

# Marine vs. terrigenous organic matter in Louisiana coastal sediments: The uses of bromine:organic carbon ratios

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## Abstract

Recent data on the sources of organic carbon buried in the ocean have emphasized the probable importance of terrigenous organic matter in burial budgets of deltaic depocenters. The many markers used to assess relative importance of marine vs. terrestrial sources each have ambiguities. We use the ratio of bromine to organic carbon (Br:OC) as a source indicator for organic matter in the Mississippi delta. Progressive increases in bromine concentrations from the river to the slope indicate increasing content of marine-derived organic matter. Quantitative estimates of marine vs. terrigenous organic matter using Br:OC ratios in a two-endmember mixing model are consistent with recent estimates using a combination of three other source markers [Gordon, E.S., Goñi, M.A. 2003. Sources and distribution of terrigenous organic matter delivered by the Atchafalaya River to sediments in the northern Gulf of Mexico. *Geochim. Cosmochim. Acta*, 67:2359–2375]. The Br:OC vs.  $\delta^{13}\text{C}$  relationship indicates seaward increase in  $\delta^{13}\text{C}$  without proportionate incorporation of marine organic matter, consistent with recent arguments that isotopically depleted terrestrial detritus derived from C3 plants is separated from C4-derived terrigenous organic matter during transport. Decreasing Br:OC ratios downcore at many sites that have significant amounts of marine organic matter indicate that the marine organic matter is preferentially lost during burial diagenesis. This preferential loss constrains the contribution of organic matter burial in deltaic environments to global removal of Br.

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## 1. Introduction

Organic carbon burial in marine sediments is a major flux in the long-term carbon cycle (Berner, 1982), affecting not only carbon flux but also other elements incorporated into organic matter. Most burial of organic

matter in the ocean occurs on continental shelves and upper slopes (Berner, 1982; Hedges and Keil, 1995). These ocean margin sediments partition into two modes of burial based on their ratio of organic carbon to mineral surface area (Mayer, 1994). Deltas of large muddy rivers, especially at lower latitudes, share lower ratios of  $\sim 0.25 \text{ mg-OC m}^{-2}$ , which is less than a third of that found in most other shelf environments. Each of these two shelf types accounts for roughly half of the

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overall marine burial flux of organic carbon (Hedges and Keil, 1995).

The proximity of these depocenters to land and the strong association between organic matter and terrigenous minerals (Mayer, 1994) means that terrigenous organic matter can make up significant fractions of the burial flux. The mix of terrigenous and marine-derived organic matter that constitutes this flux is unknown. Older literature inferred dominance of marine OM burial in oceanic sediments, based largely on lignin biomarkers and stable isotope data of the bulk organic matter pool (e.g., Hedges and Parker, 1976; Gearing et al., 1977).

More recent literature (Hedges et al., 1997; Goñi et al., 1997, 1998; Holtvoeth et al., 2005; Burdige, 2005) calls into question this presumption — especially in deltaic situations. Among the most compelling evidence is the increasingly old  $^{14}\text{C}$  ages of sedimentary organic matter in land-to-sea transects (Goñi et al., 1997, 1998; Gordon and Goñi, 2003); this trend is opposite to that predicted from addition of young planktonic material to older soil-derived organic matter (Hedges and Parker, 1976). The  $\delta^{13}\text{C}$  values of the presumed marine and terrestrial endmembers are not as clear as originally supposed, because organic matter from land-based C4 plants, upon mixing with C3 plant-derived organic matter, results in  $\delta^{13}\text{C}$  values of terrigenous organic matter similar to those generated by marine plankton (Goñi et al., 1997, 1998). Selective removal of the C3-derived detritus, by physical or diagenetic processes, can therefore alter  $\delta^{13}\text{C}$  values in a direction that simulates the addition of isotopically heavy marine organic matter. Likewise, the C:N ratios of terrigenous organic matter are usually higher than those of marine-derived planktonic remains. However, the C:N ratio of the bulk terrestrial organic matter pool results from a complex mixture of material that can become segregated during sorting in the marine environment, winnowing vascular plant detritus of high C:N which can then be transported offshore and leaving behind in nearshore regions mineral-associated soil organic matter with C:N ratios similar to those formed in the oceans (Leithold and Blair, 2001). Side reactions with inorganic phases can interfere with interpretations of other elemental ratios, such as C:P (Ruttenberg and Goñi, 1997). Various biomarkers, especially lignin, have been used as further indicators of terrigenous vs. marine origin; these approaches have advantages in specificity of origin, but can be problematic to interpret quantitatively because they do not always maintain a constant ratio to the pool which they represent (Hedges and Prahl, 1993).

The challenge of quantitatively partitioning organic matter sources would clearly benefit from the application of more markers that distinguish between the terrestrial

vs. marine origins of organic matter (Burdige, 2005). Especially beneficial would be markers that are independent of the different types of terrestrial organic matter. One such marker that has been used in the past is the ratio of bromine to organic carbon (Br:OC; Mayer et al., 1981). In transects of temperate estuaries bromine contents have been used to distinguish marine from terrigenous organic matter (Mayer et al., 1981; Malcolm and Price, 1984; Upstill-Goddard and Elderfield, 1988). This use of the Br:OC ratio relies on the low concentration of bromine in terrestrial environments and its relatively high concentrations in the oceans.

Bromine in the particulate phase of sediments is thought to be associated entirely with organic matter (Harvey, 1980), though neither the chemical nature nor origin of this association is understood. Many primary producers, especially macroalgae, are known to synthesize brominated organic compounds (Gribble, 1998). Heterotrophic organisms, especially invertebrates but including bacteria (Gribble, 1998; Van Pée, 1996), also produce brominated compounds. Last, bromination may occur via nonbiological reactions (Müller et al., 1996). Anthropogenic oxidation processes such as chlorination are well known to cause bromination of various organic moieties (e.g., Sigleo et al., 1980; Howard et al., 1984) and natural versions of this type of reaction may occur.

As part of a study examining organic matter in the Mississippi delta region, we therefore examined the bromine contents of riverine, shelf and slope sediments to assess their contribution to the question of marine vs. terrestrial origin. We concentrate on a spatial analysis of Br:OC ratios in surface sediments, and also examine possible changes in these ratios resulting from downcore diagenesis.

## 2. Methods and materials

We sampled both deposited and suspended sediments for this study, in areas including the lower Mississippi and Atchafalaya Rivers, and coastal, shelf and slope sites offshore of the Mississippi and Atchafalaya deltas (Fig. 1, Map). Suspended sediments were obtained from water samples collected on the Mississippi River at St. Francisville, LA, and Venice, LA, and on the Atchafalaya River at Morgan City, LA. Suspended particulate matter (SPM) was occasionally concentrated from large volumes of river water samples in plastic-lined garbage cans by adding Instant Ocean (TM) to reach a salinity of 5–10‰, and allowing coagulation to occur overnight. After decantation of the clarified supernatants, the concentrated suspensions were then centrifuged to remove most of the remaining water. Tests showed that insignificant changes in organic matter content result from this separation

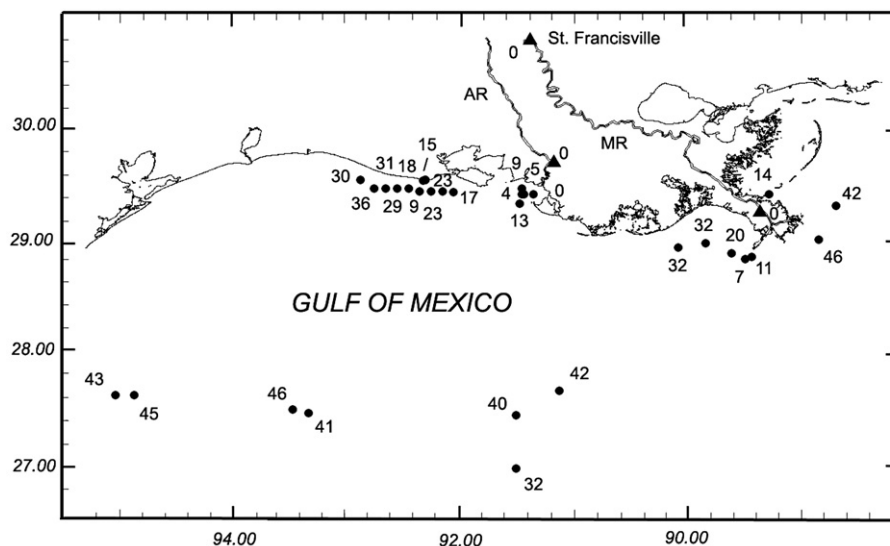


Fig. 1. Map of stations, along with the percentage of organic matter at the sediment–water interface that is marine, calculated from Br:OC ratios and the equation described in the text. Seabed samples shown by solid circles and riverine SPM samples by solid triangles.

approach as compared with direct centrifugation or filtration of bulk river water without seasalt coagulation. Deposited sediments were collected by gravity corer, Kasten corer, box corer, multicorers, and various grabs, on a number of cruises during 2003–2005. Cores were dissected using core extruders within hours of collection and samples frozen until analysis.

Bromine was analyzed by neutron activation analysis (Activation Laboratories, Ancaster, Ontario). Samples were rinsed twice in deionized water, to remove interstitial seawater with its associated bromide. We tested for possible removal of brominated organic compounds in this study by measuring solid phase bromine before and after the deionized water rinse, and comparing the decrease in bromine with that calculated from a separate determination of seasalt bromide using ion chromatography. This test showed excellent agreement between the two approaches, indicating that insignificant organic bromine was washed away. This finding confirms previous assumptions that distilled water removes Br only to the extent that would be expected from dried interstitial water (Harvey, 1980; Mayer et al., 1981). We tested for complete removal of seasalt by performing up to four washes and found no further Br loss. The coefficient of variation of Br analyses by this method was 2%.

Organic carbon was analyzed on a Perkin-Elmer 2400B Elemental Analyzer, after decarbonation by gas phase acidification (Mayer, 1994). Carbon isotope ratios were determined by isotope ratio mass spectrometry on a Europa 20-20 mass spectrometer (MBL Stable Isotope Laboratory, Woods Hole MA).

### 3. Results

The Br content of sediments (Table 1) is low in the riverine suspended particulate samples, and similar to the global average

of  $5 \mu\text{g g}^{-1}$  reported by Martin and Meybeck (1979). Br concentrations in deposited sediments just outside of the mouths of the Mississippi and Atchafalaya Rivers are similar to riverine suspended sediments, and generally increase with distance from their river mouths. The river SPM samples do not contain the lowest Br concentrations, largely because they are relatively fine-grained sediments; Br concentrations are grain size-dependent (Mayer et al., 1981) and thus coarser-grained sediments in nearshore sites often exhibit even lower concentrations. Organic carbon concentrations show the opposite trend to Br, instead generally decreasing across the river to ocean transition in keeping with trends observed in most deltaic environments (Keil et al., 1997).  $\delta^{13}\text{C}$  values also show the usual enrichment in the river-offshore direction, consistent with numerous studies from this region (e.g., Goñi et al., 1998).

Downcore changes in Br and OC concentrations were variable in sites close to shore (e.g., A-1, P4S5), likely as a result of recent and nonsteady state sedimentation. More distant sites offshore (e.g., MC-2, P4S8) showed more consistent drops in both parameters downcore, reflecting the slower sedimentation rates and hence greater time for diagenetic reactions to affect concentrations.

## 4. Discussion

### 4.1. Provenance

The only known, nonaqueous phase association for Br in marine sediments of normal salinity is organic matter (Price and Calvert, 1977; Price et al., 1970; Harvey, 1980). Harvey (1980) indicated that Br likely forms a wide variety of organic compounds. We have

Table 1

Station names, locations, water depths, depths within cores, total organic carbon (TOC) and bromine (Br) concentrations, bromine:organic carbon ratios (Br:OC), the percent of the organic matter that is of marine origin as calculated from Br:OC values by the equation in the text (MAR), and  $\delta^{13}\text{C}$  values

Sampling site	Latitude (degrees)	Longitude (degrees)	Water depth (m)	Core depth (cm)	TOC (mg/g)	Br ( $\mu\text{g/g}$ )	Br:OC (mg-Br:g-OC)	%-MAR	$\delta^{13}\text{C}$ (per mil)
<i>Suspended particulates</i>									
Atchafalaya, Morgan City 4/03 (5240)	29.7	91.17			19.0	8.9	0.47	0	-26.1
Mississippi, Venice, 3/05	29.26	89.35			23.8	8	0.34	0	-24.3
Mississippi, Venice 4/05	29.26	89.35			14.8	7	0.47	1	
Mississippi, St. Francisville 3/05 (18700)	30.47	91.23			25.1	10	0.40	0	-26.8
Mississippi, St. Francisville 4/05 (17700)	30.47	91.23			18.1	8	0.44	0	
Mississippi, St. Francisville 2/03 (21700)	30.47	91.23			10.50	4.6	0.44	0	-25.8
Coastal SPM, off Freshwater Bayou	29.53	92.3			23.9	27.8	1.16	10	-22.6
<i>Atchafalaya region</i>									
A-1	29.32	91.47	3	0–1	11.5	8.5	0.74	4	-23.3
				1–2	10.5	7.5	0.72	4	-23.2
				2–3	10.8	8.0	0.74	4	-23.0
				3–4	9.9	7.8	0.79	5	-22.7
				4–5	12.7	8.4	0.66	3	-23.0
				5–7	14.5	8.0	0.55	2	-22.6
				8–10	12.0	7.3	0.61	3	-22.8
				10–15	10.0				
				15–17	10.2	5.1	0.51	1	-23.0
				22–24	6.9	3.8	0.55	2	-22.7
				32–34	13.2				
				42–44	6.7	4.3	0.64	3	-22.1
				52–54	12.5				
A-2	29.40	91.45	2	0–1	14.4	11.3	0.78	5	-23.6
				1–2	6.1	5.3	0.86	6	-23.5
				2–3	9.7	7.7	0.79	5	-23.2
				3–4	15.2	10.8	0.71	4	-22.4
				4–5	14.0	18.6	1.33	12	-22.7
				5–7	12.8	9.7	0.75	4	-22.6
				8–10	10.4	6.7	0.65	3	-23.2
				14–16	9.4	5.5	0.58	2	-23.5
				22–24	13.1	10.2	0.78	5	-21.9
				28–30	9.5	5.3	0.56	2	-23.7
				32–34	12.4	9.4	0.75	4	-21.9
				38–40	15.3	15.7	1.03	8	-22.9
				42–46	11.4	8.1	0.71	4	-21.3
50–53	12.4	9.6	0.78	5	-21.8				
62–65	11.7	9.1	0.78	5	-21.7				
72–75	12.2	10.2	0.84	6	-21.9				
82–85	12.3	8.8	0.72	4	-23.7				
A-3	29.45	91.45	2	0–2	18.7	19.7	1.05	9	-23.2
				2–3	19.7	22.2	1.13	10	-23.0
				3–4	15.0	18.0	1.20	11	-22.8
				4–5	7.7	6.6	0.85	6	-23.3
				5–7	7.0	5.1	0.73	4	-23.5
				7–10	9.8	7.5	0.77	5	-23.5
				13–15	13.2	8.1	0.62	3	-22.7
				18–20	11.9	7.2	0.60	2	-23.1
				Atchafalaya Bay Stn	29.40	91.43			20.4
FWB-1	29.53	92.30	1	0–1	18.9	28.9	1.53	15	-22.5
				ca. 1–6	20.4	29	1.42	14	-22.5
FWB-6	29.52	92.32	3	0–1	17.4	26.1	1.50	15	-22.6
				ca.1–6	16.9	28.5	1.69	17	-22.6

(continued on next page)

Table 1 (continued)

Sampling site	Latitude	Longitude	Water depth	Core depth	TOC	Br	Br:OC	%-MAR	$\delta^{13}\text{C}$
	(degrees)	(degrees)	(m)	(cm)	(mg/g)	( $\mu\text{g/g}$ )	(mg-Br:g-OC)		(per mil)
<i>Western shelf</i>									
B7	29.53	92.87	16	0–2	7.18	19	2.65	30	
				2–4	7.20	19	2.64	30	
				4–6	7.99	21	2.63	30	
B8	29.45	92.75	15	0–2	9.41	29	3.08	36	-21.7
				2–4	9.41	27	2.87	34	-21.7
				4–6	9.14	22	2.41	27	-21.7
B9	29.45	92.65	14	0–2	15.1	40	2.65	31	
				2–4	11.8	30	2.55	29	
				4–6	10.4	26	2.50	29	
B10	29.45	92.55	12	0–2	15.0	38	2.53	29	
				2–4	13.3	31	2.33	26	
				4–6	12.5	34	2.72	31	
B11	29.45	92.45	10.5	0–2	16.3	28	1.72	18	
				2–4	16.0	19	1.19	10	
				4–6	15.7	16	1.02	8	
B12	29.43	92.35	9	0–2	15.1	16	1.06	9	
				2–4	16.0	14	0.87	6	
				4–6	15.8	32	2.02	22	
B13	29.43	92.25		0–2	13.9	31	2.23	25	
				2–4	17.4	34	1.95	21	
				4–6	14.6	26	1.78	19	
B14	29.43	92.15		0–2	15.7	33	2.10	23	
				2–4	14.8	28	1.89	20	
				4–6	14.5	24	1.65	17	
B15	29.42	92.05		0–2	15.4	26	1.69	17	
				2–4	14.0	22	1.57	16	
				4–6	8.5	13	1.52	15	
<i>Circum Birdfoot Delta</i>									
P4S2	28.85	89.42	50	0–1	17.3	21	1.21	11	
				3–5	15.7	10	0.64	3	
				11–14	14.7	15	1.02	8	
P4S5	29.40	89.27	6	0–2	15.8	23	1.46	14	
				8–11	12.8	13	1.02	8	
				20–23	20.4	18	0.88	6	
P4S6	28.88	89.6	69	0–1	19.3	37	1.91	20	
				1–4	18.2	29	1.59	16	
				7–10	16.5	33	2.00	22	
				13–16	15.9	29	1.82	19	
				16–19	15.3	26	1.70	17	
P4S7	28.97	89.83	40	19–22	15.5	25	1.61	16	
				0–1	17.6	48	2.73	32	
				1–4	16.3	45	2.76	32	
				4–7	14.9	37	2.49	28	
				7–10	13.9	38	2.73	32	
P4S8	28.93	90.07	72	10–13	13.0	32	2.46	28	
				13–16	12.1	26	2.14	24	
				0–1	12.0	33	2.76	32	-21.7
				1–3	10.7	29	2.71	31	-21.9
				3–6	7.6	18	2.37	27	-22.0
MSS-2	28.83	89.48	45	6–9	7.7	18	2.33	26	-21.6
				9–12	8.4	13	1.55	15	-21.4
				12–14	7.2	6	0.84	6	-21.2
				0–5	13.0	11.8	0.91	7	-23.4
				5–10	12.8	9.6	0.75	4	-23.4

Table 1 (continued)

Sampling site	Latitude (degrees)	Longitude (degrees)	Water depth (m)	Core depth (cm)	TOC (mg/g)	Br ( $\mu\text{g/g}$ )	Br:OC (mg-Br:g-OC)	%-MAR	$\delta^{13}\text{C}$ (per mil)
<i>Circum Birdfoot Delta</i>									
MSS-2				15–20	12.6	8.4	0.67	3	–23.1
				30–35	13.6	10.8	0.79	5	–22.4
				50–55	13.3	11.2	0.84	6	–22.6
				70–75	13.0	10.3	0.79	5	–22.7
				90–95	12.4	6.1	0.49	1	–24.1
				150–160	12.0	8.9	0.74	4	–23.5
MC-2	29.00	88.83	200	0–0.5	17.1	65	3.81	46	–21.9
				0.5–1	16.3				–21.8
				1–1.5	16.2				–22.2
				1.5–2	15.6				–21.6
				2–3	15.3	50	3.3	39	–21.5
				3–4	15.4				–21.6
				4–5	15.3				–21.9
				5–6	15.2				–21.7
				6–7	15.1				–21.4
				7–8	14.8				–21.5
				8–9	14.7				–21.6
				9–10	14.7				–21.3
				10–12	14.8	39	2.6	30	–21.5
				12–14	14.8				–21.7
				14–16	15.3				–21.6
				16–18	14.6				–21.5
				18–20	14.4				–21.5
				20–22	14.8				–21.6
				22–24	13.9				–21.3
				24–26	13.9				–21.7
				26–28	14.0				–21.8
				28–30	13.3	27	2.0	22	–21.5
MC-1	29.30	88.68	62	0–0.5	15.5	54	3.5	42	
				2–3	14.4	47	3.3	39	
				10–12	12.6	37	2.9	34	
				28–30	11.1	28	2.5	29	
<i>Slope</i>									
6T	29.63	95.03	730	SWI	12.0	45	3.6	43	
7T	27.63	94.87	713	SWI	12.0	46	3.7	45	–19.9
14T	27.50	93.47	587	SWI	11.9	45	3.8	46	
15T	27.47	93.33	662	SWI	10.3	38	3.4	41	
21T	27.67	91.12	973	SWI	10.7	39	3.5	42	–19.7
CT-7	27.46	91.50	964	4–6	12.0	40	3.3	40	–20.0 <sup>a</sup>
				28–30	11.3	17	1.5	15	
				55–57	10.5	26	2.5	28	
				73–75	9.6	24	2.5	28	
				91–93	15.4	29	1.9	20	
CT-5	26.98	91.5	2250	2–4	8.8	24	2.7	32	–21.8 <sup>a</sup>
				8–10	7.4	21	2.8	33	
				14–16	7.6	15	2.0	21	
				20–22	8.0	38	4.8	59	

Values in parentheses associated with river samples are river flow ( $\text{m}^3 \text{s}^{-1}$ ).

<sup>a</sup> From Ruttenberg and Goñi (1997).

no reason to suspect any other phase association for bromine in sediments from the Mississippi delta region and will therefore assume this association for the purposes of this paper.

We can infer provenance of bulk organic matter assuming that the Br:OC ratio, as a chemical marker, acts as a tracer for marine vs. terrestrial source. The Br:OC ratios in the river suspended particulates all fell

within the narrow range 0.34–0.47 mg-Br g-OC<sup>-1</sup> (Table 1). Values in nearshore sediments close to the two river mouths are generally close to this value, and hence indicate a largely terrigenous nature for the organic matter in these sites. The increase in Br:OC ratios with distance from the sites of river discharge presumably reflects increasing marine primary production in the overlying water column as suspended sediment levels decrease and the light field for phytoplankton improves (Lohrenz et al., 1999; Lane et al., 2002). This increase in primary production will roughly correlate with a decrease in sedimentation rate of terrigenous detritus, which settles close to shore (Wright and Nittrouer, 1995; Hitchcock et al., 1997). Lower sedimentation rates away from the river mouths or in deeper waters hence provide a greater exposure time to marine organic matter input to the sediment–water interface, as well as continued loss of terrigenous organic matter due to decay and winnowing (Gordon and Goñi, 2004; Chen et al., 2005).

Quantification of the mix of terrigenous and marine-derived organic matter could be calculated by a two-endmember mixing model, once we know each endmember. An average terrestrial endmember value of 0.43 mg-Br g-OC<sup>-1</sup> can be calculated from the river SPM samples (Table 1), and is similar to those found in soils and sediments from other terrestrial environments (Mun and Bazilevich, 1962; Song and Müller, 1993; Keppler et al., 2000). Because the Br and OC contents of our riverine suspended sediments are similar to those of other rivers (Martin and Meybeck, 1979; Meybeck, 1982), it follows that these values may well be applicable to other land–sea interfaces. While it is possible that components of terrigenous organic matter (e.g., C3-derived vascular plant detritus vs. C4-derived grassy material) have different Br:OC ratios, the bromine content of terrigenous organic matter may also result from bacterial or fungal processing of terrestrial plant detritus rather than that taken up by the original plant (Gribble, 1998). In any case, our riverine samples derive largely from winter–spring river flows, which typically dominate the delivery of sediments to the Louisiana coast, and it seems likely that the narrow range of low values we found accurately characterizes the terrestrial endmember for the purposes of a binary, linear mixing model (see below).

The appropriate marine endmember is problematic for this area, because we don't know if the highest value found (4.8 mg-Br g-OC<sup>-1</sup>) represents organic matter that is 100% marine in origin. Values from the literature, for shelf sites with likely minimal terrestrial influence, average 7.7 mg-Br g-OC<sup>-1</sup> (Table 2) — which is 60% higher than this value. The values in Table 2 represent

average ratios calculated from individual samples in the literature rather than reported slopes of regression plots, because the latter approach leads to ratios that are not representative of many of the samples. In addition, we have excluded the review compilation of Ten Haven et al. (1988) whose Fig. 5 summary incorrectly forces slopes from other papers through the origin and misrepresents the data from Mayer et al. (1981).

The choice of the marine endmember value has greater potential to affect calculations of marine vs. terrestrial carbon content than variations in the terrestrial endmember. If, as a first approximation, we use the average of the Table 2 values as a marine endmember, we can calculate percent marine organic matter (%-MAR) by the formula

$$\% - \text{MAR} = 100 \times (\text{Br} : \text{OC}_{\text{sample}} - 0.43) / (7.7 - 0.43),$$

where 7.7 and 0.43 mg-Br g-OC<sup>-1</sup> are the marine and terrigenous endmember ratios, respectively, and Br:OC<sub>sample</sub> is the sample ratio.

These calculations (Table 1) yield values for the Atchafalaya region coastal sediments that are similar to, though a bit less than, those calculated by Gordon and Goñi (2003) for nearby locations. These authors used a combination of stable carbon isotopes, lignin compositions and C:N ratios to derive their estimates, which they argued provide much better estimates of %-MAR than mass balance calculations that use the classical stable isotope approach alone. Thus Br:OC ratios provide a fourth source indicator, independent from the others, that provides inferences consistent with the combination of the other three parameters used by Gordon and Goñi (2003), and builds confidence in both approaches.

These calculations indicate that sediments within a few km of the Atchafalaya and Mississippi River mouths have %-MAR values at the sediment–water interface of generally less than 20% (Fig. 2). Shelf

Table 2  
Average Br:OC ratios (mg-Br:g-OC) of surface sediment samples from shelf sites in areas not proximal to major source of terrigenous organic matter

Br:OC (mg-Br:g-OC)	Location ( <i>n</i> )	Reference
6.6	Gulf of Maine (8)	Table 1 Mayer et al. (1981)
6.0	Namibian Shelf (15)	Fig. 3. Price and Calvert (1977)
~ 8.8	Baja California (3)	Fig. 3. Shimmield and Pedersen (1990)
7.7	Barents Sea (8)	Table 1 Price et al. (1970)

Number of samples given by *n*.

sites extending tens of km westward of mouths of the Atchafalaya River (stations A 1–3, B 7–15) and Mississippi River (stations P4 S2, 6–8) outflows, which represents the main coastal plume directions, achieve progressively greater %-MAR values of up to 36% at the sediment–water interface. Two deeper shelf sites to the east of the Mississippi Birdfoot delta (MC-1 and MC-2) showed values of 42–46%; this region receives a relatively small portion of the Mississippi River outflow and presumably has more time to accumulate marine organic matter. The offshore, slope sites (>500 m water depth) have similar %-MAR values of 32–46%. Thus in none of the sites sampled does marine phytodetritus appear to become the dominant contributor to the standing stock of sedimentary organic matter, assuming that we have used an appropriate marine endmember value for Br:OC.

The relationship between Br:OC and  $\delta^{13}\text{C}$  would be expected to be a linear one if both indicators of bulk organic matter provenance had simple endmembers — e.g., if terrigenous organic matter did not contain significant amounts of both C3 and C4 detritus. Indeed, Mayer et al. (1981) found an approximately linear trend in the Gulf of Maine, whose watershed has a lower production by C4 grasses than that of the Mississippi watershed. The relationship between Br:OC and  $\delta^{13}\text{C}$  for the Mississippi sediments is clearly nonlinear, however (Fig. 2).

The concave upward shape of the data trend could be due to a greater variation in  $\delta^{13}\text{C}$  values between C3- and C4-derived organic matter than in Br:OC ratios, coupled with sorting of these two terrigenous organic matter types in the lower river and coastal region. For example, the various riverine data points in the lower right corner of Fig. 2 show a horizontal data trend, presumably resulting from physical separation of C3-

and C4-derived terrigenous organic matter in the lower river channel (Bianchi et al., 2007). The  $\delta^{13}\text{C}$  of riverine suspended particulate organic matter from the upstream sampling site at St. Francisville is lighter than that from the downstream site at Venice (Table 1), but the Br:OC ratio is similar. This trend implies downstream loss of isotopically light, terrigenous, C3 detritus from the suspended load during river flow, and also indicates similar Br:OC ratios for C3- and C4-derived terrigenous organic matter. Separation of C3 from C4 terrigenous detritus might continue in coastal sediments as a result of differential winnowing (Goñi et al., 1998; Bianchi et al., 2002) and hence lead to the concave upward shape in the mixing line.

#### 4.2. Downcore diagenesis

The downcore behavior of Br:OC ratios provides insight into the relative loss of these two materials. Loss patterns vary among sites. Nearshore cores with low Br:OC ratios at the sediment–water interface generally show little consistent change downcore (e.g., Table 1: A-1, A-2, MSS-2). More offshore cores with higher Br:OC at the sediment–water interface, indicating a significant fraction of marine organic matter, usually exhibit decreases in the Br:OC ratio downcore. For example, of those cores having a Br:OC value >1.5 mg-Br g-OC<sup>-1</sup> at the sediment–water interface (e.g., B8, P4S8, MC-2), about 60% show consistent decreases in Br:OC ratios and none show consistent increases. It is possible that some of the changes in Br:OC ratio are due to nonsteady state sedimentation in this dynamic environment, instead of downcore diagenesis. For example, the deepest slope core (CT-5) displays a rise in Br:OC in its lowest horizon, and core A-2 from a shallow area near the Atchafalaya River mouth showed varying Br:OC values that correlate positively with <sup>210</sup>Pb activities (unpub. data) — another indicator of marine input. Nevertheless, simultaneous downcore losses in OC without any change in grain size (with grain size indicated by sediment specific surface area — Mayer, 1994) in most cores strongly imply normal diagenetic loss of OC during progressive burial rather than changes in OC concentrations due to changing types of sediment input.

Br:OC ratios in sediment cores reported from other marine studies are usually fairly constant downcore (Price and Calvert, 1977; Pedersen and Price, 1980; Mayer, unpub. data for Gulf of Maine), but downcore decreases in this ratio have occasionally been observed — e.g., in the Barents Sea shelf (Price et al., 1970). Upstill-Goddard and Elderfield (1988) found small decreases in a

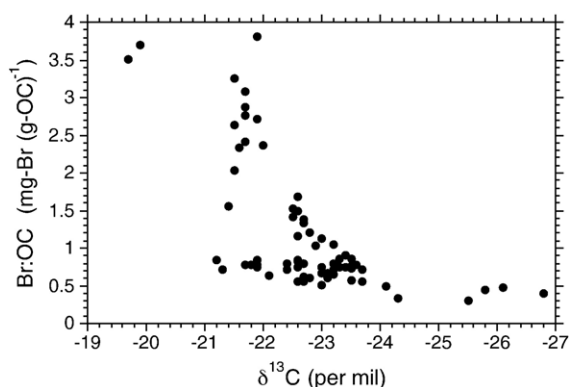


Fig. 2. Scatter plot of Br:OC (mg-Br (g-OC)<sup>-1</sup>) vs.  $\delta^{13}\text{C}$  (per mil) for all samples.



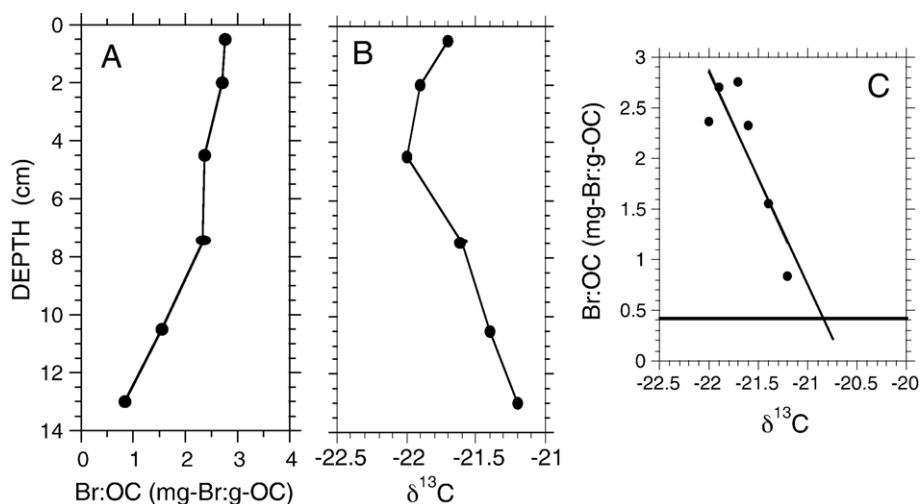


Fig. 3. Diagenetic changes in Core P4S8. Downcore changes (A) Br:OC ratio (mg-Br:g-OC) and (B)  $\delta^{13}\text{C}$  (per mil). Regression plot (C) of Br:OC vs.  $\delta^{13}\text{C}$  to find the appropriate terrigenous endmember value of  $\delta^{13}\text{C}$  at a terrigenous Br:OC value (0.4 mg-Br:g-OC).

pair of cores from an estuary, with the more terrestrially influenced core showing a  $\sim 10\%$  decrease and the more marine influenced core showing 35–40% decrease in Br:OC ratio — similar to the pattern we find in this study. These decreases are usually ascribed to preferential degradation of Br-containing compounds (Price et al., 1970; Upstill-Goddard and Elderfield, 1988, and references therein). In the context of sediments with mixtures of marine and terrigenous organic matter, we suggest that this interpretation implies preferential loss of the marine organic matter component that is enriched in Br.

It is possible that these drops in Br:OC in our study sites are instead due to dehalogenation of Br-containing compounds (Bossert et al., 2003) without remineralization of the organic carbon. However, studies of shelf environments with dominantly marine organic matter inputs (e.g., Price and Calvert, 1977) frequently show relatively constant Br:OC ratios downcore in conjunction with OC loss. Such behavior implies similar loss rates of the tracer Br and its host organic matter, and argues against a major role for simple dehalogenation of the marine organic matter component in our cores.

The explanation of more rapid loss of marine organic matter would instead agree with the scheme proposed by Aller and Blair (2004), in which modern marine organic matter makes up a small but relatively reactive component of sedimentary organic matter that decomposes in deltas. Their conclusions were based on carbon isotope compositions, especially  $^{14}\text{C}$ , which was presumed to derive preferentially from recent marine primary production. Bromine here performs this same functional role, as would any element preferentially

enriched in marine relative to terrigenous organic matter. Upstill-Goddard and Elderfield (1988) found that brominated organic compounds of marine origin were more easily oxidized chemically than brominated organic material of terrestrial origin, consistent with greater lability of marine organic matter. We stress that this inference depends on the use of Br as a tracer for the overall marine component of OM; if Br-rich compounds decay more quickly than other marine-derived OM, or if compounds are simply dehalogenated but not further degraded, then our inference is incorrect. Similar caveats would apply to any marker, including isotopes.

Downcore decreases in Br:OC were not accompanied by progressively lighter  $\delta^{13}\text{C}$  values, which we would expect if the terrigenous component of the residual organic matter had a  $\delta^{13}\text{C}$  value lighter than  $\sim 24\text{‰}$ . The core P4S8 is particularly illustrative of this trend, showing a small enrichment in  $\delta^{13}\text{C}$  rather than depletion with decreasing Br:OC downcore (Fig. 3A and B). This trend implies that the material being left behind after diagenetic loss of the marine organic matter is even more enriched than bulk organic matter. If the Br:OC and  $\delta^{13}\text{C}$  data are extrapolated (Fig. 3C) to a Br:OC value equivalent to that of the terrestrial endmember ( $\sim 0.4 \text{ mg-Br g-OC}^{-1}$ ), the predicted value of  $\delta^{13}\text{C}$  for this terrestrial component would be  $-21.1 (\pm 0.5)$  per mil, considerably heavier than the sediments delivered by the river. This relatively heavy terrestrial isotopic value should, of course, be regarded as particular only to this core, and presumably due to selective loss of the isotopically light, C3 component of its terrigenous organic matter via a process such as winnowing prior to burial. Goñi et al. (1998) used lignin

analyses to point out that the  $\delta^{13}\text{C}$  value for the terrigenous component of the organic matter varied according to the site-specific mixture of C3- and C4-derived lignin compositions; in the case of the core shown here a value of  $-21.1\text{‰}$  would correspond to roughly equal contributions from organic matter deriving from these two plant types. Of course, if terrestrial organic matter  $\delta^{13}\text{C}$  values vary among sites then they might also vary among depths in a core.

Assuming that the Br:OC ratio of the marine-derived organic matter does not change during downcore diagenesis, then the downcore decreases in Br:OC ratio that are frequently observed imply that the marine fraction of organic matter that is buried will be lower than would be inferred from Br:OC ratios at the sediment–water interface (Fig. 2). Few of our cores are more than 20–30 cm deep, in an area with high sedimentation rates, so we cannot quantitatively infer the proportion of marine organic matter transiting into the geological record. Nevertheless, to the extent that the preferential loss of marine organic matter is correctly inferred from decreasing Br:OC ratios and that this trend continues downcore, then these sediments may bury primarily terrigenous and not marine organic matter.

Marine organic matter instead appears to serve primarily as short-lived kindling that enhances the metabolism of terrigenous organic matter (Aller and Blair, 2004). Marine production may therefore dominate the incoming organic flux, but not achieve dominance in terms of the standing stocks measured in this study.

## 5. Conclusions

Marine sediments deriving from the outflow of the Mississippi River have Br:OC ratios consistent with an increase in marine organic matter along the direction of sediment transport. A simple, two-endmember mixing model with Br:OC ratios gives quantitative estimates of the fraction of marine vs. terrigenous organic matter that are consistent with estimates previously obtained from more complex suites of provenance indicators. These source calculations may misrepresent actual mixtures of marine and terrigenous organic matter if the Br:OC ratio is not conservative to the marine or terrigenous pool. For example, we have found that Br is released from sediments containing only marine organic matter upon irradiation under simulated sunlight (unpub. data), and that this release is greater than simultaneous release of bulk organic carbon (Mayer et al., 2006). However, we find similarly disproportionate changes in other source indicators such as lignin and C:N ratio (unpub. data), so that if photodissolution is important in the marine en-

vironment then other source markers may also be affected. If further research should demonstrate this caveat to be unimportant, we note that Br is a less expensive measurement (by commercial means) than stable isotopes, and as a single measurement in this deltaic system seems to provide a less ambiguous answer to questions about partitioning of marine vs. terrigenous organic matter source in marine sediments. The use of this halogen complements the recent application of iodine concentrations to determination of organic matter source in the Mississippi region (Santschi et al., 2007). To the extent that the Br:OC ratio retains accurate estimate of this mix, marine organic matter inputs are exhibited most strongly at the sediment–water interface, and are attenuated before long-term burial. Deltaic sediments may, therefore, be rather poor sinks for marine organic matter and associated bioactive elements such as bromine.

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## References

- Aller, R.C., Blair, N.E., 2004. Early diagenetic remineralization of sedimentary organic C in the Gulf of Papua deltaic complex (Papua New Guinea) — net loss of terrestrial C and diagenetic fractionation of C isotopes. *Geochim. Cosmochim. Acta* 68, 1815–1825.
- Berner, R.A., 1982. Burial of organic carbon and pyrite sulfur in the modern ocean: its geochemical and environmental significance. *Am. J. Sci.* 282, 451–473.
- Bianchi, T.S., Mitra, S., McKee, B.A., 2002. Sources of terrestrially-derived organic carbon in lower Mississippi River and Louisiana shelf sediments: implications for differential sedimentation and transport at the coastal margin. *Mar. Chem.* 77, 211–223.
- Bianchi, T.S., Galler, J.J., Allison, M.A., 2007. Hydrodynamic sorting and transport of terrestrially derived organic carbon in sediments of the Mississippi and Atchafalaya Rivers. *Estuar. Coast. Shelf Sci.* 73, 211–222.
- Bossert, I.D., Häggblom, M.M., Young, L.Y., 2003. Microbial ecology of dehalogenation. In: Häggblom, M.M., Bossert, I.D. (Eds.), *Dehalogenation: Microbial Processes and Environmental Applications*. Kluwer Academic Publishers, Boston, pp. 33–52.
- Burdige, D.J., 2005. Burial of terrestrial organic matter in marine sediments: a re-assessment. *Glob. Biogeochem. Cycles* 19, GB4011. doi:10.1029/2004GB002368.
- Chen, N., Bianchi, T.S., McKee, B.A., 2005. Early diagenesis of chloropigment biomarkers in the lower Mississippi River and

- Louisiana shelf: implications for carbon cycling in a river-dominated margin. *Mar. Chem.* 93, 159–177.
- Gearing, P., Plucker, F.E., Parker, P.L., 1977. Organic carbon stable isotope ratios of continental sediments. *Mar. Chem.* 5, 251–266.
- Goñi, M.A., Ruttnerberg, Eglinton, T.I., 1997. Sources and contribution of terrigenous organic carbon to surface sediments in the Gulf of Mexico. *Nature* 389, 275–278.
- Goñi, M.A., Ruttnerberg, K.C., Eglinton, T.I., 1998. A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico. *Geochim. Cosmochim. Acta* 62, 3055–3075.
- Gordon, E.S., Goñi, M.A., 2003. Sources and distribution of terrigenous organic matter delivered by the Atchafalaya River to sediments in the northern Gulf of Mexico. *Geochim. Cosmochim. Acta* 67, 2359–2375.
- Gordon, E.S., Goñi, M.A., 2004. Controls on the distribution and accumulation of terrigenous organic matter in sediments from the Mississippi and Atchafalaya river margin. *Mar. Chem.* 92, 331–352.
- Gribble, G.W., 1998. Naturally occurring organohalogen compounds. *Acc. Chem. Res.* 31, 141–152.
- Harvey, G.R., 1980. A study of the chemistry of iodine and bromine in marine sediments. *Mar. Chem.* 8, 327–332.
- Hedges, J.I., Parker, P.L., 1976. Land-derived organic matter in surface sediments from the Gulf of Mexico. *Geochim. Cosmochim. Acta* 40, 1019–1029.
- Hedges, J.I., Prahl, F.G., 1993. Early diagenesis: consequences for applications of molecular biomarkers. In: Engel, M., Macko, S.A. (Eds.), *Organic Geochemistry*. Plenum Press, New York, pp. 237–253.
- Hedges, J.I., Keil, R.G., 1995. Sedimentary organic matter preservation: an assessment and speculative synthesis. *Mar. Chem.* 49, 81–115.
- Hedges, J.I., Keil, R.G., Benner, R., 1997. What happens to terrestrial organic matter in the ocean? *Org. Geochem.* 27, 195–212.
- Hitchcock, G.L., Wiseman, W.J., Boicourt, W.C., Mariano, A.J., Walker, N., Nielsen, T.A., Ryan, E., 1997. Property fields in an effluent plume of the Mississippi river. *J. Mar. Syst.* 12, 109–126.
- Holtvoeth, J., Kolonic, S., Wagner, T., 2005. Soil organic matter as an important contributor to late Quaternary sediments of the tropical West African continental margin. *Geochim. Cosmochim. Acta* 69, 2031–2041.
- Howard, A.G., Pizzic, R.A., Whitehouse, J.W., 1984. Studies of the halogenation of dissolved organic material during the chlorination of saline cooling waters, using the model compound resorcinol. *Water Res.* 18, 735–743.
- Keil, R.G., Mayer, L.M., Quay, P.D., Richey, J.E., Hedges, J.I., 1997. Loss of organic matter from riverine particles in deltas. *Geochim. Cosmochim. Acta* 61, 1507–1511.
- Keppler, F., Eiden, R., Niedan, V., Pracht, J., Schöler, H.F., 2000. Halocarbons produced by natural oxidation processes during degradation of organic matter. *Nature* 403, 298–301.
- Lane, R.R., Day, J.W., Marx, B., Reyes, E., Kemp, G.P., 2002. Seasonal and spatial water quality changes in the outflow plume of the Atchafalaya River, Louisiana, USA. *Estuaries* 25, 30–42.
- Leithold, E.L., Blair, N.E., 2001. Watershed control on the carbon loading of marine sedimentary particles. *Geochim. Cosmochim. Acta* 65, 2231–2240.
- Lohrenz, S.E., Fahnenstiel, G.L., Redalje, D.G., Lang, G.A., Dagg, M.J., Whittedge, T.E., Dortch, Q., 1999. Nutrients, irradiance and mixing as factors regulating primary production in coastal waters impacted by the Mississippi River plume. *Cont. Shelf Res.* 19, 1113–1141.
- Malcolm, S.J., Price, N.B., 1984. The behaviour of iodine and bromine in estuarine surface sediments. *Mar. Chem.* 15, 263–271.
- Martin, J.-M., Meybeck, M., 1979. Elemental mass balance of material carried by major world rivers. *Mar. Chem.* 7, 173–206.
- Mayer, L.M., 1994. Surface area control of organic carbon accumulation in continental shelf sediments. *Geochim. Cosmochim. Acta* 58, 1271–1284.
- Mayer, L.M., Macko, S.A., Mook, W.H., Murray, S.M., 1981. The distribution of bromine in coastal sediments and its use as a source indicator for organic matter. *Org. Geochem.* 3, 37–42.
- Mayer, L.M., Schick, L., Skorko, K., Boss, E., 2006. Photodissolution of particulate organic matter from sediments. *Limnol. Oceanogr.* 51, 1064–1071.
- Meybeck, M., 1982. Carbon, nitrogen, and phosphorus transport by world rivers. *Am. J. Sci.* 282, 401–450.
- Müller, G., Nkusi, G., Schöler, 1996. Natural organohalogens in sediments. *J. Prakt. Chem.* 338, 23–29.
- Mun, A.I., Bazilevich, Z.A., 1962. Distribution of bromine in lacustrine bottom muds. *Geochemistry* 2, 199–205.
- Price, N.B., Calvert, S.E., 1977. The contrasting geochemical behaviours of iodine and bromine in recent sediments from the Namibian shelf. *Geochim. Cosmochim. Acta* 41, 1769–1775.
- Price, N.B., Calvert, S.E., Jones, P.G.W., 1970. The distribution of iodine and bromine in the sediments of the southwestern Barents Sea. *J. Mar. Res.* 28, 22–34.
- Pedersen, T.F., Price, N.B., 1980. The geochemistry of iodine and bromine in sediments of the Panama Basin. *J. Mar. Res.* 38, 397–411.
- Ruttnerberg, K.C., Goñi, M.A., 1997. Phosphorus distribution, C:N:P ratios, and  $\delta^{13}\text{C}_{\text{OC}}$  in arctic, temperate, and tropical coastal sediments: tools for characterizing bulk sedimentary organic matter. *Mar. Geol.* 139, 123–145.
- Santschi, P.H., Oktay, S.D., Cifuentes, L., 2007. Carbon isotopes and iodine concentrations in a Mississippi River delta core recording land use, sediment transport, and dam building in the river's drainage basin. *Mar. Environ. Res.* 63, 278–290.
- Shimmield, G.B., Pedersen, T.F., 1990. The geochemistry of reactive trace metals and halogens in hemipelagic continental margin sediments. *Aquat. Sci.* 3, 255–279.
- Sigleo, A.C., Helz, G.R., Zoller, W.H., 1980. Organic-rich colloidal material in estuaries and its alteration by chlorination. *Environ. Sci. Technol.* 14, 673–679.
- Song, Y., Müller, G., 1993. Freshwater sediments: sinks and sources of bromine. *Naturwissenschaften* 80, 558–560.
- Ten Haven, H.L., deLeeuw, J.W., Schenck, P.A., Klaver, G.T., 1988. Geochemistry of Mediterranean sediment. Bromine/organic carbon and uranium/organic carbon ratios as indicators for different sources of input and post-depositional oxidation, respectively. *Org. Geochem.* 13, 255–261.
- Upstill-Goddard, R.C., Elderfield, H., 1988. The role of diagenesis in the estuarine budgets of iodine and bromine. *Cont. Shelf Res.* 8, 405–430.
- Van Pée, K.-H., 1996. Biosynthesis of halogenated metabolites by bacteria. *Annu. Rev. Microbiol.* 50, 375–399.
- Wright, L.D., Nittrouer, C.A., 1995. Dispersal of river sediments in coastal seas: six contrasting cases. *Estuaries* 18, 494–508.