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Transport of Particulate Organic Carbon by the Mississippi River and Its Fate in the Gulf of Mexico

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ABSTRACT: This study was designed to determine the amount of particulate organic carbon (POC) introduced to the Gulf of Mexico by the Mississippi River and assess the influence of POC inputs on the development of hypoxia and burial of organic carbon on the Louisiana continental shelf. Samples of suspended sediment and supporting hydrographic data were collected from the river and >50 sites on the adjacent shelf. Suspended particles collected in the river averaged 1.8 ± 0.3% organic carbon. Because of this uniformity, POC values (in μmol l^{-1}) correlated well with concentrations of total suspended matter. Net transport of total organic carbon by the Mississippi-Atchafalaya River system averaged 0.48 × 10^{12} moles y^{-1} with 66% of the total organic carbon carried as POC. Concentrations of POC decreased from as high as 600 μmol l^{-1} in the river to <0.8 μmol l^{-1} in offshore waters. In contrast, the organic carbon fraction of the suspended matter increased from <2% of the total mass in the river to >35% along the shelf at ≥10 km from the river mouth. River flow was a dominant factor in controlling particle and POC distributions; however, time-series data showed that tides and weather fronts can influence particle movement and POC concentrations. Values for apparent oxygen utilization (AOU) increased from ~ 60 μmol l^{-1} to >200 μmol l^{-1} along the shelf on approach to the region of chronic hypoxia. Short-term increases in AOU were related to transport of more particle-rich waters. Sediments buried on the shelf contained less organic carbon than incoming river particles. Organic carbon and $\delta^{13}C$ values for shelf sediments indicated that large amounts of both terrigenous and marine organic carbon are being decomposed in shelf waters and sediments to fuel observed hypoxia.

Introduction

Suspended particles are a landmark feature of the Mississippi River and its seaward plume. These particles play an important role in the transport of organic carbon to the Gulf of Mexico. Once introduced by the river or fixed in shelf waters, particulate organic carbon (POC) is carried along and across the Louisiana shelf to be deposited, remi-

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neralized, or moved on to the open Gulf of Mexico. Along the way, decomposition of POC in the water column and sediments plays a key role in the creation and persistence of observed hypoxia. This study quantifies riverine inputs of organic carbon to the Louisiana shelf and considers the distribution and fate of terrigenous and marine POC in the Gulf of Mexico.

Globally, rivers are estimated to carry about 15 $\times 10^{12}$ moles of POC and about 17 $\times 10^{12}$ moles of dissolved organic carbon (DOC) to the oceans per year (Meybeck 1982; Smith and Hollibaugh 1993). Work by Milliman et al. (1984) on the Yangtze River suggests that POC transport by rivers with particle loads >500 mg l^{-1} may be greater than previously reported and that total riverine POC transport may be as much as 19 $\times 10^{12}$ mol yr^{-1}. Oceanic budgets for carbon show that only ~9 $\times 10^{12}$ mol yr^{-1} are buried in deltaic-shelf sediments (Berner 1989). Part of the explanation for the low burial rate of carbon in coastal sediments follows from studies such as that by Ittekkot (1988), who estimated that at least 35% of the riverborne POC is chemically labile and readily decomposed. Furthermore, Smith and Hollibaugh (1993) presented arguments to support net heterotrophy in the coastal ocean. In their scenario, the 18 $\times 10^{12}$ mol of missing C yr^{-1} in oceanic budgets is slowly respired in the open ocean. Regionally, data on transport of total organic carbon (TOC) by the Mississippi River are rather limited. A 1969–1970 survey by Malcolm and Durum (1976) reported that the Mississippi River carries 0.28 $\times 10^{12}$ mol TOC yr^{-1}, with 54% as POC.

Terrigenous inputs of organic carbon (OC) by the Mississippi-Atchafalaya river system (MARS) are augmented substantially by new marine production. Continuous increases in the nitrate load of the river system during the past few decades are hypothesized to have enhanced primary productivity in shelf waters (Rabalais et al. 1991). This OC fuels oxygen consumption and leads to observed instances of chronic hypoxia along the Louisiana continental shelf (Rabalais et al. 1994). Bacterial decomposition of OC in both the water column and sediments is important; however, the relative importance of each is not well established for the Louisiana shelf (Dagg et al. 1991; Benner et al. 1992). Globally, Smith and Hollibaugh (1993) estimate that 70% of respiration in the coastal zone occurs in the water column and 30% on the bottom, with respiration exceeding primary production by only ~1%. Knowledge of the sources, transport, and fate of biogenic carbon on the Louisiana shelf is critical to understanding the development and persistence of shelf hypoxia, as well as to the overall cycling of carbon.

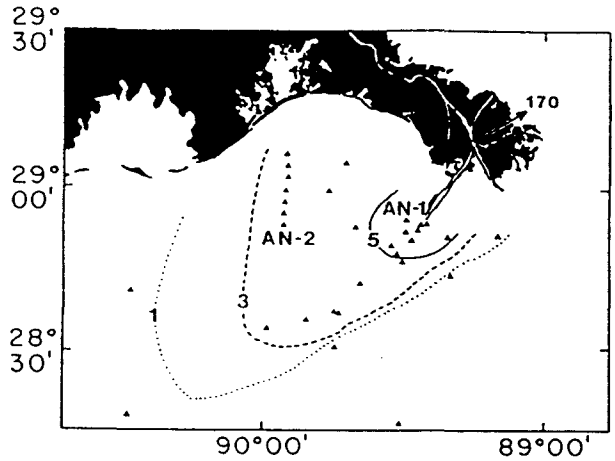

Fig. 1. Map showing study area at the Mississippi River and adjacent continental shelf with generalized distribution of total suspended matter (TSM) in surface waters (0–5 m) for February 1991. Numbers given on the map show TSM values in mg l^{-1} for Head of Passes and broad areas seaward of the river. Solid triangles identify key station locations, including anchor stations 1 and 2 (AN-1, AN-2). Additional sites were sampled to the west of the area shown here.

Materials and Methods

During July–August 1990 and February–March 1991, 50 stations were occupied on each of two cruises of the Nutrient-Enhanced Coastal Ocean Productivity (NECOP) Program of the National Oceanic and Atmospheric Administration (NOAA). The area shown in Fig. 1, plus an additional 50 km to the west, were sampled using a rosette equipped with a Neil Brown conductivity-temperature-depth (CTD) system, Sea Tech transmissometers, and General Oceanics Go-Flo water bottles. To best match real-time data with results from water samples, the CTD sensor and optical path of the transmissometer were placed approximately at the vertical center of the Go-Flo bottles. The CTD and transmissometer data were used to provide snapshots of the hydrography and distribution of suspended particles throughout the study area.

Sample sites were chosen to provide a river mouth to shelf edge transect, a transect from the head of the Mississippi Canyon to the area of chronic hypoxia, the hypoxia area, and offshore stations. In addition to the sample sites described above, two anchor stations (AN-1 at 28°54.4'N, 89°29.9'W and AN-2 at 28°53.5'N, 89°56.1'W) were occupied for approximately 36 h each on both cruises (Fig. 1). Anchor station 1 (AN-1) was chosen to characterize temporal variations in the concentrations and composition of particles within hundreds of meters of the river mouth at Southwest Pass. Anchor station 2 (AN-2) was situated 30

km west of Southwest Pass within an area of chronic hypoxia as established by the ongoing monitoring of Rabalais et al. (1991). At each anchor station, a current record was obtained in the near-bottom flow field using a General Oceanics winged current meter.

To complement the data obtained by CTD, transmissometer, we collected 400 particle samples on both glass-fiber filters and polycarbonate filters during the July–August 1990 and February–March 1991 cruises for chemical analysis. The water samples were collected either with 10-l Go-Flo bottles or by in-situ pumping. All filtrations of water samples were carried out immediately upon collection in a NOAA clean van aboard ship.

Suspended matter collected on precombusted, 13-mm Whatman GF/F glass-fiber filters was used to determine concentrations of POC and particulate organic nitrogen (PON). To obtain the OC fraction of each sample, all filters were placed in a desiccator along with a small beaker containing 10 ml of concentrated HCl. Fumes that evolved from the acid in this closed container decomposed any $CaCO_3$ present in the samples. The complete efficiency of this technique was tested using replicate aliquots of $CaCO_3$. Following acid treatment, analyses for POC and PON were carried out by placing a filter in a 10-mg tin cup and combusting the samples at 1,000°C using a Carlo Erba NA1500 NCS system. Measurements for particulate nitrogen include organic nitrogen as well as adsorbed ammonia; however, the fraction of total particulate nitrogen that is inorganic is small (Meybeck 1982) and PON is used to identify the resultant data in this paper. Instrumental precision was generally 2% or better based on analysis of numerous triplicate samples. Reproducibility for field replicates tended to be higher, as much as 20% in some surface water samples. Where such large variations were observed, they most likely resulted from particle inhomogeneities at low total suspended matter (TSM) values along with possible particle settling in the Go Flo bottles, even though the bottles were shaken regularly during the filtration process. The accuracy of the technique was within 2% of values obtained by the National Research Council of Canada for their standard sediments MESS-1 and BCSS-1.

The OC content of sediments from the Mississippi Delta was determined for samples pretreated with acid to remove any inorganic carbon present. Initially, 5 ml of H_2SO_3 were added to preweighed aliquots of sediment to remove any $CaCO_3$ present in the samples and then oven dried at 70°C. Approximately 10–15 mg of pretreated sediment were added to the tin cups and analyzed as described above.

Water samples for carbon isotope analysis were carefully vacuum-filtered through precombusted (4 h @ 400°C), 47-mm Whatman GF/F glass-fiber filters. When the filtration rate slowed significantly, the filter was evacuated to dryness and the vacuum broken. Approximately 10 ml of 1 N HCl were added to a funnel and allowed to drip through the filter to remove $CaCO_3$. Each filter was rinsed with ~5 ml of distilled water, vacuum-dried, and stored frozen in a precleaned plastic Petri dish.

In preparation for $\delta^{13}C$ analysis, filters were cut into quarters, rolled with some precombusted CuO, placed in a 9-mm Vycor sample tube and evacuated to dryness. Approximately 2 g of CuO and 1 g of Cu were then added to the sample, and the sample was evacuated and sealed. Samples were combusted for 6 h at 750°C, cooled to 600°C for 2 h, and then allowed to cool to ambient temperature. Carbon dioxide was separated by cryogenic vacuum distillation and $\delta^{13}C$ was measured using a VG PRISM isotope ratio mass spectrometer. Results are reported versus the PDB standard with an analytical precision of 0.1‰.

Concentrations of inorganic (carbonate) C in suspended matter and sediment samples were determined by the gasometric method of Schink et al. (1978). Samples of 2–5 g were analyzed to obtain reliable data. The method was standardized using pure $CaCO_3$. Precision of 5% or better was obtained at levels of 1–2% carbonate.

Concentrations of suspended matter along with particulate Al were determined in samples collected on 0.4-μm pore size polycarbonate filters. Analysis for Al was by atomic absorption spectrophotometry following complete digestion with HF-HNO_3 in a sealed Teflon tube (Trefry and Trocine 1991).

River Particles and POC

Concentrations of suspended particles in the Mississippi River at Head of Passes averaged 44 mg l^{-1} and 170 mg l^{-1} for the July–August 1990 and February–March 1991 cruises, respectively (Table 1). Higher values during February–March 1991 were consistent with increased water flow and sediment discharge (Table 1). In addition to the 1990 and 1991 samples, we also have collected multiple samples from the Mississippi River on eight previous occasions that include four seasonally-spaced periods during 1982–1983 and four times during 1974–1975. Our river data span 17 yr and include a variety of water depths from the surface to 11 m at Head of Passes (Table 1). Values for total suspended matter (TSM) at Head of Passes vary seasonally by a factor of 10 or more (Table 1; Everett 1971), with highest values generally measured dur-

TABLE 1. Mean concentrations of total suspended matter (TSM), particulate organic carbon (POC), particulate organic nitrogen (PON), and supporting parameters for selected dates at Head of Passes in the lower Mississippi River.

Date	TSM (mg l^{-1})	POC (μmol l^{-1})	POC (%)	PON (μmol l^{-1})	PON (%)	C/N (molar ratio)	Water Flow (10^6 l s^{-1})[a]	Sediment Discharge (10^6 g s^{-1})[a]
February 1991	170	330	2.28	—	—	—	26.0	5.4
July 1990	44	105	3.72	11.4	0.48	9.2	13.1	2.7
November 1983	21	38	2.15	4.3	0.28	8.8	8.0	0.7
April 1983	200	212	1.40	20.7	0.14	10.2	30.0	7.1
September 1982	85	118	1.78	11.4	0.19	10.4	11.0	3.0
May 1982	110	172	1.93	17.1	0.22	10.1	14.0	4.9
November 1975	38	93	2.80	—	—	—	8.8	3.2
September 1975	11	68	7.70	—	—	—	6.8	0.9
August 1975	136	217	1.91	23.6	0.24	9.2	13.3	4.5
March 1975	119	155	1.56	15.0	0.18	10.3	21.2	5.4
May 1974	144	254	2.12	25.0	0.24	10.2	16.4	7.3

[a] At Tarbert Landing, downstream of the diversion channel to the Atchafalaya River.

ing the late-winter and spring runoff and lowest values during late summer and early fall.

Concentrations of POC in the Mississippi River at Head of Passes averaged 105 μmol l^{-1} (1.26 mg l^{-1}) during the summer 1990 cruise and 330 μmol l^{-1} (4.0 mg l^{-1}) during the winter 1991 cruise. Although POC values (in μmol l^{-1}) were higher during winter, these particles contained less OC on a weight percent basis than observed during the low TSM summer period (Table 1). Within our multiyear dataset (n = 27), POC values ranged from 40 μmol l^{-1} to 600 μmol l^{-1} and correlated well with concentrations of TSM (Fig. 2). Data from the 1969–1970 study of Malcolm and Durum (1976) also fit the trend we observed very well (Fig. 2). Thus, the strong POC versus TSM relationship shown in Fig. 2 and discussed below suggests that we can predict POC values from TSM concentrations.

Good correlations between POC (in μmol l^{-1}) versus TSM, resulted from a relatively uniform %OC in Mississippi River particles. At TSM concentrations >50 mg l^{-1}, our values for %POC in the river particles averaged 1.8 ± 0.3% (Fig. 3). These results compare well with values of 2.0 ± 0.4% POC reported by Malcolm and Durum (1976) for Mississippi River samples with TSM > 50 mg l^{-1} (Fig. 3). As TSM concentrations decreased below 50 mg l^{-1}, the %OC content of the particles increased sharply. This trend is consistent with previously defined patterns for world rivers by Meybeck (1982) and Milliman et al. (1984) as shown on Fig. 3. We have chosen to present our data in Fig. 3 with linear coordinates, rather than

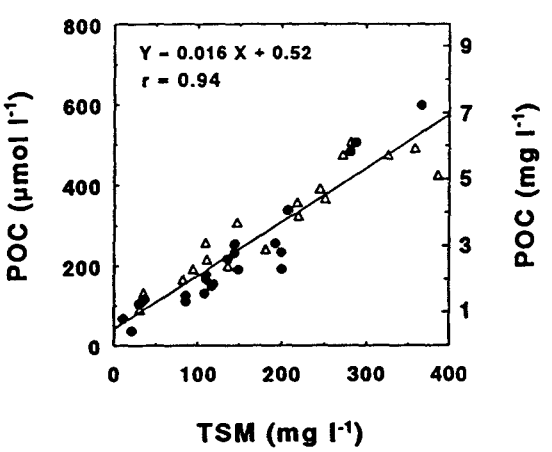

Fig. 2. Scatter plot showing concentrations of particulate organic carbon (POC) versus total suspended matter (TSM) for the lower Mississippi River. Solid circles are for data from this study and open triangles are for data from Malcolm and Durum (1976). The line, equation, and correlation coefficient (r) are from linear regression of both datasets.

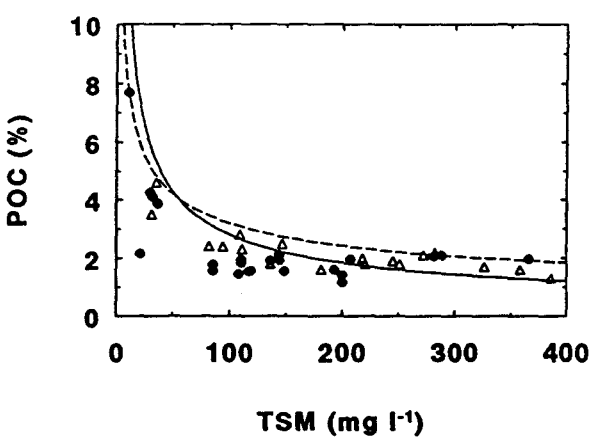

Fig. 3. Plot showing concentrations of particulate organic carbon (POC) on a weight percent basis versus total suspended matter (TSM) for the lower Mississippi River. Solid circles are from data reported in this study and open triangles are for data from Malcolm and Durum (1976). Solid line shows trend for world rivers from Meybeck (1982) and dashed line shows trend for Yangtze River from Milliman et al. (1984).

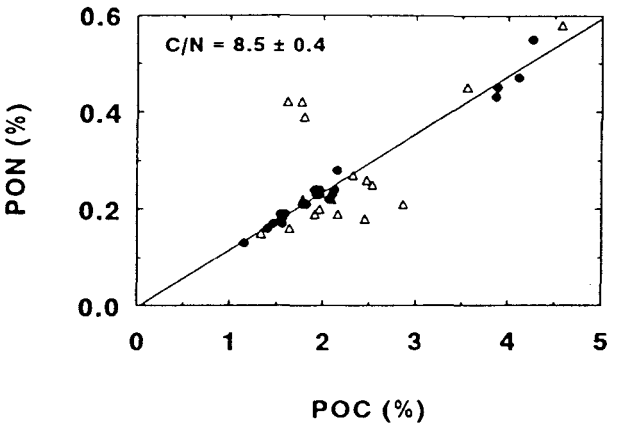

Fig. 4. Scatter plot showing concentrations of particulate organic carbon (POC) versus particulate organic nitrogen (PON) on a weight percent basis for the lower Mississippi River. Solid circles are from data reported in this study and open triangles are for data from Malcolm and Durum (1976). The line is from a linear regression fit for data from this study.

on logarithmic scales, to more clearly show the relatively uniform %POC in the river on most occasions.

Our measured values for POC also correlate well with those for PON ($r = 0.99$) with an average C:N ratio of 8.5 on a weight percent basis (Fig. 4). This C:N ratio is the same as that shown by Meybeck (1982) for selected North American rivers and within the range of 8 to 10 typically found for world rivers. Meybeck (1982) ascribed this range of ratios in suspended particles to a mixture of aquatic plants (C:N = 5.7 by wt), terrestrial plants (C:N = 6 by wt), and average soil (C:N = 10 by wt). Although somewhat more scattered, data from Malcolm and Durum (1976) fit the same overall trend we observed. They suspect that some of the deviant points may be related to seasonal shifts in the composition of terrigenous POC.

The long-term uniformity of the %POC values from our work and those of Malcolm and Durum (1976) justify a straightforward approach to calculating POC transport wherein the total suspended sediment load of the river is multiplied by an average value for %POC. Meade and Parker (1985) calculated an annual sediment load of 210 $\times 10^{12}$ g yr^{-1} for the Mississippi-Atchafalaya river system, averaged for the past 25 yr. R. H. Meade (personal communication) has just compiled a 29-yr mean value of 140 $\times 10^{12}$ g yr^{-1} (Fig. 5a) for just the Mississippi River, which carries about 70% of the total transport of the MARS. Using a value of 140 $\times 10^{12}$ g suspended sediment yr^{-1} and 1.8% POC for the Mississippi River, we calculated a long-term average of 0.21 $\times 10^{12}$ mol POC yr^{-1}. One possible limitation to this estimate is that few samples were collected during very high sediment flow. For example, only three of the TSM values obtained by Malcolm and Durum (1976) and one of our values are close to or above the reported 360 mg TSM l^{-1} average for the river (Fig. 2). Unpublished reports from the United States Geological Survey (USGS) suggest that the long-term average POC concentration may be closer to 1.5% or 1.6%. However, assuming that %POC does not decrease considerably as TSM levels increase above 400 mg l^{-1} (Fig. 3; Milliman et al. 1984), our estimate of POC transport based on sediment load seems within 10–15% of probable levels. Assuming similar %POC values for the Atchafalaya River, total POC transport by the MARS is 0.32 $\times 10^{12}$ mol yr^{-1}.

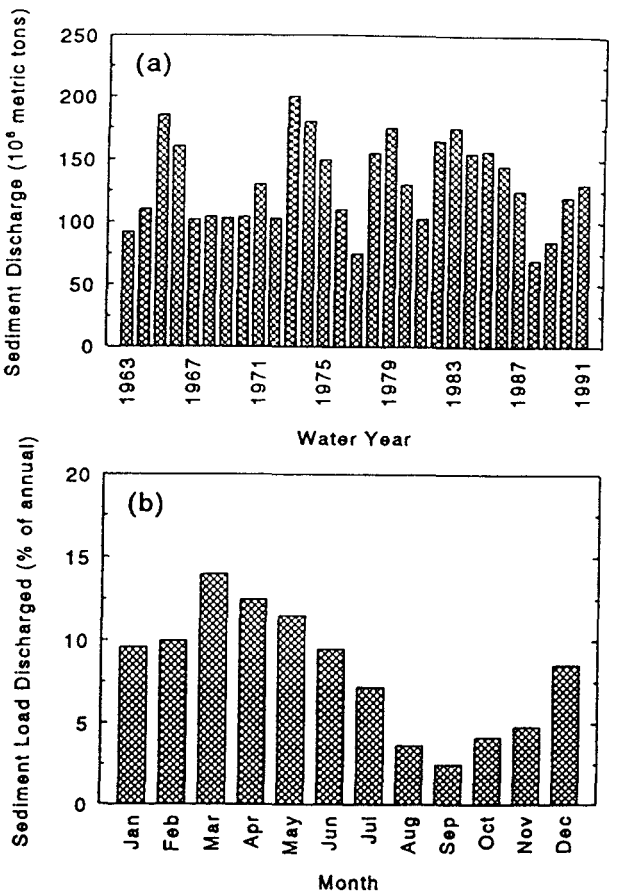

Fig. 5. (a) Annual suspended-sediment discharges of the Mississippi River at Tarbert Landing, Mississippi, from 1963 (the year the Old River Control Structure was completed and regulation of the Atchafalaya River began) to 1991. (b) Monthly averages of suspended-sediment discharges for 1963–1991. Data compiled in May 1993 by R. H. Meade from data of the United States Army Corps of Engineers, New Orleans District, and the United States Geological Survey, Baton Rouge.

We also measured an average of 0.15% particulate inorganic carbon (~1.3% $CaCO_3$) for sus-

pended matter samples from Head of Passes. This value is the same as Malcolm and Durum (1976) reported for the Mississippi River but considerably lower than the world average value of 0.9% particulate inorganic carbon (PIC) presented by Meybeck (1982). Based on our value, the PIC load of the Mississippi River is 0.018×10^{12} mol yr^{-1} (0.026×10^{12} mol PIC yr^{-1} for the MARS) and represents ~8% of the total particulate carbon (POC + PIC).

Reported concentrations of DOC in the Mississippi River do not vary greatly on a per liter basis. Trefry and Presley (1976) found an average of 270 ± 30 μmol DOC l^{-1} during 1974–1975 and Malcolm and Durum (1976) reported 280 ± 50 μmol DOC l^{-1} for 1969–1970. Benner et al. (1992) measured values of 330 μmol l^{-1} and 270 μmol l^{-1} for summer 1990 and winter 1991, respectively. During most sampling periods, concentrations of DOC behave conservatively (± 10%) across the freshwater-seawater mixing zone. Taking an overall average of 280 μmol l^{-1} (3.4 mg l^{-1}) and an annual water flow for the Mississippi River of 4.1×10^{14} l yr^{-1} (Milliman and Meade 1983), DOC transport is calculated at 0.11×10^{12} mol yr^{-1} (or 0.16×10^{12} mol DOC yr^{-1} for the MARS).

Using grand averages, we calculate overall TOC transport of the Mississippi-Atchafalaya river system to be 0.48×10^{12} mol yr^{-1}, with 66% of the TOC associated with particles. Our total transport value is about 20% higher than that calculated for a single water year by Malcolm and Durum (1976); however, it is consistent with annual variations in sediment and water transport (Fig. 5a). Overall, our results show that large amounts of particulate organic carbon are carried by the Mississippi-Atchafalaya river system to the Gulf of Mexico, with about 80% of the sediment transport, and thus POC transport, occurring during the 7-mo period from December to June (Fig. 5b).

Shelf Trends for Suspended Particles and POC

As the Mississippi River empties into the Gulf of Mexico, a sharp decrease in TSM values for surface waters (0–5 m) to <10% of levels at Head of Passes occurs within 5 km of the river mouth at Southwest Pass. A further decrease of TSM in surface waters to <3 mg l^{-1} was observed 15–30 km from the river in July–August 1990 and 30–70 km in February–March 1991 (Fig. 1). The generalized spatial extent of particle loadings during the higher-flow winter 1991 sampling can best be compared with the low-flow summer 1990 period by noting that the 3 mg l^{-1} contour for winter (shown in Fig. 1) approximately matched the 1 mg l^{-1} boundary for the summer sampling.

Seasonal variations in the concentrations of suspended matter near the river mouth contribute to shifts in the sites of maximum productivity. Lohrenz et al. (1992) found generally lower primary production at low salinities near the mouth of the Mississippi River, with highest levels at intermediate salinities. Comparison of Lohrenz et al.'s (1992) contour maps for integral biological production with our distributions of TSM show that productivity is low in the >5 mg TSM l^{-1} area near the river mouth with maximum productivity values in the region where TSM values are between 3 mg l^{-1} and 5 mg l^{-1}. The negative influence of river-borne particles combined with the positive effect of river-derived nutrients seem to be optimized for productivity some 20–100 km west of the mouth of Southwest Pass. This area of high productivity coincides with the eastern region of documented seasonal hypoxia (Rabalais et al. 1991).

The spatial distribution of POC during winter 1991, follows the trend for suspended particles in the area (Fig. 1), with values decreasing from 50 μmol l^{-1} near the river mouth to about 15 μmol POC l^{-1} in surface water by station AN-2. Beyond that point, the pattern is patchy, with values of <2 μmol POC l^{-1} to 50 μmol POC l^{-1}. In contrast, even though river flow and particle loading were lower during the summer 1990 cruise, POC levels on the shelf were generally higher, with values of 30–90 μmol POC l^{-1} for more than 100 km along the Louisiana shelf. Thus, more organic-rich particles and higher levels of POC were present during the summer sampling period.

In addition to broad spatial patterns for TSM and POC, short-term (hours to days) shifts in the concentrations of suspended particles and POC were also observed along the shelf at AN-1 and AN-2, located adjacent to the mouth of Southwest Pass and within the area of chronic hypoxia, respectively. For example, at AN-1 during February–March 1991, surface salinities varied from <5‰ to 18‰; TSM concentrations varied indirectly with salinity and ranged from 4 mg l^{-1} to 25 mg l^{-1} over about 30 h. This observation is common in this area and is related to tidal effects.

Within the near-bottom nepheloid layer (~27 m) at AN-1, salinity remained at about 36‰; however, short-term variations in TSM values from <1.5 mg l^{-1} to 9 mg l^{-1} were observed (Fig. 6). These changes in concentrations of suspended particles in near-bottom water can be directly related to passage of a short-duration weather front over the site. As the front passed, bottom current velocities increased from about 5 cm s^{-1} to about 35 cm s^{-1} (Trefry et al. 1992), with a concurrent increase in concentrations of TSM (Fig. 6). Even though levels of TSM increased considerably during passage of the front, the %POC content of the parti-

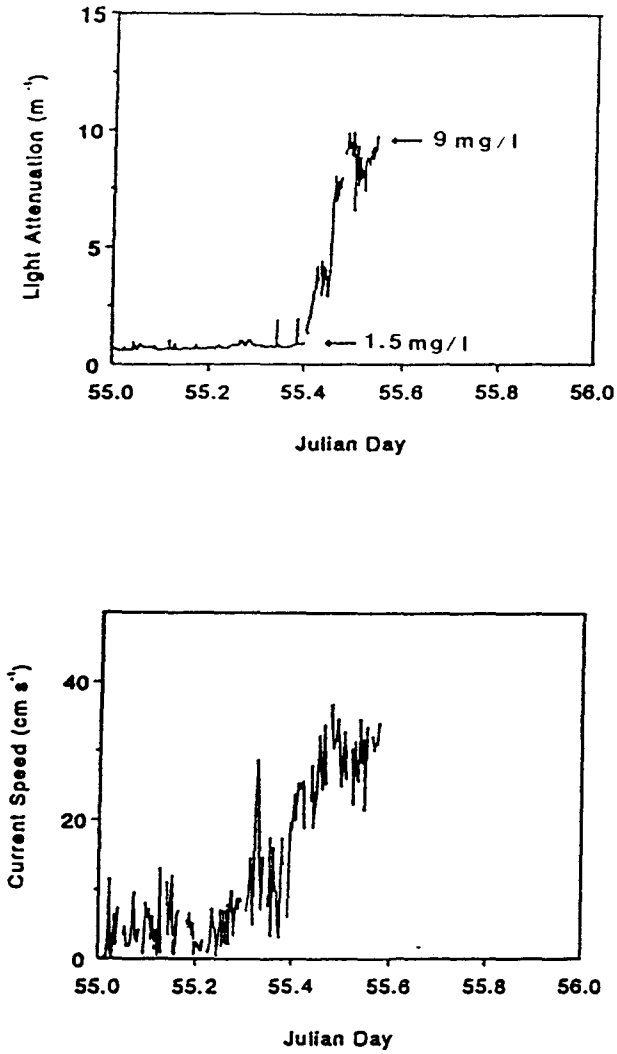

Fig. 6. Upper graph illustrates light attenuation for 25-cm path length transmissometer versus time with corresponding total suspended matter concentrations noted in mg l^{-1} and lower graph illustrates current speed versus time for February 24, 1991, at anchor station 1 (AN-1) at the mouth of the Mississippi River modified (from Trefry et al. 1992).

cles remained relatively uniform at 4.4 ± 1.2%. Thus, the net transport of POC followed the trend observed for TSM. These changes in particle loading share a direct relationship with oxygen depletion as will be described below.

Concentrations of POC for the waters of the Louisiana shelf can be divided into terrigenous and marine components using both the POC:Al ratio and $\delta^{13}C$ values. The POC:Al ratio at Head of Passes varies somewhat seasonally, with values of 0.49 for July–August 1990 and 0.32 for February–March 1991. Higher POC:Al ratios for the summer 1990 samples are consistent with lower TSM values (Fig. 3) and possibly more autochthonous POC. However, these river differences are small relative to POC:Al ratios of >50 along the shelf when terrigenous material settles out of the plume and production of marine POC begins. By multiplying the Al concentration for a given sample by the riverine POC:Al ratio, we can estimate the terrigenous fraction of the POC as shown by

$$\text{Terrigenous OC} = [\text{Al}]_{\text{sample}} \times (\text{POC/Al})_{\text{MARS}} \quad (1)$$

The marine POC is calculated by subtracting the terrigenous POC from the total POC. Values for $\delta^{13}C$ can be used in the same manner. The $\delta^{13}C$ of terrigenous POC in the Mississippi River is about −25.5‰, increasing to −19.5‰ in the marine POC. By assuming a $\delta^{13}C$ of −25.5‰ for the terrigenous endmember and −19.5‰ for the marine endmember, we can estimate the relative contributions of river runoff versus new production using the $\delta^{13}C$ value for a given sample. Agreement between the two approaches is good in most instances. A tendency to overestimate the terrigenous POC using the POC:Al ratio may be a potential problem in aged samples as the more labile components of this fraction are decomposed. However, because the terrigenous component of the POC generally decreased quickly away from the river mouth, this effect seems to be minimal. Thus, the overall combined approach provides a good along-shelf perspective of sources and transport of POC.

Temporal and spatial trends in POC can be seen in Fig. 7 at anchor stations 1 and 2 for the summer 1990 and winter 1991 cruises. At AN-1, the terrigenous POC in surface waters is almost 50 μmol l^{-1} in February–March 1991 relative to 20 μmol l^{-1} in July–August 1990 (Fig. 7). This difference occurs in response to an increased particle load and POC levels in the river during the late winter period (Table 1). The seasonal difference in marine POC in surface water at AN-1 is equally dramatic; however, the trend is reversed in the summer with a five times higher marine component (Fig. 7). In subsurface waters, the terrigenous component is an important fraction of the total POC during both sampling periods. Collectively, these trends for POC at AN-1 reflect the seasonal influence of riverine inputs of POC and nutrients, along with shelf hydrography, on levels of terrigenous and marine POC in near-river-mouth waters.

At AN-2, some 30 km to the west, values for terrigenous POC (Fig. 7) were lower than at AN-1 during both cruises with all values <5 μmol l^{-1}. Values for marine POC at AN-2 are similar throughout the water column for both the summer and winter cruises. If we compare integrated values for marine POC over the entire water column (0–38 m), the integrated value at AN-2 of 370 mmol

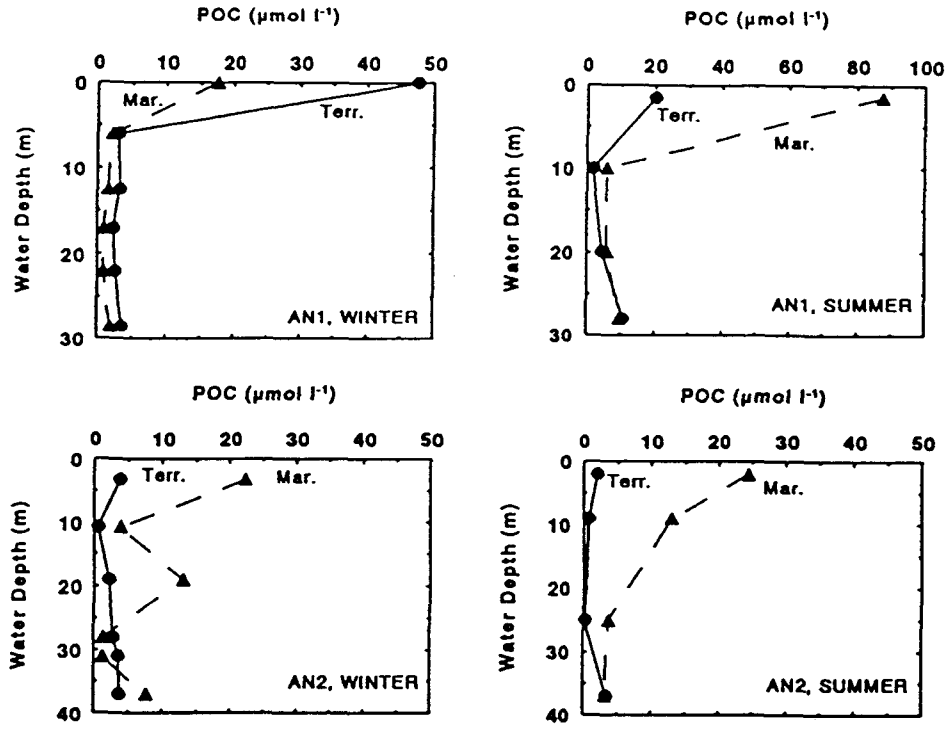

Fig. 7. Graphs showing values for terrigenous (Terr.) and marine (Mar.) particulate organic carbon (POC) versus depth for anchor stations 1 and 2 (AN-1 and AN-2) during July–August 1990 (Summer) and February–March 1991 (Winter).

POC m^{-2} for summer 1990 is only 25% higher than calculated for winter 1991. In near-bottom water samples, the terrigenous POC is again an important fraction of total POC during both summer and winter.

A primary focus of the NECOP program is to understand the mechanisms that lead to development of seasonal hypoxia along the Louisiana shelf. Hypoxia (dissolved oxygen concentrations <60 μmol l^{-1} or <2 mg l^{-1}) has been found to extend over areas as large as 9,000 km^2 in bottom waters along the Louisiana shelf (Rabalais et al. 1991). One method for assessing and tracking trends in oxygen distribution is by apparent oxygen utilization (AOU) values. Concentrations for AOU are calculated here in μmol l^{-1} using the equations of Chen (1981):

$$\ln O_{sat} = -1268.9782 + 36063.19/T_{Kelvin} + 220.18329(\ln T_{Kelvin}) - 0.351229(T_{Kelvin}) + \text{Salinity}(0.006229 - 3.5912/T_{Kelvin}) + 0.00000344(\text{Salinity})^2 \quad (2)$$

$$AOU = [-(D_{O_2} - O_{sat})/22393] \times 1{,}000{,}000 \quad (3)$$

where

O_{sat} = the dissolved oxygen concentration in ml l^{-1} at saturation.

D_{O_2} = observed dissolved oxygen concentration for a given sample (ml l^{-1}).

Values for AOU at AN-1 of 50–100 μmol l^{-1} during July–August 1990 are only slightly greater than those for February–March 1991 (Fig. 8). However, during the summer sampling period a distinct trend of increasing AOU with depth is observed. Maximum values for AOU of 100 μmol l^{-1} at station AN-1 represent consumption of about 60% of the dissolved oxygen in these waters from near the mouth of the Mississippi River.

During both time periods, values for AOU between stations AN-1 and AN-2 increase significantly in the bottom water (Table 2). This trend is consistent with continued oxygen consumption west of the river mouth. In contrast with this spatial trend, seasonal differences in verical profiles for AOU between the July–August and February–March sampling periods are relatively small (Fig. 8). In many ways, the bottom water at station AN-2 is poised near hypoxia during both periods (Table 2).

Spatial trends for POC and AOU observed between AN-1 and AN-2 can be followed farther west into an area of more intense seasonal hypoxia. At

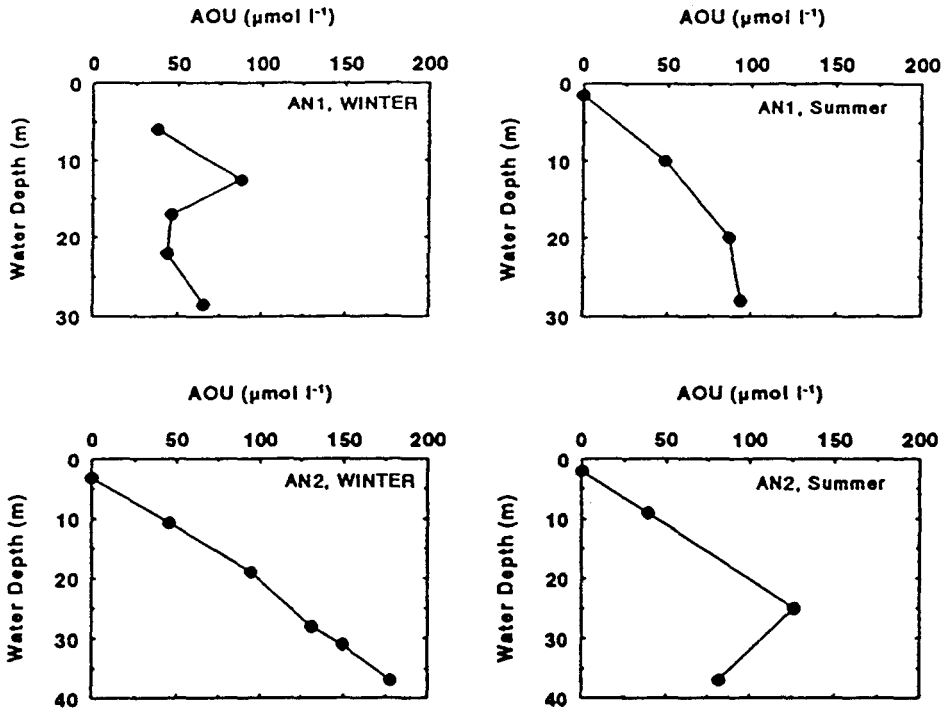

Fig. 8. Graphs showing values for apparent oxygen utilization (AOU) versus depth for anchor stations 1 and 2 (AN-1 and AN-2) during July–August 1990 (Summer) and February–March 1991 (Winter).

station 26, some 100 km west of station AN-2 (28°36.4′N, 91°00.8′W), during February–March 1991, POC values were 6–26 μmol l^{-1}, essentially all marine and similar to concentrations observed at station AN-2 (Fig. 7). However, levels of AOU at station 26 of 100 μmol l^{-1} were somewhat less than observed at station AN-2 (Table 2) during this time of year. In contrast to our winter observations, POC values during July–August 1990 in this area at 91°W were 6–50 μmol l^{-1} and levels of AOU approached 200 μmol l^{-1}. Measured concentrations of dissolved oxygen were as low as 12 μmol l^{-1} (0.4 mg l^{-1}). Thus, AOU values continue to increase toward the west during the summer.

In addition to the seasonal and spatial changes discussed above, we also have observed small but consistent short-term shifts in TSM and AOU while occupying the anchor stations. For example, data for bottom water from station AN-2 during summer 1990 show a statistically significant increase in TSM of 0.5 mg l^{-1} coupled to an AOU increase of 10 μmol l^{-1} over a 3-h time period (115–298 min, Fig. 9). Salinity varied by <0.01‰ and tempera-

TABLE 2. Hydrographic and chemical data for bottom water samples from anchor stations 1 and 2 located 0.5 km and 30 km, respectively, west of Southwest Pass. TSM = total suspended matter, POC = particulate organic carbon, AOU = apparent oxygen utilization.

	Anchor 1		Anchor 2	
	July 1990	March 1991	July 1990	March 1991
Depth (m)	27.6	27.5	37.1	36.2
Salinity (‰)	35.8	36.2	36.0	36.4
Temperature (°C)	24.88	20.64	24.80	20.65
TSM (mg l^{-1})	5.0	1.7	2.9	1.6
POC (μmol l^{-1})	15.2	5.5	16.2	11.2
POC (%)	3.6	3.8	6.6	6.6
Measured				
O_2 (μmol l^{-1})	80	160	85	103
AOU (μmol l^{-1})	95	65	127	178

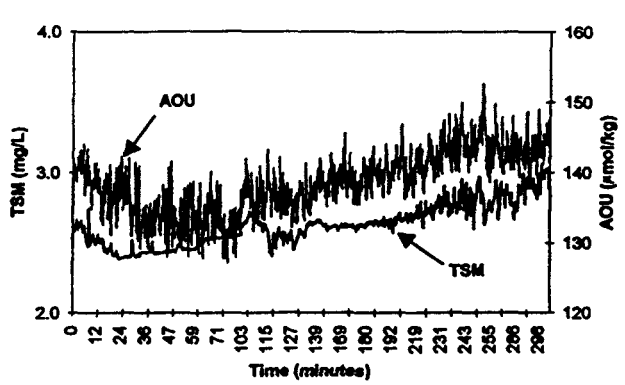

Fig. 9. Plot showing trends in total suspended matter (TSM) and apparent oxygen utilization (AOU) versus time for near-bottom water at 28 m for anchor station 2 (AN-2).

ture by <0.04°C during the same time period. Similar events were observed during each occupation of the anchor sites.

One possible explanation for the coincident TSM and AOU increases is that particles are serving as a substrate for bacterial activity as described by Benner et al. (1992) and that net consumption of oxygen is related to the mass of particles moving along with a given parcel of water. Thus, as the particle load of the water shifts, a corresponding shift in AOU is observed. Given a change in AOU of 10 μmol l^{-1} over the time interval shown in Fig. 9, along with a ratio of 1.3 for the ratio of oxygen utilization:OC consumption, an additional 13 μmol of OC l^{-1} had been decomposed in the waters that flowed by station AN-2 near the end of the time interval. The 13 μmol OC l^{-1} that would need to decompose in order to produce the observed ΔAOU represent about 10% of the TOC in the bottom water at the end of the observation period (POC ~30 μmol l^{-1} and DOC ~80 μmol l^{-1}). The relative consumption of POC versus DOC is not well-defined at this time; however, the particles certainly serve as an important bacterial substrate (Benner et al. 1992). This scenario for oxygen consumption along the Louisiana shelf enroute to station AN-2 invokes a continuous process of OC consumption in the water column by bacteria during particle transport and water mass movement over distances of 30 km and a period of one to several days.

Water-column POC is eventually delivered to the sediments; however, concentrations of sediment organic carbon on the Louisiana shelf are far below those predicted from combined inputs of riverine POC plus primary productivity. Analyses of more than 50 surficial sediments from the Mississippi Delta show that sediments typically contained 1.4 ± 0.2% OC, whereas particles from the Mississippi River averaged 1.8 ± 0.3% OC. Superimposed on riverine inputs of terrigenous OC is carbon fixed during primary productivity. Using primary production rates of 50–300 g C m^{-2} yr^{-1} (Redalje et al. 1992) for an area where sediment accumulation rates average 5,000 g m^{-2} yr^{-1}, we predict that sediments could contain a range of ~3–8% OC [(1.8% terrestrial) + (1–6% marine)]. Comparing this value with the 1.4 ± 0.2% OC present in sediments indicates that only 20–50% of the TOC is actually buried. Furthermore, $\delta^{13}C$ values for shelf sediments (Eadie et al. 1994) suggest that <40% of the OC buried is terrigenous. One possible explanation for this observation is that POC is transported off the shelf and buried in slope sediments as postulated by Walsh et al. (1981). However, concentrations of OC in slope sediments are consistently less than the 1.8% OC observed in riverine particles. Therefore, the conclusion at this time is that respiration of sizable amounts of both terrigenous and marine OC on the shelf, as well as export of OC to the open waters of the Gulf of Mexico balance the coastal carbon budget along the Louisiana shelf in the same manner as projected globally by Smith and Hollibaugh (1993).

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