

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

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Abstract

Onshore–offshore trends in phosphorus (P), organic carbon (OC), and total nitrogen (TN) concentration, P distribution, elemental organic C:N:P ratios, and stable carbon isotopic composition of OC ($\delta^{13}\text{C}_{\text{oc}}$) of surficial sediments, are presented from three river-dominated coastal regimes: the Mackenzie River/Beaufort shelf in the Canadian Arctic; the Mississippi Delta and Louisiana shelf in the temperate Gulf of Mexico; and the tropical Amazon shelf. These parameters, measured in surficial sediments from the three sites, are used to assess changes in the importance of terrestrial and marine organic matter sources to sediments as a function of distance from the locus of riverine discharge.

Trends in elemental ratio data from the Arctic transect, and a portion of the Gulf of Mexico transects, can be explained in terms of a two-end-member mixture of terrestrial and marine phytodetritus. In the arctic transect, covariation of organic C:P ratios with $\delta^{13}\text{C}_{\text{oc}}$ is consistent with a two-end-member mixture of terrestrial and marine organic matter. A similar relationship between C:P ratios and $\delta^{13}\text{C}_{\text{oc}}$ is not evident in Gulf of Mexico or Amazon shelf sediments. At these sites the two-end-member model fails to explain the data adequately.

The most striking feature of the onshore–offshore trends in elemental OC:OP and OC:TN ratios is the occurrence of low ratios in sediments from deep-water stations in the Gulf of Mexico and all stations on the Amazon shelf, resulting from P and N enrichments exceeding the Redfield Ratio for marine plankton. Three explanations are discussed to account for these low ratios: (1) the dominance of refractory OP- and ON-compounds in the residuum of degraded organic matter; (2) differential sorption of OP- and N-compounds, regardless of lability, on the surfaces of the fine-grained sediments characteristic of these sites; and (3) a dominance of bacterial biomass, or components derived from bacterial biomass. Elemental ratios and $\delta^{13}\text{C}_{\text{oc}}$ signatures indicate that differential sorption may be most important in the deep-water Gulf of Mexico sites. In contrast, elemental ratios and $\delta^{13}\text{C}_{\text{oc}}$ on the Amazon shelf are most consistent with a sedimentary organic matter pool dominated by bacterial biomass, or derivative substances.

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1. Introduction

The use of elemental ratios as indicators of organic matter source is a common approach in geochemical studies. Studies of this type typically focus on C:N ratios (e.g. Hartmann et al., 1973; Müller, 1977; Hedges et al., 1986; Meyers, 1994); whereas the use of C:P ratios as indicators of organic matter source is uncommon. There are at least two reasons for the preponderance of C:N ratio data relative to C:P data. The first is purely a result of the analytical ease of quantifying nitrogen (N) along with carbon (C) using a CHN elemental analyzer. While CHN analyses are routine and ubiquitous in studies of sediment geochemistry, there is no simple analytical analogue for quantifying P. Second, elemental C:P ratios in aquatic plants and bacteria can show greater variability than elemental C:N ratios, due to luxury P consumption and storage exhibited by algae and bacteria (Cembella et al., 1984; Gächter and Meyer, 1993).

Elemental ratios alone can be ambiguous indicators of organic matter source because marine sediments contain mixtures of organic matter of different origins. Furthermore, original ratios may be altered during transport and early diagenesis (e.g. Pomeroy, 1970; Hartmann et al., 1973; Krom and Berner, 1981; Rice, 1982). Use of multiple tracers, such as elemental ratios in conjunction with stable isotopic signatures, improves the certainty with which organic matter sources can be identified (e.g. Fry and Sherr, 1984).

In this study we use organic-C:organic-P ratios, organic-C:total-N ratios, and the carbon isotopic composition of bulk sediment organic matter (hereafter abbreviated as OC:OP, OC:TN, and $\delta^{13}\text{C}_{\text{OC}}$, respectively) to determine the source and nature of organic matter in surficial marine sediments from three river-dominated coastal environments. Sample sites were chosen along onshore-offshore transects to provide a gradient between the two dominant sources of organic matter to marine sediments: terrestrial plants and marine phytoplankton. We present data from the Mackenzie River/Beaufort shelf in the Canadian Arctic, the Mississippi Delta and Louisiana shelf in the temperate Gulf of Mexico, and the tropical

Amazon shelf (Fig. 1, Tables 1 and 2). Study sites are arrayed along flow trajectories of the dominant rivers to assess changes with increasing distance from the locus of riverine input. Finally, we infer the identity of sedimentary organic P and N at some of the sites using elemental ratios and carbon isotopic composition of the bulk sedimentary organic matter pool.

2. Methods

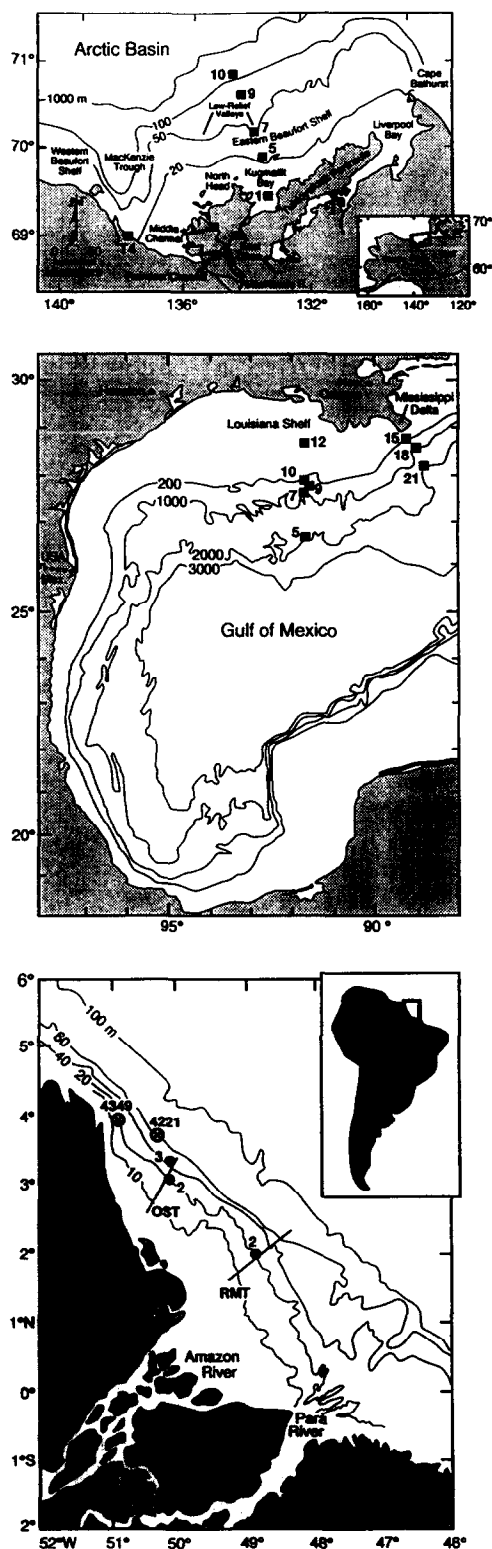
2.1. Sample collection

Samples from the Arctic were graciously supplied by Mark Yunker at the Institute of Ocean Sciences, B.C., Canada (Fig. 1, Tables 1 and 2). Suspended sediment from the Mackenzie River was collected using continuous flow centrifugation, and surficial Beaufort shelf sediment was collected using a grab sampler (Yunker et al., 1993). The location and method of collection of the peat sample (T4, Yunker et al., 1993) is as described in Yunker et al. (1991).

Sediment from two shore-perpendicular transects in the Gulf of Mexico was collected in January 1987 on the R/V *Gyre* (Fig. 1, Tables 1 and 2). The Delta transect runs along the seaward extension of Southwest Pass, one of the main tributaries of the Mississippi Delta. The Louisiana shelf transect runs along the 91°30' longitude line, which is roughly the longitude of Atchafalaya River inflow. At five of the eight stations, paired box and gravity cores were collected.

Sediment from the Amazon shelf was collected during the AmasSeds IV cruises (October 1991) on the R/V *Iselin* (Fig. 1, Tables 1 and 2). Amazon shelf box and piston cores were taken on two separate legs of AmasSeds IV; four sites were revisited for collection of paired box and piston cores: RMT-2, OST-2, OST-3, and the relict mud site (RM). Cores from both the Gulf of Mexico and the Amazon were sectioned in an inert (N_2) atmosphere immediately after collection, and pore water was removed via centrifugation.

Surficial sediments analyzed for this study equate to the upper ≈ 2 cm for Mackenzie shelf



grab samples, the (0–2 cm) interval for Gulf of Mexico box and gravity cores, the (0–0.25 cm) interval for AmasSeds box cores, and the (3–13 cm) interval for piston cores. Samples were stored frozen (-20°C) after collection, and were freeze dried upon return to the laboratory. Splits of all freeze dried samples were ground in an agate mortar and pestle and passed through a $125\ \mu\text{m}$ sieve prior to analysis.

2.2. Analytical methods

Bulk sediment total-P (TP) and inorganic-P (IP) were determined by leaching two sample splits in 1 M HCl, the TP split initially having been ashed at 550°C . Organic-P (OP) was determined by difference (TP–IP) (Aspila et al., 1976; Ruttenberg, 1992). The error in reproducibility of TP, IP, and OP is better than 1.5%, 1.5%, and 5.6%, respectively. The efficiency of the ashing method for quantifying TP was verified by Ruttenberg (1992), who found comparable TP recoveries from a variety of pure plant tissues and sediments using both the ashing method and the well accepted method of fuming nitric/perchloric acid digestion (Black, 1965; Strickland and Parsons, 1972). Since OP is derived from the difference of two independently measured parameters (TP and IP), uncertainties in the accuracy of OP may exceed analytical reproducibility, especially if TP and IP are of similar magnitude. Other potential artifacts include underestimation of IP due to incomplete IP recovery from clays and ferric iron phases during 1 M HCl extraction of the unashed split (Mach et al., 1987; Ruttenberg, 1992). A portion of this insoluble IP may become soluble in 1 M HCl after ashing at 550°C , resulting in overestimation of OP (Ruttenberg, unpubl. results). Labile forms of OP may be extracted by 1 M HCl from the unashed split. This will result

Fig. 1. Location maps. Upper: Mackenzie River and Beaufort shelf sampling stations (after Yunker et al., 1993). Middle: Gulf of Mexico sampling stations: Mississippi Delta front and Louisiana shelf (after Lin, 1990). Lower: Amazon shelf sampling stations. RMT=River Mouth Transect, OST=Open Shelf Transect, stations denoted by ⊗ are the Relic Mud (RM) sites (after Blair and Aller, 1995).

Table 1
Location and description of stations

Station, Core	Latitude	Longitude	Water Depth (m)	Site name, Description	Sedimentation rate (cm/y)	Distance from river mouth (km)
<i>Arctic: Mackenzie River and shelf</i>						
G1 STN 1	69°32.5'N	133°17.5'W	7	Surface sediment	—	15
G7 STN 5	70°01.0'N	133°26.0'W	30	Surface sediment	—	60
GRM 1	69°32.5'N	133°17.5'W	40	Mid-shelf sediment homogenate	—	70
G12 STN 9	70°44.2'N	134°09.9'W	75	Surface sediment	—	135
G9 STN 10	70°56.8'N	134°35.4'W	200	Surface sediment	—	160
G10 STN 10	70°56.8'N	134°35.4'W	200	Replicate of G9 STN 10	—	160
RM			1	RSPM: East channel 6/87	n/a	n/a
SS-3-1			1	RSPM: Reindeer channel 7/87	n/a	n/a
1-SS-2-1			1	RSPM: Middle channel 6/87	n/a	n/a
SS-1-1			1	RSPM: East channel 7/87	n/a	n/a
T4			n/a	Coastal low tundra peat	n/a	n/a
<i>Temperate: Gulf of Mexico</i>						
15BC6	28°47.77'N	89°19.14'W	107	Delta transect	0.8 ^a	17
15GC4	28°47.75'N	89°19.11'W	110	Delta transect	0.8 ^a	17
18BC7	28°29.90'N	89°08.90'W	574	Delta transect	0.2 ^b	34
18GC5	28°30.30'N	89°06.80'W	598	Delta transect	0.2 ^b	34
21BC8	28°06.26'N	88°50.05'W	1470	Delta transect	0.005 ^b	110
21GC6	28°06.20'N	88°50.40'W	1470	Delta transect	0.005 ^b	110
12BC5	28°14.90'N	91°30.00'W	74	Louisiana shelf transect	^c	120
10BC4	27°46.90'N	91°30.00'W	606	Louisiana shelf transect	^c	170
10GC3	27°47.00'N	91°29.80'W	605	Louisiana shelf transect	^c	170
9BC3	27°40.30'N	91°31.50'W	688	Louisiana shelf transect	^c	180
7BC2	27°27.30'N	91°30.20'W	947	Louisiana shelf transect	^c	200
7GC2	27°27.30'N	91°30.10'W	964	Louisiana shelf transect	^c	200
5BC1	26°58.86'N	91°30.06'W	2250	Louisiana shelf transect	^c	310
<i>Tropical: Amazon shelf</i>						
4318-BC	02°04.30'N	48°52.55'W	21	River mouth transect: RMT-2	^d	200
4228-PC	02°04.94'N	48°51.52'W	19	River mouth transect: RMT-2	^d	200
4345-BC	03°11.74'N	50°06.37'W	25	Open shelf transect: OST-2	^d	350
4204-PC	03°07.70'N	50°06.25'W	20	Open shelf transect: OST-2	^d	350
4344-BC	03°18.77'N	50°00.81'W	37	Open shelf transect: OST-3	^d	375
4213-PC	03°21.34'N	50°02.19'W	39	Open shelf transect: OST-3	^d	375
4349-BC	04°02.98'N	50°55.88'W	16	Relict muds: RM	—	450
4221-PC	03°39.11'N	50°17.12'W	56	Relict muds: RM	—	450

n/a = not applicable. — = data not available. RSPM = Riverine Suspended Particulate Matter.

^aRuttenberg (1990). ^bLin (1990). ^cData not available for these cores; sedimentation rates are generally lower on the Louisiana shelf than on the Delta (Lin, 1990). ^dSpatially variable, 0–10 cm/yr (Kineke et al., 1991).

in overestimates of IP and underestimates of OP only when the HCl-extractable OP is hydrolyzed, however, which is not always the case (Ruttenberg, 1992). The net effect of these artifacts is difficult to quantify because of the difficulty in obtaining representative analogue phases to determine their magnitude empirically, and also because the different artifacts act in opposition. These artifacts

can largely be avoided by use of the more complex SEDEX method (Ruttenberg, 1992); however, the ease and rapidity of the ashing method recommend it for reconnaissance studies.

Total N (TN) was determined on bulk sediment samples using a Perkin Elmer model 2400 CHN Elemental Analyzer. Organic C (OC) was determined as the difference between total C (TC) of

Table 2
Study site characteristics

Site	Climate	Major rivers	Drainage basin area (km ²)	Runoff (mm/yr)	Load (t/yr)	Yield (t/km ² /yr)	Description	Marine shelf sediment grain size and composition	Marine productivity (g C/m ² /yr)
Mackenzie shelf	Arctic: seasonally ice covered shelf. River hydrograph extends from spring ice break-up to fall freeze-up (Hill et al., 1991; Macdonald and Thomas, 1991)	Mackenzie	1.8 × 10 ⁶	170	42 × 10 ⁶	23	Largest N. American River draining into the Arctic; contributes 95% of the total sediment to the Beaufort Shelf (Hill et al., 1991). Drains subarctic forests and tundra (Yunker et al., 1993).	Dominantly clay-sized, becoming siltier at water depths ≤ 20m (Hill et al., 1991). <2 μm fraction is dominated by illite with minor smectite, kaolinite, chlorite, and mixed layer clays (Naidu and Mowatt, 1974).	20–40
Mississippi Delta and Louisiana shelf	Temperate: Smoothly varying, seasonally controlled river hydrograph (Demas and Curwick, 1988).	Mississippi and Atchafalaya	3.3 × 10 ⁶	150	210 × 10 ⁶	120	Largest water shed in the U.S. Drains 41% of the coterminous U.S.; contributes > 90% of freshwater to the Gulf of Mexico. Drains agricultural lands, hardwood forests and swamps (Turner and Rabalais, 1991; Rabalais et al., 1994)	Northeastern Gulf of Mexico sediments: 50–75% clay, 25–45% silt, 1–10% fine sand (Lin, 1990). Clay mineralogy: 45–70% montmorillonite, 10–38% illite, 5–20% kaolinite (Griffin, 1962).	≥ 100
Amazon shelf	Tropical: Smoothly varying, seasonally controlled river hydrograph (Nitttrouer et al., 1995)	Amazon	6.1 × 10 ⁶	100	1200 × 10 ⁶	190	Contributes 20% of the world's river discharge to the ocean. Drainage basin includes savannah and world's largest tropical rain forest (Richey et al., 1990).	Homogeneous silty clay at water depths < 60 m, except along river mouth transect, which has interbedded fine sand to clayey silt (Nitttrouer et al., 1983). Fine sediment fraction composed of montmorillonite, kaolinite, illite, feldspars and quartz (Gibbs, 1977).	90

The Atchafalaya River is considered part of the Mississippi River system; ≈ 30% of the Mississippi River discharge is diverted to the Atchafalaya at Tarbert Landing, LA. The Red River joins the Atchafalaya River south of Tarbert Landing and contributes an additional ≈ 33% to the Atchafalaya River discharge (Bratkovich et al., 1994).

Drainage basin area, runoff, load, and yield are from Milliman and Syvitski (1992) unless otherwise indicated.

Load = mass of sediment transported annually by the river.

Yield = 'sediment yield'; normalization of sediment load to size of river basin makes possible comparison of disparate river basins (Milliman and Syvitski, 1992).

Marine productivity estimates are from (Walsh, 1988).

bulk sediment determined by CHN analyzer, and inorganic C (IC) of bulk sediment determined coulometrically as the quantity of CO₂ generated upon sample acidification with 100% H₃PO₄ (Ostermann et al., 1990). The average mean deviations of TC and TN was $\pm 2\%$, and the precision of IC measurements is better than 1%. Stable carbon isotopic composition of bulk sediment total organic carbon ($\delta^{13}\text{C}_{\text{OC}}$) was measured at the Ecosystems Center of the Marine Biological Laboratory (Woods Hole, MA, USA) on pre-acidified samples (2 N HCl) by high-temperature combustion coupled with mass spectrometry. All stable carbon isotopic compositions are reported as δ values relative to the PDB carbonate standard in the usual parts per thousand (‰) notation. The reproducibility of this measurement is better than 0.1‰.

3. Results

Elemental concentrations, elemental ratios, and carbon isotopic data for sediments from all three sites are given in Table 3. Data for the Beaufort shelf, the Mississippi Delta, and the Louisiana shelf transects are listed in order of increasing water depth, which is roughly equivalent to distance from the locus of the Mackenzie, the Mississippi, and the Atchafalaya River input, respectively (Table 1). Water depth cannot be used as an index of distance from the source of Amazon River input. The Amazon River flow trajectory bends north along the shelf under the influence of the Brazilian Current and flows roughly parallel to the isobaths (Nittrouer et al., 1995). Instead, we use latitude as an index of distance from the locus of Amazon River input; the further north the station, the greater the distance from the source of riverine material. In an attempt to remove the complication of diagenetic over-printing, and therefore more closely track the nature of the input material, we looked at surficial sediments only. Nevertheless, we believe that some of the samples discussed have been altered by diagenesis. The data reported in Table 3 are contrasted graphically in Figs. 2 and 3.

Arctic marine surficial sediments are enriched in

TP relative to the temperate and tropical sediments due to higher IP content (Fig. 2A). This site is also characterized by the widest range in TP and IP, while the Amazon is characterized by the narrowest range. The mean OP content of the three sites are statistically indistinguishable.

Mean sedimentary OC content decreases from the Arctic to the temperate to the tropical regime (Fig. 2B). Gulf of Mexico sediments show the widest range of OC, whereas the Amazon shows the narrowest range; the Mackenzie is intermediate. The mean TN content of the three transects are statistically indistinguishable (Fig. 2C). We assume that the quantity TN reflects the N content of organic matter (ON). There may be an inorganic nitrogen component, probably in the form of ammonia associated with clays, included in the quantity TN (Müller, 1977). Therefore, although we assume that $\text{ON} = \text{TN}$ in pure plant tissues used as end-members, this assumption cannot be made for bulk sediment. We will address this caveat and its implications for the interpretation of sources of sedimentary organic matter in the discussion of results.

The range of Gulf of Mexico OC:OP overlaps that of both the Mackenzie and the Amazon (Fig. 3A). The mean OC:OP of the Mackenzie and Gulf of Mexico are not significantly different, however, both are distinctly higher than the Amazon. Since the mean OP of the three sites are statistically indistinguishable (Fig. 2A), most of the variability evident in the mean OC:OP ratio results from different characteristic OC content (Fig. 2B).

The mean OC:TN ratio of Mackenzie sediments is statistically higher than either Gulf of Mexico or Amazon sediments, and the range overlaps that of the Gulf of Mexico, but not the Amazon (Fig. 3B). Mean OC:TN ratios of the Gulf of Mexico and the Amazon are statistically indistinguishable. As is the case for the OC:OP ratios, most of the variability in this ratio is due to the inter-site difference in OC (Fig. 2B). The mean TN:OP of the Mackenzie sediments is statistically indistinguishable from both the Gulf of Mexico and the Amazon, but the mean TN:OP of the Gulf of Mexico is distinctly higher than that of the Amazon (Fig. 3C). Differences in mean TN:OP

Table 3
Phosphorus, carbon, nitrogen, C:N:P ratios, and carbon isotopic composition

Station, Core	Water depth (m)	Total P (TP) (μmol/g)	Inorg. P (IP) (μmol/g)	Porg (OP) (μmol/g)	Corg (OC) (wt%)	Total-N (TN) (wt%)	OC:OP (molar)	OC:TN (molar)	TN:OP (molar)	δ ¹³ C (OC) (Per mil)
<i>Arctic: Mackenzie River and shelf</i>										
G1 STN 1	7	25.45	19.08	6.37	1.13	0.14	148	9	16	−25.9
G7 STN 5	30	35.47	27.59	7.88	1.97	0.17	208	14	15	−25.5
GRM 1	40	34.75	25.33	9.42	1.44	0.14	127	12	11	−25.7
G12 STN 9	75	51.19	40.44	10.75	1.54	0.20	119	9	13	−24.4
G9 STN 10	200	37.09	28.90	8.19	1.23	0.12	125	12	10	−25.1
G10 STN 10	200	32.82	24.64	8.18	1.20	0.10	122	14	9	−25.5
RSPM: RM	RSPM	28.39	21.12	7.27	1.46	0.14	167	12	14	−26.4
RSPM: SS-3-1	RSPM	26.47	19.60	6.86	1.67	0.13	203	15	14	−26.4
RSPM: 1-SS-2-1	RSPM	26.80	18.91	7.89	1.57	0.13	166	14	12	−26.2
RSPM: SS-1-1	RSPM	26.91	21.34	5.57	1.84	0.18	275	12	23	−26.9
Peat: T4	Peat	29.28	14.07	15.21	17.05	0.98	934	20	46	−26.0
{Omit Peat and RSPM}:										
Transect mean		36.13	27.66	8.46	1.42	0.15	142	12	12	−25.4
Stdev		8.43	7.11	1.48	0.31	0.04	34	2	3	0.5
Rel (%)		23	26	18	22	25	24	18	23	2
n		6	6	6	6	6	6	6	6	6
<i>Temperate: Gulf of Mexico</i>										
Delta: 15BC6	107	22.66	15.13	7.53	1.37	0.19	152	8	18	−21.1
Delta: 15GC4	110	23.93	15.91	8.02	1.26 ^a	0.18 ^a	131	8	16	n.d.
Delta: 18BC7	574	24.43	17.59	6.84	1.42	0.20	173	8	21	−20.4
Delta: 18GC5	598	24.49	18.09	6.40	1.30	0.18	169	8	20	−20.6
Delta: 21BC8	1470	20.26	12.53	7.72	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Delta: 21GC6	1470	20.10	12.53	7.58	0.91	0.17	100	6	16	−19.7
Shelf: 12BC5	74	21.79	15.78	6.00	0.92	0.14	128	8	17	−20.9
Shelf: 10BC4	606	21.29	14.45	6.84	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Shelf: 10GC3	605	27.01	19.27	7.74	1.24	0.18	134	8	17	−21.6
Shelf: 9BC3	688	33.67	27.85	5.82	1.53	0.18	219	10	22	−24.1
Shelf: 7BC2	947	19.55	13.01	6.54	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Shelf: 7GC2	964	20.66	12.94	7.72	0.57	0.13	62	5	12	−20.0
Shelf: 5BC1	2250	18.23	12.97	5.26	0.34	0.08	54	5	11	−21.8
{Omit Seep Stn (9BC3)}:										
Transect mean		22.03	15.02	7.02	1.04	0.16	122	7	16	−20.8
Stdev		2.53	2.35	0.85	0.38	0.04	43	1	3	0.7
Rel (%)		11	16	12	37	24	35	20	20	4
n		12	12	12	9	9	9	9	9	9
<i>Tropical: Amazon Shelf</i>										
4318-BC (RMT-2)	21	14.93	9.75	5.18	0.43	0.07	69	7	10	−24.9
4228-PC (RMT-2)	19	20.55	11.01	9.54	0.44	0.08	38	6	6	−25.8
4345-BC (OST-2)	25	21.60	11.97	9.62	0.71	0.12	62	7	9	−24.3
4204-PC (OST-2)	20	23.00	12.03	10.97	0.63	0.16	48	5	10	−24.4
4344-BC (OST-3)	37	22.34	12.38	9.95	0.80	0.14	67	7	10	−24.8
4213-PC (OST-3)	39	21.53	12.28	9.25	0.80	0.16	72	6	12	−24.9
4349-BC (RM)	16	18.24	14.88	3.27	0.63	0.09	161	8	20	−24.1
4221-PC (RM)	56	18.21	13.38	4.84	0.60	0.12	103	6	18	−25.5
{Omit relict muds (RM)}:										
Transect mean		20.66	11.57	9.09	0.64	0.12	59	6	10	−24.9
Stdev		2.93	1.02	2.00	0.17	0.04	13	0	2	0.5
Rel (%)		14	9	22	26	32	22	15	22	2
n		6	6	6	6	6	6	6	6	6

OC=(TC−TIC). See text for discussion of method. OP=(TP−IP). See text for discussion of method. RSPM= Riverine suspended particulate matter; BC= box core; GC= gravity core; PC= piston core. n.d.= not determined.

^aData from Ruttenberg (1990).

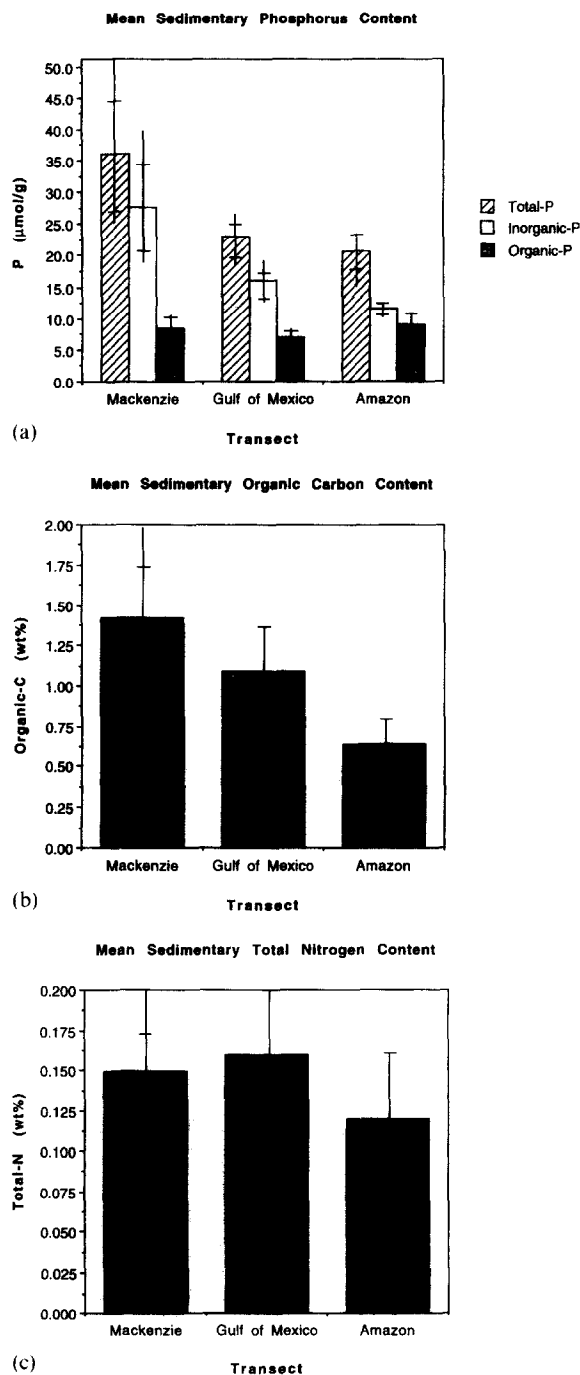


Fig. 2. Mean P, OC, and TN concentrations of surficial sediment over the marine transects of the three climatic regimes. Coastal peat and RSPM samples were omitted from the Mackenzie data set so that mean concentrations represent the marine transect only. Anomalous depositional environments at

ratios from one site to another are driven principally by differences in TN (Fig. 2C).

The mean $\delta^{13}\text{C}_{\text{OC}}$ of surficial sediments from the Mackenzie and the Amazon are statistically indistinguishable (Fig. 3D). Surficial sediments at both sites are significantly depleted in ^{13}C relative to surficial sediments from the Gulf of Mexico. The range of variability observed for the three marine transects is similar, with the Gulf of Mexico displaying the widest range.

4. Discussion

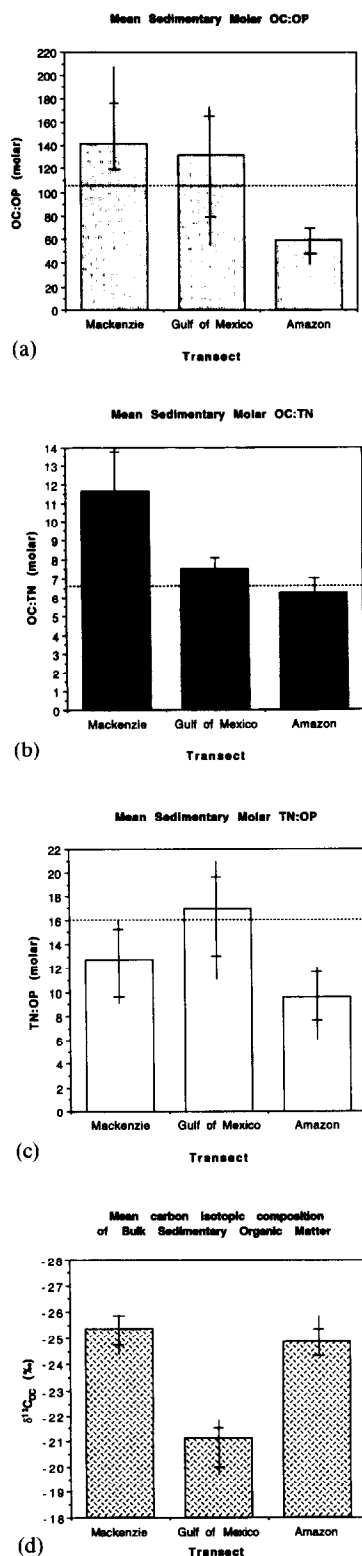
4.1. Characteristic elemental composition of organic matter

We have presented mean values of elemental concentrations and ratios, and carbon isotopic compositions (Table 3, Figs. 2 and 3), to enable us to make an assessment of the characteristic composition of organic matter of sediments from the three sites. Our goal was to assess whether the organic matter from these three different climatic regimes is characterized by distinctly different elemental compositions, elemental ratios, and carbon isotopic compositions. Recognizing the small size of our data set, we caution that conclusions drawn in this discussion must be viewed as preliminary.

The significantly higher TP content of Mackenzie shelf sediments, and the higher proportion of IP relative to the other sites (Fig. 2A), may indicate less extensive chemical weathering of particulate matter delivered to coastal marine sediments at this site. The more extensive continental vegetation, and year-round growing season in tropical and temperate climates may result in more efficient retention of P in living organic matter in

(Fig. 2 continued)

station 9 in the Gulf of Mexico and relic mud sites 4221-PC and 4349-BC on the Amazon shelf were omitted from mean calculations because they are not representative of present-day sediment input (see text). The vertical bars drawn through the columns represent the range of values observed. The short horizontal bars which bisect the vertical range bars denote the standard deviation about the mean. (A) Mean TP, IP, and OP ($\mu\text{mol/g}$). (B) Mean OC (wt%). (C) Mean TN (wt%).



these lower latitude regimes, and more extensive transformation of IP to OP. An alternative explanation for the higher IP content of Mackenzie shelf sediments is the possibility of a more P-enriched source terrane. Conclusive evaluation of the effect of differential weathering and plant uptake on transport of particulate P from the continent to the ocean, and the role these processes play in producing the mean P concentrations and P distribution observed in proximal coastal sediments, requires a more comprehensive study than the one summarized here.

Elemental ratios in surficial sediments from the three depositional environments are significantly different in some cases (Fig. 3A–C). In all cases, differences in OC:OP and OC:TN appear to be driven mostly by intra-site differences in OC concentration (Fig. 2B). Since changes in OC:OP and OC:TN between transects are driven by changes in OC concentration, and have little to do with OP and TN concentrations, it is difficult to use these bulk ratios to infer the nature of specific OP and TN compounds present in the sediments. A possible exception to this is the low OC:TN and OC:OP ratios observed in certain Gulf of Mexico and Amazon shelf sediments (Table 3), which approach the ratios of specific biochemicals; for example, proteins (C:N \approx 5) and phospholipids (C:P \approx 40).

The Amazon shelf data exhibit the narrowest range of all elemental concentrations and ratios measured (Figs. 2 and 3), indicating either that the source is homogeneous, or that heterogeneous source material underwent extensive homogenization once delivered to the shelf. The Amazon shelf is known to be subjected to shelf-wide physical resuspension (Kuehl et al., 1995), and resuspended sediments can be transported laterally in the form of thick bottom-hugging suspensions, known as

Fig. 3. Mean elemental ratios and carbon isotopic signatures of bulk surficial sediment over the marine transects of the three climatic regimes. Samples omitted from calculated means are the same as for Fig. 2, and the range and standard deviation about the mean are indicated as described in Fig. 2. (A) Mean OC:OP ratios. (B) Mean OC:TN ratios. (C) Mean TN:OP ratios. (D) Mean $\delta^{13}C_{oc}$. The dashed lines in (A)–(C) indicate the Redfield Ratio for marine plankton.

'fluid muds' (Kineke and Sternberg, 1995). We believe that the documented physical reworking of Amazon shelf sediments plays a key role in the limited variance of the elemental composition observed in surficial sediments. The broader ranges exhibited in the Arctic and temperate transects for all reported geochemical parameters (except OP) are likely due, in part, to the larger range in water depth sampled. Surficial sediments at deeper sites will have undergone more extensive biogeochemical modification, due to longer exposure time to water column remineralization processes, and thus are not expected to maintain a clear bulk signature imparted from the riverine source. Also, input of marine organic matter will dilute the progressively weaker terrestrial signal at deeper sites. In addition, it is unknown whether fluid muds exist in either the Mackenzie or Gulf of Mexico shelf environments, and the absence of this homogenizing force would contribute to the persistence of heterogeneities.

The narrow range of OP concentrations at each site, and the similarity in the mean OP concentration across the three sites, is striking (Fig. 2A). Given the differences in the terrestrial source terranes of the three regions (Table 2), this may imply that OP in river-dominated depositional environments undergoes similar modification during transport to coastal sediments, regardless of climatic regime and drainage basin characteristics, with the result that OP concentrations end up within a narrow concentration range.

4.2. Trends in composition with distance from locus of riverine input

4.2.1. Phosphorus concentration and distribution

Total, inorganic, and organic phosphorus (TP, IP and OP) concentrations are shown as a function

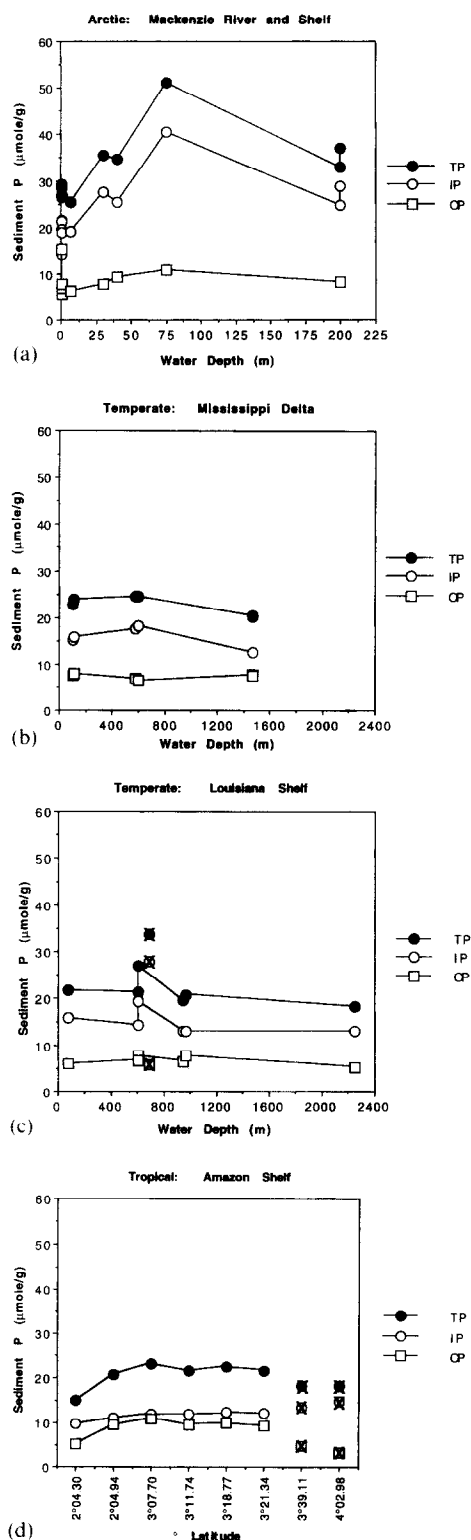


Fig. 4. Sediment P concentration (total, inorganic, and organic P) as a function of distance from the locus of riverine input. (A) Mackenzie River and Beaufort shelf. (B) Mississippi Delta. (C) Louisiana shelf. (D) Amazon shelf. Station 9 (seep site) on the Louisiana shelf and stations 4221-PC and 4349-BC (relict muds) on the Amazon shelf, which are anomalous depositional environments (see text), are disconnected from the transect lines and distinguished by crossed symbols.

of water depth for the Mackenzie and Gulf of Mexico, and as a function of latitude for the Amazon shelf (Fig. 4). This presentation provides a view of changes roughly as a function of distance from the locus of riverine input. Our expectation in designing this comparative study was that we would observe systematic trends in the P concentration and P distribution of sediments with increasing distance from the locus of riverine input, and systematic differences between the three sites due to differences in climatic regime. However, we observe surprisingly little variability (the analytical uncertainty in these measurements is equal to or smaller than the size of the symbols). Three samples are from anomalous depositional environments, and are set apart from the others by crossed symbols. Station 9, at mid-transect on the Louisiana shelf in the Gulf of Mexico, is located in the vicinity of a cold hydrocarbon seep (Fig. 4C). Such seeps are a common feature in the Gulf of Mexico (Brooks et al., 1990; Sassen et al., 1994). Stations 4349 and 4221 on the Amazon shelf are relic muds (Fig. 4D); pore water CH_4 and SO_4^{2-} profiles at Stn. 4221 indicate that the mud currently residing at the sediment–water interface had previously been buried ≈ 10 m below the surface (Blair and Aller, 1995). Samples from these anomalous environments have distinctly different P distribution than other sites on the same transect.

Riverine Suspended Particulate Matter (RSPM) samples and the coastal peat sample, plotted at zero water depth on the Mackenzie plot (Fig. 4A), have similar TP content, but the peat has a higher OP and lower IP content (Table 3). Sediment from the shallowest station (7 m) has a P content and P distribution similar to that of the RSPM samples, indicating that these sediments are heavily influenced by riverine particulate matter. There is an apparent mid-shelf maximum in IP, but a more detailed and spatially comprehensive study of the P distribution in Mackenzie shelf sediments is required to explore whether this is a shelf-wide feature, and to reveal the mechanisms for its creation.

No systematic trend is apparent in the TP, IP, and OP concentrations along the Gulf of Mexico transects (Fig. 4B,C). The water depth span

sampled is larger and the water depths are greater than either the Mackenzie or the Amazon transects. This hampers our ability to make a direct comparison with the other two regimes, which would require samples from similar depth ranges. The seep site has slightly higher organic carbon than the other sites along the transect (Table 3), but its sedimentary phosphorus is dominated by IP (Fig. 4C). Since such sites are often heavily populated by chemosynthetic biological communities (Sassen et al., 1994), one might expect elevated sediment OP content. However, such sites are also characterized by large volumes of authigenic carbonate phases (Sassen et al., 1994), and it is conceivable that authigenic, inorganic phosphatic phases form at such sites, at the expense of organic phosphorus. If the high degree of enrichment in IP is due to precipitation of remineralized organic P, this would imply that there must, at one time, have been an elevated supply of OP to provide the phosphorus required for formation of secondary inorganic phosphate minerals.

No systematic trend is obvious with increasing distance along the Amazon flow trajectory (Fig. 4D). The differences between the box and piston cores at RMT-2 (River Mouth Transect, ca. 2°N. Lat., Fig. 1) may result from grain-size heterogeneities, common in sites directly in line with the river mouth (Nittrouer et al., 1983; Kuehl et al., 1986; Table 2). Surficial sediment P distribution at OST-2 and OST-3 (Open Shelf Transect, ca. 3° N. Lat., Fig. 1) varies little, and the TP is comprised of almost equivalent parts OP and IP. The OST stations are located within a narrow water depth range (20–39 m), and the shelf environment is known to be extremely dynamic with regard to sediment resuspension (Kuehl et al., 1995). Both of these factors could create a laterally homogeneous surface layer of sediment, resulting in a transect which looks invariant along the river flow trajectory. The relic mud (RM) sites, furthest north on the transect, diverge from this homogeneous trend. They are markedly depleted in OP relative to the other stations, slightly depleted in TP, and have higher IP concentrations. These observations are consistent with the relic nature of these sediments. Having at one time been buried ≈ 10 m below the surface (Blair and Aller, 1995),

they would have undergone diagenetic alteration which typically results in the formation of inorganic authigenic phosphate phases, which derive their phosphate from the destruction of organic phosphorus (e.g., Ruttenberg and Berner, 1993; Louchouart et al., this volume).

A progression in P distribution appears evident from the Arctic to the temperate to the tropical sites, which may be due to differences in climatic regime. IP dominates in Mackenzie shelf sediments, whereas in Amazon shelf sediments the IP and OP reservoirs are of equivalent size; the Gulf of Mexico is intermediate. The higher TP and IP content of the Arctic Mackenzie shelf surficial sediments, and the fact that OP comprises a progressively more significant fraction of TP in progressively warmer climatic regimes, could result from different continental weathering regimes linked to climatic differences, or from differences in the extent of modification of particulate material after it enters the marine shelf environment.

The lack of variability in P concentration and speciation observed in the Gulf of Mexico and Amazon shelf transects, from samples proximal to the river mouth to those at distal sites, was unanticipated. The observed homogeneity along the transects may result from extensive biogeochemical processing of particulate matter, either in transit to the sea bottom, or post-depositional alteration of surficial sediments. In contrast, the variability seen in the Mackenzie shelf sediments may imply that less extensive biogeochemical modification of particulate matter occurred prior to sedimentation.

4.2.2. *Elemental OC:OP and OC:TN ratios*

The two major sources of organic matter to marine sediments are terrestrial and marine plants; each have distinctive C:N:P ratios. Marine phytoplankton have a mean molar organic OC:OP ratio of 106:1, and a mean molar OC:ON ratio of 6.6:1 (Redfield et al., 1963). In contrast, terrestrial plants are relatively impoverished in P and N, with characteristic OC:OP ratios ranging from 300 to 1300 and OC:ON ratios ranging from 10 to 100 for soft tissues, OC:OP ratios greater than 1300 and OC:ON ratios ranging from 100 to 1000 for woody tissues (e.g., Likens et al., 1981; Hedges et al., 1986, 1988; Goñi and Hedges, 1995;

Ruttenberg, unpubl. data). Microbial communities may be an important component of sedimentary organic matter, and bacterial OC:OP ratios range from 7 to 80 (Luria, 1960; Gächter and Meyer, 1993), while bacterial OC:ON range from 4 to 6 (e.g., Luria, 1960; Goñi and Hedges, 1995).

If marine sedimentary organic matter in river-dominated coastal regimes can be characterized as a two-end-member mixture of terrestrial and marine phytodetritus, elemental ratios should trend from high (above Redfield Ratios) OC:OP and OC:TN ratios in sediments closest to the locus of riverine input, to progressively lower ratios, approaching the Redfield Ratio, with distance away from the river mouth. This pattern would result from a monotonic gradient from nearshore sediments enriched in terrestrial organic matter to more distal sediments in which marine organic matter becomes a progressively more important component of the total sedimentary organic matter pool. Superimposed on this simple mixing trend will be any biogeochemical modification of the particulate matter in transit to the seabed, and post-depositional (diagenetic) modification of surficial sediments. Despite possible modification of riverine particulate matter in transit to marine sediments, the high runoff and large sediment loads which characterize the rivers in the study sites (Table 2) should result in a strong riverine signal in stations nearest the river mouth. A weaker terrigenous signal might be detected at distal sites, as well.

All measured OC:OP and OC:TN ratios in the Mackenzie transect lie above the Redfield Ratio (Fig. 5A,D), indicating the presence of an important terrestrial organic matter component. OC:OP ratios are highest at shallow water depths, and trend toward the Redfield Ratio with increasing water depth, consistent with the two-end-member mixing model. The OC:OP and OC:TN ratios of the coastal peat, one source of terrestrial organic matter to this site, are 934 and 20, but the elemental ratios of RSPM are significantly lower (OC:OP ranging from 166 to 275, and OC:TN from 12 to 15, Table 3), indicating that organic matter enriched in P and N, perhaps freshwater plant material, including freshwater phytoplankton, has mixed with terrestrial phytodetritus in the river.

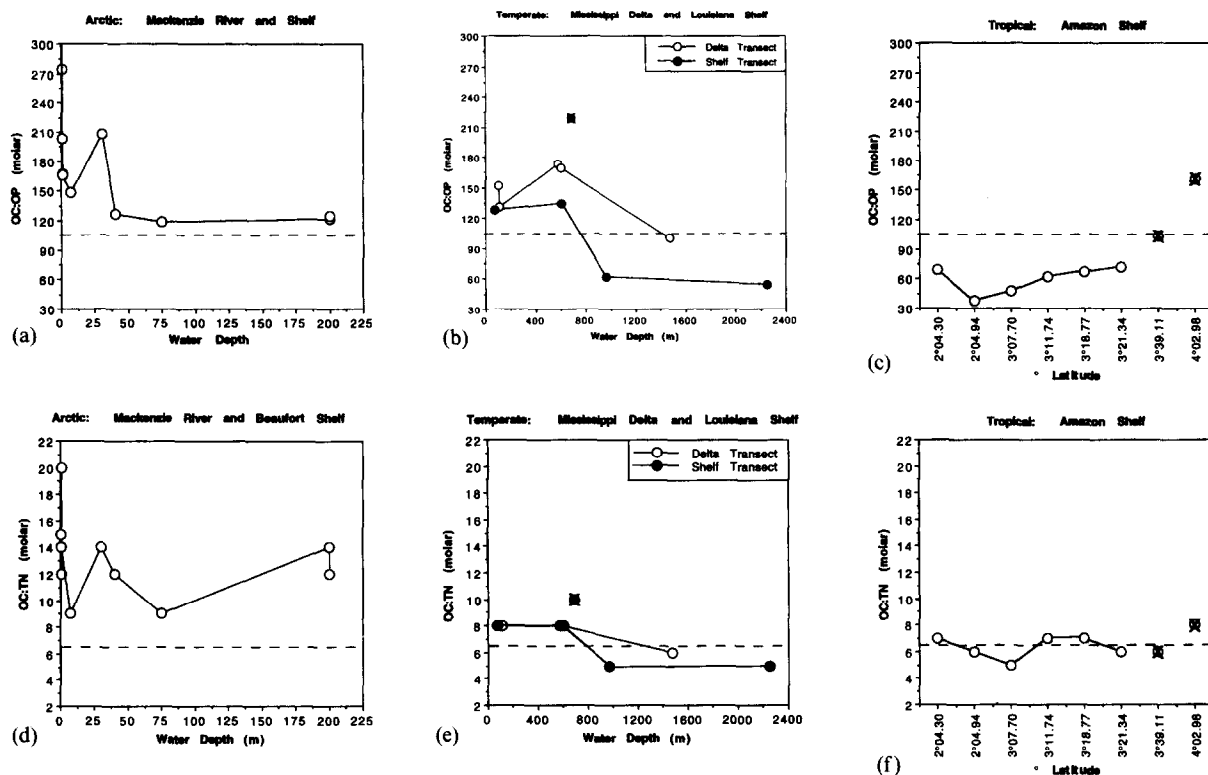


Fig. 5. Variations in surficial sediment OC:OP and OC:TN ratios as a function of distance from the locus of riverine input. The dashed line represents the Redfield Ratio for marine plankton. Analytical uncertainty is equal to or smaller than the size of the symbols; ratios which differ by an amount greater than the symbol size are therefore considered significantly different. (A) OC:OP ratios for the Mackenzie River and Beaufort shelf (peat sample excluded). (B) OC:OP ratios for the Mississippi Delta and Louisiana shelf. (C) OC:OP ratios for the Amazon shelf. (D) OC:TN ratios for the Mackenzie River and Beaufort shelf. (E) OC:TN ratios for the Mississippi Delta and Louisiana shelf. (F) OC:TN ratios for the Amazon shelf. Stations at anomalous depositional environments are distinguished as in Fig. 4.

Several large and numerous small lakes on the Mackenzie River and Delta (Reeder, 1972; Lesack et al., 1995) could provide a source of P- and N-enriched freshwater plants to the river. The OC:OP ratio of 208 at 30 m water depth (Stn. 5) falls above the otherwise smooth trend of decreasing OC:OP with increasing water depth, and the trend in OC:TN shows even more variability, suggesting that processes other than simple mixing of two distinct end-members must be occurring.

Both transects in the Gulf of Mexico are similar to the Mackenzie transect in that they trend from higher OC:OP and OC:TN ratios at shallow water depths to lower ratios with increasing water depth (Fig. 5B,E). Again, this is consistent with a

stronger terrestrial signal at shallow depths, giving way to a more strongly marine signal at distal stations. The shallowest stations of both transects have similar OC:OP and OC:TN ratios, both higher than the Redfield Ratio. Ratios at the deepest Mississippi Delta station drop to very near the Redfield Ratio, and ratios of sediments from the two deepest stations on the shelf transect are significantly lower than the Redfield Ratio. The relatively high OC:OP and OC:TN ratios encountered at Stn. 9 on the Louisiana shelf transect reflect the presence of a natural petroleum seep at this station, where the sedimentary organic matter is presumed dominated by P- and N-poor hydrocarbons.

In contrast to the other two sites, all Amazon shelf stations (excluding the relict mud sites) have OC:OP ratios significantly lower than the Redfield Ratio, ranging from 38 to 72. OC:TN ratios from all stations on the Amazon shelf are at, or very close to, the Redfield Ratio; the transect mean is $\text{OC:TN} = 6 \pm 1$ (Table 3). The observation of these low ratios is striking considering their proximity to the Amazon River outflow, where one would expect high OC:OP and OC:TN ratios, due to terrestrial organic matter input. The relict mud sites, which, as discussed previously, are not comparable to surficial sediments from the other sites, are characterized by OC:OP ratios at or above the Redfield Ratio.

Low OC:OP ratios have been observed previously in pelagic sediments (Froelich et al., 1982; Mach et al., 1987; Ingall and Van Cappellen, 1990; Ruttenberg, 1990), however, the occurrence of such low OC:OP ratios in near-shore sediments has not previously been reported, to our knowledge. Two alternative explanations have been advanced for the 'anomalously low' ratios observed in pelagic sediments (Froelich et al., 1982; Ingall and Van Cappellen, 1990). Either these low ratios reflect an organic matter residuum enriched in refractory OP compounds, a departure from the accepted notion that OP compounds are inherently labile, or they represent a dominance of bacterial biomass, which is characterized by low OC:OP ratios. Both hypotheses can reasonably be applied to explain the low OC:OP ratios we observe in these near-shore sediments. We consider these, along with the possible role of sorption of OP onto particle surfaces, as mechanisms for preserving elevated OP relative to OC in these sediments, in the final section of this discussion.

OC:TN ratios of Amazon River particulate organic matter (POM) are significantly more depleted in N than those we observe on the shelf, with coarse riverine POM ($> 60 \mu\text{m}$) characterized by a mean OC:TN ratio of 24, and fine POM ($< 60 \mu\text{m}$) by a mean OC:TN ratio of 11 (Hedges et al., 1986). This indicates that the N enrichment observed in shelf sediments must be the result of processes occurring after deposition on the shelf. Arguments parallel to those presented for the low OC:OP ratios can be constructed to explain the

observed trends in OC:TN. The trend in TN:OP (not shown) does not differ significantly from that of OC:OP.

In summary, the trends in elemental ratios observed for the Arctic and temperate transects show a progression from high ratios indicative of a significant terrestrial component in stations proximal to the source of riverine input, to low ratios at distal stations, indicating a more important marine organic matter component. The absence of a monotonic gradient between proximal and distal sites along these transects, which would result from progressive dilution of terrestrial organic matter by marine organic matter, indicates that processes in addition to simple mixing of two well constrained end-members are active. The anomalous depositional environments in both the Gulf of Mexico (the seep site) and the Amazon shelf (the relict mud sites), and the unexpectedly low ratios observed at deep Gulf of Mexico sites and on the Amazon shelf, demonstrate the complexity of factors which may play a role in imparting elemental ratios to organic matter in marine sediments. The differences observed in the elemental ratio trends between the three sites could be due to differences in climatic regime (weathering and the strength of river-supplied terrestrial source), depositional environmental characteristics (overlying water productivity, water column length, sediment accumulation rate and rate of organic matter remineralization), or, more likely, a combination of these factors.

4.2.3. Carbon isotopic composition of bulk organic matter ($\delta^{13}\text{C}_{\text{OC}}$)

Terrestrial C3 plants are characterized by $\delta^{13}\text{C}_{\text{OC}}$ ranging from -23‰ to -34‰ , marine plankton are enriched relative to C3 terrestrial plants (-18‰ to -24‰), and on the basis of this difference the $\delta^{13}\text{C}_{\text{OC}}$ signature of bulk organic matter has been used to distinguish terrestrial from marine organic sources (e.g. Degens, 1969; Fry and Sherr, 1984). Terrestrial C4 plants are enriched in $^{13}\text{C}_{\text{OC}}$ relative to both C3 plants and marine plankton, with $\delta^{13}\text{C}_{\text{OC}}$ ranging from -6‰ to -23‰ (e.g. Degens, 1969; Fry and Sherr, 1984). Clearly, if there is significant input of C4 terrestrial plant material, the sources of marine sedimentary

organic matter can no longer be interpreted according to a simple two-end-member mixing model. In addition, the isotopic signature of phytoplankton is an indirect function of temperature, and phytoplankton from high latitudes can be significantly depleted in $^{13}\text{C}_{\text{OC}}$, with $\delta^{13}\text{C}$ signatures ranging from -18‰ to -30‰ (Rau et al., 1982; Schell, 1983). Bacteria have highly variable $\delta^{13}\text{C}_{\text{OC}}$; their isotopic composition tends to reflect their dominant food source (Fry and Sherr, 1984).

Onshore-offshore trends in $\delta^{13}\text{C}_{\text{OC}}$ of surficial sediments along the transects in the three climatic regimes, where present, are extremely muted (Fig. 6). In the Arctic, the RSPM and peat samples cluster between -26‰ and -28‰ , which is well within the range of terrestrial C3 plants (Fig. 6A). With distance offshore, sediments become slightly heavier, falling outside the range given above for average marine plankton, but within the range reported for marine plankton from high-latitude regions (Rau et al., 1982; Schell, 1983).

With the exception of the seep site, stations along the Gulf of Mexico transects all display carbon isotopic signatures within the range accepted as typical for marine plankton (Fig. 6B). Hedges and Parker (1976) observed similar values in this region of the Gulf. There is a slight trend toward more ^{13}C -enriched organic matter (from -21.1‰ to -19.7‰ ; note that analytical uncertainty is 0.1‰) along the Delta transect, suggesting the presence of a ^{13}C -depleted source of organic matter (e.g. terrestrial C3 plant material) at near-shore stations; no systematic trend is evident in the shelf transect. The highly depleted sedimentary organic matter at the seep site is further evidence for a hydrocarbon-dominated organic matter pool.

Sediments from the Amazon shelf display no systematic variation in $\delta^{13}\text{C}_{\text{OC}}$ with distance from the locus of riverine input (Fig. 6C). The isotopic composition of these surficial sediments ranges from -24.1‰ to -25.8‰ , which is closest to the

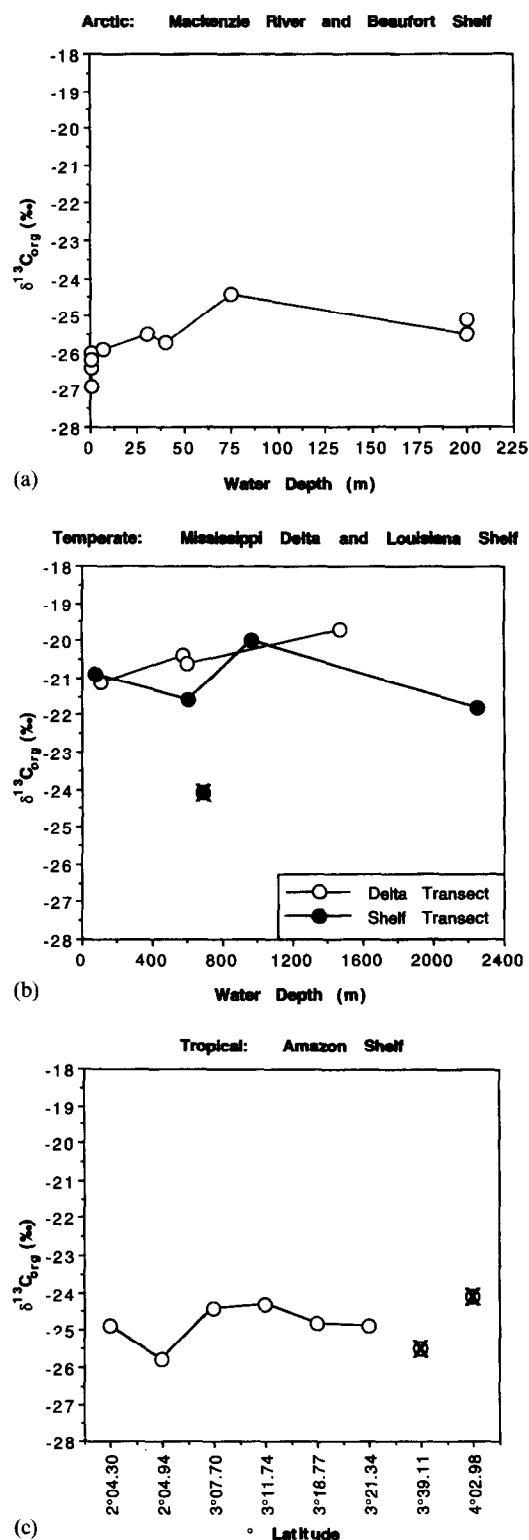


Fig. 6. Carbon isotopic composition of bulk sedimentary organic matter as a function of distance from the main locus of riverine input. (A) Mackenzie River and Beaufort shelf. (B) Mississippi Delta and Louisiana shelf. (C) Amazon shelf. Stations at anomalous depositional environments are distinguished as in Fig. 4.

range described by terrestrial C3 plants. Showers and Angle (1986) found similar values in a broad survey of the Amazon shelf. The observed isotopic composition is consistent with expectations for a river-dominated coastal system with significant terrigenous input, in this case due to Amazon River inflow.

4.3. Reconciling elemental ratios and $\delta^{13}\text{C}_{\text{OC}}$ as indicators of organic matter source

The degree to which the OC:OP ratios co-vary with carbon isotopic composition of bulk organic matter can be used to indicate the applicability of a two-end-member mixing model of organic matter sources to sediments. A systematic relationship exists between OC:OP ratios and $\delta^{13}\text{C}_{\text{OC}}$ for Mackenzie River and shelf samples (Fig. 7A). The hyperbolic trend observed is characteristic of the mixing line obtained between two end-members in ratio-to-ratio plots (Faure, 1986). The Mackenzie shelf data are therefore consistent with sediments comprised of a mixture of terrestrial and marine organic matter. Samples which are isotopically lighter are characterized by higher OC:OP ratios, consistent with a terrestrial organic matter component, whereas samples which are isotopically heavier have lower OC:OP ratios, consistent with a marine component (Fig. 7A). This also accords with the onshore–offshore trends observed in surficial Mackenzie shelf sediment OC:OP ratios (Fig. 4A). The fact that the more distal stations never actually reach the Redfield Ratio can be explained by invoking a persistent terrestrial component, and the generally low marine productivity of this region relative to the temperate and tropical regions (Table 2). The onshore–offshore $\delta^{13}\text{C}_{\text{OC}}$ trend, although slight, is also consistent with a binary mixture of terrestrial and marine organic matter. The $\delta^{13}\text{C}_{\text{OC}}$ signature does not provide a strong constraint on source at this site, however,

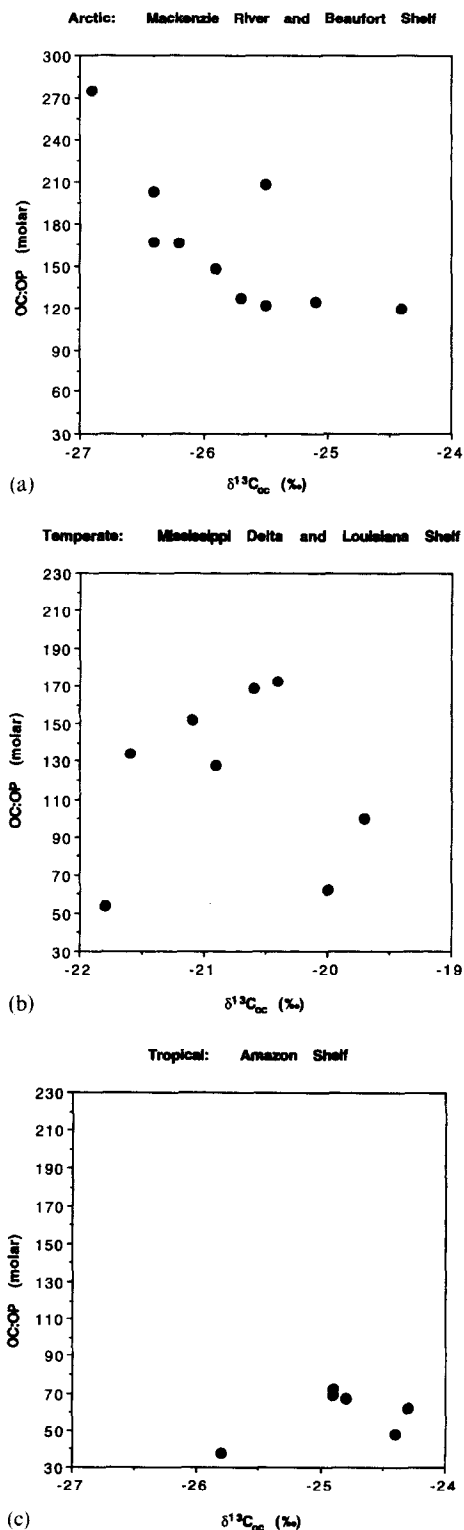


Fig. 7. Sediment OC:OP ratios versus $\delta^{13}\text{C}_{\text{OC}}$. (A) Mackenzie River and Beaufort shelf (peat sample excluded). (B) Mississippi Delta and Louisiana shelf (seep site excluded). (C) Amazon shelf (relic mud sites excluded).

because of the possibility of ^{13}C -depleted plankton at high latitudes (Rau et al., 1982; Schell, 1983).

There is no discernible correlation between OC:OP ratios and $\delta^{13}\text{C}_{\text{OC}}$ in sediments from the Gulf of Mexico or Amazon shelf (Fig. 7B,C), indicating that data from these sites cannot be interpreted according to a simple two-end-member mixing model. Although the elemental ratio trends in the Gulf of Mexico transects are suggestive of two-end-member mixing (Fig. 5B,E), the $\delta^{13}\text{C}_{\text{OC}}$ values imply that terrestrial C3 plant material is not an important constituent of organic matter in these surficial sediments (Fig. 6B). We observed vascular plant debris in these sediments, however, which could only have derived from a terrestrial source. These apparently conflicting observations suggest that an important fraction of the terrestrial organic matter exported to the Gulf of Mexico may derive from C4 plants. The drainage basin of the Mississippi and Atchafalaya rivers includes mature grasslands, large areas of grain-producing agricultural lands (Turner and Rabalais, 1991), and extensive marshes in the deltaic plain (DeLaune, 1986). Therefore river-borne terrestrial phytodetritus could include a significant C4 plant component. A $\delta^{13}\text{C}_{\text{OC}}$ value of -19.7‰ was obtained from a single suspended matter sample from the lower Mississippi River at Venice, LA (Ruttenberg, unpubl. data). This relatively enriched $\delta^{13}\text{C}_{\text{OC}}$ value supports the hypothesis that terrestrial C4 plants contribute to the heavy carbon isotopic signature of near-shore surficial sediments. The overlap in carbon isotopic signatures of organic matter sources to Gulf of Mexico sediments hinders the use of a simple two-end-member mixing model to explain the measured $\delta^{13}\text{C}_{\text{OC}}$ values.

The isotopic signature of surficial sediments on the Amazon shelf (Fig. 6C), which indicates that terrestrial phytodetritus dominates the organic matter pool, is at odds with the elemental ratios, which are enriched in both OP and TN relative to OC (Fig. 5C,F). It is unlikely that marine phytoplankton or the phytodetritus which they contribute to surficial sediments could have such depleted carbon isotopic signatures in a tropical regime. In any case, the elemental ratios of the Amazon sediments are far too enriched in OP and TN to

be consistent with a terrestrial phytodetrital source. The contradictory indications of source provided by the isotopic and elemental ratio data make it impossible to view these surficial sediments in terms of a simple two-end-member mixture of terrestrial and marine organic matter.

The degree of P and N enrichment in sediments from the three deepest stations in the Gulf of Mexico and all sites on the Amazon shelf, such that the elemental ratios are below the Redfield Ratio, precludes explanation of organic matter sources to these sediments using the two-end-member model. In order to explain these low ratios, the presence of a third, P- and N-enriched end-member (e.g. bacteria), or a process which fractionates C from P and N (e.g. preferential C regeneration) must be invoked.

Sediments enriched in refractory OP compounds, such as inositol phosphates and phosphonates, have been discussed as a plausible explanation for low OC:OP ratios observed in pelagic sediments (Froelich et al., 1982; Ingall and Van Cappellen, 1990). However, it has been demonstrated that inositol phosphates, which have their origin in terrestrial phytodetritus, are readily degraded in marine sediments (Hedges and Weliky, 1989; Suzumura and Kamatani, 1994). Phosphonates have been identified in marine sediments (Ingall et al., 1990) and organisms (Kittredge et al., 1969), but their quantitative importance remains unresolved. Furthermore, C–P bond-cleaving enzymes have been isolated from marine bacteria (McMullan and Quinn, 1992), suggesting that phosphonates are not immune to degradation.

Proteins, and their constituent amino acids, account for the majority of N in primary producers (e.g. Cowie and Hedges, 1992). In most sedimentary environments, proteins are considered more labile (e.g. Cowie and Hedges, 1992) than other forms of organic carbon. This diagenetic lability generally results in higher OC:TN ratios in sediments relative to the source organisms (e.g. Cowie and Hedges, 1992). In some cases, however, degradation of proteins can be hindered if they are present within protective matrices, such as cell wall proteins in diatom siliceous tests (Cowie et al., 1992). Other refractory nitrogenous compounds,

for example pheopigments (e.g. Keeley and Brereton, 1986; Furlong and Carpenter, 1988) and peptoglycans (e.g. de Leeuw and Largeau, 1993) may also contribute to sedimentary nitrogen. The quantitative significance of these compounds in these marine sediments has not yet been established, however, which precludes an assessment of their role in lowering OC:TN ratios to the levels we observe. Bacterially mediated accumulation of N during decomposition of phytodetritus (Rice and Tenore, 1981; Rice, 1982) is another mechanism for N-enrichment of organic matter. This N-enrichment process results in lower OC:TN ratios relative to the initial fresh plant material; however, the end ratios observed in decomposition studies are significantly higher than those we observe in surficial sediments from the deep Gulf of Mexico and the Amazon shelf (OC:TN ≥ 10 ; Rice and Tenore, 1981). Therefore, although this could be a contributory process, it may not fully account for the low OC:TN ratios observed.

Sorption of OP and ON compounds, both refractory and labile, could protect them from remineralization (e.g. Lee, 1992; Keil et al., 1994). Preservation of P- and N-enriched organic matter by this mechanism would require preferential sorption of OP and ON compounds relative to purely OC compounds, which is reasonable given the more ionic nature of the phosphate and amino moieties of OP and ON compounds. The fine-grained nature of all the sediments in which low OC:OP and low OC:TN ratios have been observed (Table 2) is consistent with the sorption/protection hypothesis, since the high surface area which accompanies small grain size promotes sorption.

Plots of OC versus TN can be used to assess the contribution of sorbed inorganic N to the organic matter pool (Hedges et al., 1986). Linear least-squares regression lines through the data in OC versus TN plots for the three sites (Fig. 8) indicate that the relationship between OC and TN is significant for both the Gulf of Mexico

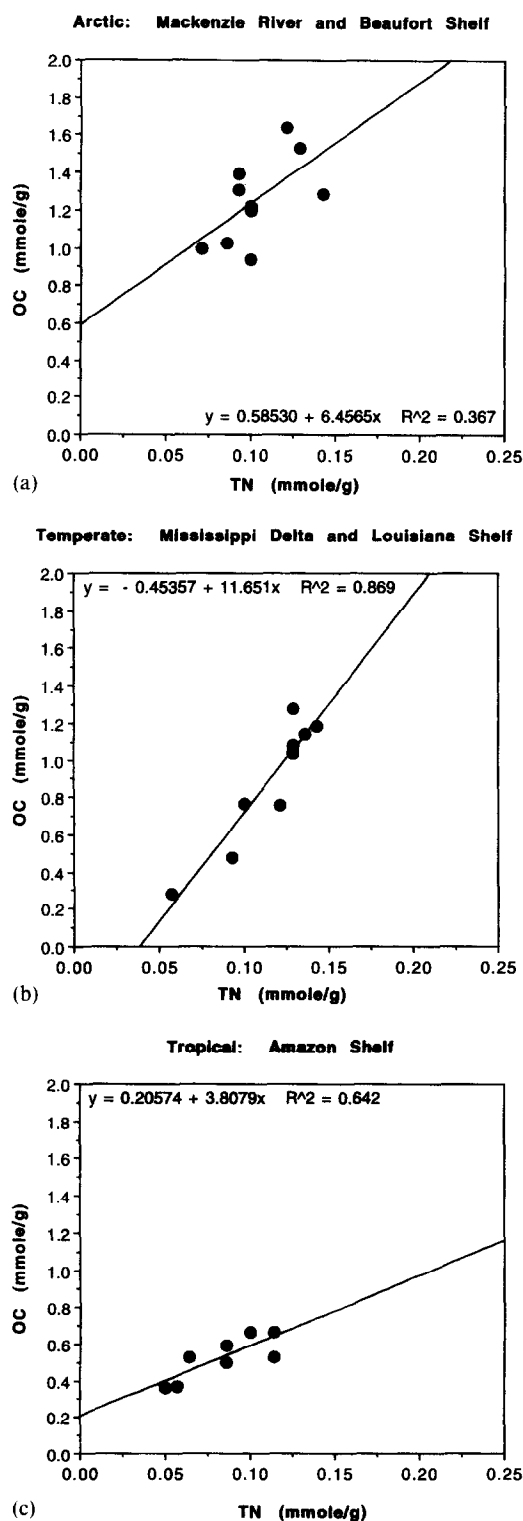


Fig. 8. Sediment OC versus TN concentration. (A) Mackenzie River and Beaufort shelf (peat sample excluded). (B) Mississippi Delta and Louisiana shelf. (C) Amazon shelf. Best fit lines are shown; the correlation coefficients associated with these linear fits to the data are given as R^2 values.

($R^2 > 0.8$) and the Amazon shelf transects ($R^2 > 0.6$); a less significant correlation exists for the Arctic transect ($R^2 > 0.3$). The poor correlation in Arctic sediments (Fig. 8A) indicates the presence of variable quantities of marine and terrestrial organic matter end-members with different elemental ratios, consistent with the previous discussion indicating simple two-end-member mixing. The significant correlation between OC and TN in the Gulf of Mexico and Amazon transects indicates that the distinct organic matter sources which supply organic matter to these sediments are present in nearly invariant proportions. For the Gulf of Mexico, this homogeneity is attributed to the greater water depth relative to the Arctic site; at the depth of the shallowest Gulf of Mexico station the terrestrial and marine sources have already homogenized. For the Amazon, we attribute the homogeneity of organic matter pool derived from different sources to the resuspension regime and the lateral homogenization promoted by migrating fluid mud.

We interpret the positive TN intercept at OC = 0 observed in the Gulf of Mexico (Fig. 8B) as an indication of a background of inorganic N in the TN pool, most likely NH_4 sorbed to sediment surfaces (Müller, 1977), which is mixing with a relatively homogeneous organic matter pool. The positive TN intercept leads us to conclude that the low (OC:TN) ratios observed in the deep-water Gulf of Mexico stations are most likely due to sorption of inorganic N. Given this intercept, sorbed inorganic N may account for 20–50% of the TN pool in these sediments. The higher mean TN content and TN:OP ratios observed in Gulf of Mexico sediments, as contrasted to these parameters at the other sites (Figs. 2C and 3C) may, therefore, reflect the presence of an important sorbed inorganic-N component.

In contrast, the plot of OC versus TN for the Amazon shelf (Fig. 8C) yields a positive OC intercept at TN = 0. This suggests that there is an extremely N-poor pool of organic matter (OC:TN = ∞), for example, terrestrial organic matter, which is mixed with an N-rich organic matter pool. Unlike the Gulf of Mexico, therefore, the low OC:TN ratios in the Amazon cannot be explained by the inorganic-N sorption hypothesis.

Fine suspended matter from the Amazon River has OC:TN ratios of 10–11, reflecting an organic matter pool dominated by soil humus (Hedges et al., 1986). This is considerably higher than the OC:TN ratio we observe for the shelf sediments (between 5 and 7), which leads us to invoke the presence of a more N-enriched end-member in Amazon shelf sediments. Having ruled out the sorption hypothesis, we conclude that Amazon shelf sedimentary organic matter at these sites may be dominated by bacterial biomass or substances derived therefrom.

The possibility that bacteria may constitute a significant fraction of organic matter in some sediments, and may act as a repository for C, N, and P derived from remineralized terrestrial and/or marine organic matter, has been raised by others (e.g. Lee, 1992). A significant bacterial contribution is likely in sediments unfavorable to grazers of bacteria (e.g. protozoans). Low porosity in fine-grained sediments renders them unfavorable for protozoan colonization because there is less interstitial space for them to live in (Lee, 1992). The Amazon shelf sites under discussion are characterized by fine-grained sediments (Table 2), and therefore meet this criterion. Temporally and spatially extensive bottom sediment resuspension on the Amazon shelf (Kineke and Sternberg, 1995; Kuehl et al., 1995) is another factor which could discourage grazer colonization (Aller and Stupakoff, 1996). Whether the organic matter pool on the Amazon shelf is comprised of living bacteria, bacterial excreta, or molecular components from dead bacterial cells, the elemental ratios would be expected to reflect the composition of the bacterial source. If these bacterially derived components become fixed in sediments via sorption or other immobilization processes (e.g. Rice, 1982), it would be difficult to distinguish between a sorbed versus a biomass component because the two pools would mirror each other compositionally.

5. Summary and conclusions

Mackenzie shelf sediments are more enriched in IP than Gulf of Mexico or Amazon shelf sedi-

ments, and the relative size of the OP reservoir increases from Arctic to temperate to tropical sediments. This pattern may result from progressively more efficient weathering, accompanied by more effective transformation of IP to OP, in temperate and tropical climates. Conclusive evaluation of the effect of differential weathering and plant uptake on transport of particulate P from the continent to the ocean, and the role these processes play in producing the P distribution observed in proximal coastal sediments, requires further study.

Although the proportion of OP relative to IP differs from site to site, absolute OP concentrations are strikingly similar. The similarity in mean OP concentrations across the three sites is surprising given the dramatic differences in climate and depositional settings. We cannot resolve the factors responsible for this similarity, but speculate that it may result from similar biogeochemical modification of particulate OP in transit to shelf sediments.

Elemental ratios for the Mackenzie and shallow Gulf of Mexico sites are consistent with a two-end-member mixture of terrestrial- and marine-derived organic matter. Carbon isotopes do not provide a strong constraint, however, due to the possible role of variable end-members (e.g. ^{13}C -depleted phytoplankton in the Arctic, C_4 terrestrial plants in Gulf of Mexico sediments). The relationship between OC:OP ratios and $\delta^{13}\text{C}_{\text{OC}}$ is consistent with a binary mixture of marine and terrestrial organic matter in Mackenzie shelf sediments. Such a relationship is not evident in Gulf of Mexico or Amazon shelf data, indicating that the two-end-member mixing paradigm does not adequately explain these data.

OC:OP and OC:TN ratios lower than the Redfield Ratio for marine plankton are observed in the deepest Gulf of Mexico stations and in Amazon shelf stations. This observation is especially striking in the Amazon shelf sediments, given the strength of the riverine source of terrestrially derived, ^{13}C -depleted, high OC:OP and OC:TN ratio organic matter to these sites. In order to reconcile these conflicting observations, either the presence of a N- and P-enriched third end-member (e.g. bacteria) must be invoked, or a process which fractionates C from N and P is required. OC versus TN plots for these sites suggest that prefe-

rential sorption of inorganic N is the most likely explanation for low OC:TN ratios in Gulf of Mexico sediments, whereas a bacterially derived component is the best explanation for Amazon shelf sediments.

There is considerable interest in using bulk sediment parameters, such as elemental ratios and $\delta^{13}\text{C}_{\text{OC}}$, to characterize bulk sedimentary organic matter. However, atypical depositional environments, anomalous elemental ratios, and poorly constrained end-members can seriously confound attempts to identify sources of organic matter to marine sediments. In this study, inconsistencies between OC:OP and OC:TN ratios and $\delta^{13}\text{C}_{\text{OC}}$ led us to consider non-traditional end-members (e.g. bacteria and C_4 terrestrial plants), and processes other than simple mixing of two well constrained end-members, to explain our data. Thus, in spite of potential pitfalls, careful consideration of these coupled bulk parameters can prove useful in revealing the complex nature of marine sedimentary organic matter.

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