

Transport and fate of dissolved organic carbon in the Lake Pontchartrain estuary, Louisiana, U.S.A.

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Abstract. Cycling dynamics of dissolved organic carbon (DOC) were examined in Lake Pontchartrain estuary, Louisiana, in relation to changes in freshwater inputs. DOC concentrations ranged from 5.3 to 8.5 mg C L⁻¹ reaching their highest during high river inflow. The percentage of DOC represented by HMW DOC (or colloidal material) was greatest (ca. 11%) at stations where freshwater discharge from rivers and surrounding wetlands was most significant. Moreover, the lignin-phenol content of this material (λ ranged from 0.09 to 0.33 and Λ from 0.11 to 0.39) confirmed that a significant fraction of colloidal organic carbon was derived from terrestrial sources. Riverine and benthic fluxes represented the dominant sources of DOC to the estuary. On an annual basis, riverine and benthic DOC concentrations were estimated to be 2.8×10^{10} g C yr⁻¹ and 8.8×10^{10} g C yr⁻¹, respectively, while the total DOC pool in the estuary was 3.8×10^{10} g C. Annual average concentrations of dissolved inorganic carbon (DIC) (1298 μ M) and pCO₂ (5774 μ atm) were comparable to those found in other freshwater systems that reached CO₂ saturation levels. Net losses of DOC in the Lake Pontchartrain estuary appeared to be primarily controlled by heterotrophic consumption (conversion of CO₂) – which may have been amplified by the long residence time (approximately 120 days) of DOC in this system.

Introduction

A diverse array of allochthonous and autochthonous dissolved organic carbon (DOC) sources enter into the food webs of riverine and estuarine ecosystems (Wetzel 1984; Valiela 1995). Temporal variations of these carbon sources usually vary seasonally with maximum phytoplankton production in summer and peak allochthonous inputs in spring and winter or late fall. Recent work in coastal and oceanic systems has shown that there is a correlation between chlorophyll-*a* (an indicator of phytoplankton biomass) and DOC concentrations, because phytoplankton represents the dominant source of the DOC pool (Guo et al. 1994; Santschi et al. 1995). Conversely, other work has shown that chlorophyll-*a* is not well correlated with DOC concentrations

in estuarine and freshwater ecosystems, due to allochthonous DOC inputs from vascular plants (Bianchi et al. 1997). It has been well established that high concentrations of DOC typically found in freshwater systems are due to inputs from non-planktonic sources (i.e., littoral macrophytes, terrestrial and wetland inputs) (Wetzel 1984; Malcolm 1990; Mann & Wetzel 1995; Wetzel et al. 1995). Moreover, it has also been shown using biomarkers of terrestrial sources of organic carbon (i.e., lignin-phenols) that a substantial fraction of the DOC (40 to 60%) pools in estuarine and coastal systems can be comprised of land-derived materials (Moran et al. 1991).

A significant fraction (10 to 70%) of the total DOC in marine systems is usually represented by high molecular weight (HMW DOC) material usually greater than 1 kD (Carlson et al. 1985; Benner et al. 1992; Ogawa & Ogura 1992; Guo et al. 1994, 1995; Buesseler et al. 1996). This material is colloidal in nature rather than “truly” dissolved (Carlson et al. 1985; Benner et al. 1992; Guo et al. 1994; Santschi et al. 1995). Although colloids are formed by a variety of abiotic and biotic processes (Sholkovitz 1976; Carlson et al. 1985); direct exudation from phytoplankton appears to be the major pathway in the open ocean and in some estuarine systems (Sigleo et al. 1983; Kirchman et al. 1991; Kepkay et al. 1993; Bianchi et al. 1995). The major biochemical components of colloidal material, derived from fragmentation or digestion of algal cells are likely to be proteins, lipids, and nucleic acids (Lewin 1974; Lee & Henrichs 1993). While many of the estuarine and freshwater systems have HMW DOC that is derived from terrestrial sources, recent studies have shown that this colloidal material is more degradable – according to the size-reactivity continuum model (Amon & Benner 1996). Furthermore, experimental work has shown that a large fraction (22–99%) of this DOC can effectively be consumed by bacteria after the addition of nutrients (Zweifel et al. 1995). As a result of this heterotrophic consumption of DOC, freshwater systems receiving high inputs of DOC can also have very high CO₂ levels. For example, recent work has shown that many of the freshwater lakes in the world as well as some estuaries, are saturated with CO₂ and represent sources and not sinks to the atmosphere (Cole et al. 1994; Frankignoulle et al. 1996).

The flux of porewater DOC across the sediment-water interface has also been shown to represent an important source to the total DOC pool in both coastal and oceanic environments (Alperin et al. 1992; Burdige et al. 1992; Martens et al. 1992; Burdige & Homstead 1994). For example, it has been suggested that benthic fluxes are a significant source to coastal systems ($0.1\text{--}0.9 \times 10^{14} \text{ g C yr}^{-1}$) and may represent about the same magnitude as riverine inputs of DOC to the oceans ($2\text{--}2.3 \times 10^{14} \text{ g C yr}^{-1}$) (Burdige et al. 1992; Burdige & Homstead 1994). Near-bottom ¹⁴C-DOC data from the North Pacific indicates that sediments may also represent a significant source of

DOC to deep oceanic waters (Williams & Druffel 1987). Recent work has also shown that groundwater flux of ^{226}Ra to coastal waters of the south Atlantic Bight may be as much as 40% of the riverine flux (Moore 1996). While benthic DOC fluxes have been shown to be significant in estuarine systems (Burdige et al. 1982; Burdige & Homstead 1994), the relative importance of these fluxes in comparison to wetland and riverine inputs needs further work.

In this study, we investigated the cycling of DOC in the Lake Pontchartrain estuary in relation to the total freshwater discharge. We also used DOC inputs from rivers and sediments to develop a conceptual model that estimated the residence time of DOC in this system. Our objectives were as follows: 1) To determine the temporal and spatial distribution of DOC ($<0.2\ \mu\text{m}$) and HMW DOC ($>3\ \text{kD}$ to $<0.2\ \mu\text{m}$) at selected stations in the estuary; 2) To use porewater DOC profiles to estimate fluxes of DOC across the sediment-water interface in the estuary; and 3) To use lignin-phenols as biomarkers of terrestrial sources of HMW DOC at selected stations in the Lake Pontchartrain estuary.

Materials and methods

Site description

The Lake Pontchartrain estuary is located in the central Gulf Coastal Plain Province adjacent to New Orleans, Louisiana (Figure 1). The system is composed of two lakes, Pontchartrain (1,645 square kilometers, average depth of 4 m) and Maurepas (241 square kilometers, average depth of 2 m). Average riverine discharges into Lake Maurepas and Lake Pontchartrain are estimated to be $144\ \text{m}^3\ \text{sec}^{-1}$ and $228\ \text{m}^3\ \text{sec}^{-1}$, respectively (Flowers & Isphording 1990). Additional discharge into Lake Pontchartrain occurs from stormwater drainage as well as freshwater diversion from the Mississippi through the Bonnet Carré spillway. Bottom sediments are typically dominated by clays and silts representing 43 and 38% of the total sediment fraction, respectively (Flowers & Isphording 1990).

Sampling regime

In this study, three transects were sampled (each with three stations), representing the upper (1, 4, 7), middle (2, 5, 8) and lower (3, 6, 9) estuarine regions, respectively (Figure 1). During the period from May 1995 to May 1996, water and sediment samples were collected bimonthly aboard the R/V *Callinectes* at all nine stations. In March 1996, water samples for DOC analyses were collected from rivers (Amite River, Tangipahoa River, and Tchefuncta River) that drain into the Lake Pontchartrain ecosystem. Water samples were also collected from Lake Maurepas and Manchac Pass at this time; while these

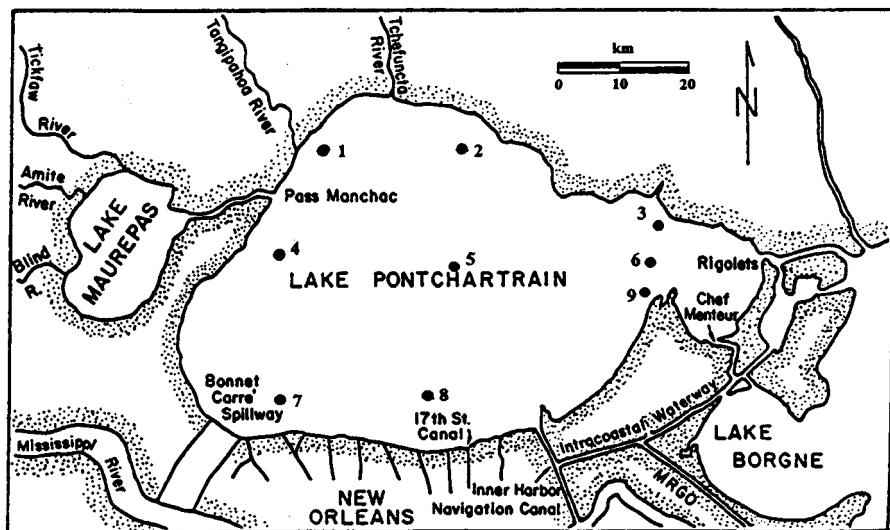


Figure 1. Map of the Lake Pontchartrain estuary, showing the nine stations (St 1, 4, 7, upper-region; St 2, 5, 8, middle-region; St 3, 6, 9, lower-region), sampled from May 1995 to May 1996.

systems were not included within our sampling stations – these regions are a part of the Lake Pontchartrain ecosystem.

Surface and bottom water samples were collected and filtered from each station using a peristaltic pump for suspended particulate matter (SPM), DOC and HMW DOC analyses. Filtration of water samples was carried out immediately upon collection and the filters frozen. Duplicate sediment samples were collected from each station using a hand-held corer. Cores were sectioned immediately at 1 cm depth intervals at a depth of 15 cm, centrifuged for porewater DOC analysis (described later), and stored frozen.

Water column

Hydrographic data such as salinity, temperature, dissolved oxygen, pH, alkalinity, and light attenuation were measured using methods described by Bianchi et al. (1997). Dissolved inorganic carbon concentrations (DIC) were calculated using alkalinity and pH data (Wetzel & Likens 1979). DIC values were also determined directly using a Shimadzu TOC 5000 analyzer. Partial pressure ($p\text{CO}_2$) and concentration of CO_2 [CO_2] were calculated, as described by Millero & Sohn (1992), assuming a Henry's law content of 0.036, $k_1 = 5 \times 10^{-7}$, $k_2 = 8.8 \times 10^{-11}$ (for a salinity range of 0.0 to 3.0‰) and $k_2 = 1.9 \times 10^{-10}$ (for a salinity range of 3.0 to 8.0‰).

DOC analysis

DOC water samples were initially filtered using pre-combusted (450 °C) GF/F Whatman filters. All DOC measurements were made using a Shimadzu TOC 5000 Analyzer according to the methods of Guo et al. (1994). Our instrument blank was 5 to 6 $\mu\text{M C}$ and our water blank was typically $<4 \mu\text{M C}$. The precision of the DOC analyses, expressed as a coefficient of variation (CV), was $<2\%$.

HMW DOC analysis

Surface waters were sampled in September 1995, and January 1996, from selected stations (St 4, 5, 6) for HMW DOC analysis. Water samples were pumped directly through a 0.2 μm Nuclepore pre-filter (in-line) into a 20 L acid-cleaned container and returned to the laboratory. HMW DOC material was then fractionated using tangential cross-flow ultrafiltration (Guo et al. 1994). An Amicon hollow-fiber polysulfone cartridge with a nominal molecular weight cut-off of 3 kD was used during September 1995 and January 1996 cruises. HMW DOC is operationally defined here as the fraction >3000 Daltons and $<0.2 \mu\text{m}$. Aliquots of pre-filtered water, ultrafiltered water, and HMW DOC concentrated water, were analyzed for DOC (Carlson et al. 1985; Guo et al. 1994). Diafiltration (removal of salts) was carried out immediately after ultrafiltration using 10 L of Nano-pure water in the same ultrafiltration system. The permeate and concentrate from diafiltration were also sampled for DOC analysis to test for any losses of DOC during ultrafiltration. The HMW DOC concentrate was frozen, lyophilized, and the HMW DOC "powder" used for lignin-phenol analysis. The ultrafiltrate cartridge was cleaned between samples using 1 N HCl and 0.5 N NaOH solutions, and then flushed with large volumes of Nanopure water before, between, and after cleaning solutions.

The DOC mass balance was assessed by measuring all fractions of organic carbon involved in ultrafiltration, such as the pre-filtered water, ultrafiltered, and HMW DOC fractions (Carlson et al. 1985; Guo et al. 1995). Recovery of $>100\%$ indicated contamination by the ultrafiltration system or other sources, while $<100\%$ indicated losses in the system. Our DOC recovery (R) ranged from 85 to 104% (with an average of 96%); this suggested that losses or contamination from the system were negligible.

Lignin-phenol analysis

Lignin-phenol concentrations were measured in HMW DOC (ca. 15–35 mg of freeze-dried material) samples using the CuO oxidation method described by Hedges & Ertel (1982). Samples were analyzed by capillary GC using a Shimadzu Model GC-14 APSCF. Verification of lignin-phenols were performed using a Finnigan GC-MS.

Sediments

Porewater DOC analysis

Porewaters analyzed for DOC as previously described were extracted by centrifugation (5000 rpm) for 5 minutes. At stations where porewater DOC concentrations increased with depth, compared to overlying waters, diffusive fluxes of DOC out of sediments were estimated. Profiles of porewater DOC concentration were used to estimate benthic DOC fluxes, based on the Fickian diffusion equation as modified for marine sediments (Berner 1980). The DOC concentration gradient, $(\partial c / \partial z)_0$, at the sediment-water interface was estimated from the concentration difference (∂c) between the overlying waters and the porewaters at the first and second sediment intervals, and the depth of the mid-point (∂z) of this sediment interval (Burdige et al. 1992; Burdige & Homstead 1994). Diffusion coefficients for these sediments were calculated to be 2.3 to $5.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

Statistical analyses

An F_{max} was used prior to analysis of variance (ANOVA) to check for homogeneity of variances (Sokal & Rohlf 1995). One-way ANOVA was used to test for significant effects within and among hydrographic data, SPM, DOC, and river inflow (Sokal & Rohlf 1995). When ANOVA differences were significant, a Scheffé multiple range test was performed to detect differences among stations and among different sampling dates. Spearman Rank Correlation analysis was also performed to test for relationships between all the variables.

Results

Water column

Throughout most of the study there were no significant differences (based on ANOVA analyses) for SPM and DOC measured between stations. While this estuary is well mixed and does not appear to have pronounced spatial differences among these measured parameters, there is a significant gradient of freshwater flow (via river) into the estuary that generally moves from west to east. Based on this gradient of freshwater inflow, the data from the individual stations were combined and presented here as averaged regional data; the estuary was divided into upper (St 1, 4, 7), middle (St 2, 5, 8), and lower (St 3, 6, 9) regions across a west to east direction (Figure 1). Due to the lack of spatial heterogeneity we will focus on temporal differences between these regions.

Hydrographic data

Monthly precipitation varied from 2 to 55 cm, reaching its highest in May 1995 and its lowest in May 1996 (Figure 2). Total river inflow (Amite, Tickfaw, and Tangipahoa and Tchefuncta Rivers) as monitored by the U.S. Geological Survey (USGS) was lowest in May 1996 ($63 \text{ m}^3 \text{ s}^{-1}$) and highest in May 1995 ($276 \text{ m}^3 \text{ s}^{-1}$) (Figure 2). The high river inflow in May 1995 was due to extensive flooding (100 yr flood) that New Orleans experienced at that time. The highest total freshwater (rivers and spillway) discharges ($291 \text{ m}^3 \text{ s}^{-1}$) occurred at the end of June 1995, just after the flooding event, due to leakage from the Bonnet Carré Spillway (Figure 2). The flow of water from Lake Maurepas into Lake Pontchartrain, via a tidal channel known as Manchac Pass, was assumed to be equal to river discharge into Lake Maurepas. However, since the Blind River was not monitored by USGS, our calculated inputs were likely underestimated. Water temperatures over the entire sampling period ranged from 10 to 31°C (data not shown). No significant differences in temperature were observed between the three regions of the estuary ($P > 0.05$). However, water temperatures were significantly different between sampling dates ($P < 0.05$); the lowest average temperature occurred in March 1996 ($10.7 \pm 0.4^\circ\text{C}$, $n = 18$) and the highest in July 1995 ($30.7 \pm 0.4^\circ\text{C}$, $n = 18$). Dissolved oxygen (DO) ranged from 2 to 13 mg L^{-1} with no significant differences between regions of the estuary (data not shown); the highest ($P < 0.05$) average concentration of DO (9.4 ± 1.2 , $n = 18$) occurred during March 1996.

Average salinities ranged from below detection to 8 ppt (data not shown). Average salinity was significantly different among the three regions of the estuary ($P < 0.05$) with the upper region $<$ mid $<$ lower ($P < 0.05$). Alkalinity typically ranged from 120 to $910 \mu\text{eq L}^{-1}$ (Table 1), and was significantly correlated ($P < 0.05$) with temperature. Dissolved inorganic carbon (DIC) ranged from 609 to $4620 \mu\text{M}$ (Table 1); the highest value was observed in September 1995 at Station 6. DIC values obtained by two methods (described earlier) agreed well. The pH throughout the estuary for the whole sampling period ranged between 6.0 to 8.0, except in January 1996 where pH values in the upper region dropped to 5.0 (data not shown).

Dissolved and HMW DOC organic carbon measurements

Average regional DOC concentrations ranged from 5.3 to 8.5 mg C L^{-1} ; the highest ($P < 0.05$) DOC concentrations occurred in May 1995 ($6.9 \pm 0.9 \text{ mg C L}^{-1}$), January 1996 ($8.4 \pm 1.4 \text{ mg C L}^{-1}$), and March 1996 ($6.5 \pm 0.5 \text{ mg C L}^{-1}$) in the upper region (Figure 3). DOC concentrations were significantly correlated with total river discharge ($R = 0.44$, $n = 178$, $P < 0.05$). HMW DOC ranged from 0.2–0.9 mg C L^{-1} (Table 2). The highest percentages of

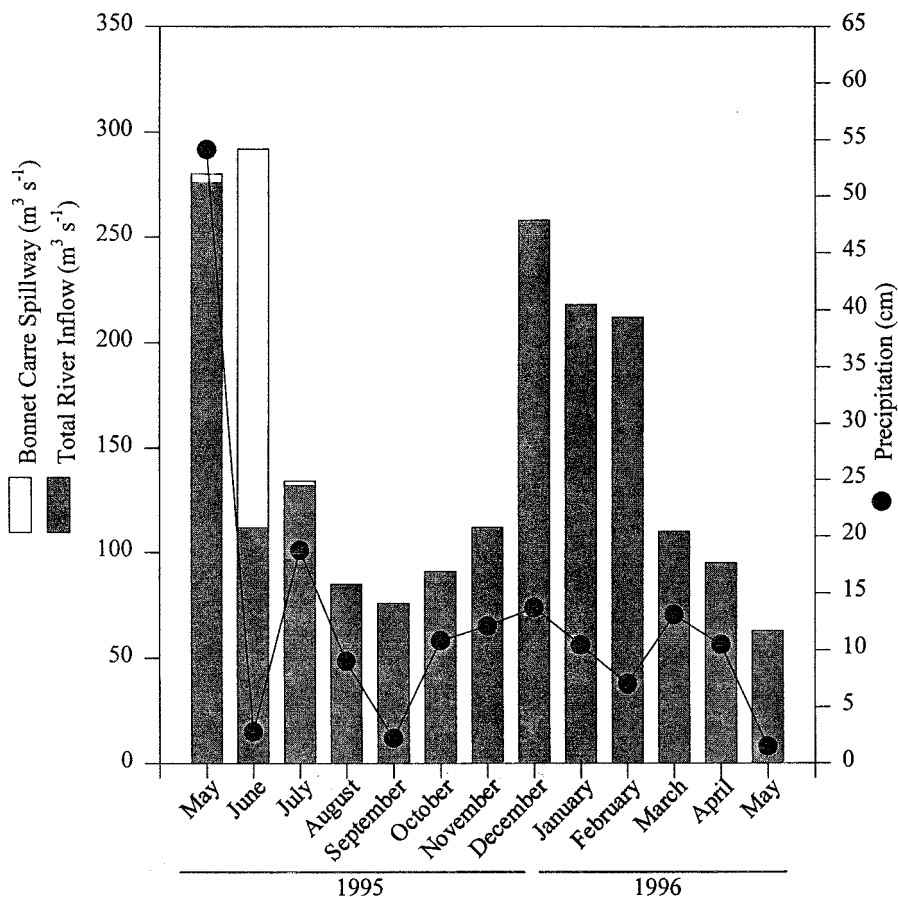


Figure 2. Monthly precipitation (cm) and total freshwater inflow ($\text{m}^3 \text{s}^{-1}$) from the Amite, Tickfaw, Tangipahoa, Tchefuncta Rivers and Bonnet Carré Spillway into the Lake Pontchartrain estuary from May 1995 to May 1996.

Table 1. Alkalinity and dissolved inorganic carbon (DIC) concentrations in the Lake Pontchartrain estuary. The means and range are based on the concentrations found at all nine stations in 1995 and 1996. \pm = standard deviation.

Sampling date	Alkalinity ($\mu\text{eq L}^{-1}$)		DIC (μM)	
	Range	Mean	Range	Mean
July 1995	120–780	598.9 ± 207.8	609.3–3960.2	3040.6 ± 1055.1
September 1995	340–910	671.1 ± 210.1	1726.2–4620.2	3407.3 ± 1066.7
November 1995	280–570	413.3 ± 96.0	1421.6–2995.5	2155.0 ± 554.2
January 1996	260–460	387.8 ± 65.5	1320.1–2335.5	1968.8 ± 332.3
March 1996	330–550	445.6 ± 62.6	1675.5–2792.4	2262.1 ± 317.6
May 1996	340–450	396.3 ± 36.4	1726.2–2284.7	2011.8 ± 184.7

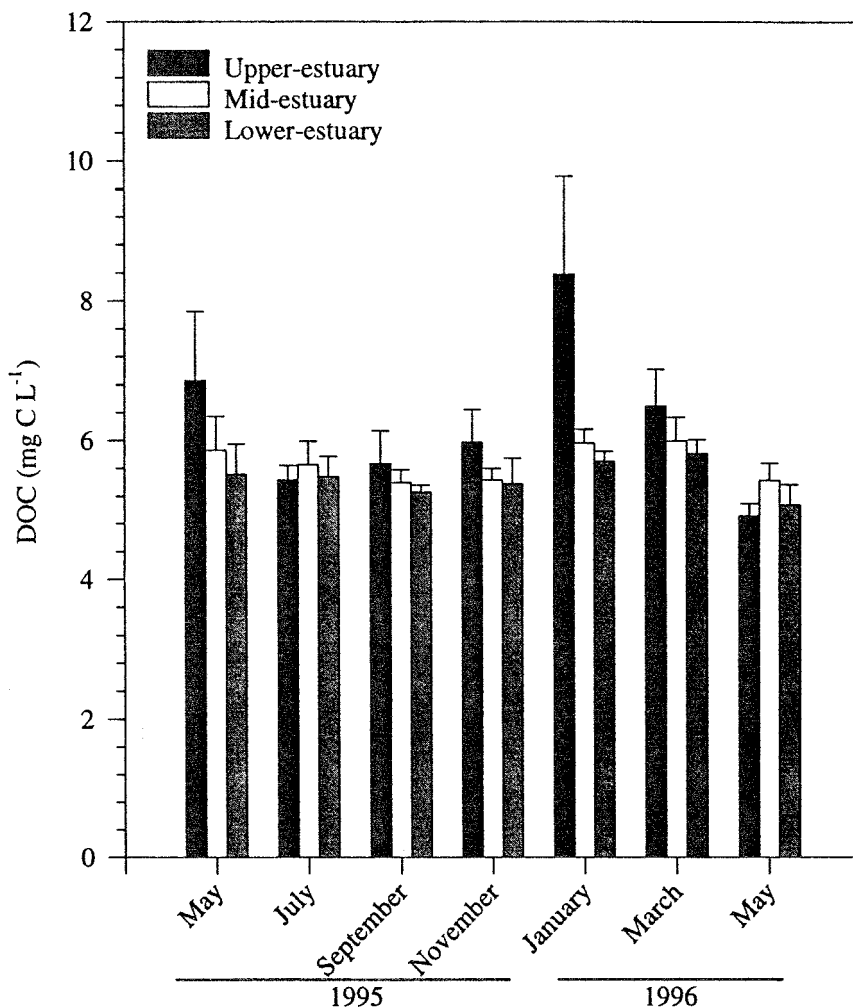


Figure 3. Water column dissolved organic carbon (DOC) concentrations (mg C L^{-1}) from all three regions of the Lake Pontchartrain estuary, sampled from May 1995 to May 1996.

HMW DOC (10 and 11%) were observed in September 1995 and January 1996 at station 4.

Lignin-phenols concentrations in HMW DOC

Lignin oxygen products are expressed in terms of organic carbon through the use of λ (the sum of vanillyl and syringyl phenols in $\text{mg } 100 \text{ mg OC}^{-1}$) and Λ (the sum of vanillyl, syringyl, and cinnamyl phenols in $\text{mg } 100 \text{ mg OC}^{-1}$). Lignin-phenols in HMW DOC in the Lake Pontchartrain estuary indicated

Table 2. Dissolved organic carbon fractions in the Lake Pontchartrain estuary in September 1995, January 1996, and May 1996. SPM – suspended particulate matter; DOC – total dissolved organic carbon ($<0.2 \mu\text{m}$); HMW DOC –high molecular weight dissolved organic carbon ($>3 \text{ kD}$ to $<0.2 \mu\text{m}$). \pm = standard deviation.

Date	Station	SPM (mg L^{-1})	DOC (mg L^{-1})	HMW DOC (mg L^{-1})	HMW DOC/DOC (%)	Recovery (%)
September 1995	4	3.6 ± 0.2	5.8	0.6	10	104
September 1995	5	3.7 ± 0.5	5.4	0.3	6	89
September 1995	6	6.7 ± 0.5	5.1	0.4	7	95
January 1996	4	30.4 ± 2.4	8.4	0.9	11	85
January 1996	5	16.6 ± 0.6	5.7	0.2	4	100
January 1996	6	6.5 ± 0.1	5.8	0.3	5	103

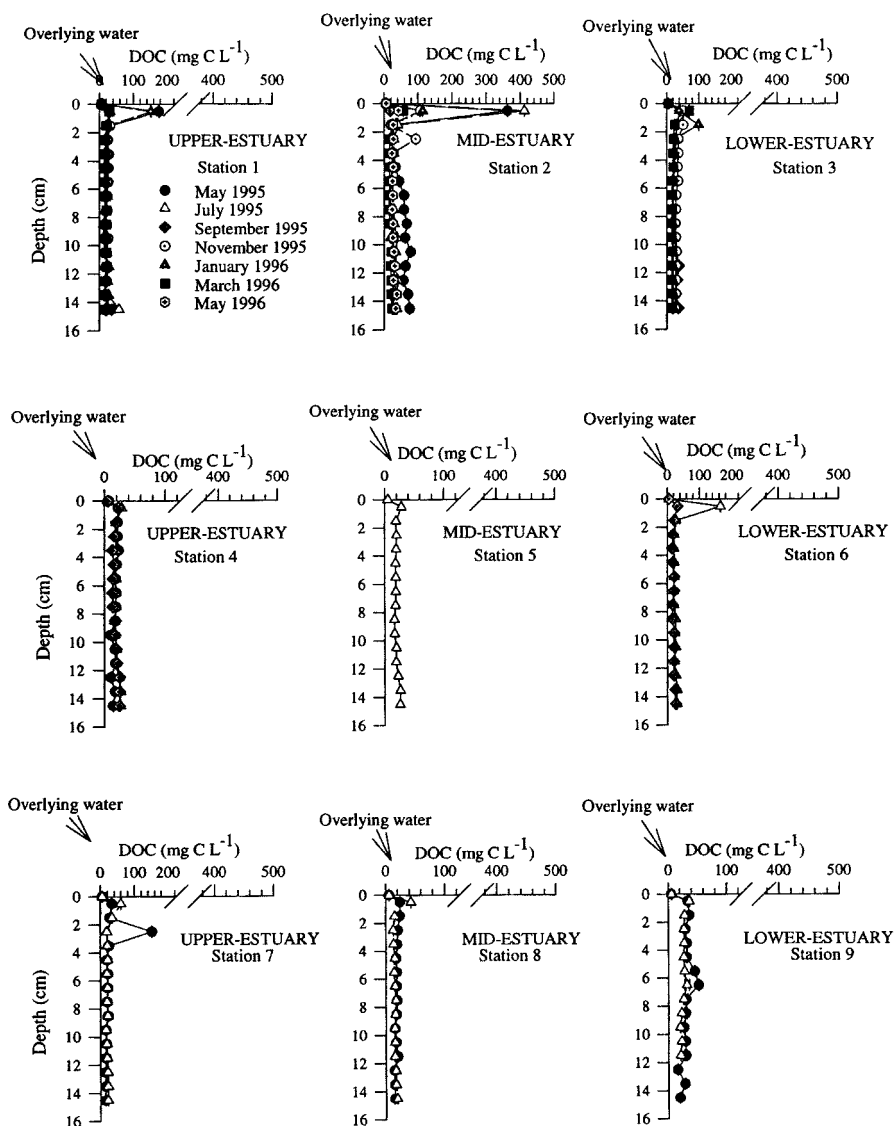


Figure 4. Porewater DOC profiles in sediments from all three regions of the Lake Pontchartrain estuary, sampled from May 1995 to May 1996.

that station 4 had significantly higher λ ($0.33 \text{ mg } 100 \text{ mg}^{-1} \text{ OC}$), and Λ ($0.39 \text{ mg } 100 \text{ mg}^{-1} \text{ mg } 100 \text{ mg}^{-1} \text{ OC}$) in September 1995 than those in January 1996, respectively.

Sediments

Porewater DOC measurements

Porewater DOC profiles in sediments of all stations are shown in Figure 4. In general, depth-profiles increased slightly in surface cm layers and remained constant at depth, with a mean concentration of 20 to 30 mg C L⁻¹ compared to DOC concentrations in bottom waters (5 to 8.5 mg C L⁻¹) (Figure 4). In some cases, DOC showed significantly higher subsurface concentrations in the upper 2 cm of sediments (150 to 410 mg C L⁻¹ versus the typical average concentration of ~20 mg C L⁻¹). The highest DOC subsurface maxima were observed in May 1995 and July 1995 at the mid-region (station 2) of the estuary (Figure 4).

Benthic flux measurements

Benthic DOC fluxes were calculated separately for two distinct sediment sections – an upper section which included the subsurface maxima, and a lower section where asymptotic porewater DOC concentrations were constant (shown in Table 4). In general, DOC fluxes ranged between 4.8 to 46.5 mmol m⁻² d⁻¹ with an average of 12.3 mmol m⁻² d⁻¹ (Table 4); the highest DOC flux (46.5 ± 0.3 mmol m⁻² d⁻¹) occurred in May 1995 at station 2. No significant ($P > 0.05$) differences in benthic DOC fluxes were observed between stations; however, average DOC fluxes were significantly ($P < 0.05$) higher in May 1995. Estimated benthic DOC fluxes from the upper sediment section, which include the subsurface maxima and bottom waters, varied from 46.1 to 1821.5 mmol m⁻² d⁻¹ (data not shown). These fluxes were significantly different ($P < 0.05$) than those calculated from the lower asymptotic values. In fact, calculated benthic DOC fluxes between bottom waters and the lower section were in good agreement with those measured during a 4-h flux experiment (Argyrou 1996). Thus, we will use the calculated fluxes based on the lower sedimentary section for our annual estimates in this study.

Discussion

DOC dynamics

Allochthonous inputs of DOC to the Lake Pontchartrain estuary vary with freshwater discharge. High DOC water is transported to the estuary via rivers and adjacent wetlands drainage. DOC concentrations in some of the creeks that drain these rivers and wetlands into the Lake Pontchartrain estuary reach concentrations as high as 28 mg C L⁻¹ during February and March (Bianchi, unpublished data). A significantly higher fraction of HMW DOC (<0.2 μm to >3 kD) was found at stations 1, 4 and 7 which received greater freshwater

Table 3. Lignin-phenols in HMW DOC collected in September 1995 and January 1996 for stations 4–6 of the Lake Pontchartrain estuary. The symbol λ is the sum of the vanillyl and syringyl phenols in mg for 100 mg OC, whereas Λ is the sum of the vanillyl, syringyl, and cinnamyl phenols in mg for 100 mg OC. ND = No data.

Station	λ		Λ	
HMW DOC				
4	0.33	0.27	0.39	0.30
5	0.24	0.14	0.29	0.17
6	0.11	0.09	0.14	0.11

inputs from rivers and adjacent wetlands. Based on previous studies, much of the HMW DOC in freshwater systems is likely to be derived from vascular plant sources (Wetzel 1984; Malcolm 1990; Mann & Wetzel 1995; Wetzel et al. 1995).

In the Lake Pontchartrain estuary, the HMW DOC fraction showed a decreasing gradient of lignin-phenol concentrations from the upper to the lower region (Table 3), indicating that much of the HMW DOC coming into the estuary is transported via riverine and wetland inputs from the west. In fact, lignin values of λ and Λ (in the HMW DOC fraction) observed in this study were similar to those found in several blackwater rivers along the coastlines of South Carolina and Georgia (Moran et al. 1991). If DOC were primarily derived from phytoplankton sources, a significant correlation between chlorophyll-*a* and DOC would be expected (Guo et al. 1994; Santschi et al. 1995), but this was not observed in the Lake Pontchartrain estuary. Moreover, the long hydraulic residence time (volume of estuary/total riverine inputs) in this estuary (537 days) may allow heterotrophic processes (i.e., photooxidation, bacterial consumption) to effectively degrade this material. This may also explain why the percentage of HMW DOC in Lake Pontchartrain is considerably lower (4 to 10%) than other aquatic systems (10 to 70%) (Benner & Hedges 1993; Hedges et al. 1994; Amon & Benner 1996). It should also be noted that our molecular weight cutoff was at 3 kD as compared with 1 kD used in many of these other studies. Studies that have used 3 kD as a molecular weight cutoff found that the percentage of HMW DOC ranged from 10 to 24% lower than at the 1 kD cutoff (Guo et al. 1995).

Riverine inputs and benthic fluxes of DOC were similar in magnitude and represented the dominant sources of DOC to the Lake Pontchartrain estuary. Riverine DOC inputs for the month of March 1996 ranged from 6.5 to 7.3 mg C L⁻¹. Some of these rivers (e.g., Tchefuncta River) that discharge into the Lake Pontchartrain estuary are blackwater systems with high DOC concentrations

of $7.3 \pm 0.1 \text{ mg C L}^{-1}$; a value typical of blackwater rivers (Vegas-Villarrubia et al. 1988; Doering et al. 1994). Water column DOC concentrations in the Lake Pontchartrain estuary ranged from 5.3 to 8.5 mg C L^{-1} throughout the estuary for the entire sampling period (Table 3). Calculated benthic DOC fluxes ranged from 4.8 to $46.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Table 4). Based on these values, the annual input of DOC versus the total DOC pool in the Lake Pontchartrain estuary could be calculated, taking into consideration the average annual discharge of the rivers to the Lake Pontchartrain estuary ($142 \text{ m}^3 \text{ s}^{-1}$), as well as the surface area (1645 km^2) and total volume ($6580 \times 10^6 \text{ m}^3$) of the estuary. Annual riverine loadings of DOC into the Lake Pontchartrain estuary were estimated to be $2.8 \times 10^{10} \text{ g C yr}^{-1}$ while annual benthic DOC fluxes were calculated to be $8.8 \times 10^{10} \text{ g C yr}^{-1}$. These benthic DOC fluxes were greater than those found in considerably larger estuaries, such as Chesapeake Bay ($1.2\text{--}3.1 \times 10^{10} \text{ g C yr}^{-1}$) (Burdige et al. 1992; Burdige & Homstead 1994). Based on an annual average DOC concentration of 5.8 mg L^{-1} the total DOC pool in the estuary was estimated to be $3.8 \times 10^{10} \text{ g C}$. Using the total annual DOC inputs ($11.6 \times 10^{10} \text{ g C yr}^{-1}$) and the total pool of DOC in the estuary ($3.8 \times 10^{10} \text{ g C}$), the DOC residence time (pool/inputs) was estimated to be 120 days. Thus, the residence time of DOC (120 days) was found to be significantly shorter than the hydraulic residence of the system (537 days).

The difference between hydraulic and DOC residence times (417 days) is likely due to heterotrophic transformations of DOC which result in losses of CO_2 from the system. The three dominant mechanisms that may explain this imbalance are export of DOC (currents and tides), photooxidation (Mopper et al. 1991; Wetzel et al. 1995), and heterotrophic activity (i.e., bacterioplankton) (Findlay et al. 1991). Export of DOC due to physical mixing is expected to be negligible due to the fact that the residence time of the estuary is much longer than the DOC residence time, in addition to the minimal tidal exchange that typically ($<1 \text{ m}$) occurs in this system. Photooxidation of DOC is likely to be an important mechanism governing the DOC losses in the Lake Pontchartrain estuary. Recent work has shown that HMW DOC treated by UV can effectively be degraded into more available forms (i.e., fatty acids such as acetic, formic, pyruvic) that can fuel bacterial metabolism (Wetzel et al. 1995). Although the Lake Pontchartrain estuary is characterized by highly turbid waters, the combination of a long hydraulic residence time and resuspension events results in materials frequently being exposed to the surface where they can be photodegraded. Another possible mechanism controlling the losses of DOC is the metabolic respiration by bacteria. It has been well established that DOC consumption by bacteria in aquatic ecosystems is an important

Table 4. Benthic DOC fluxes in the Lake Pontchartrain estuary sediments.

Sampling date	Stations	DOC flux ($\text{mmol m}^{-2} \text{d}^{-1}$)
May 1995	1	13.50 ± 0.03
May 1995	2	46.50 ± 0.03
May 1995	4	6.75 ± 0.03
May 1995	7	10.95 ± 0.06
May 1995	8	12.18 ± 0.20
May 1995	9	18.36 ± 0.30
July 1995	1	11.70 ± 0.60
July 1995	2	20.50 ± 0.45
July 1995	4	7.86 ± 0.20
July 1995	5	9.03 ± 0.10
July 1995	6	12.90 ± 0.10
July 1995	7	10.80 ± 0.03
July 1995	8	9.90 ± 0.12
July 1995	9	14.70 ± 0.05
September 1995	3	11.70 ± 0.08
September 1995	4	4.80 ± 0.14
September 1995	6	9.03 ± 0.30
November 1995	1	13.50 ± 0.10
November 1995	2	12.60 ± 0.50
November 1995	3	17.10 ± 0.12
January 1996	1	5.70 ± 0.35
January 1996	2	7.80 ± 0.21
January 1996	3	8.70 ± 0.15
March 1996	1	11.10 ± 0.80
March 1996	2	6.90 ± 0.55
March 1996	3	7.80 ± 0.35

mechanism in the cycling of carbon (Findlay et al. 1991; Kirchman et al. 1982; Wetzel 1992; Coveney & Wetzel 1995).

While much of the DOC in Lake Pontchartrain appears to be derived from allochthonous sources, heterotrophic consumption remains the most likely explanation for losses of DOC from the system. DOC that is released into the water column from the sediment-water interface has an average molecular weight that ranged between 1 and 10 kD (Burdige et al. 1992; Burdige & Homstead 1994). It has been shown that HMW DOC in aquatic systems can be efficiently consumed by bacteria (Wetzel 1983; Tranvik 1990; Mann & Wetzel 1995; Zweifel et al. 1995). Moreover, the HMW DOC in coastal waters and the open ocean is preferentially utilized by bacterioplankton over low molecular weight DOC (Amon & Benner 1994, 1996). Zweifel et al. (1995) further demonstrated that a large portion (22–99%) of allochthonous DOC in

Table 5. pH, dissolved inorganic carbon (DIC) concentration, and partial pressure of CO₂ (pCO₂) in the Lake Pontchartrain estuary in comparison with other freshwater systems. LPE = Lake Pontchartrain estuary, *n* = number of lakes or samples used in each study.

Lakes	Samples	pH	DIC (μ M)	pCO ₂ (μ atm)	Basis of pCO ₂ estimate	Reference
LPE (1)	45	6.6–7.9	609–4,620	2,844–8,428	PH, Alk., DIC	This study
37	390	4.7–9.5	4.9–2,500	107–4,128	Direct measurement	Cole et al. 1994
1612	1612	3.8–9.4	13.3–4,077	20–9,789	pH, DIC	Hesslein et al. 1991
60	179	4.9–9.3	11–3,578	5–7,991	pH, DIC	Caraco et al. 1992
59	79	6.0–9.9	43–145,790	32–20,249	pH, DIC	Kling 1987

the Bothnian Sea was degradable by bacteria after inorganic nutrients were added. It is also well known that phosphorus availability is an important factor controlling bacterioplankton productivity (Cotner & Wetzel 1992; Zweifel et al. 1993). While the Lake Pontchartrain estuary is a system deficient in inorganic forms of nitrogen, phosphorus concentrations were moderately high and relatively stable throughout the study period (Bianchi & Argyrou 1997).

Assuming that DOC losses are primarily due to heterotrophic consumption, increases in CO₂ concentrations should be coupled with increases in DOC loading. This balance between DOC input and CO₂ export may explain for the stability of DOC values observed throughout the estuary. Calculated DIC concentrations and pCO₂ in the system ranged from 609 to 4620 μ M and 2840 to 8428 μ atm, respectively (Table 5). These values are similar to those found in other freshwater systems that had reached saturation levels (Devol et al. 1987; Findlay et al. 1993; Cole et al. 1994; Frankignoulle et al. 1996). Furthermore, it has recently been shown that many lakes are sources and not sinks for CO₂ (Cole et al. 1994). Since this estuary appears to have residence times similar to that of freshwater lakes, it is not surprising to expect that the net loss of DOC is primarily from CO₂ export. Thus, the Lake Pontchartrain estuary appears to be driven by heterotrophic processes which results in the conversion of terrestrial-derived DOC to CO₂ that fluxes to the atmosphere.

Conclusions

On the basis of our field study in the Lake Pontchartrain estuary, we concluded that:

- 1) The percentage of DOC represented by HMW DOC (or colloidal material) was greatest (ca. 11%) at stations where freshwater discharge from rivers and surrounding wetlands was most significant.
- 2) The lignin-phenol content of HMW DOC (λ ranged from 0.09 to 0.33 and Λ from 0.11 to 0.39) indicated that a significant fraction of colloidal organic carbon was derived from terrestrial sources.
- 3) Net losses of DOC in the Lake Pontchartrain estuary appeared to be primarily controlled by heterotrophic consumption (conversion to CO₂) – which may have been amplified by the long residence time (approximately 120 days) of DOC in this system.

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