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Marine Chemistry 89 (2004) 103–125

MARINE CHEMISTRY

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High-resolution measurements of chromophoric dissolved organic matter in the Mississippi and Atchafalaya River plume regions

Robert F. Chen*, G. Bernard Gardner

Environmental, Coastal and Ocean Sciences, University of Massachusetts Boston, 100 Morrissey Boulevard, Boston, MA 02125-3393, USA

Received 17 January 2003; received in revised form 5 February 2004; accepted 17 February 2004
Available online 15 June 2004

Abstract

Chromophoric dissolved organic matter (CDOM) was measured in the spring and summer in the northern Gulf of Mexico with the ECOShuttle, a towed, instrumented, undulating vehicle. A submersible pump mounted on the vehicle supplied continuously flowing, uncontaminated seawater to online instruments in the shipboard laboratory and allowed discrete samples to be taken for further analysis. CDOM in the northern Gulf of Mexico was dominated by freshwater inputs from the Mississippi River through the Birdfoot region and to the west by discharge from the Atchafalaya River. CDOM was more extensively dispersed in the high-flow period in the spring but in both time periods was limited by stratification to the upper 12 m or so. Thin, subsurface CDOM maxima were observed below the plume during the highly stratified summer period but were absent in the spring. However, there was evidence of significant *in situ* biological production of CDOM in both seasons.

The Mississippi River freshwater end member was similar in spring and summer, while the Atchafalaya end member was significantly higher in the spring. In both time periods, the Atchafalaya was significantly higher in CDOM and dissolved organic carbon (DOC) than the Mississippi presumably due to local production and exchange within the coastal wetlands along the lower Atchafalaya which are absent along the lower Mississippi. Nearshore waters may also have higher CDOM due to outwelling from coastal wetlands. High-resolution measurements allow the differentiation of various water masses and are indicative of rapidly varying (days to weeks) source waters. Highly dynamic but conservative mixing between various freshwater and marine end members apparently dominates CDOM distributions in the area with significant *in situ* biological inputs (bacterial degradation of phytoplankton detritus), evidence of flocculation, and minor photobleaching effects also observed. It is clear that high-resolution measurements and adaptive sampling strategies allow a more detailed examination of the processes that control CDOM distributions in river-dominated systems.

Keywords: CDOM; Mississippi; Dissolved organic carbon; Undulating vehicle; Fluorescence; Atchafalaya

* Corresponding author. Tel.: +1-617-287-7491; fax: +1-617-287-7474.
E-mail address: bob.chen@umb.edu (R.F. Chen).

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doi:10.1016/j.marchem.2004.02.026

1. Introduction

1.1. Dissolved organic matter in coastal waters

Dissolved organic matter (DOM) in seawater is one of the largest reactive reservoirs of carbon on earth (Hedges, 1992). Coastal waters, due to their high primary productivity and horizontal advection rates, may act as important sinks for atmospheric carbon dioxide and as such need to be assessed as to their importance in the global carbon cycle (Walsh et al., 1981, 1988). Estuaries and unconfined river plumes show large gradients in DOM due to advective transport of terrestrial organic matter as well as high productivity, but are complex regions for studying organic geochemical processes due to the intense mixing of coastal currents, tides, seasonal variability and multiple freshwater inputs. Therefore, the sources and transformations of DOM at the land–water interface are not well understood. Although conservative mixing of riverine and marine waters has been suggested to control distributions of dissolved organic carbon (DOC) in some estuaries (Mantoura and Woodward, 1983; Alvarez-Salgado and Miller, 1998), other processes such as phytoplankton and salt marsh grass (*Spartina* spp.) production or anthropogenic inputs have been observed to be significant DOC contributors in others (Aminot et al., 1990; Fry et al., 1992; Peterson et al., 1994; Winter et al., 1996). Photochemical transformations of DOM has been suggested to be the major sink of refractory marine DOM (Mopper et al., 1991) and have been seen to act in concert with bacteria to degrade DOM in coastal waters (Miller and Moran, 1997). Estuarine DOC flows across the entire US eastern continental shelf (Moran et al., 1991; Vlahos et al., 2002) is entrained into major ocean current systems such as the Gulf Stream (Atkinson et al., 1978; Vlahos et al., 2002) and therefore may represent a major flux of carbon from land to sea.

DOC in several English estuaries has been shown to act conservatively throughout the year (Mantoura and Woodward, 1983; Alvarez-Salgado and Miller, 1998). On the other hand, several studies on the East Coast of the United States (Fry et al., 1992; Peterson et al., 1994; Winter et al., 1996), especially in salt marsh-dominated tidal estuaries, have shown in situ DOC production and therefore net carbon export from the estuaries. The resulting Outwelling Hypothesis was extended to include tropical mangrove estuaries as well (Wattayakorn et al., 1990; Hemminga et al., 1994; Lee, 1995). The ensuing debate has continued—some estuaries act as passive transport areas, others are regions of active producers of organic carbon, and still others act as net sinks of terrestrial organic matter (Findlay et al., 1992; Argyrou et al., 1997). In a few cases, while there is little net production or consumption of organic carbon, the estuary clearly acts as a reactor to convert the molecular and isotopic composition of DOM from terrestrial to marine (Peterson et al., 1994; Taylor and Allanson, 1995; Soetaert and Herman, 1995). It is therefore difficult to generalize about the effect of an estuary on the delivery of terrestrial (vascular plant, soil, riverine) DOM to the coastal ocean.

1.2. Chromophoric dissolved organic matter

Chromophoric or colored dissolved organic matter (CDOM) is an important fraction of the total DOM for several reasons. First, this pool consists of the photochemically active fraction of DOM, meaning that all sunlit-induced reactions of nonliving systems are mediated by the CDOM pool. CDOM absorbs energetic photons leading to the presence of reactive intermediates such as hydrated electrons, hydrogen peroxide, superoxide radicals and hydroxy radicals that control metal speciation (Moffett and Zika, 1987), photodegradation of refractory macromolecules (Mopper et al., 1991) and production of trace gases (Conrad and Seiler, 1980) in surface waters. Second, CDOM affects the quality and quantity of light reaching photosynthetic cells. Light limitation in highly turbid and organic-rich estuarine and coastal waters is common. Third, CDOM appears to be somewhat refractory, certainly less labile than the glucopolysaccharide fraction that may turn over in hours to days (Arnosti et al., 1994). As such, CDOM appears to have a residence time longer than time scales of most estuarine and coastal mixing processes and can therefore represent a significant portion of the DOM that is exported to the open ocean. Fourth, CDOM affects the overall ocean color as seen by satellite remote sensing efforts (Carder et al., 1989). Knowledge of distributions and characterization of CDOM is essential for retrieving accurate chlorophyll *a* concentrations in the

world's oceans from satellite measurements. In their own right, coastal CDOM distributions will yield great insight into the interaction of terrestrial sources of DOM with the marine carbon cycle. Finally, CDOM represents the most readily measured fraction of the total DOM pool as will be discussed below. Because CDOM is much more concentrated in terrestrial waters than marine waters, large gradients in optical properties yield a sensitive tool for tracking the influence of terrestrial DOM offshore.

The optical properties of DOM in natural waters are dominated by the presence of a complex mixture of chromophores (those molecules that absorb UV and visible light) and fluorophores (those molecules that reemit absorbed light in the visible). The absorption of light in seawater due to DOM has been well studied (Armstrong and Boalsch, 1961) and can be described as an exponential decrease in absorption with increasing wavelength. The slope of the log-linearized absorbance changes with CDOM composition (Carder et al., 1989; Green and Blough, 1994; Blough and Del Vecchio, 2002). The magnitude of this absorption changes temporally and spatially, especially in coastal and estuarine waters, due to a number of complex physical, biological and chemical processes. While CDOM absorption is an inherent optical property of seawater that needs to be measured directly in order to correctly interpret apparent optical properties measured remotely, it is often difficult to measure CDOM absorption consistently. Inherently, absorption (the difference in the intensity of light before and after it interacts with seawater) is a much less sensitive measurement than fluorescence (the measurement of photons against a dark background). Reliable CDOM absorption measurements when concentrations of CDOM are low (e.g., offshore) or when they are above 400 nm are often difficult (Blough and Del Vecchio, 2002). Fortunately, the fluorescence of CDOM has been shown to correlate with CDOM absorption (Hoge et al., 1993; Green and Blough, 1994; Vodacek et al., 1995; Nieke et al., 1997; Chen et al., 2002), especially in coastal waters.

1.3. High-resolution measurements

Coastal areas, where tidal and wind mixing, source variations and intense biological and chemical transformations drive gradients over centimeter to kilometer spatial scales and changes over minute to day temporal scales, require rapid three- and four-dimensional observational capabilities (Robinson and Glenn, 1999; Bissett et al., 2001) to study the biogeochemical processes controlling DOM distributions. Currently available observational capabilities include satellites, airborne systems, moorings, autonomous underwater vehicles, gliders, ship surveys and towed packages (Glenn et al., 2000). Of these, towed vehicles offer intermediate resolution with nearly synoptic coverage of coastal areas in three dimensions. For coastal work, towed vehicles can either operate in "tow-yo" or undulating mode. In the tow-yo mode, depth is controlled by the amount of tow cable paid out, the vessel speed and the weight and drag of the vehicle, but normally, tow-yo vehicles can only operate at slow (< 5 knots) speeds (Klinkhammer et al., 1997). Undulating vehicles offer the advantage of high speed (5–10 knots) and do not lead to undo wear and tear on the cable or winch. The SeaSoar (Pollard, 1986; Griffiths and Pollard, 1992; Fucile et al., 1998; Hales and Takahashi, 2002), the Batfish and/or MiniBat (Guildline Instruments, Lake Mary, FL; Herman and Denman, 1977; Hains and Kennedy, 2002) and the ScanFish (formerly GMI, now Chelsea) have been used for various oceanographic studies. Two very similar undulating vehicles, the Nu-Shuttle (formerly the AquaShuttle; Dunning, 1998) manufactured by Chelsea Instruments and the UTow manufactured by WS Envirotech, have been used in coastal waters on a regular basis worldwide (Dunning, 1998). *In situ* CDOM fluorometers mounted on undulating vehicles have recently played a critical role in the study of coastal CDOM dynamics (Chen, 1999; Chen et al., 2002).

1.4. The Mississippi River plume

The Mississippi River is the sixth largest river in terms of discharge in the world (Milliman and Meade, 1983) and, like many of the major rivers in the world, enters the coastal ocean as an unconfined river plume. The Mississippi River watershed drains 41% (1,245,000 square miles) of the area of the 48 contiguous United States. The upper reaches drain mostly agricultural areas, leading to increased nutrient loads to the Gulf of Mexico (Turner and Rabalais, 1991), while the lower alluvial valley is a

relatively flat plain. At Old River Junction, the Army Corps of Engineers has developed a system of controlling the flow of the Mississippi River to the Gulf of Mexico with ~70% of the flow draining out of the Birdfoot region and 30% being diverted to the Atchafalaya basin (Addison, 1998). The lower Atchafalaya River passes through wetland, salt marsh and bayou, and the shallow Atchafalaya Bay (~2 m) with a large capacity to trap sediment and where a highly productive ecosystem can interact with riverine and estuarine waters (Pakulski et al., 2000; Lane et al., 2002). The Lower Mississippi, on the other hand, has been highly channelized, greatly reducing the interaction of the river with historical flood plains. The major flow in the Birdfoot region exits three major outflows, Southwest Pass, South Pass, and Pass a Loutre, of which Southwest Pass is the largest, while numerous cuts and channels allows drainage of river waters throughout the region (Hitchcock et al., 1997). The plume, under normal (average) wind conditions, initially flows west and is turned anticyclonically toward the coast (to the northwest) into the Louisiana Bight (Hitchcock et al., 1997).

It is the goal of this paper to gain a better understanding of the coastal processes that affect CDOM production, distribution and fate in the northern Gulf of Mexico by using a high-resolution undulating vehicle equipped to measure CDOM.

2. Methods

2.1. Area of study

The Mississippi River plume and surrounding waters were investigated on two cruises aboard the *R/V Pelican* on June 21–28, 2000 and April 5–11, 2001. These two time periods were chosen in order to compare contrasting flow conditions, low flow in summer (average 12,700 m^3/s, rising from 10,137 to 16,169 m^3/s during the cruise) and high flow in spring (average 20,127 m^3/s, falling from 27,934 to 23,166 m^3/s during the cruise; US Army Corps of Engineers, Hydraulics Branch, 2002). The drought conditions in 2000 preceding the June cruise were anomalous, while 2001 was a typical spring with high river flow preceding the cruise. Traveling at ~8 knots, we surveyed approximately 1600 km in ~120 h of ECOShuttle operation in June 2000 and 1450 km in ~110 h of operation in April 2000.

The cruise track in June 2000 was designed to investigate the plume on both the western side of the Birdfoot region as well as the eastern side, Chandaleur Sound, the Mississippi River end member and the Atchafalaya plume to its freshwater end member (Fig. 1A). Our general approach was to cross the plume from nearshore (~10 m depth contour) to the shelf break (or high salinity 36 surface water) at various distances from the freshwater source as well as carry out transects into the Mississippi and Atchafalaya rivers to sample the major salinity gradients. Satellite data preceding the cruise as well as daily images electronically sent to the ship offered some additional guidance as to where and when to sample the plume (P. Bissett, personal communication). The plume was generally limited to the upper 12 m, and a sharp salinity gradient (salt wedge) was present in the Mississippi River itself.

In April 2001, we focused on the western side of the Birdfoot region (Fig. 1B) and had the following goals: (1) sample salinity gradients of both the Mississippi and Atchafalaya rivers, (2) conduct cross-shelf transects of the main Mississippi plume, (3) investigate nearshore waters (influenced by local freshwater sources) in the Louisiana Bight, and (4) follow Lagrangian drifters released as a triad in Southwest Pass. The high-flow period forced the freshwater end member out to the mouth of Southwest Pass, but complex mixing as this water jetted out onto the shelf (Hitchcock et al., 2004, this issue) and ship traffic resulted in our deployment of three drifters at salinities of ~8–9. Freshwater (salinities <25) were present throughout the area, and drifters demonstrated the typical anticyclonic movement of the plume west and northeast back toward the shore (Hitchcock et al., 1997, 2004).

2.2. Underway measurements

2.2.1. ECOShuttle

The ECOShuttle is a towed, undulating vehicle based on the Nu-Shuttle manufactured by Chelsea Instruments (Surrey, UK). It carries a Sea Bird Electronics (Bellevue, WA) SBE 9/11 CTD system which provides temperature, salinity and depth measurements. Fluorescent dissolved organic matter is measured by a SeaTech (Corvallis, OR; CDOM—

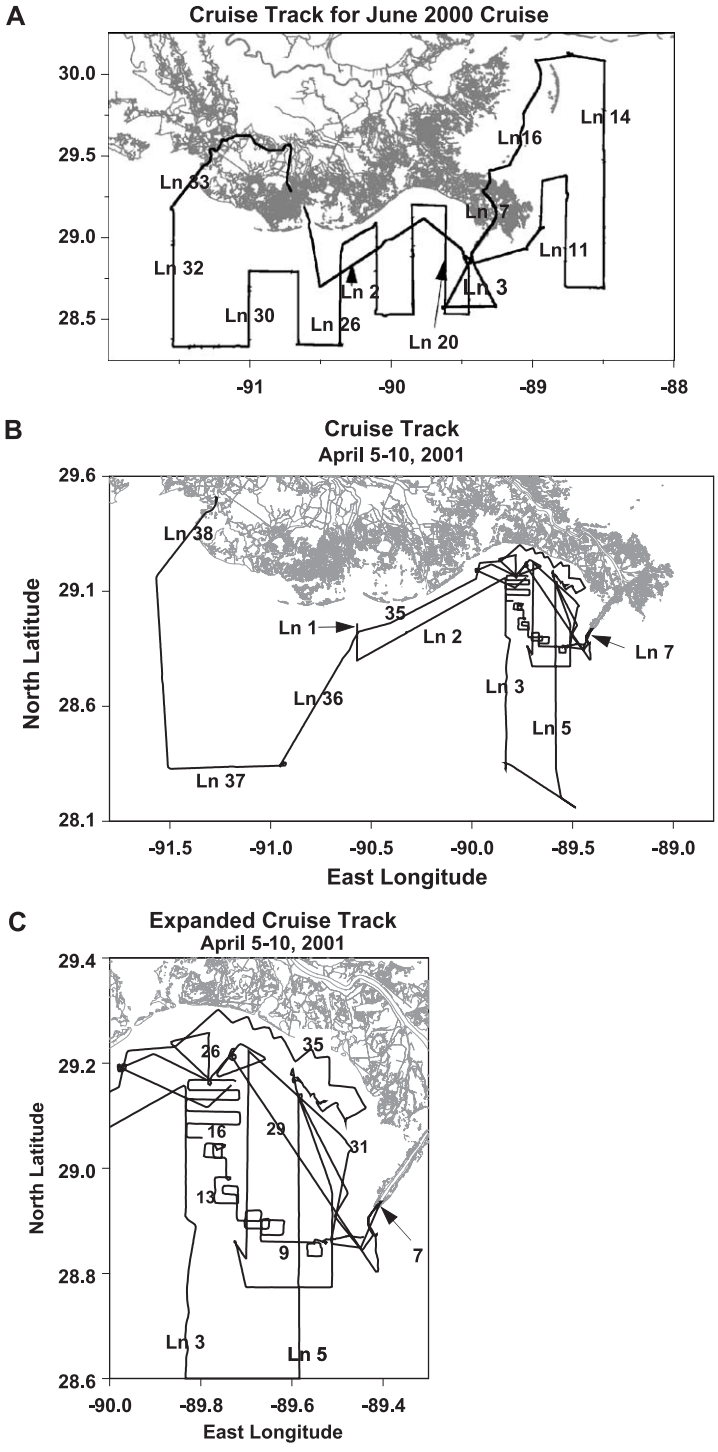


Fig. 1. Cruise tracks for the June 2000 (A) and April 2001 (B) cruises aboard the *R/V Pelican* in the northern Gulf of Mexico. Expanded cruise track for April 2001 in the Louisiana Bight (C).

λ_{ex} = 330 nm, λ_{em} = 450 nm; band width = 60 and 65 nm, respectively) fluorometer. A Chelsea Instruments UV Aqua-Tracka fluorometer (λ_{ex} = 239 nm, λ_{em} = 360 nm) also provides an indication of hydrocarbon concentration. Other instrumentation includes a chlorophyll fluorometer and optical backscatter sensor (OBS) manufactured by Sea Point Instruments (Exeter, NH) and a YSI dissolved oxygen sensor provided by Sea Bird Electronics. An altimeter facilitates safe operation within a few meters of the bottom. With the current cable, the maximum depth of operation is about 40 m at 8 knots.

In addition to on-board instrumentation, the ECOShuttle also incorporates a stainless steel, submersible pump which allows water to be continually supplied to the shipboard lab via a 0.5-in. ID Teflon tube in the tow cable (Falmat; San Marcos, CA). This water may be distributed to a variety of in-line instruments and also allows discrete samples to be obtained for further analysis. In-line instruments include a time-resolved laser-induced fluorometry system which determines both CDOM spectra (λ_{ex} = 337 nm) as well as pyrene concentrations (Rudnick and Chen, 1998), an AC-9 multispectral absorption meter (Wetlabs; Philomath, OR), a SaFIRE multiple-wavelength spectrofluorometer (Wetlabs) and a SeaBird thermosalinograph. A fluid rotary and electrical slip-ring (Focal Technologies; Dartmouth, Nova Scotia) incorporated into the winch (SeaMac, Houston, TX) allow data, control and fluid connections between the shipboard laboratory and the ECOShuttle. Complete details of this system are presented elsewhere (Gardner et al., in preparation).

2.2.2. Surface measurements

In April 2001, we deployed a depressor vein and a tow body with a 0.5-in. Teflon tube sampler off the port side of the *R/V Pelican*. A compressed air-driven Teflon diaphragm pump pulled water from the tow body set at 1–2 m depth. The clean seawater was then sent to a laboratory van where it entered a polycarbonate flow cell (~ 2 l volume). A Falmouth Scientific (Cataumet, MA) Micro-CTD and a SeaPoint CDOM fluorometer were mounted in the flow cell. Data (with ship's GPS) were recorded with a laptop and later synchronized with the ECOShuttle data.

The *R/V Pelican*'s SAIL system also provided underway temperature, salinity, chlorophyll fluorescence and turbidity measurements on seawater from the ship's uncontaminated seawater pumping system (3 m depth).

2.3. Discrete samples

2.3.1. Sampling and filtration

Discrete samples were drawn from the sampling port supplied by the ECOShuttle pumping system. The time of sampling was generally determined by the ECOShuttle depth (for surface samples, minimum depth was about 3 m; the ECOShuttle was programmed to rise only to 3 m depth to avoid ship propeller mixing behind the ship), the sampling lag time (~ 3 min) and the location. When a sample was to be taken, an instantaneous (page printout) record of the *in situ* data was produced, and a stopwatch started to determine the exact time for collection. Samples were drawn precisely (nearest second, although filling the bottle generally took ~ 5 s) after the determined delay time had passed (the ECOsuttle generally spent 10–20 s at the surface). The delay time was determined by pumping tonic water (containing the highly fluorescent quinine sulfate) through the ECOShuttle pumping system and visual observation of a bright blue fluorescence in the laser-induced fluorescence flow cell prior to the cruise. The delay time apparently shifted several times (between two or three quasi-states) during a cruise, so delay times were occasionally determined on the June 2000 cruise by aligning the maximum CDOM concentrations (AC-9, Safire, LIF) with the minimum salinities (ECOShuttle CTD). Careful alignment of in-line data with ECOShuttle data was made after the cruise. Only for a few samples taken in the strong vertical salinity gradient was this data difficult to align, and for these samples, salinity was determined on discrete samples in the lab. For April 2001, we used a thermosalinograph placed in the in-line flow so that minimum salinities (surface waters in the plume area) could be observed at the sampling port. This offered good alignment of sample collection with *in situ* data.

This guided sampling strategy allowed routine measurement of surface waters every 30–60 min of the cruise as well as targeted sampling (increased sampling frequency of a salinity gradient based on observed salinities, subsurface features, matched samples of two separate water masses, etc). The vast

majority of the samples were collected from the surface.

DOC and fluorescence samples were drawn directly from a Teflon sampling port from the ECOShuttle pumping system into precombusted (4 h at 500 °C) 250-ml Pyrex bottles. Bottles (12–24 for the whole cruise) were reused after rinsing with sample water three to five times, and this sampling strategy showed no sample carry-over as tested by occasional Milli-Q water blank filtrations. Samples were filtered (within 2 h of collection) through precombusted 25-mm glass fiber filters (Whatman GFF, 0.7-μm nominal pore size) under positive pressure (< 15 psi) using ultra-high-purity nitrogen and placed in precombusted 40-ml vials (clear for DOC, amber for fluorescence/absorbance). Filtered DOC samples were acidified using 200 μl of 50% (v/v) phosphoric acid to bring the pH to 2 and stored at 4 °C until analysis. Filtered fluorescence/absorbance samples were frozen in 40-ml amber vials and remained frozen until analysis. Comparisons of filtered and unfiltered samples showed little or no filtration artifact (generally < 2% for fluorescence/absorbance). Milli-Q water blank filtration showed less than 5% blanks. Replicate sampling demonstrated reproducibility for CDOM fluorescence and absorbance measurements to < 1% and reproducibility for DOC to < 5%. Comparisons of ship-board analysis to laboratory analysis up to 12 months later showed no measurable storage artifact (unpublished data).

2.3.2. DOM fluorescence

Fluorescence of filtered seawater samples was measured with a Photon Technologies International (London, Ontario) Quantum Master-1 spectrofluorometer equipped with a double excitation monochromator, a single emission monochromator and a cooled photomultiplier assembly. All slits widths were set to 4 nm. Emission spectra were obtained at 337-nm excitation and were integrated from 350 to 600 nm. Spectra were blank subtracted (to remove the water Raman scattering peak) and compared with four to five quinine sulfate (pH = 2) standards run each day that samples were analyzed. CDOM fluorescence is expressed as quinine sulfate units (QSU) where 1 QSU is equivalent to the fluorescence emission of 1 μg/l quinine sulfate solution integrated from 350 to 600 with excitation wavelength = 337 nm. The blank (Milli-Q) subtraction differed by less than 1% from a multipoint curve fitting routine used to remove the Raman scattering peak. Fluorescence measurements reported in this way are equivalent to those normalized to the water Raman peak (F_n; Hoge et al., 1993) since Raman areas were consistent within 1% for all samples. Samples were thawed quickly in a warm water bath to minimize the formation of insoluble precipitates during the freeze–thaw cycle.

The voltage output of the SeaTech and SeaPoint CDOM fluorometers was calibrated against discrete sample measurements (Fig. 2) which show that the *in situ* measurements are consistent with discrete methods and that calibration did not drift significantly over the entire cruise period (see Section 3.1).

2.3.3. DOM absorbance

CDOM absorption spectra (190–800 nm) was measured on filtered samples with a Cary 50 spectrophotometer fitted with a 10-cm path length cell. We have found that shipboard filtration through precombusted glass fiber filters (Whatman GFF) in combination with the freeze–thaw cycle sometimes yields artifacts due to scattering off glass fibers dislodged during filtration. We therefore refiltered (0.2-μm Poretics polycarbonate filters) thawed seawater samples immediately preceding absorption measurements. In addition to full spectra, absorption at 337 nm is indicative of the concentration of CDOM and can be compared with fluorescence measurements excited at this wavelength.

2.3.4. Dissolved organic carbon

DOC samples were analyzed in triplicate by high-temperature combustion (Peltzer and Brewer, 1993; Chen et al., 1996). Briefly, 50 μl of sparged, acidified seawater samples were injected into a two-stage furnace (800 °C upper, 600 °C lower) with a carrier gas of ultra-high-purity O_2. Quartz chips were used at the top of the combustion tube to provide catalytic sites for oxidation (Qian and Mopper, 1996). DOC was converted to CO_2 in the combustion column and then flowed through a $AgNO_3$ trap (chloride) that was cooled to 2 °C (water), a $MgClO_4$ trap (water) and particle traps (2 μm, 0.2 μm) (aerosols) and into a LiCor nondispersive infrared detector. Peaks were integrated using HP Chemstation chromatography software and were compared with a five-point stan-

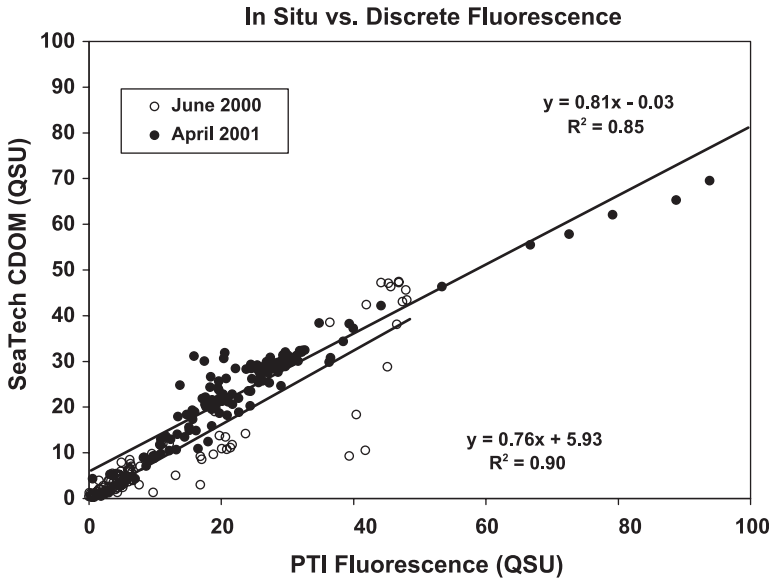


Fig. 2. *In situ* fluorescence measurements (SeaTech CDOM fluorometer mounted on the ECOShuttle) vs. discrete, filtered fluorescence measurements on samples pumped onboard for June 2000 and April 2001.

dard of potassium acid phthalate to establish daily response factors and Milli-Q UV water used to determine shifting instrument blanks. Both response factors and blanks were compared with intercomparison standards provided by J. Sharp (U. Delaware) and D. Hansell (Bermuda Biological Lab).

3. Results

3.1. CDOM measurements

Discrete fluorescence measurements (337-nm excitation) correlated very well with absorption (337 nm)

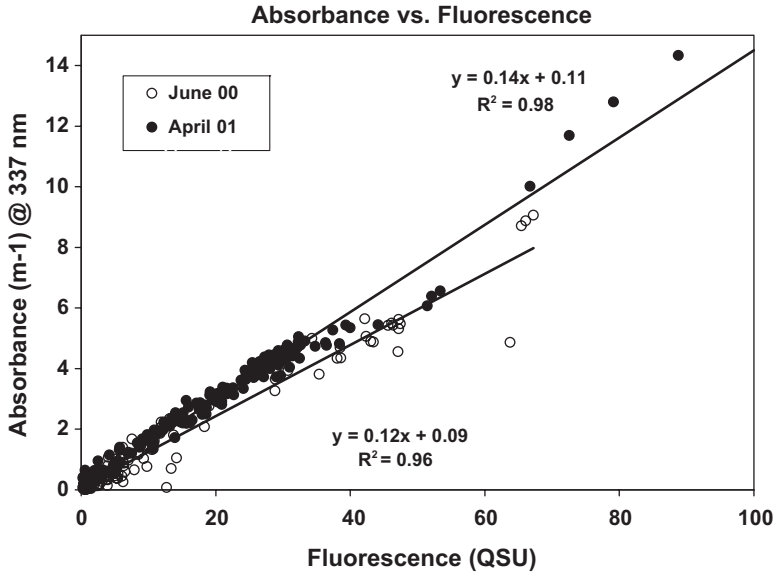


Fig. 3. CDOM absorbance (at 337 nm) vs. CDOM fluorescence taken on discrete samples for June 2000 and April 2001.

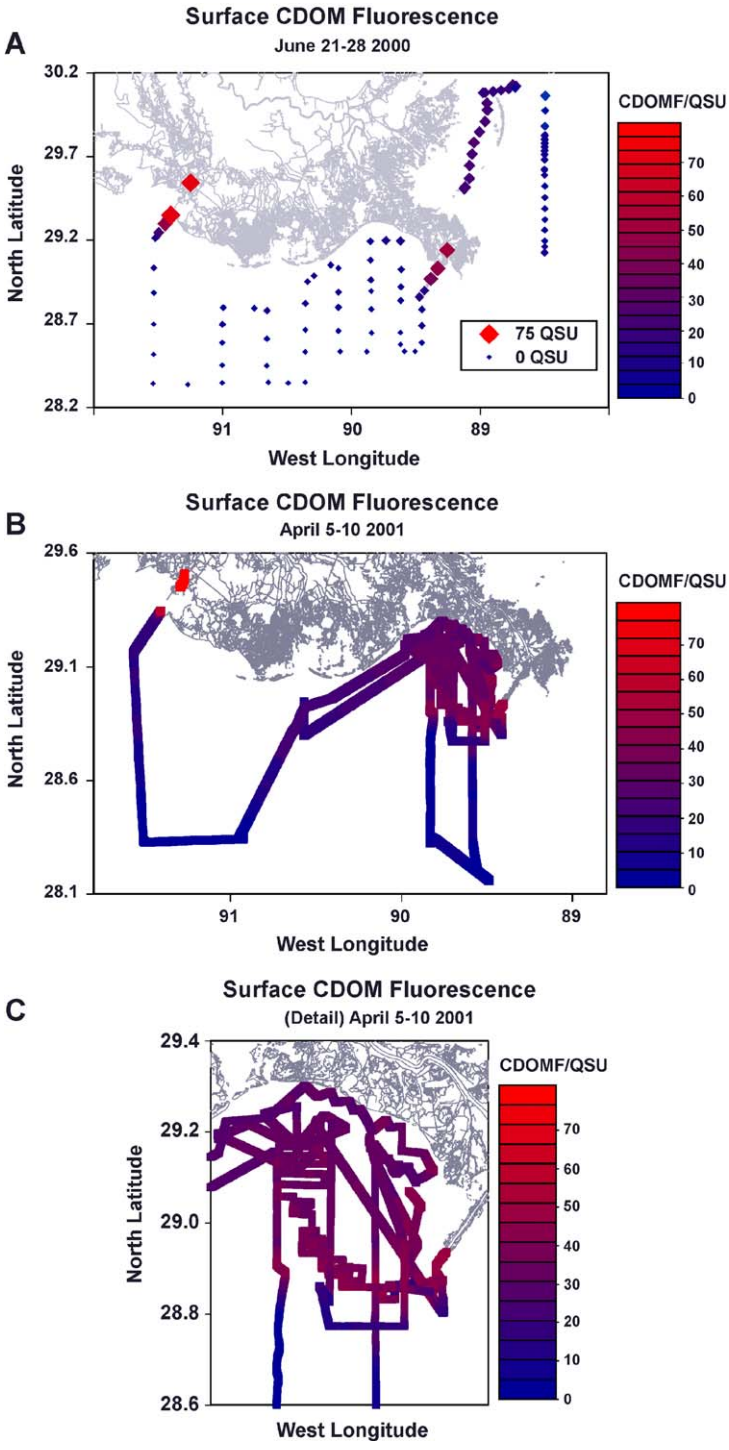


Fig. 4. Surface CDOM concentrations from the SeaTech fluorometer aboard the ECOShuttle in June 2000 (A) and the SeaPoint fluorometer in the shipboard on-line pumping system in April 2001 (B). A more detailed distribution is shown in (C).

measurements ($r^2 = 0.96$, $n = 206$ for June 2000; $r^2 = 0.98$, $n = 221$ for April 2001; Fig. 3), so it appears for this study that DOM fluorescence and absorbance are interchangeable and reliable measurements of CDOM. Discrete CDOM fluorescence measurements agreed fairly well with *in situ* measurements ($r^2 = 0.85$, $n = 126$ for June 2000; $r^2 = 0.90$, $n = 143$ for April 2001; Fig. 2). The mismatch is due to the different band widths of fluorescence measurements of the *in situ* and discrete measurements, the misalignment of the timing of sample collection and the presence of particles (discrete samples are filtered). The better correlation in April 2001 suggests that ~ 10% of the error was due to switching the gain settings on the SeaTech fluorometer during the June 2000 cruise (constant setting for the entire April 2001 cruise) as well as better synchronization of the two measurements in April 2001 (using the thermosalinograph).

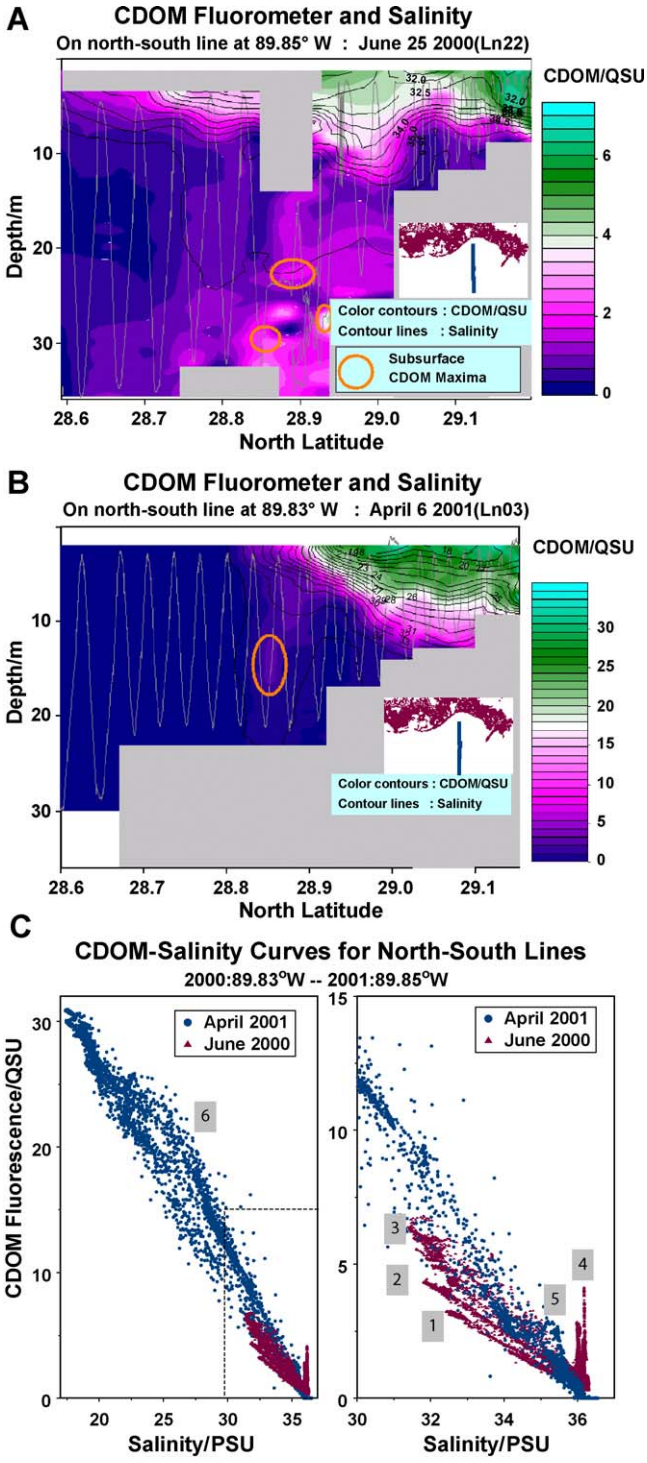
3.2. Summer vs. Spring

Surface distributions of CDOM in the Mississippi plume region are presented in Fig. 4. The extent of high CDOM concentrations is clearly related to flow. With a higher flow of ~ 20,000 m^3/s in the spring (US Army Corps of Engineers, Hydraulics Branch, 2002), fluorescence values of >25 QSU are observed in surface waters throughout the region. During the low-flow period of June 2000, these highly colored surface waters are only observed at the mouths of the Mississippi and Atchafalaya Rivers. The high color in surface waters is correlated to low salinities that are more pervasive in the high-flow period.

Cross-shelf (cross-plume) transects of CDOM along 89.8° W longitude for June 2000 (Line 22) and April 2001 (Line 3) are presented in Fig. 5A and B. The distribution of CDOM generally correlates with the distribution of salinity in the region (Fig. 5). While lower salinities and higher CDOM are present in the plume region in April 2001, high concentrations of CDOM are generally constrained to the upper 12 m of the water column. The base of the plume is quite variable in June 2000, indicative of complex three-dimensional mixing of an unconfined river plume (Durand et al., 2002). A slightly deeper penetration and more constrained plume (towards the shore) are evident in the higher velocity, higher turbulence period in April 2001. A deep penetration (to >20 m) of low-salinity, high-CDOM plume water is apparent at the seaward edge of the plume, a feature that has been observed in the fall (Walker et al., 1996). This deep intrusion of the plume at the seaward edge of the plume, coincident with presumably high shear velocities, is probably a common feature and may be a mechanism for injecting high-CDOM surface waters below the plume. Due to the stratification during June 2000 and the degradation of organic matter and production of CDOM at depth (Chen et al., 2004, this issue), deep maxima of CDOM can be seen below the plume in June 2000 (Fig. 5A). This biological production is not accompanied by lower salinities (Fig. 5A and C).

Fig. 5C shows CDOM as a function of salinity for the two seasons. Again, the lower salinities and higher CDOM can be seen in the region of interest for the April 2001 data set. The subsurface, biological production of CDOM at high salinity is clearly seen in June 2000, where CDOM increases at constant and high salinity (feature "4"). Additionally, three mixing lines with different apparent freshwater end members are present. The lowest mixing curve "1" is farthest offshore, the middle curve "2" is the main plume, and the highest apparent end member mixing line, "3," is nearshore and somewhat variable. The Mississippi River is the major source of freshwater in this area, so it is unlikely that some other river system (e.g., Atchafalaya) is influencing this region. Therefore, there are two possible interpretations for this data. First, the Mississippi River end member varies temporally and was lower previous to our cruise. This older water (farther offshore) represents a separate water mass (as shown by a temperature–salinity relationship; data not shown) and shows a distinct mixing line of lower freshwater CDOM end member

Fig. 5. CDOM color contours across the Mississippi plume in June 2000 (Line 22) (A) and April 2001 (B). Salinity is represented by the contour lines. Inset maps show the location of the line in relation to the Birdfoot region. Please note the change in scale for CDOM color contours. Areas where there was no data were masked off. Bottom depths were approximately 5 m below the maximum depths of the ECOShuttle. Subsurface CDOM maxima (A) and the plume feature mentioned above (B) are highlighted with orange circles. CDOM (calibrated to QSU by comparing to discrete samples; Fig. 2) vs. salinity for both cruises (C). The panel on the right shows more detail at the higher salinities.


A
CDOM Fluorometer and Salinity
On north-south line at 89.85° W : June 25 2000(Ln22)
CDOM/QSU
Depth/m
North Latitude
Color contours : CDOM/QSU
Contour lines : Salinity
Subsurface
CDOM Maxima
B
CDOM Fluorometer and Salinity
On north-south line at 89.83° W : April 6 2001(Ln03)
CDOM/QSU
Depth/m
North Latitude
Color contours : CDOM/QSU
Contour lines : Salinity
C
CDOM-Salinity Curves for North-South Lines
2000:89.83°W -- 2001:89.85°W
CDOM Fluorescence/QSU
Salinity/PSU
April 2001
June 2000

with the same marine source. The mixing line labeled "2" in Fig. 5C is the main mixing line of the present Mississippi river plume in the region, and the end member is that in the Mississippi River at the time of the cruise. It has been shown that at high-flow periods, the plume normally turns toward shore and is clearly identifiable for about 2 days (Hitchcock et al., 1997). The highest mixing line labeled "3" is near the shore. The coastline of the Louisiana Bight is a series of swamps and wetlands that have been observed to outwell nutrients and dissolved organic matter (Inoue and Wiseman, 2000; Engelhaupt and Bianchi, 2001) and are therefore expected to have high CDOM end members, but possibly low freshwater flows (Inoue and Wiseman, 2000). Temperature and salinity data suggest this water mass is highly influenced by the Mississippi River water (TS data for mixing line "3" look similar to that for mixing line "2"). Therefore, we expect this nearshore water mass might be an older Mississippi River plume water mass with a higher end member value or that is influenced by the local wetlands and is isolated from the Mississippi River plume (more on this below). Flushing times for these Louisiana bays is estimated to be about 27 days (Inoue and Wiseman, 2000), suggesting an increased residence time for interactions compared with plume waters (2 days; Hitchcock et al., 1997).

The second interpretation is that the low apparent end member offshore ("1") has experienced photodegradation previous to mixing. In this scenario, Mississippi water with a constant end member flows out and is isolated at the surface due to density gradients. The older water (we do not have a way to determine time scales, but weeks seems reasonable) has been photobleached, so that the apparent CDOM end member is reduced. What we are measuring on Line 22 in June 2000 is the mixing of this low-salinity, photobleached surface plume water with the same marine end member. Given a constant Mississippi end member, photobleaching processes cannot explain the nearshore water "3" being higher than "2" (plume at the mouth of Southwest Pass), since water mass "3" has been exposed to more sunlight than "2," so the previous explanation of the coastal influence on this nearshore water mass is the only explanation for this relationship. Two more pieces of information are needed to differentiate between these two hypotheses. First, some sense of time scales for water mass mixing of older plumes is necessary to see if photobleaching rates are large enough to explain this discrepancy, and second, temporal measurements of the freshwater end member are needed to gain an understanding of variability and mixing. While these data are not currently available, we are working on both fronts, using Lagrangian drifters to understand the dynamics of the plume better (see below and Hitchcock et al., 2004, this issue), and we will soon deploy a CDOM fluorometer year-round in the Mississippi River.

In April 2001, significantly higher CDOM concentrations and more turbulent mixing obscure the observation of subsurface biological CDOM production (Chen et al., 2004, this issue) and the crossing of different water masses (Fig. 5C). However, the variability seen in Fig. 5C shows that many of the same processes are probably working to control the observed relationships. Feature "5" in Fig. 5C shows an increase in CDOM at high salinity, and while it is not as clear as the increase in the highly stratified June 2000 data set, subsurface biological production in April 2001 appears to be of the same magnitude of increase as in June. Additionally, Feature "6" shows a higher apparent mixing curve for nearshore, subsurface waters, suggestive that the Mississippi River end member is either varying temporally or that increased residence times and increased input from coastal wetlands increases the apparent end member.

In April 2001, at any given salinity, considerable variability in CDOM demonstrates that *in situ* biological production of CDOM, of a similar magnitude to that in June, may be occurring throughout the water column rather than being concentrated on an isopycnal. Overall, there is evidence for *in situ* production of CDOM in the Louisiana Bight during both seasons in the region of the Mississippi plume. This is consistent with measurements of increased productivity at mid-salinities in the plume (Lohrenz et al., 1990, 1999; Chin-Leo and Benner, 1992).

3.3. Excess CDOM

One method of visualizing the production or degradation of CDOM in an area of complex dynamics is to normalize CDOM to salinity. This effectively removes the dominant control of CDOM so that secondary influences might be observed. In order to

do this, we calculate "excess" CDOM as the difference between the observed CDOM concentration and the CDOM concentration on the conservative mixing line at the same salinity.

$$\mathrm{CDOM}_{\mathrm{excess}} = \mathrm{CDOM}_{\mathrm{in\ situ}} - [(S_{\mathrm{m}} - S_{\mathrm{in\ situ}}) \times (\mathrm{CDOM}_{\mathrm{f}} - \mathrm{CDOM}_{\mathrm{m}})/S_{\mathrm{m}} + \mathrm{CDOM}_{\mathrm{m}}] \quad (1)$$

$\mathrm{CDOM}_{in\ situ}$ is the measured CDOM at any given point, $\mathrm{CDOM}_{\mathrm{f}}$ is the freshwater end member determined from the river transect (46 QSU for June, 53 QSU for April), and $\mathrm{CDOM}_{\mathrm{m}}$ is the marine end member (0.3 QSU) at S_{m} (36). Fig. 6A shows "excess CDOM" for Line 22. In June 2000, a significant amount of CDOM is produced below the Mississippi plume at around 28.85°N latitude. This is likely due to bacterial degradation of phytoplankton detritus and is isolated on isopycnals (Chen et al., 2004). Excess CDOM is also apparent towards the coast due to a higher previous Mississippi end member and/or influence from coastal wetlands as discussed above. In April 2001, excess CDOM is

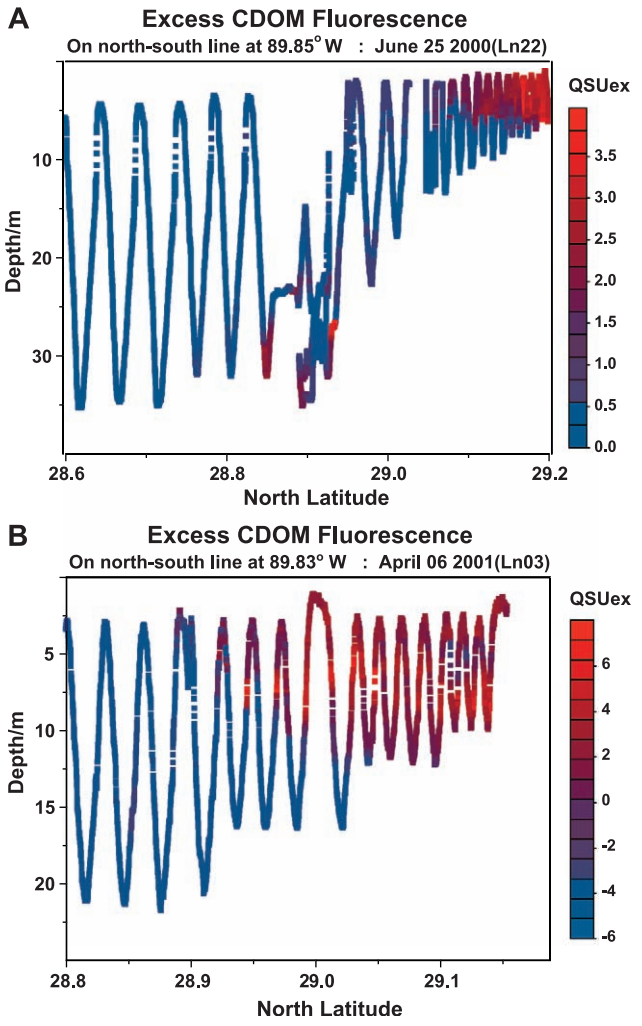


Fig. 6. "Excess" CDOM on Line 22 from June 2000 (A) and on Line 3 from April 2001 (B). Excess CDOM is determined by subtracting the measured CDOM from the CDOM at the same salinity calculated from the conservative mixing line determined by the river transect (Eq. (1)).

most apparent in the subsurface nearshore waters (Fig. 6B). This may be due to an increased residence time of this colder water mass and influence from coastal wetlands or *in situ* biological production. There is also some evidence for subsurface biological production at ~ 15 m depth at 28.85°N latitude (Figs. 5B, 5C and 6B). These biologically produced CDOM signals are more vertically dispersed due to a more intense mixing period in April 2001 (Fig. 6B). The thin layers and pycnoclines that lead to easily visible subsurface maxima (Chen, 1999; Chen et al., 2004) of CDOM do not form; however, it is apparent from Figs. 5C and 6B that biological production of CDOM continues at magnitudes similar to those during the summer (Bissett et al., 2001; Chen et al., 2002).

3.4. Atchafalaya vs. Mississippi

By comparing the Mississippi and Atchafalaya systems, CDOM production mechanisms might be elucidated because the lower watersheds of the two systems contrast sharply. The source water for both systems is the same at Old River Junction (~ 480 km upstream from Southwest Pass), and the Army Corps of Engineers controls the distribution of freshwater to the two systems. The Atchafalaya River water interacts with a complex system of productive wetlands in its 833,000-acre basin (Inoue and Wiseman, 2000; Engelhaupt and Bianchi, 2001). In contrast, the Mississippi has minimal interaction with vegetation and soils due to anthropogenic controls of the channelized river system (Pakulski et al., 2000). Fig. 7 shows a transect into the Atchafalaya for June 2000 (A) and April 2001 (B). Unlike the complex Mississippi Delta region, the Atchafalaya drains completely into Atchafalaya Bay where it is semi-confined with increased trapping of dissolved and particulate materials within the delta region (Lane et al., 2002). Increase mixing and longer residence times lead to a typical salt wedge (Fig. 7A and B). Fig. 7C shows CDOM–salinity relationships for Line 32 in June 2000 and Line 29 in April 2001. The relationship above salinity ~ 25 for both seasons is driven by the Mississippi River plume offshore of Atchafalaya Bay. The line with a clearly higher apparent end member in June 2000 shows the markedly different characteristics of the Atchafalaya River-influenced water mass (temperature and salinity data confirm this; data not shown). In April 2001, the nearly vertical mixing line around salinity 20 represents a rapid transitional area where the ship crossed from the Mississippi plume waters into the Atchafalaya-influenced waters over a distance of < 1 km. In both cases, the Atchafalaya freshwater end member is considerably higher than the Mississippi freshwater end member.

Fig. 8 shows discrete CDOM vs. salinity (A) and DOC vs. salinity (B) relationships for the two rivers. It is clear that the Atchafalaya river CDOM end member (70 QSU in June 2000; 100 QSU in April 2001) is higher than the Mississippi River CDOM end member (46 QSU in June 2000; 52 QSU in April 2001). It is also apparent that the seasonal variability of the CDOM end member is more significant for the Atchafalaya River. The Atchafalaya freshwater end member is ~ 43% higher in spring that summer, while the Mississippi freshwater end member is only 13% higher in spring (Fig. 8A).

Despite significant variability in DOC between salinity 10 and 30 suggesting local production and degradation mechanisms, DOC end members show similar trends (Fig. 8B) to the fluorescence data with the Atchafalaya end member being ~ 33% higher in DOC than the Mississippi end member in June 2000 and ~ 66% higher in April 2001. End member DOC concentrations in spring are similar to those in summer in the Atchafalaya, while DOC is slightly higher in the Mississippi in summer. This suggests that slightly more colorless DOC is produced in summer in the Mississippi, more colored DOC is produced in the Atchafalaya in the spring, and that apparent quantum yields (fluorescence per μM C) are similar for both systems in the same season, but are 50% higher in spring than summer (Table 1).

These observations are consistent with the hypothesis that the quality of the material is dependent on season, and the amount of CDOM produced is significantly affected by the interactions with coastal wetlands. Stable carbon isotope data suggest that the Atchafalaya and Mississippi rivers have a similar values of −25.0‰ to −29.0‰ (Wang et al., 2003,

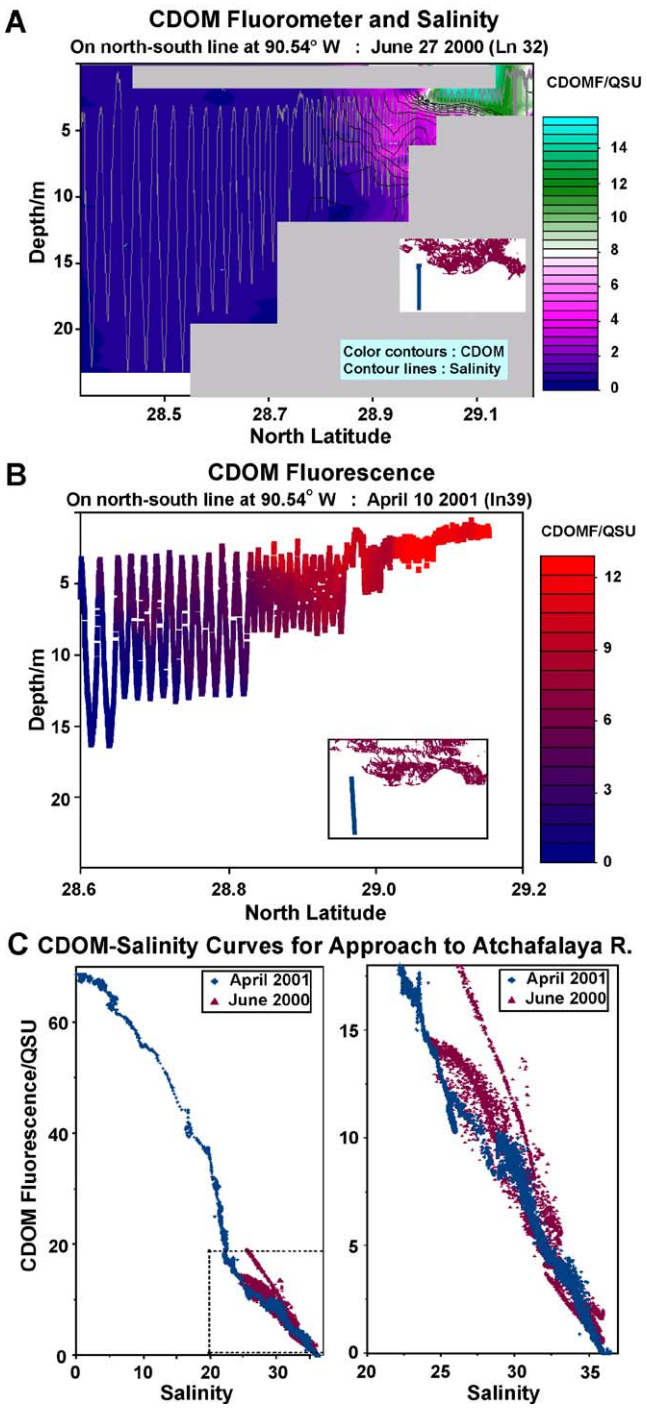


Fig. 7. CDOM color contours on a transect entering Atchafalaya Bay in June 2000 (A). Line contours are salinity. CDOM is plotted (color) as a function of latitude and depth for a similar transect in April 2001 (B). Contouring of this data set was not representative of the data due to the depth distribution of the measurements and is therefore not shown. CDOM vs. salinity is presented for both seasons in (C).

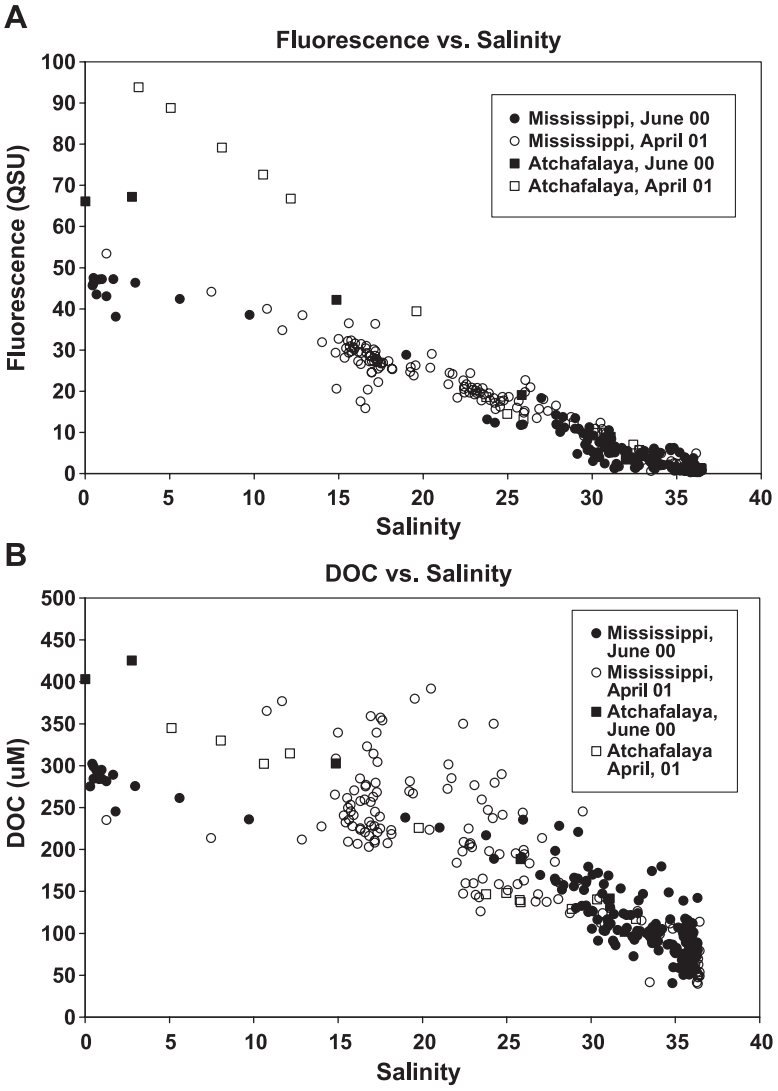


Fig. 8. Fluorescence vs. salinity (A) for the Mississippi and Atchafalaya plumes in June 2000 and April 2001. DOC vs. salinity for both plumes on both cruises (B).

this issue) so it does not appear that C-4 plants (e.g., salt marsh grasses) contribute significantly to the total DOC in either system. Plants have been found to be greater contributors to Louisiana Bay DOM than soils (Engelhaupt and Bianchi, 2001), and plants might be expected to have a greater seasonal

Table 1
River end members

End member	June 2000 DOC (μM)	June 2000 fluorescence (QSU)	April 2001 DOC (μM)	April 2001 fluorescence (QSU)	June 2000 Flu/DOC (QSU/μM)	April 2001 Flu/DOC (QSU/μM)
Mississippi	307	46	241	52	0.15	0.22
Atchafalaya	408	70	401	100	0.17	0.25

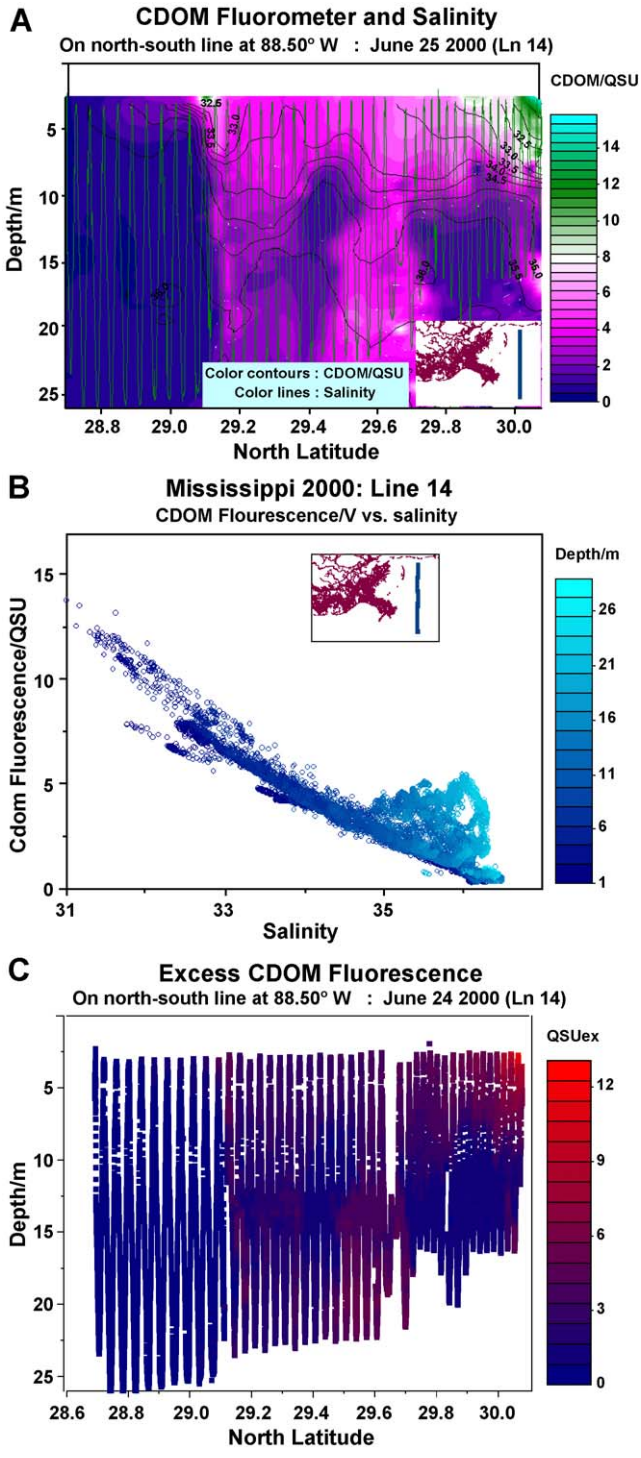


Fig. 9. CDOM color contours on a cross-shelf transect (Line 14) on the east side of the Birdfoot region into Chandaleur Sound in June 2000 (A). CDOM vs. salinity for this transect (B). "Excess" CDOM on this transect (C).

variability than soils due to a combination of light and temperature.

3.5. Westside vs. Eastside

In June 2000, the eastern side of the Birdfoot region was investigated to see if the shallow Chandaleur Sound acted as a source or potentially a photochemical reactor for CDOM. Fig. 9A shows Line 14, a cross-plume transect from blue water into the Chandaleur Sound. Fig. 9B shows CDOM vs. salinity for this transect. CDOM trends on the eastern side of the Birdfoot region can be seen on the western side. High CDOM in the upper 10 m within the plume with subsurface production along pycnoclines in the subsurface are evident. Additionally, CDOM is high in Chandaleur Sound, a shallow water mass influenced by coastal wetlands and isolated from the plume somewhat by barrier islands. High-salinity production was apparent over large areas (EXCESS Fig. 9C). Chandaleur Sound showed higher than plume CDOM with respect to salinity, similar to nearshore Louisiana Bight waters where local wetlands are leaking out higher end member CDOM than the Mississippi River plume. There was no clear evidence for photochemical bleaching, and in fact, the shallow nearshore regions acted as a local source for CDOM to the region.

3.6. Nearshore waters

By examining CDOM–salinity relationships as we crossed the plume/nearshore water interface multiple times in April 2001, we could examine the nearshore waters with respect to the Mississippi plume waters. This interface was visible to the human eye with higher particle loads in the plume waters. However, CDOM–salinity relationships do not show a significant difference in apparent freshwater end members in surface waters. In deeper waters (>5 m) (see Fig. 6B) nearshore, cold water with a higher apparent end member was observed. Our interpretation of this higher CDOM ("excess" CDOM) in deeper nearshore waters is that either material is being collected in salinity structures created when plume pycnoclines break down or a higher amount of CDOM is being added to the subsurface plume from nearby coastal embayments such as Barataria Bay. This is consistent with the fact that coastal waterways do not represent a significant freshwater flux, but are often higher in plant-derived organic matter than plume waters (Engelhaupt and Bianchi, 2001).

3.7. Temporal evolution

In April 2001, a triad of Lagrangian drifters were released at the mouth of Southwest Pass. The ECOShuttle was towed in boxes around the drifters for ~ 24 h, and then various transects of the plume were conducted while continuously tracking and revisiting the drifters. The drifters were retrieved 55 h after deployment. The Mississippi River plume traveled west and then curved back up towards shore to the northeast in a typical anti-cyclonic flow (Hitchcock et al., 2004). The addition of a time scale for the same water mass being mixed allows for the investigation of the temporal evolution of CDOM within the plume. By picking points that were close to the drifter location in latitude, longitude and time, we compiled SeaTech CDOM measurements on a temporal scale. Because plume water was constantly being mixed with marine end member water, CDOM decreased with time. However, a salinity correction can be made as was done to calculate "excess CDOM" (Section 3.3) based on the Mississippi River transect (Line 7) so that trends in CDOM not related to salinity can be graphed vs. time (Fig. 10). There appears to be an initial drop (~ 20%) in CDOM fluorescence in the first 20 h possibly due to flocculation or sorption of CDOM to particles or increased bacterial respiration (Chin-Leo and Benner, 1992). The decrease then slows to about 5% per day as the plume spreads, possibly due to photobleaching of surface waters as particles sink and water clarity increases. The drifters remained in waters of ~ 15 salinity and were taken up in the drift line between nearshore waters and plume waters. In the 2–3 days it takes for the plume to flow north and lose its energy, CDOM is reduced by about 25% compared to the shelf-wide average of CDOM. Even with temporal time scales, however, it is

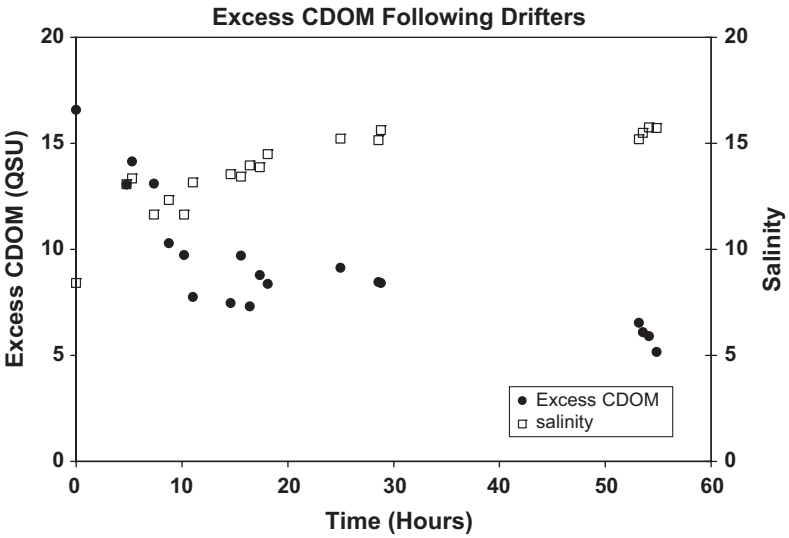


Fig. 10. CDOM normalized to salinity vs. time along the Lagrangian drifter tracks.

difficult to differentiate photobleaching, *in situ* production and flocculation processes.

4. Discussion

4.1. Terrestrial DOM inputs

CDOM and DOC freshwater end members in the northern Gulf of Mexico vary temporally. CDOM and DOC in freshwater are generally higher during higher flow conditions, presumably due to the larger leaching capacity (deeper penetration, larger area) of rain and surface waters through soils during high-flow periods. Hour to week time scales for this end member variability is possible depending on residence times of water in the watershed. Smaller systems generally have shorter time scales (hours; Gardner et al., in preparation), while large systems like the Mississippi may vary on time scales of days to weeks. Seasonal variability due to plant growth cycles has also been observed. The production of CDOM and DOC in wetlands and salt marshes have been found to be highest in late summer (Engelhaupt and Bianchi, 2001; Gardner et al., in preparation). Variability on time scales of days to weeks as well as seasonally will affect CDOM distributions in the northern Gulf of Mexico and interpretations of mixing (conservative or nonconservative), production and degradation as freshwater is diluted by marine end members.

Both fluorescence and DOC are elevated in the surface waters of the northern Gulf of Mexico. As both are affected by some of the same factors, especially conservative mixing of river and marine end members, the two properties are loosely related (Fig. 11). The production of colorless DOC, the variability in apparent quantum yields (QSU/μMC) and photobleaching of CDOM all lead to a considerable variability in this relationship, however, and therefore, it would be difficult to estimate total DOC with CDOM measurements in this system (Chen et al., 2002).

4.2. Marine DOM production

Production of CDOM below high-productivity plume waters was observed in June 2000 where thin layers of high CDOM were concentrated on isopycnals (Fig. 5A; Chen et al., 2004, this issue). Fig. 5C shows that CDOM is likely produced in April 2001 at similar magnitudes to that in the summer, but excess CDOM is more vertically and horizontally dispersed (Fig. 6). DOC appears to be produced in the mid-salinities of 15–30 where primary productivity reaches a maximum (Lohrenz et al., 1990, 1999; Fig. 8B). As shown through a mass-balance approach in

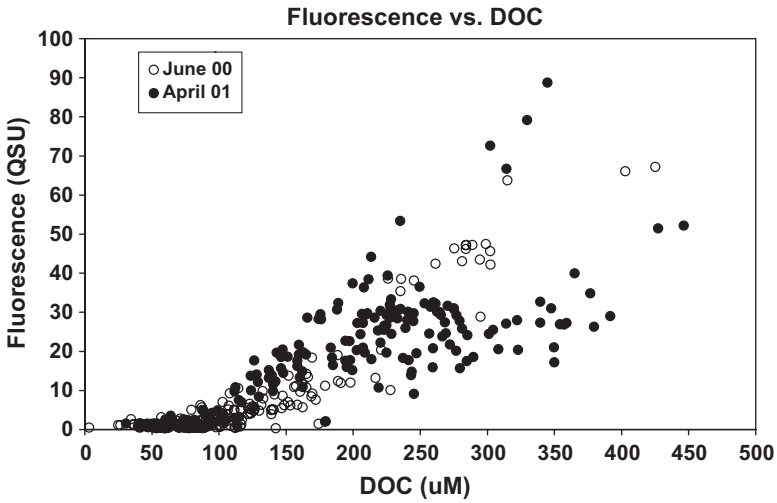


Fig. 11. Fluorescence vs. DOC for both cruises.

the Mid-Atlantic Bight, *in situ* productivity of CDOM may in fact greatly outweigh the delivery of terrestrial organic matter to coastal waters. A similar mass balance approach is difficult in the northern Gulf of Mexico because the Mississippi plume is unconfined, and the general physics of the area are not as well constrained as in the Mid-Atlantic Bight (Chen et al., 2002). While terrestrial biomarkers can be found in plume waters (Opsahl and Benner, 1997), DOC in general is quite reactive with terrestrial organic matter being replaced by marine organic matter at salinities <30 (Wang et al., 2004, this issue).

4.3. Mixing

Mississippi plume water flows out into the northern Gulf of Mexico quickly 2 days before it stalls out in the Louisiana Bight. Complex three-dimensional mixing is evident from ECOShuttle cross-sections (e.g., Fig. 5A and B and is more thoroughly discussed in Hitchcock et al., 2004). The Mississippi plume generally curves back from its initial westward direction to the northeast into the Louisiana Bight. A nearshore coastal current generally flows in the opposite direction, to the west, and is influenced by the Mississippi water mass, but its flow and mixing are controlled by local winds, bottom topography and tidal flushing of local shallow embayments (Inoue and Wiseman, 2000). While freshwater discharge from coastal embayments is small, tidal mixing allows organic matter to be flushed out into these nearshore waters.

4.4. Photobleaching

Vodacek et al., (1997) has shown evidence for shelf-wide photobleaching of CDOM in the Mid-Atlantic Bight during summer-stratified conditions. Residence times on the MAB are estimated to be weeks to months with mixing depths of 10–20 m. Also in the MAB, Chen et al. (2002) found evidence for photobleaching in August, although this was less clear in the spring. Using a mass-balance approach to the shelf, they found that it was difficult without measurements of temporal scales to determine rates of photobleaching on the shelf and could only identify that a net positive production of CDOM occurred in the summer for the whole water column compared with the spring (*in situ* production; photobleaching) (Chen et al., 2002). The intent of the April 2001 cruise was to track a single water mass with Lagrangian drifters (Hitchcock et al., 2004, this issue) in an attempt to observe photobleaching processes. Over the course of 2.5 days, there was some evidence (5%/day) for photobleaching after an initial drop of 20% probably due to flocculation in the turbid Mississippi plume waters (Fig. 10). It is difficult to differentiate photobleaching of this water mass from other pro-

cesses such as sorption and particle sinking, however. CDOM–salinity relationships for both cruises on over 60 individual lines crossed by the ECOShuttle from 2 to ~30 m show little evidence of photobleaching (CDOM measurements below a hypothetical conservative mixing line). Premixing photobleaching (photobleaching of fresher water masses before mixing with marine end members) was offered as an interpretation of variable freshwater apparent end members (Fig. 5C), but it seems unlikely that mid-salinity photobleaching was not observed on the three-dimensional surveys (Fig. 5) at two time periods if this were the case. Therefore, the various mixing lines observed on these cruises (e.g., Figs. 5C and 7C) are more easily explained by a Mississippi River end member that varies on time scales of weeks by as much as 50% in CDOM.

While photobleaching has been shown to be a significant process controlling CDOM concentrations in irradiation studies (Miller and Moran, 1997), and *in situ* (Vodacek et al., 1997) and model studies (Bissett et al., 2001), conclusive evidence that this is a significant process in the highly turbid, rapidly mixing (<2 weeks) coastal waters in the northern Gulf of Mexico is lacking.

5. Summary

High-resolution CDOM fluorescence measurements allowed the observation of several important processes controlling CDOM in an unconfined river plume. First, mixing is complex, varies with flow and wind, and is three-dimensional, resulting in multiple fronts between plume and gulf waters and plume and nearshore waters. Second, multiple mixing curves result from a temporally varying freshwater end members in both the Mississippi and Atchafalaya systems. Third, the high productivity in coastal wetlands leads to higher CDOM in waters that interact with these wetlands (e.g., Atchafalaya or nearshore waters), while lower CDOM results from extensive channelizing and non-interaction with coastal wetlands (e.g., the lower Mississippi). Fourth, apparently, the CDOM that is produced locally in coastal wetlands has a similar quantum yield (fluorescence per unit DOC) in both systems, but this ratio varies with season. Finally, it does not appear that photobleaching of CDOM in the turbid, rapidly flowing portion of the Mississippi plume may not be significant. Overall, high-resolution (both temporal and spatial) measurements are necessary to elucidate the complex biological, chemical and physical processes controlling CDOM distributions in river-dominated systems.

Acknowledgements

We thank the Office of Naval Research (especially Program Manager Joan Cleveland) for continued support of this research (Award numbers N00014-97-1-0720 and N00014-00-1-0325). We also than the Captain and crew of the *R/V Pelican*, Ayora Berry, Julie Callahan and Xuchen Wang for DOC analysis, Yixian Zhang for fluorescence and absorbance analysis, Sarah Oktay and Joseph Smith for onboard filtration, Peter Edwards for assistance with the ECOShuttle and the entire scientific crew on the two *R/V Pelican* cruises for collaboration).

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