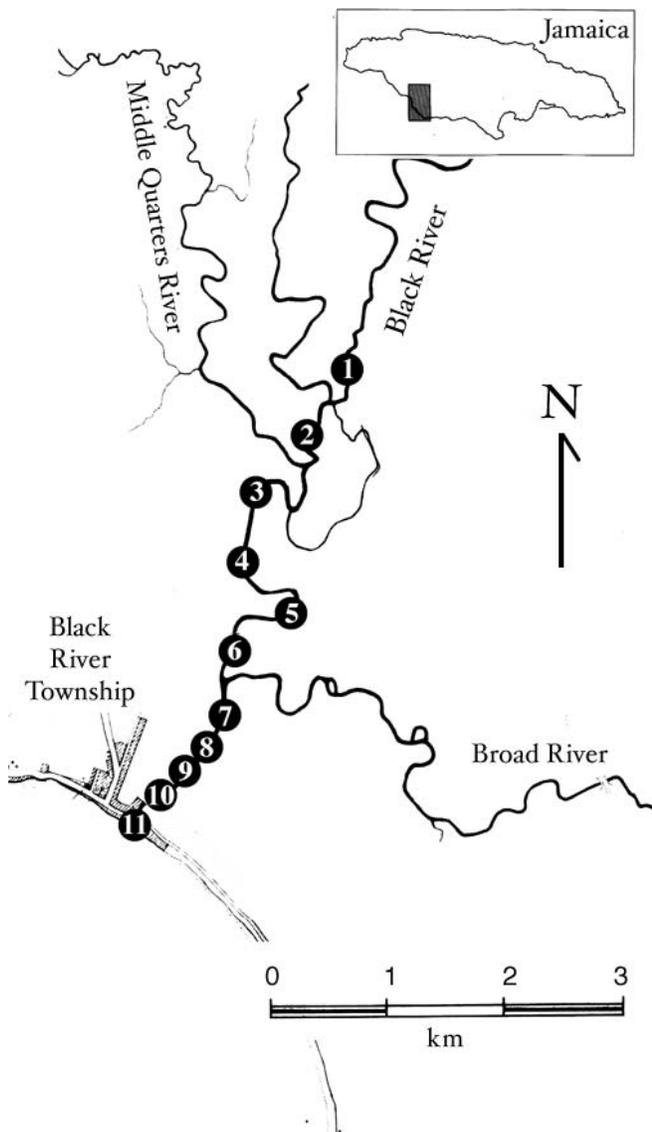


FIGURE 1—Map of sites sampled along the Black River in southwestern Jamaica. One additional site was sampled from within the Black River Bay, at least 10 m away from the mouth of the Black River, in order to represent the local marine environment.

($\text{NaCl} < 0.1 \text{ g} \cdot \text{l}^{-1}$), water associated with river sediments could span a salt-content gradient of one to three orders of magnitude, depending on the evaporative status of the body of water that receives the river. The presence of significant salt content within the depositional environment, however, could affect the ability to reconstruct $\delta^{13}\text{C}_2$ from organic matter in several ways. First, classic studies have shown that the $\delta^{13}\text{C}$ value of plant tissue can be altered—for example, by subjecting a plant to increased soil salt content (Guy et al., 1980). Thus, plants growing in an estuarine environment and contributing to organic matter in the sedimentary system may be isotopically heavy relative to plants growing in a fully freshwater environment. Second, changes in NaCl concentrations within fluids have a strong effect on cell membranes, even at concentrations well below that of seawater (Miroshnikov et al., 2006), leading to questions about the integrity of plant tissues recently contributed to the riverine system. Third, it has been shown that ambient NaCl concentration strongly affects the processes of decomposition and nutrient cycling (e.g., Liang et al., 2005; Riffat and Krongthamchat, 2006), which could have significant effects on the preservation of total organic matter after burial. Finally, decreasing salt content will exclude marine photosynthesizers,

TABLE 1—Properties of the Black River Bay, Jamaica. PDB and AIR are the stable isotope standards of PeeDee Belemnite and Air, for which $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are reported against, respectively.

Latitude; longitude	18.0 °N; 77.5 °W
Mean annual temperature	22 °C
Salinity	69.5 g/L NaCl
Sediment	29.0% carbonate by mass <1.0% organic C by mass <0.1% organic N by mass
Isotopic composition	
$\delta^{13}\text{C}$ of carbonate	−0.2‰ [vs. PDB]
$\delta^{18}\text{O}$ of carbonate	+1.5‰ [vs. PDB]
$\delta^{13}\text{C}$ of total organic carbon	−21.8‰ [vs. PDB]
$\delta^{15}\text{N}$ of total organic nitrogen	+4.6‰ [vs. AIR]

which make up a large portion of the organic carbon that is sequestered in marine sediments (Popp et al., 1989). In order to test the effects of variable salt content on this method of reconstructing $\delta^{13}\text{C}_2$ from different fractions of total organic matter, recent sediment from a fluvial system was sampled, and predicted $\delta^{13}\text{C}_2$ was compared to measurements of today's atmosphere.

FIELD SITE

In order to test the hypothesis that C3 land-plant isolates can be used to reconstruct the $\delta^{13}\text{C}_2$ of the atmosphere under complex field conditions, a highly productive ecosystem dominated by C3 plants was needed. C3 plants dominate most terrestrial environments today and in the past, while C4 plants form a relatively recent addition, first appearing in the Cenozoic (Tippie and Pagani, 2007). A salt-content gradient within this environment further provides a test of the effect of NaCl concentration on the accuracy of this isotopic indicator. For these reasons, field sites were located in southwestern Jamaica, specifically within the 400 square-mile area (104,000 hectares) watershed of the Black River. Rates of discharge from the Black River are among the highest in the country (median discharge = $10 \text{ m}^3 \cdot \text{s}^{-1}$) and are well correlated with concurrent rates of precipitation (Nkemdirim, 1979). The entire region rests on limestone bedrock of Cenozoic age.

According to the Jamaican State of the Environment Report (Jamaican Natural Resources Conservation Authority, 1997), the basin is dominated by three ecological settings: riparian swale (*Typha domingensis*), riparian forest (*Rhizophora mangle*, *Avicennia germinans*, *Laguncularia racemosa*), and swamp forest (*Grias cauliflora* and *Roystonea princeps*). In addition, *Calyptronoma occidentalis*, *Sabal jamaicensis*, *Psidium guajava*, *Haematoxylum campechianum*, and abundant *Thelypteris interrupta* were also observed. Overall, the site can be characterized as a highly productive riparian environment, overwhelmingly dominated by C3 plants. Thus, the climate and many of the sedimentary features (except for the species composition of the vegetation) of this region parallel those of the ancient environments previously studied (Arens and Jahren, 2000, 2002).

METHODS

Water and sediment samples were collected at 12 sites along the Black River (Fig. 1). Site 12 sampled the Black River Bay, a hypersaline evaporating pond ~10 m from the mouth of the Black River. At each site, 10 0.5 l Nalgene bottles were filled with surface water and sealed, and 10 0.5 kg containers were filled with sediment. Care was taken to obtain the 10 replicates across an $\sim 5 \times 5 \text{ m}$ plot to capture any heterogeneity associated with the site. Water was collected at a depth of 1 m; sediment was collected below the first 1–2 cm in order to exclude very recently settled debris. At no point was the water deeper than ~2 m, so samples could be easily collected by hand at site positions determined by a handheld global positioning unit.

TABLE 2—Properties of water and sediment samples.

Site	NaCl [g/L]	Organic mass-%	Carbonate mass-%	C ($\pm\sigma$) ^a mass-%	N ($\pm\sigma$) mass-%	C:N	Pollen ^b [gr/g]	Pollen:dino ^c
1	0.5	11.3	5.8	8.1 \pm 0.2	0.7 \pm 0.1	11.5	27500	17.3
2	0.7	2.5	6.1	5.3 \pm 1.6	0.5 \pm 0.1	10.2	25115	18.2
3	1.0	4.0	6.5	7.0 \pm 2.0	0.7 \pm 0.1	10.3	33775	4.4
4	1.5	4.7	6.1	7.9 \pm 1.3	0.7 \pm 0.1	11.2	32594	7.2
5	2.5	26.0	7.0	9.5 \pm 0.7	0.8 \pm 0.1	12.0	55660	7.2
6	2.7	21.0	8.2	10.2 \pm 0.6	0.7 \pm 0.1	14.0	102178	3.4
7	2.9	1.3	12.8	6.2 \pm 1.4	0.5 \pm 0.1	12.4	72151	1.6
8	3.5	5.7	22.2	5.1 \pm 0.6	0.4 \pm 0.1	11.6	99654	2.1
9	3.6	23.7	19.0	5.8 \pm 0.7	0.4 \pm 0.1	12.8	146975	2.8
10	3.8	1.5	15.1	8.4 \pm 0.3	0.5 \pm 0.1	15.9	165149	0.5
11	4.4	4.5 ^d	24.7	— ^e	—	—	—	—

^a σ = standard deviation seen across 10 replicates.

^b Number of pollen grains identified per gram of sediment (see text for extrapolation).

^c Ratio of pollen grains to dinoflagellates identified within sediment.

^d Standard deviation associated with 10 samples > 5 mass-%.

^e Not determined.

All samples were refrigerated at $\sim 5^{\circ}\text{C}$ during transport to the laboratory for analysis. Atomic absorption spectroscopy was used to determine sodium concentration for each water sample; all sodium was assumed to be in the form of NaCl, which allowed for calculation of salt content in the form of $\text{g NaCl}\cdot\text{l}^{-1}$ of water. For each site, the variability across 10 replicates was less than the error associated with measurement ($<0.1\text{ g}\cdot\text{l}^{-1}$). Sediment samples were dried for 10 days at 100°C . To characterize particle-size distribution in the samples, 25 g of dry-sieved ($<2\text{ mm}$) sediment was suspended in a sodium hexametaphosphate solution, and settling was monitored via hydrometer. This technique permitted classification of sediment by grain-size ratios: clay ($<2\text{ }\mu\text{m}$), silt ($2\text{--}50\text{ }\mu\text{m}$), and sand ($50\text{ }\mu\text{m}\text{--}2\text{ mm}$) content. The $>2\text{ mm}$ size fraction

was sorted manually at $20\times$ magnification, and components were identified when possible. Dried samples were also subjected to pure phosphoric acid under vacuum (25°C for 24 hours) to produce CO_2 via the reaction of acid with carbonate. Resultant CO_2 was drawn off and measured manometrically and used to infer the mass percent of carbonate sediment within the sample. For each site, the variability across 10 replicates was less than the error associated with measurement (<1 mass percent).

One-hundred gram aliquots of dried sediment, which had been acidified for 24 hours with 1 M HCl and thoroughly rinsed, were subjected to 550°C for 5 hours in order to crudely estimate mass-percent organic content from the remainder. Results were variable between replicates, yet this variability did not exceed the significant error associated with the measurement (<5 mass percent). In order to refine the estimate of organic content, a relatively large aliquot of HCl-acidified sediment ($\sim 150\text{ mg}$) from each replicate was combusted under vacuum in the presence of Cu, CuO, and Ag to produce CO_2 and N_2 gas, which was then measured manometrically and used to calculate the mass percent of carbon and nitrogen within the noncarbonate portion of the sediment. For both carbon and nitrogen, the variability across 10 replicates from each site was less than the error associated with measurement (<0.1 mass percent).

Stable isotope determination was made for carbon, nitrogen, and oxygen within organic and carbonate fractions of the sediment. In order to measure the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ value of sediment carbonate, 50 mg of dried and ground sediment from 10 replicates per site were reacted in evacuated vessels with 5–10 cm^3 of 100% phosphoric acid for 24 hours at 25°C (McCrea, 1950). For $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of bulk organics, 50 mg of dried, ground, and acidified sediment from 10 replicates per site were combusted within evacuated quartz tubes containing excess Cu, CuO, and Ag reagents (Minagawa et al., 1984). Similarly, $\sim 20\text{ mg}$ of leaf and stem fragments (Fig. 2) were isolated by hand under $25\times$ magnification from each of 10 replicate samples per site and combusted within quartz tubes. Resultant purified CO_2 and N_2 gases were analyzed for $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ in the case of carbonates and for $^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ in the case of bulk organics and isolates, using an Isoprime stable isotope ratio mass spectrometer at the Johns Hopkins University. Total variability of $\delta^{13}\text{C}$ values across 10 replicates was $\leq 0.2\text{‰}$ for each site, for both leaf and stem isolates. Instrumental error associated with measurements was within ± 0.1 in all cases. All results are presented in standard δ -notation relative to PeeDee Belemnite for C and O, and atmospheric air for N reporting standards (Sharp, 2006).

Palynomorphs provide an additional assessment of the terrestrial-plant

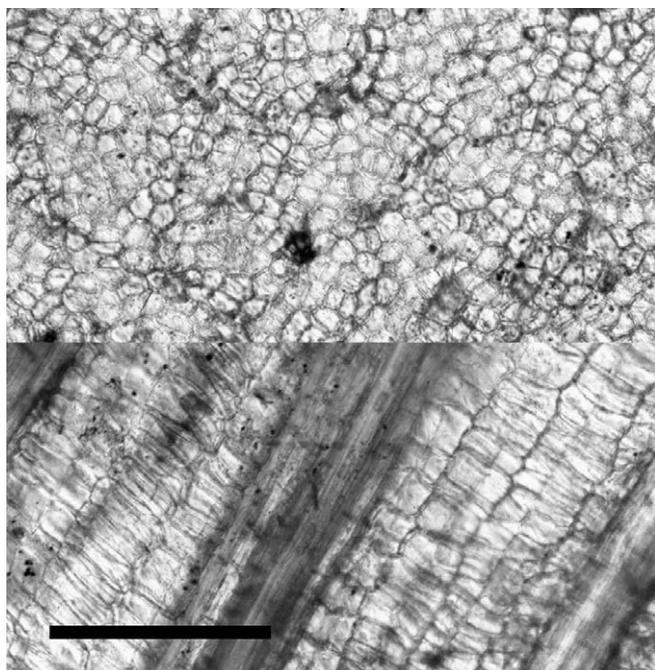


FIGURE 2—Adaxial leaf cuticle sheet (above) and stem fragment with vascular bundles (dark) and ground tissue (below). Leaf tissue was identified by the characteristic pattern of epidermal cells. Stem tissue was recognized by cell-wall thickenings on xylem. Scale = 1 mm.

TABLE 3—Stable isotope composition of sediment samples. PDB and AIR are the stable isotope standards of PeeDee Belemnite and Air, for which $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are reported against, respectively.

Site ^a	Carbonate ^b		Total organic matter ^c		Isolates ^d	
	$\delta^{13}\text{C} \pm \sigma$ [‰]	$\delta^{18}\text{O}$ [‰]	$\delta^{13}\text{C} \pm \sigma$ [‰]	$\delta^{15}\text{N} \pm \sigma$ [‰]	Leaf $\delta^{13}\text{C}$ [‰]	Stem $\delta^{13}\text{C}$ [‰]
1	-9.8 ± 0.1	-4.5	-24.5 ± 0.1	4.2 ± 0.1	-27.2	-25.0
2	-9.9 ± 0.1	-4.0	-24.1 ± 0.1	4.8 ± 0.1	-28.5	-25.3
3	-9.2 ± 0.1	-4.1	-24.6 ± 0.1	4.2 ± 0.2	-28.7	-27.2
4	-8.6 ± 0.1	-3.6	-24.5 ± 0.1	4.1 ± 0.1	-27.9	-27.5
5	-7.3 ± 0.2	-3.4	-25.5 ± 0.1	4.8 ± 0.1	-28.1	-27.2
6	-9.1 ± 0.1	-4.3	-26.1 ± 0.2	5.3 ± 0.1	-27.9	-28.4
7	-7.6 ± 0.1	-3.5	-25.7 ± 0.1	5.1 ± 0.1	-28.8	-27.7
8	-1.3 ± 0.1	-1.7	-25.2 ± 0.1	4.6 ± 0.1	-29.3	-25.9
9	-3.5 ± 0.1	-2.1	-25.2 ± 0.2	4.8 ± 0.1	-28.9	-28.4
10	-5.0 ± 0.1	-2.9	-26.3 ± 0.1	5.1 ± 0.1	-29.2 ± 0.1	-26.7
11	-0.0 ± 0.1	-1.2	— ^e	—	—	—

^a Site 1 is the most landward, site 11 the most seaward.

^b σ = standard deviation seen across 10 replicates; for all $\delta^{18}\text{O}$ measurements, $\sigma < 0.1$; standard is PDB.

^c σ = standard deviation seen across 10 replicates; ^{13}C standard is PDB; ^{15}N standard is AIR.

^d Values represent the mean for 10 replicates for which $\sigma < 0.1$; standard is PDB.

^e Not determined.

contribution to the river sediments. Samples for palynological analysis were demineralized using HCl and HF, and nonpalynomorph organic material was removed by acetolysis following standard laboratory procedures (Traverse, 1988). The number of palynomorphs per volume of sediment was estimated as follows:

$$X = (\text{BD}/\text{CA}), \quad (2)$$

where X is the number of palynomorphs per gram of sediment, A is the sediment mass (before acidification or other processing), B is the mass of maceration residue and mounting medium, C is the mass of the maceration residue and mounting medium on each microscope slide, and D is the total number of palynomorphs counted on the slide. The ratio of land-plant pollen and spores to aquatic algae (marine dinoflagellates and acritarchs) was also calculated from palynomorph count data as an additional index of marine influence.

RESULTS

Table 1 characterizes site 12, the Black River Bay, ~10 m away from the mouth of the Black River. As expected, this is a hypersaline depositional environment with minimal total organic matter input; most of the sediment is inorganic mineral material, with 29% of the total mass composed of Ca and Mg carbonates. Carbon and nitrogen isotopic values of the small amount of organics present reflect typical marine values (Fry, 1991; Fry and Wainright, 1991), as do the carbon and oxygen values of the carbonate (Coplen and Schlanger, 1973; Douglas and Savin, 1973). The salt content of the Black River Bay is fully double that of average seawater (69.5 vs. 30 g·l⁻¹ NaCl, respectively); apparently the bay is subject to evaporation relative to the well-mixed ocean near Jamaica.

In comparison, all of the 11 sites sampled along the Black River display properties in keeping with a more terrestrially dominated environment (Tables 2–4). Salt content varies systematically from the most upstream site (NaCl = 0.5 g·l⁻¹) to the most downstream (NaCl = 4.4 g·l⁻¹; see Fig. 3, upper left). Some properties of the sediment held nearly constant across this transect; for example, particle-size distribution (approximately equal parts sand, silt, and clay; see, e.g., discussion on site 11 below) and organic versus mineral content (mineral content $\geq 75\%$ by mass) were uncorrelated with position along the transect (Fig. 3, upper right and lower left). The amount of organic matter deposited with the Black River channel clastic sediment was much less than that found within the adjacent Great Morass, a stagnant, peaty wetland (20%–60% organic matter). Similarly, clay was much less predominant in the channel, as expected (Azan and Webber, 2007). Some characteristics, however, did

change systematically along the salt-content gradient. For example, mass-percent carbonate increased steadily from 5% to 25% as salt content increased (Fig. 3, lower right), probably due to the increased influence of marine organisms with carbonate skeletons. Marine foraminifera were absent in the landward extreme of the transect, appearing at low abundance (from 1% at site 7 to 7% at site 12) closer to the mouth of the river. These, along with coral fragments, likely represent marine sediment transported upstream during storm events.

Figure 4 shows that the concentration of pollen grains in sediment increased steadily toward the mouth of the river. This distribution is correlated with the silt ($r = 0.66$, $p < 0.001$) and clay ($r = 0.27$, $p < 0.001$) fraction, as would be expected from patterns of physical sedimentation (Traverse, 1988; Holmes, 1994). Conversely, the concentration of palynomorphs is inversely related ($r = -0.48$, $p < 0.001$) to the sand fraction. The absolute abundance of palynomorphs did not parallel total organic carbon (Fig. 3) but did track salt content ($r = 0.50$, $p < 0.001$). In the upstream portions of the transect, palynomorphs were dominated by pollen and spores (Fig. 4) from the local terrestrial vegetation. Very

TABLE 4—Summary of measured and calculated organic and carbonate characteristics. PDB is the stable isotope standard of PeeDee, for which $\delta^{13}\text{C}$ is reported against.

Property	Mean (n) ^a	Range	Dependence on salinity (R ²) ^b	Prediction of atmospheric $\delta^{13}\text{CO}_2$ [‰] ^c
C content [mass-%]	6.7 (10)	5.1	— ^d	n/a ^e
N content [mass-%]	0.6 (10)	0.4	—	n/a
C:N	12.2 (10)	5.7	1.0 (0.53)	n/a
TOC $\delta^{13}\text{C}_{\text{PDB}}$ [‰]	-25.2 (10)	2.1	0.5 (0.66)	-6.5
TON $\delta^{15}\text{N}_{\text{AIR}}$ [‰]	+4.7 (10)	1.1	—	n/a
Leaf isolate $\delta^{13}\text{C}_{\text{PDB}}$ [‰]	-28.4 (10)	2.1	—	-9.7*
Stem isolate $\delta^{13}\text{C}_{\text{PDB}}$ [‰]	-26.9 (10)	3.4	—	-8.2*
Carbonate $\delta^{13}\text{C}_{\text{PDB}}$ [‰]	-6.5 (11)	9.8	2.2 (0.74)	n/a
Carbonate $\delta^{18}\text{O}_{\text{PDB}}$ [‰]	-3.2 (11)	3.3	0.7 (0.69)	n/a

^a n = number of sites sampled for this property.

^b dependence reported as m within $y = mx + b$, where y = property and x = [NaCl]; R² is the correlation statistic for the regression.

^c Prediction of atmospheric $\delta^{13}\text{CO}_2$ using the relationship described in Arens et al., 2000; * indicates that the prediction is within 1‰ of the measured $\delta^{13}\text{CO}_2$ value of the present-day atmosphere.

^d R² < 0.50

^e n/a indicates that the calculation does not apply.

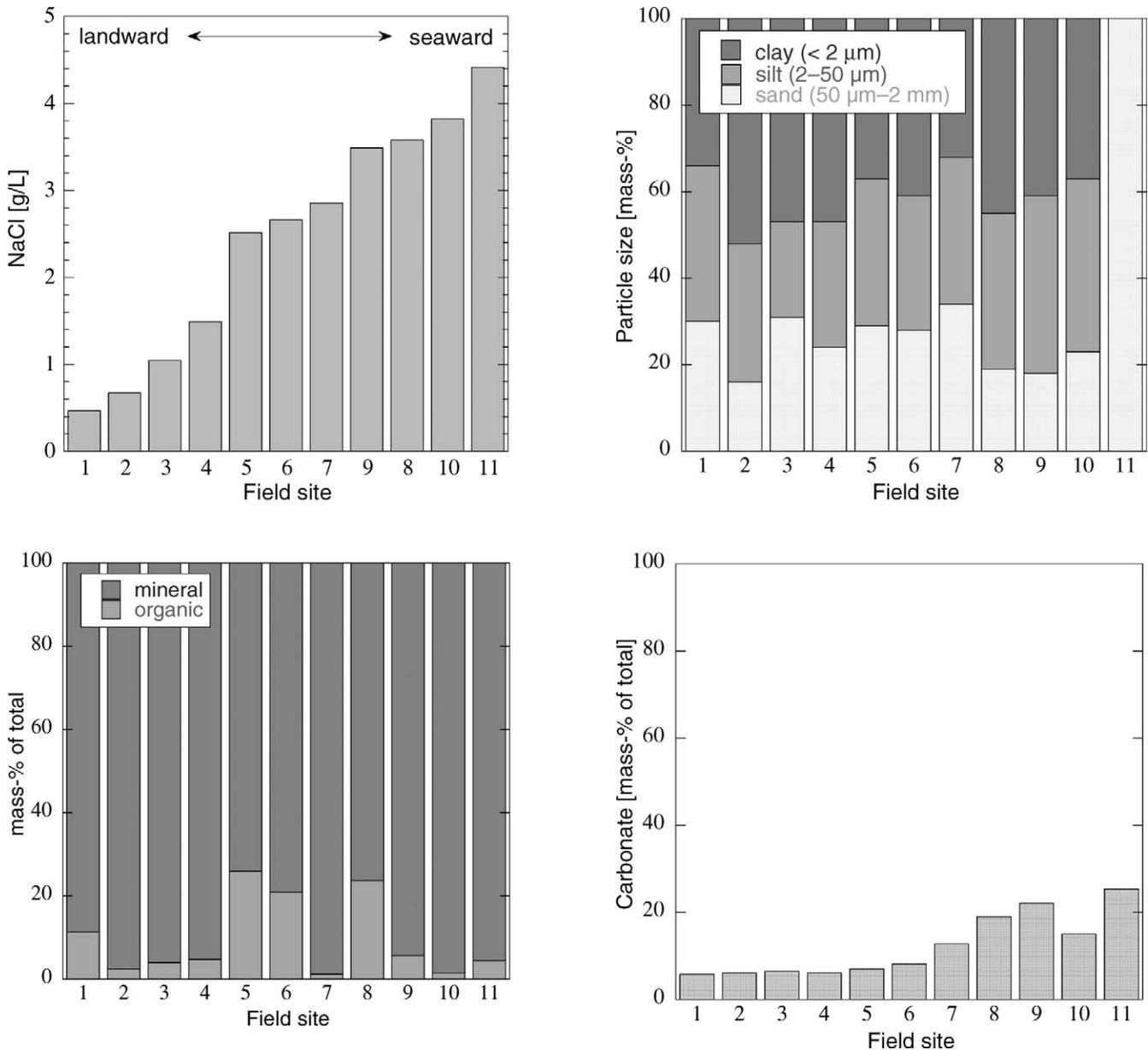


FIGURE 3—Characterization of the sedimentary environment of samples taken from terrestrial sites (see Fig. 1), including concentration of NaCl within river water (upper left), particle-size distribution (upper right), organic versus mineral content (lower left), and carbonate content (lower right).

few species from outside the immediate drainage of the Black River were noted; however a quantitative documentation of this pattern was not made. Near the mouth of the river, marine algae, particularly dinoflagellates, were more abundant (Fig. 4), suggesting greater marine influence. No organic-walled microfossils were recovered from bay sediments. This is likely the consequence of the higher-energy characteristic of this environment (Brush and Brush, 1994).

The ratio of terrestrially derived palynomorphs (pollen) to marine palynomorphs (e.g., dinoflagellates) is inversely related ($r = -0.48$, $p < 0.001$) to the concentration of pollen in sediment (Fig. 4). This pattern is created by a relatively constant concentration of pollen and spores throughout the portion of the river's reach that was sampled, with increasing representation of marine algae toward the mouth of the river. Since the ratio of terrestrial to marine palynomorphs is not correlated with the silt fraction, as would be expected if the pattern were a taphonomic artifact, the decreasing ratio toward the river's mouth appears to record marine influence.

Because NaCl concentration increases evenly, by $\sim 0.5 \text{ g} \cdot \text{l}^{-1}$, with each increase in site number (Table 2 and Fig. 3, upper left), isotopic and other characteristics of the sediments can be presented in relation to NaCl concentration, a proxy for position along the transect. Because of the very coarse grain size at site 11 (near the mouth of the river, with all particles $> 2 \text{ mm}$; see Fig. 3, upper right), only inorganic carbon and oxygen-isotope determinations were performed on this sample (Table 3). Figure 5 shows the relatively monotonic values of mass-percent C and mass-percent N across the NaCl gradient. Interestingly, these values are similar to those determined for organic horizons in Inceptisols (e.g., Werts and Jahren, 2007), which, by definition, contain only terrestrial influence. The ratio of C:N showed a weak correlation with NaCl concentration ($r = 0.73$; Table 4), possibly confirming the role of NaCl in the inhibiting decomposition (Riffat and Krongthamchat, 2006). Nevertheless, the $\delta^{13}\text{C}$ value of total organic carbon systematically decreased with increased NaCl concentration across a range of 2‰ ($R^2 = 0.66$; see Fig. 6, Table 4). The $\delta^{15}\text{N}$ value of total organic nitrogen did not change across the

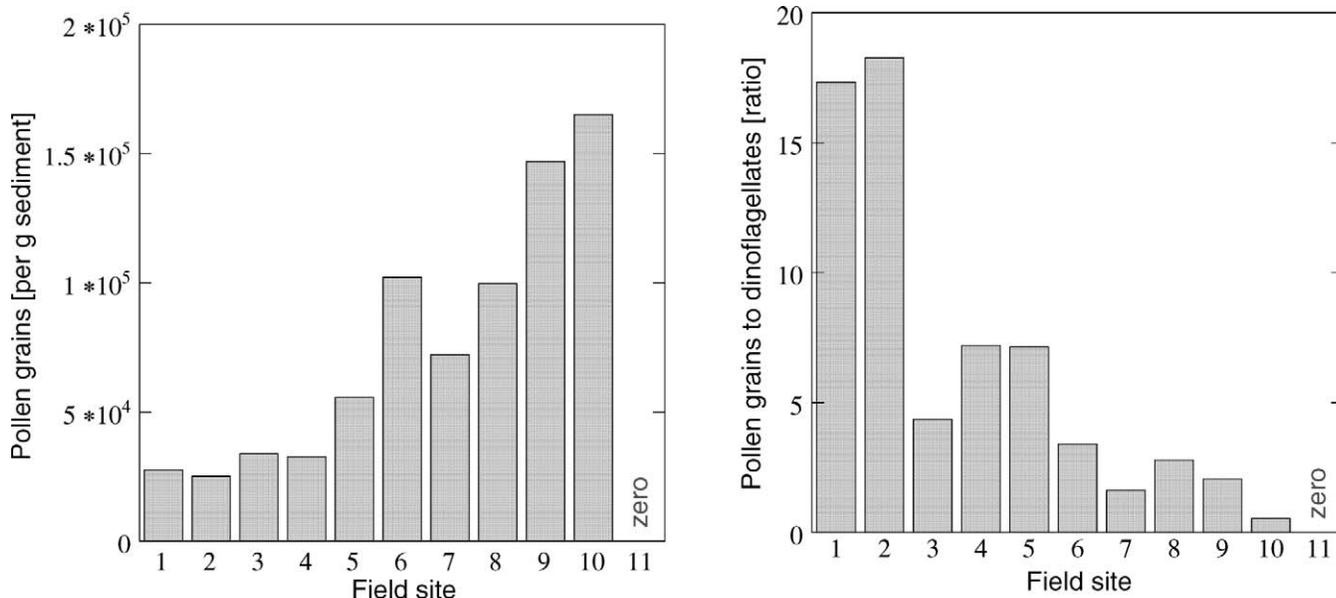


FIGURE 4—Estimated number of pollen grains per gram of sediment (left) and ratio of terrestrial (pollen grains + spores) to marine algae (dinoflagellates + other marine algae producing resistant walls; right). No determinations were performed on samples from site 11 because of the very large particle size of the sediment (>2 mm; see Fig. 3, upper right).

transect, although these values may be considered less reliable given the very small mass of N in each sample (Table 2, Fig. 5). Both sets of values are within the range of values expected for mixed marine-terrestrial environments (Fry, 1991; Fry and Wainright, 1991).

There is a larger variability between sites in the $\delta^{13}\text{C}$ values of leaf and stem fragments, especially for stem isolates (Table 4); however, measurements reveal no significant relationship between $\delta^{13}\text{C}$ value and NaCl concentration for either leaf or stem isolates. This is significant because it suggests that the isotopic signature of the integrated terrestrial contribution is independent of the salt content of the depositional environment (Fig. 6). In contrast, the isotopic value of sediment carbonate shows a strong dependence on NaCl concentration (Fig. 7, Table 4), and values vary across a large range ($\Delta\delta^{13}\text{C} = 9.8\text{‰}$; $\Delta\delta^{18}\text{O} = 3.3$). Carbonate $\delta^{18}\text{O}$ values increase with salt content, likely in response to the input of relatively depleted rainwater upstream, compared to Standard Mean Ocean Water (Bowen and Wilkinson, 2002). The low values of carbonate $\delta^{13}\text{C}$ upstream reflect the influence of CO_2 produced by the decay and respiration of terrestrial plant material (Holmes et al., 1995). Irrespective

of whether the carbonate sampled here was derived from *in situ* biomineralization or from abiotic precipitation, respired and dissolved isotopically light CO_2 would give rise to low carbonate $\delta^{13}\text{C}$ values.

INTERPRETATION AND CONCLUSIONS

In order to test the hypothesis that the $\delta^{13}\text{C}$ value of accumulated land-plant tissue can be used to reconstruct the $\delta^{13}\text{C}\text{O}_2$ value of the atmosphere under which it grew, the numerical relationship detailed in Arens et al. (2000) was applied to the mean values of all isolates retrieved from the Jamaican sediments (Table 4). This work involved previously published values of 176 C3 land-plant species and demonstrated an average isotopic depletion of -18.72‰ ($R^2 = 0.91$) in plant tissue relative to the atmosphere (Arens et al., 2000). When this relationship is applied to the mean values of leaf and stem isolates recovered from Jamaican sediments, $\delta^{13}\text{C}\text{O}_2$ values of $-9.7 (\pm 1.0)$ for leaf and $-8.2 (\pm 1.7)$ for stem tissues are predicted. Both of these values are within $\sim 1\text{‰}$ of recent

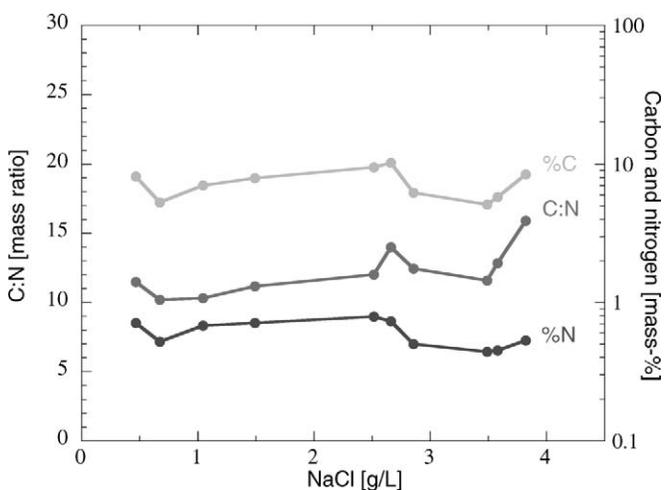


FIGURE 5—Carbon and nitrogen by mass percent versus NaCl concentration (right y-axis); C:N also presented (left y-axis).

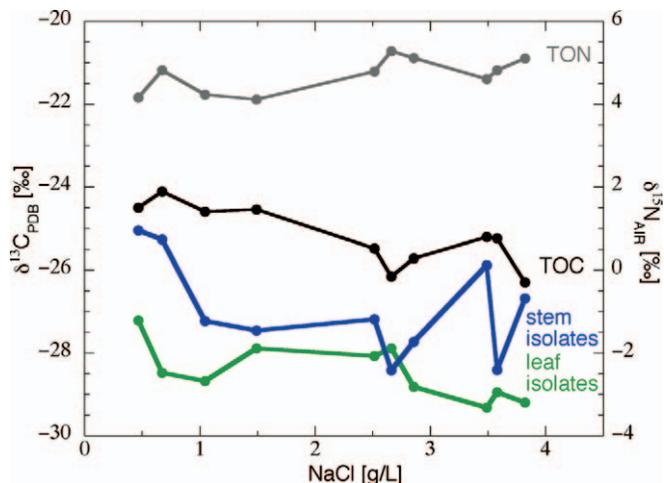


FIGURE 6—The stable-isotope composition of total organic carbon (TOC, left y-axis) and total organic nitrogen (TON, right y-axis) versus NaCl concentration. Also presented are the carbon isotope values of stems and leaves isolated from sediment sampled (left y-axis). PDB = PeeDee Belemnite; AIR = atmospheric air.

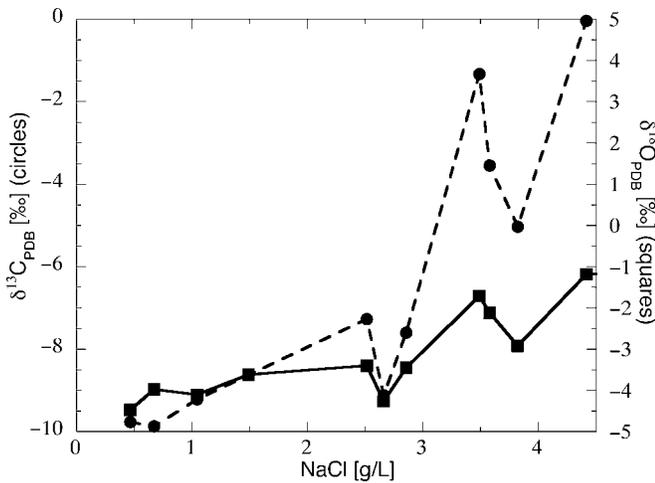


FIGURE 7—The carbon (left y-axis; dashed line with circles) and oxygen (right y-axis; solid line with squares) isotope composition of bulk carbonate within sediment sampled versus NaCl concentration. PDB = PeeDee Belemnite.

regional-scale measurements of atmospheric $\delta^{13}\text{C}\text{O}_2$ values in Europe. The common, unpolluted end member in the Ile-de-France region is -9.4 (± 0.3 ; see Widory and Javoy, 2003); while the long-term average for eastern Europe is -9.6 (Kuc et al., 2007). Because the atmosphere is in long-term equilibrium, the $\delta^{13}\text{C}\text{O}_2$ of the global atmosphere is thought to be well mixed (Ciais et al., 1995), and the isotopic similarity seen in the values above supports this idea. For these reasons, we conclude that both leaf and stem isolates from the Black River sediments successfully reflect the isotopic composition of the modern atmosphere. The isotopic composition of the atmosphere has changed $>1\%$ in the last century, and so the more recent inputs of terrestrial organic matter may reflect this variability. Furthermore, the $\delta^{13}\text{C}$ of total organic carbon from the sediments fails to predict the isotopic composition of atmospheric carbon dioxide (-6.5 ± 1.0 ; see Table 4), as discussed previously. In this depositional environment this substrate is not purely terrestrial in origin but likely contains considerable marine organic carbon input. Leaf matter gives slightly more accurate results than stem material. This might be because stem isolates were dominated by *Typha* (cattail), which was extremely abundant along the banks of the river and on its proximal floodplain. *Typha* is rich in lipids, which are concentrated in the stem. Furthermore, the lipid constituents of *Typha* are isotopically heavy relative to those of most C3 plants (Shtemenko et al., 2005). Plant fragments isolated from sediment were generally too small to identify to genus; thus, this possibility cannot be rigorously tested with the data at hand. Sedimentary leaf litter likely consisted of a wider range of species, thus allowing better reconstruction of $\delta^{13}\text{C}\text{O}_2$ (Elder et al., 2000). It may be advisable to avoid fossil substrates clearly dominated by a single tissue type (such as *Typha* stems) for use in atmospheric reconstruction.

A substrate comprising the contribution of multiple species and many individual plants is necessary for accurate prediction. Studies of single species grown under controlled atmospheric $\delta^{13}\text{C}\text{O}_2$ values have yielded carbon isotope fractionations notably different than those in Arens et al. (2000), for example, -25.4% for *Raphanus sativus* in Jahren et al. (2008). Fortunately, sedimentary organic material in floodplain settings commonly includes contributions from many species and individuals within a few cubic centimeters (Elder et al., 2000) and thus constitutes the best substrate for $\delta^{13}\text{C}\text{O}_2$ reconstruction. Furthermore, the current reconstruction of $\delta^{13}\text{C}\text{O}_2$ based on sedimentary organic material derived from terrestrial sources was not noticeably sensitive to salt content. Our results also indicate that the introduction of significant marine productivity into total organic matter could bias the reconstruction; however, this influence may be gauged using the terrestrial:marine palynomorph ratio.

In closing, our study indicates that rocks containing terrestrial plant matter, characterized in terms of depositional environment and biotic content, should be a source of accurate $\delta^{13}\text{C}\text{O}_2$ reconstruction applicable throughout the Phanerozoic.

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