



Source characterization of dissolved organic matter in a subtropical mangrove-dominated estuary by fluorescence analysis

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Abstract

Measurements of dissolved organic carbon (DOC), UV–visible, fixed wavelength fluorescence, and synchronous fluorescence were performed in an effort to characterize spatial and temporal variability in concentration and source of dissolved organic matter (DOM) in surface waters of the southwest coast of Florida. Concentrations of DOC in the surface water ranged from 318 to 2043 μM and decreased from the upper estuary to the coastal areas, and were not only influenced by source strength but also by the hydrology and geomorphology of the mangrove-dominated southwest Florida estuarine area of Everglades National Park. Mangroves provided a significant input of DOM to the estuarine region. This terrestrially derived DOM underwent conservative mixing in these estuaries, but at salinities ≥ 30 a clear switch from terrestrial to marine DOM was observed indicating a change in the nature and origin of the dominant DOM. The results show that the dynamics of DOM in these subtropical estuaries are complex and that geomorphologically compartmentalized estuarine subregions can be distinguished based on the optical characteristics of their DOM.

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1. Introduction

DOM in aquatic environments has been widely studied because of its importance in a variety of physical, geochemical, and biological processes (e.g. Scully and Lean, 1994; Cai et al., 1999; Alberts and

Takacs, 1999; Del Castillo et al., 2000). DOM is often classified into two major categories, (a) biochemically defined compounds (non-humic substances) such as proteins, carbohydrates, and lipids and (b) humic substances (Thurman, 1985). As a main fraction of terrestrial DOM, humic substances influence physicochemical characteristics of natural aquatic systems by increasing light attenuation, maintaining pH by organic acid buffering, acting as a strong ligand for many elements and affecting the redox chemistry of trace metals (e.g. Scully and Lean, 1994; Alberts and Takacs, 1999; Cai et al., 1999; Lu and Jaffé, 2001).

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Although the importance of estuarine and coastal waters in the global DOM cycling has been recognized, sources, transport, and transformation of DOM are not well understood. For example, it is unclear whether conservative or nonconservative mixing of riverine and marine waters control distribution of DOM in estuaries (Miller, 1999; Kattner et al., 1999). According to Coble et al. (1998), terrestrially derived humic substances from runoff are a major source of colored DOM (CDOM) to the ocean and near-shore areas. However, autochthonous DOM sources, such as phytoplankton (freshwater or marine) and marsh- and mangrove-derived DOM, have also been shown to be important contributors to estuarine and coastal pools (Moran et al., 1991; Mueller and Ayukai, 1998; Del Castillo et al., 2000; Dittmar et al., 2001; Hernes et al., 2001). In addition to multiple potential sources of aquatic DOM, microbial transformations (Amon and Benner, 1994, 1996; Moran et al., 1999; Tranvik, 1993) and photochemical degradation of DOM (Mopper et al., 1991; Vodacek et al., 1997; Ziegler and Benner, 2000; Moran et al., 2000) play an important role in altering the physicochemical characteristics of these materials. Bacteria depend on labile DOM as a source of energy and nutrients which fuel the microbial loop and regulate trophic transfers in aquatic food webs (Pomeroy, 1980). For example, DOM leached from algae is available for heterotrophic bacteria production (Kaplan and Bott, 1989; Kelly, 1989).

Due to the easy operation, high sample throughput, and high sensitivity, UV–visible and fluorescence spectroscopic techniques have been used to characterize sources, degree of degradation, and transformation of DOM in many aquatic environments (Cabaniss and Shuman, 1987; De Souza Sierra et al., 1994, 1997; Coble, 1996; Nieke et al., 1997; Battin, 1998; Lombardi and Jardim, 1999; Mounier et al., 1999; McKnight et al., 2001; Clark et al., 2002). A UV–visible index, (a_{254}/a_{436}) and a related parameter, S (where $S = \ln(a_{254}/a_{436})/182$) have been successfully applied to assess the source and transformation history of CDOM (Zepp and Schlotzhauer, 1981; Blough et al., 1993; Blough and Green, 1995; Battin, 1998). For example, S values of about 0.011 nm^{-1} were reported for the Orinoco Basin CDOM (Battin, 1998) while brown coastal waters and blue oligotrophic waters were characterized by values of 0.018 and 0.02, respectively

(Blough et al., 1993). The photodegradation of DOM through exposure to sunlight may however mask the source signal obtained with UV–visible spectroscopic techniques, and was attributed to the selective photochemical degradation of long wavelength ($>380 \text{ nm}$) chromophores (Vodacek et al., 1997). For this reason, alternative optical characterizations such as fluorescent techniques have been applied for source characterization of DOM. These include the emission-based fluorescence index ($f_{450/500}$) which was used by Battin (1998) to differentiate between autochthonous and allochthonous CDOM in blackwater rivers from the Orinoco Basin as did McKnight et al. (2001) for a variety of bodies of water. In the later study, the terrestrial and aquatic/microbial fulvic acid end-members values for the index were reported as 1.4 and 1.9, respectively, and were successfully applied for source discriminations in real environmental samples.

In addition to the optical methods described above, other fluorescence techniques have been successfully applied to DOM source characterization. The three-dimensional excitation–emission matrix (EEM) fluorescence technique has been widely applied for such purposes (e.g. Coble, 1996; Del Castillo et al., 1999; Marhaba et al., 2000; Parlanti et al., 2000). The presence of different EEM fluorescence maxima allows for the characterization of DOM into humic-like, marine humic-like and protein-like contributions (e.g. Coble, 1996; Parlanti et al., 2000). Synchronous excitation–emission fluorescence is a two-dimensional fluorescence method which has been applied in a variety of DOM studies (e.g. De Souza Sierra et al., 1994; Ferrari and Mingazzini, 1995; Kalbitz et al., 2000; Lu and Jaffé, 2001). Synchronous fluorescence spectra of DOM usually show the presence of four relatively broad peaks (Ferrari and Mingazzini, 1995), which can be assigned to: (1) mono-aromatic and proteinaceous materials (270–300 nm, Peak I); (2) compounds of two condensed ring systems (310 and 370 nm, Peak II); (3) fulvic acids (370–400 nm, Peak III); and (4) humic acids and other humic-like substances ($\geq 460 \text{ nm}$, Peak IV). It has been suggested that Peak I is indicative of fresh, marine-derived, possibly protein-like DOM components in estuaries (De Souza Sierra et al., 1994; Ferrari and Mingazzini, 1995; Lu et al., 2003). As such, Peak I has the potential to be used to

discriminate between marine and terrestrial DOM in estuaries. However, it is important to keep in mind that polyphenols may also produce a fluorescent signal in this region (Ferrari and Mingazzini, 1995).

The combination of multiple DOM sources (freshwater marsh vegetation, mangroves, phytoplankton, seagrass, etc.), along with seasonal variability of source, photolytic exposure history, diagenetic transformation/degradation processes, and complex advective circulation, makes the study of DOM dynamics in estuarine and coastal areas of South Florida particularly difficult using standard schemes of estuarine ecology. We conducted a detailed study of the optical characteristics of the DOM, using UV–visible and fluorescence spectroscopic techniques, at 46 estuarine sites in SW Florida. We conducted three consecutive monthly surveys of DOM at these sites in an attempt to distinguish among potential DOM sources and to characterize DOM dynamics within this geomorphologically compartmentalized system. To our best knowledge, this study is the first of its kind to combine CDOM optical techniques with geomorphological compartmental analysis to characterize DOM dynamics in estuaries. The Florida coastal Everglades, because of its complexity, provided for a unique model system. Through this study we obtained a better understanding of the DOM dynamics and ecological processes of estuaries.

2. Materials and methods

2.1. Site description

Sampling sites were located in the Ten Thousands Islands (TTI) and Whitewater Bay (WWB) areas of Everglades National Park (Fig. 1) in conjunction with an on-going estuarine water quality monitoring program (<http://www.serc.fiu.edu/wqmnetwork>). Although these are areas mainly surrounded by mangrove forests, they are influenced by freshwater-transport of organic matter from Everglades' wetlands where periphyton and sawgrass are major biomass components (Jaffé et al., 2001). The bulk of Shark River Slough, which drains the greater Everglades, empties into the mangrove rivers in the southern sampling range. However, this area can be

further compartmentalized into five subregions based on their water quality characteristics (Boyer and Jones, 2001; Fig. 1).

Estuaries within the TTI–WWB region are highly compartmentalized by local geomorphology, making it difficult to study DOM biogeochemistry using standard schemes of estuarine ecology. In addition, the sources of both freshwater and nutrients are difficult to quantify, owing to the nonpoint source nature of runoff from the Everglades and the dendritic cross channels in the mangroves. A previous statistical analysis of the 16 water quality parameters collected monthly during a 6-year period, resulted in the spatial aggregation of the 47 stations into five distinct zones having robust similarities in water quality (Fig. 1; Boyer and Jones, 2001). The zones were classified as Whitewater Bay (WWB), the Mangrove Rivers (MR), the Inner Waterway (IW), the Gulf Islands (GI), and the Blackwater River estuary (BLK). Marked differences in physical, chemical, and biological characteristics among zones were illustrated by this technique and the observed gradients are believed to be the result of coastal geomorphology and watershed characteristics in the region.

The Whitewater Bay zone is a semi-enclosed body of water with a relatively long residence time, which receives overland freshwater input from the Everglades marsh. The relatively long water residence time may explain the very low *P* concentrations (from biological uptake), while the high evaporation rate would tend to concentrate dissolved organic matter (DOM). The estuaries in the Mangrove Rivers zone are directly connected to the Shark River Slough and therefore have a huge watershed relative to their volume. Freshwater inputs from this source are very low in *P* while the extensive mangrove forest contributes much DOM. The Inner Waterway zone is an intermediate zone in all respects; having extensive channelization but lower freshwater input. The Gulf Island zone has very low freshwater input due to the poorly drained watershed of the Big Cypress Basin. Instead of mangrove river channels there are many mangrove islands set in low tidal energy environments. Finally, there is the Blackwater River region with highest salinity and *P*. There is much agricultural activity in the Blackwater River watershed, which may contribute significant amounts of *P* to the system via drainage ditches. In addition, the bedrock geology

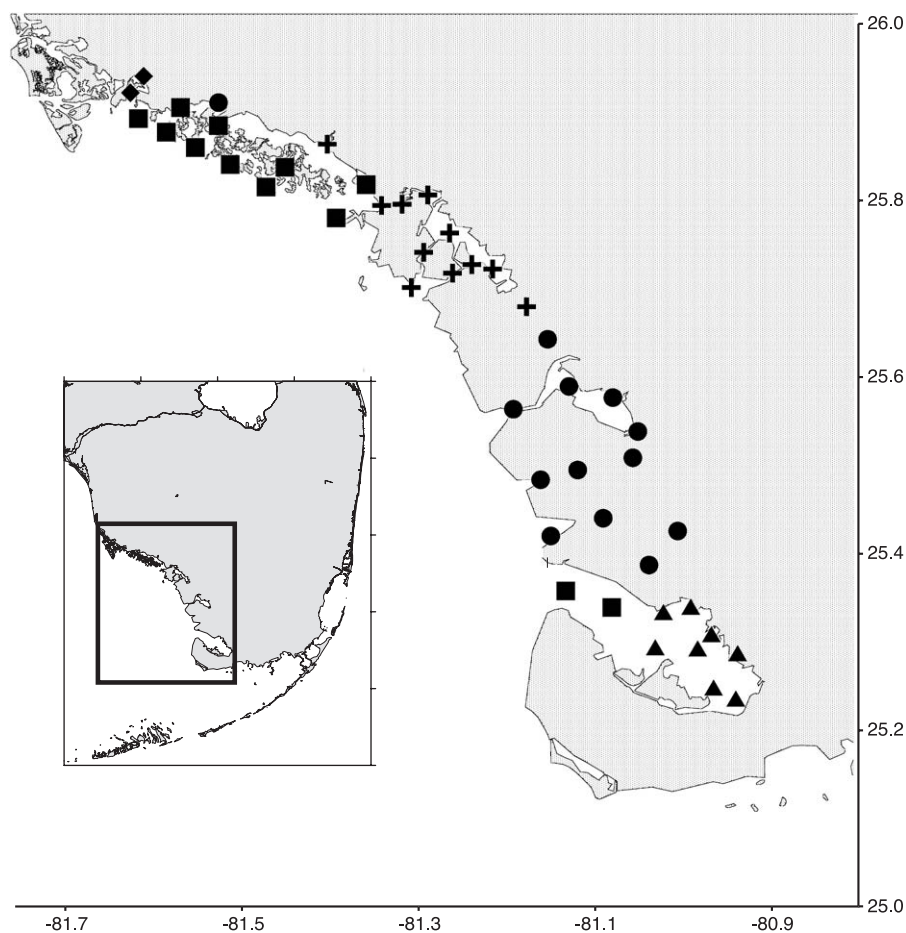


Fig. 1. Map showing sampling sites in the southwest Florida coastal Everglades. Site clusters are based on spatial statistical analysis of water quality and defined as Whitewater Bay (WWB—▲), Mangrove Rivers (MR—●), Inner Waterway (IWW—+), Gulf Islands (GI—■), and Blackwater River (BLK—◆).

in this region shifts from carbonates to silicates, which allows more transport of *P* through the watershed.

2.2. Sample collection

Surface water samples were taken from the southwest coast of Florida (see Fig. 1) during 3 months of the dry season over a 3-year period (March, April, and May of 1999, 2001, and 2002). The samples were collected using pre-washed, brown high-density polyethylene bottles. Salinity of the water samples was measured in the field using an Orion salinity meter. The pH was measured using an AR15 pH meter (Fisher, Pittsburg, PA). The

samples were stored on ice and returned to the laboratory within 8 h for analysis. Subsamples for spectroscopic analysis were filtered through pre-combusted (470 °C for 8 h) Whatman GF/F glass fiber filters once received in the laboratory and analyzed immediately.

2.3. Chemical analysis of DOM

TOC concentrations were measured by Pt-catalyzed high temperature combustion (950 °C), using a Shimadzu TOC-5000A total organic carbon (TOC) analyzer, coupled to a nondispersive infrared CO₂ detector. Ancillary physical and chemical parameters

shown in Table 1 were measured using standard methods reported elsewhere (Jones and Boyer, 2002). All chemicals used were analytical reagent grade and were purchased from Fisher, Sigma, (Bellefonte, PA), and Supelco (St. Louis, MO).

2.4. UV–visible absorbance analysis

UV–visible measurements of the water samples were carried out with 1 cm quartz UV–visible cells at room temperature (20 °C), using a Shimadzu UV-2101PC UV–visible double beam spectrophotometer. MilliQ water was used as a reference. The absorption index, a_{254}/a_{436} , was calculated for the DOM samples according to Battin (1998).

2.5. Fluorescence emission analysis

Fluorescence emission spectra were recorded at wavelengths ranging from 250 to 550 nm, at an excitation wavelength of 370 nm in a 1 cm quartz fluorescence cell at room temperature (20 °C), using a Perkin Elmer LS50B spectrofluorometer equipped with a 150-W Xenon arc lamp as the light source. Slit widths were set at 10 nm; scan speed was set at 400 nm/min. MilliQ water was used as a reference for all fluorescence analysis. The UV–visible data were used to correct for optical density differences in the fluorescence measurements as described elsewhere (McKnight et al., 2001). Total maximum fluorescence intensity (F_{\max}) and the fluorescence index, ($f_{450/500}$; Battin, 1998; McKnight et al., 2001) were determined at an excitation wavelength of 370 nm. In order to facilitate comparisons with other studies, the F_{\max} was expressed in quinine sulfate units (QSU; 1 QSU = 1 $\mu\text{g/l}$ of quinine sulfate = 1 ppb). A quinine sulfate standard calibration curve was determined for each

sample set to ensure data accuracy and normalization of instrument conditions. The maximum fluorescence emission wavelength (λ_{\max}) was determined using an excitation wavelength of 313 nm (De Souza Sierra et al., 1997).

2.6. Synchronous fluorescence analysis

Synchronous excitation–emission fluorescence spectra of the water samples were obtained at constant offset value between excitation and emission wavelengths ($\delta\lambda = \lambda_{\text{em}} - \lambda_{\text{ex}}$). All spectra were recorded at an offset value of 30 nm with slit width of 10 nm (Lu and Jaffé, 2001; Lu et al., 2003). The intensities of the four main peaks in the spectrum, namely at 275–286 nm (Peak I), 350 nm (Peak II), 385 nm (Peak III) and 460 nm (Peak IV) were determined and the relative intensity of Peak I within this group was reported as %Peak I. Fluorescence intensities were corrected for optical density differences using the method of McKnight et al. (2001) adapted for synchronous fluorescence scans. Fluorescence spectra for water blanks were also obtained to correct for Raman spectral overlap.

2.7. Statistical analysis

Typically, the degree of asymmetry of the distribution of water quality variables is usually skewed to the right resulting in non-normal distributions; therefore, it is more appropriate to use the median as the measure of central tendency. Data distributions of selected water quality variables are reported as box-and-whiskers plots. The center horizontal line of the box is the median of the data, the top and bottom of the box are the 25th and 75th percentiles (quartiles), and the ends of the whiskers are the 5th and 95th

Table 1
Water quality variables and optical properties of samples collected from SW Florida estuaries

Zone	DIN	TON	TP	CHLA	TOC	Salinity	a_{254}/a_{436}	$f_{450/500}$	%Peak I	λ_{\max}	F_{\max}	F_{\max}/TOC
BLK	1.34	20.05	1.56	3.13	412.10	37.20	19.52	1.549	34.28	426.8	37.95	0.082
GI	0.62	19.26	1.01	2.23	443.70	36.80	23.46	1.552	33.14	419.1	39.31	0.079
IWW	1.62	26.95	0.89	2.15	734.38	33.30	25.89	1.532	28.41	426.5	67.27	0.089
MR	2.00	31.71	0.78	2.26	982.60	27.40	20.30	1.510	27.01	430.0	120.27	0.132
WWB	1.20	39.43	0.58	1.18	1144.69	24.54	27.45	1.520	29.32	422.0	121.69	0.101

Results are medians of three sampling events where dissolved inorganic nitrogen (DIN), total organic nitrogen (TON), and total phosphorus (TP) are in μM , chlorophyll *a* (CHLA) in $\mu\text{g l}^{-1}$, total organic carbon (TOC) in ppm, and salinity reported on the practical salinity scale.

percentiles. The notch in the box is the 95% confidence interval of the median. When notches between boxes do not overlap, the medians are considered significantly different. Outliers (<5th and >95th percentiles) were excluded from the graphs to reduce visual compression. The box-and-whisker plot is a powerful statistical tool as it shows the median, range, distribution of the data as well as serving as a graphical, nonparametric ANOVA. In addition, differences in parameters among classes were quantified using the Kruskal–Wallace test with significance set at $P < 0.05$.

2.8. Photobleaching experiments

Mangrove leaves (50 g) were placed in 2 l of 0.2 μm filtered MR (Shark River) water and incubated in the dark at 20 °C for 24 h. The sample was again filtered through a 0.2 μm filter and 500 ml leachate samples irradiated for 72 h at 20 °C with a Suntest XLS+ solar simulator set at 765 W m² in three water cooled 33 × 11 × 6 cm Plexiglas vessels. A treatment control sample was placed separately in the dark. Treated samples were used directly for optical analysis as described above.

3. Results and discussion

3.1. TOC concentrations

Surface water TOC concentrations ranged from 318 to 2043 μM , depending upon the location and sampling event. No significant differences in TOC concentration among years were observed for the five zones so they were pooled for further analyses (data not shown). Median TOC concentrations in the Whitewater Bay proper sites were consistently higher than in the other Ten Thousand Islands sites (Fig. 2A), mainly due to differences in geomorphology and watershed characteristics between the two regions (Boyer and Jones, 2001). Overall, TOC was highest in the upper oligohaline tidal creeks (WWB and MR) and lowest in the mesohaline estuaries (IWW) and coastal zones (GI and BLK).

DOM is subject to a variety of physical processes in estuarine areas. Most commonly, terrestrially derived DOM undergoes conservative mixing once

introduced into estuaries (Del Castillo et al., 2000), and an inverse linear relationship between its concentration and salinity has been frequently reported (Laane, 1980; Dorsch and Bidleman, 1982; Hayase et al., 1987; Clark et al., 2002). Fig. 2B presents TOC vs. salinity correlations for the 3 months sampling periods for the dry season of years 1999, 2001 and 2002 for the MR and WWB sites. While the data present quite some scatter due to the geographically wide-spread nature of the sampling stations (vs. a direct transect in a gradual estuarine setting; e.g. Clark et al., 2002) the data for 2001 and 2002 suggest a correlation that would indicate conservative mixing in these estuaries. However, unlike 2001 and 2002, the data for 1999 seem to exhibit a nonconservative mixing behavior, showing a source in the mesohaline area (salinity 10–22). This type of pattern is not commonly observed in temperate estuaries (Mantoura and Wooddard, 1983; Woodruff et al., 1999) but is consistent with long-term data from this region (Jones and Boyer, 2002) and with other mangrove-dominated estuaries (Lee, 1995; Guo et al., 1999; Dittmar et al., 2001). The bump in TOC concentration in the mesohaline zone for 1999 may be the result of advection from the upper estuary and local input of DOM from the mangrove forests. In addition, the year 1999 was an unusually wet year, which is reflected in the increased number of low salinity measurements for this period. DOM rich waters from the freshwater marshes of the Everglades mix with mangrove-derived DOM in the mesohaline zone. This process was not observed for 2001 (a particularly dry year) and for 2002, both of which present TOC–salinity correlations suggesting conservative mixing.

Restricting the regression analysis to salinities ≥ 22 suggests that a conservative mixing model holds for the estuaries downstream of mangrove input ($R^2 = 0.504$, $P < 0.001$) for the three study periods. Using this euhaline mixing model, the extrapolation of TOC concentrations out to the salinity end-member of 36 lead to a TOC concentration of 612 μM . This value is much higher than median TOC concentrations of open oceans (80 μM , Druffel et al., 1992) and that found offshore in the Florida Keys (175 μM , Boyer and Jones, 2002), but is closer to the inshore median of 417 μM for the SW Florida Shelf (Jones and Boyer, 2002).

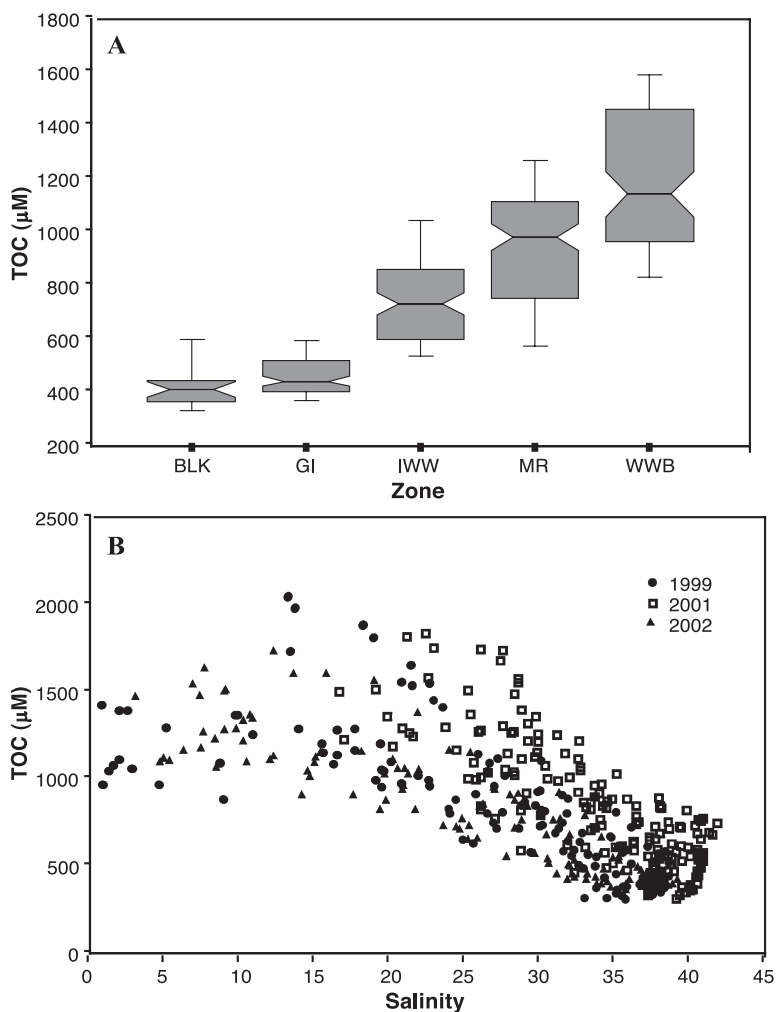


Fig. 2. (A) Box-and-whisker plot of total organic carbon (TOC, μM) in the five distinct water quality zones. The center horizontal line of the box is the median of the data, the top and bottom of the box are the 25th and 75th percentiles (quartiles), and the ends of the whiskers are the 5th and 95th percentiles. The notch in the box is the 95% confidence interval of the median. Outliers are suppressed for the sake of clarity. (B) Property–salinity plot of TOC showing a potential mesohaline source from mangrove forests for years 1999, 2001 and 2002.

3.2. Optical properties

All surface water samples showed similar UV–visible spectral patterns and were quite consistent with those reported in the literature (e.g. Battin, 1998). In general, the UV–visible spectra were featureless, showing an increase in absorbance with decreasing wavelength. The differences in absorbance intensities observed were most likely caused by the difference in chromophore concentrations. UV–visible absorbance at wavelength of 254 nm (A_{254}) has

been suggested as a measure of the contribution of colored dissolved organic matter (CDOM) as it is known to be rich in humic-like substances (high in aromatic components, Martin-Mousset et al., 1997). A significant linear regression ($R^2=0.88$) between the TOC concentrations and A_{254} suggests that a relatively consistent proportion of the terrestrially derived DOM was composed of humic substances (Martin-Mousset et al., 1997). Because the DOM was primarily of humic origin, the regression of A_{254} with salinity resulted in an inverse relationship with $R^2=0.72$.

The slopes from these correlations were not significantly different for the three sampling periods, indicating that the chromophores of the water samples had similar absorbance characteristics (Cooper et al., 1987) and therefore, that the compositions of the DOM inputs were similar as well (De Souza Sierra et al., 1997).

3.3. UV–visible index

As previously mentioned, a commonly applied source indicator of DOM is the UV–visible absorption ratio, a_{254}/a_{436} . Battin (1998) reported a_{254}/a_{436} ratio values in the range from 4.37 to 11.34 in river water from the Orinoco Basin. Such values are common for terrestrial/allochthonous DOM, which has a greater aromatic carbon content associated with the presence of tannin-like and/or humic-like substances derived from higher plants and soil organic matter (e.g. Ertel et al., 1986; Battin, 1998). Much higher ratios (ca. 38) were reported for marine/autochthonous DOM sources (Blough and Green, 1995).

Unexpectedly, in the coastal Everglades estuaries, the absorption index (a_{254}/a_{436}) showed a median value of 28.7 (Table 1), suggesting that most of the DOM in these waters was derived from microbial sources. In addition, the index was not significantly related to salinity nor did it show any significant spatial trend (data not shown). We had expected to see lower values for those sites most heavily influenced by terrestrial DOM and higher index values for the more marine/microbially influenced sites. That there was no significant change in the a_{254}/a_{436} values suggests that its applicability in the assessment of estuarine DOM sources has serious limitations. One reason for this may be the fact that this index changes dramatically during photobleaching of freshly leached CDOM. Experiments performed using CDOM leached from mangrove leaves showed that an initial a_{254}/a_{436} value of 12.98 changed to 24.03 (± 1.62 ; $n = 3$) and to 38.68 (± 4.81 ; $n = 3$) after 48 and 72 h of exposure to simulated natural light, respectively. These results are in agreement with previous studies (Vodacek et al., 1997), where sunlight induced photodegradation of CDOM was shown to cause a change in the UV–visible spectra. The elevated a_{254}/a_{436} values observed in this study, and the lack of correlation with surface water salinity could be a result of CDOM photo-

bleaching. Therefore, this parameter will not be discussed further.

3.4. Fluorescence emission

Total fluorescence (F_{\max}) ranged from 15 to 387 QSU with a median of 73 QSU. This is a wider range than reported by Clark et al. (2002) for the same geographic area, but given the greater number of samples analyzed (332 vs. 11), it is not an unreasonable observation. The spatial distribution of F_{\max} was similar to that of TOC, showing greatest intensities in the WWB and MR zones (Fig. 3A). As with TOC, F_{\max} was inversely related to salinity but there was a difference in the slope for the 2001 and 2002 data (Fig. 3B). Such inverse linear relationships between F_{\max} and salinity have previously been described (e.g.: Laane, 1980; Dorsch and Bidleman, 1982; De Souza Sierra et al., 1997; Clark et al., 2002) and are mostly explained through dilution/conservative mixing effects. The difference in the slope is likely caused by climatic differences during the 2 years, where the year 2001 was significantly dryer than 2002, resulting in hydrological differences (i.e. reduced freshwater discharge from the Everglades marshes during 2001) that account for this observation. This can also be observed in Fig. 2B where TOC concentrations for 2001 were higher than for 1999 or 2002. While the observed inverse relationship between the fluorescence and salinity is likely influenced by dilution of terrestrially derived DOM with marine waters, De Souza Sierra et al. (1997) clearly showed, that in addition to a dilution, DOM composition and abundance in estuaries can be affected by flocculation processes at the lower salinity, followed by mixing with marine-derived DOM at the higher salinities.

F_{\max} was significantly related to TOC ($R^2 = 0.605$, $P < 0.001$) for both years 2001 and 2002. Carbon-specific fluorescence (F_{\max}/TOC) among zones was also determined (Table 1 and Fig. 4), and results of the nonparametric Kruskal–Wallace test showed that the F_{\max}/TOC (for the combined 2001 and 2002 data set) for the MR zone ($0.132 \text{ QSU } \mu\text{M}^{-1}$) was significantly higher than WWB ($0.101 \text{ QSU } \mu\text{M}^{-1}$) which was in turn higher than the IWW, GI, and BLK combined ($0.085 \text{ QSU } \mu\text{M}^{-1}$). Our C-specific fluorescence values in the MR zone are similar to other Shark River data calculated from Clark et al. (2002; 0.145

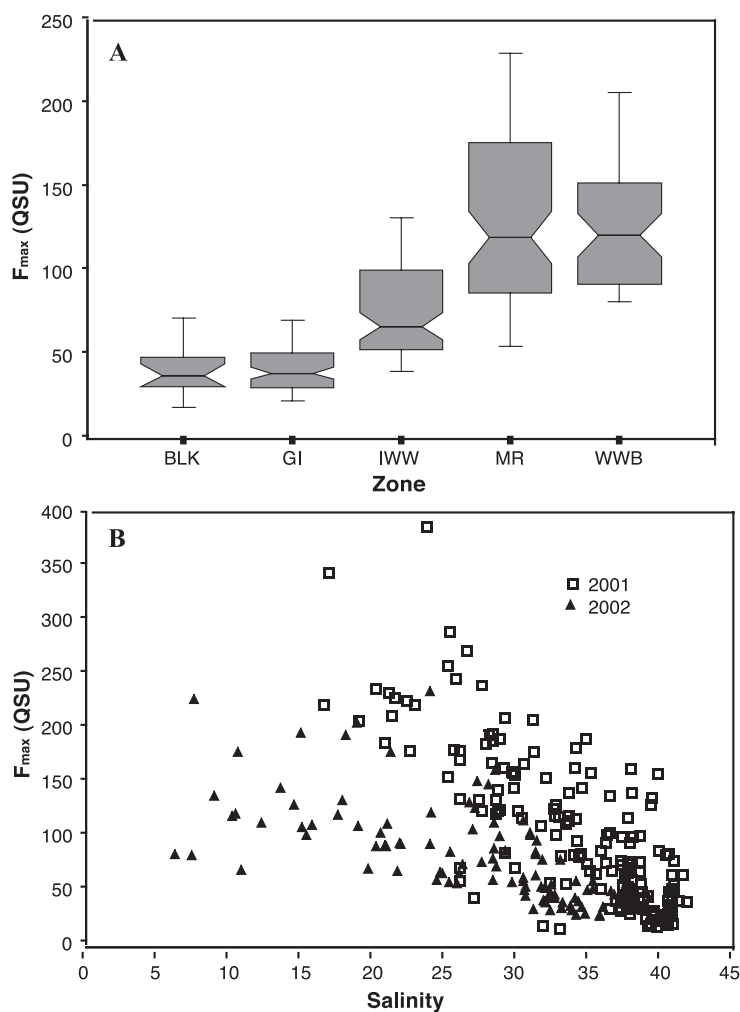


Fig. 3. (A) Box-and-whisker plot of the total fluorescence (F_{\max} , in QSU) in distinct water quality zones. (B) Property–salinity plot of F_{\max} . Note differences between years.

and $0.149 \text{ QSU } \mu\text{M}^{-1}$ for stations 14 and 15). In addition, this study, as well as data from Clark et al. (2002) and Del Castillo et al. (2000), show that C-specific fluorescence decreased strongly with increase in marine influence (Tables 1 and 2).

Maximum emission wavelength (λ_{\max}) determined for years 2001 and 2002, ranged from 397 to 435 nm with a median of 426 nm; however, there were marked differences in λ_{\max} among zones (Fig. 5A). Highest λ_{\max} was observed in the MR and BLK zones with GI and WWB lowest and IWW intermediate. We observed a similar decline in λ_{\max} with salinity (Fig. 5B) as did Del Castillo et al. (2000) and Coble (1996).

While there was significant scatter in the data, the general trend of a hypsochromic shift at salinity ≥ 30 can clearly be observed, the exception being most of the samples from WWB. Previous studies have shown that the usual cut off for terrestrially dominated DOM in estuaries occurs at salinity ≥ 30 (e.g. De Souza Sierra et al., 1997; Del Castillo et al., 1999, 2000). Such a change from terrestrial to marine-dominated DOM in coastal waters occurs through an inflection point for the hypsochromic shift, for waters from the West Florida Shelf. The point at which this source change occurs is likely related to the concentration of terrestrially derived DOM, the flux of this material to

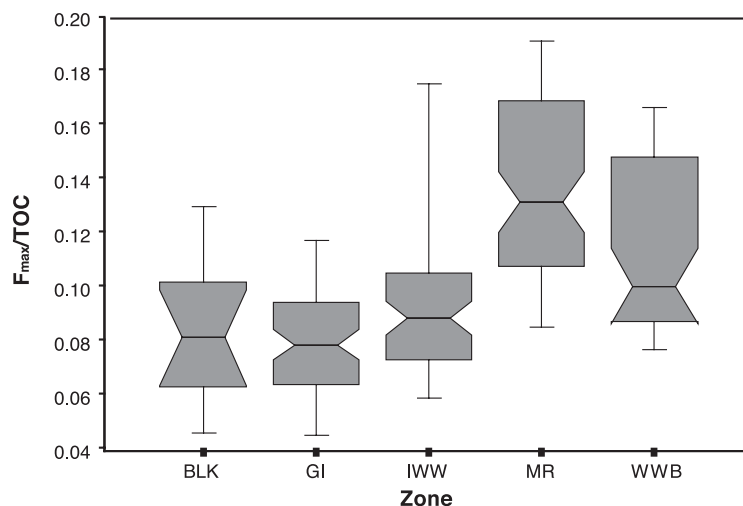


Fig. 4. Box-and-whisker plot of the carbon specific fluorescence (F_{\max}/TOC) in the different water quality zones.

coastal waters, and the mixing efficiency of fresh/riverine and marine waters in the estuary.

While flocculation of terrestrial DOM may have an effect on the optical properties of estuarine water samples (De Souza Sierra et al., 1997), the DOM input from the mangroves seems to overwhelm the visualization of any such effect. The conservative behavior of DOM in water of salinity ≥ 22 in the lower estuarine areas suggests that flocculation and particulate adsorption processes were not significant during our sampling events. This is in agreement with Del Castillo et al. (2000), who reported that CDOM in

the West Florida Shelf is dominated by riverine-derived material only close to the river mouth, and subject to conservative mixing without noticeable flocculation upon salinity increments. With the potential exception of WWB, our data seem to agree with these observations. These samples, which show a more gradual change in the λ_{\max} with increasing salinity, suggesting the potential for DOM flocculation in this region. The geomorphological characteristics of the WWB area may induce conditions that favour DOM flocculation.

Fluorescence emission spectra of DOM in natural water samples typically show a broad featureless peak, which is a common observation for spectra of complex natural organic substances (Lombardi and Jardim, 1999; McKnight et al., 2001). Due to this lack of structural information, the fluorescence index ($f_{450/500}$) has been introduced as a means to differentiate between DOM sources (e.g.: Battin, 1998; McKnight et al., 2001). Terrestrial and microbial end-member values were reported as 1.4 and 1.9, respectively. For the Florida coastal Everglades, $f_{450/500}$ values in surface waters ranged from 1.25 to 1.72, with the median being 1.53 (see also Table 1). The $f_{450/500}$ values as plotted for each of the five zones (Fig. 6) are consistent with the expected gradient of the marine-influenced DOM at the BLK and GI sites shifting to terrestrially derived DOM at the IWW, MR, and WWB sites. We observed that while the inter-site

Table 2

Range of carbon specific fluorescence (F_{\max}/DOC , in QSU μM^{-1}) in the region of study

Area of study	Clark et al. (2002)	Del Castillo et al. (2000)	This study
Shark River	0.145–0.149 (2)		0.044–0.298 (70)
Shark River Offshore	0.116–0.119 (2)		0.024–0.148 (67)
SW Florida Shelf	0.046–0.077 (3)		
Florida Bay	0.037–0.053 (4)		0.006–0.075 (754) ^a
NW Florida Shelf		0.002–0.075 (12)	

Value in parentheses is number of samples analyzed.

^a Yang (2002).

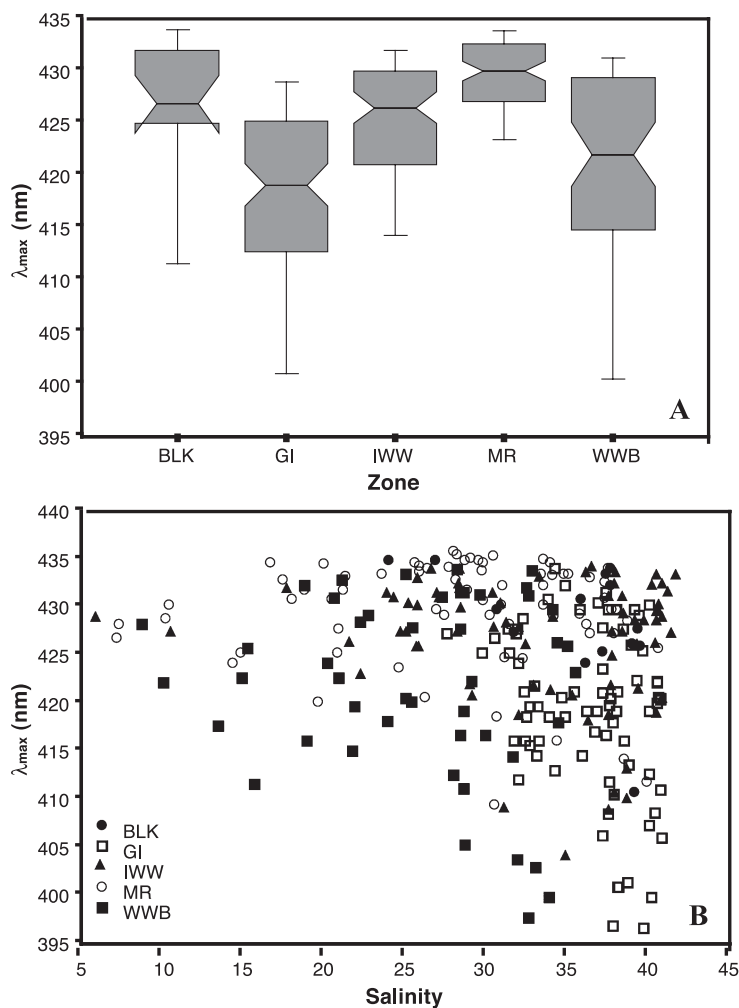


Fig. 5. (A) Box-and-whisker plot of the maximum fluorescence wavelength (λ_{\max} , nm) in the different water quality zones. (B) Hypsochromic shift in λ_{\max} with salinity.

variability was still significant, it was much reduced compared to that of a_{254}/a_{436} for the same samples. The fact that true end-member values were not observed neither at the strongly mangrove-influenced MR sites, nor at the marine-influenced GI sites, and that a quite substantial range in the value was observed within the different subregions, suggests that it may not be accurate to use f_{450}/f_{500} as a quantitative measure of DOM source material in these ecosystems (McKnight et al., 2001). While the f_{450}/f_{500} index may be a sensitive DOM source indicator in environments where most terrestrial/soil-derived DOM is highly degraded (e.g. Battin, 1998), it may be less sensitive

in wetlands and mangrove-dominated environments where continuous (or episodic) input of 'fresh' DOM from local higher plant biomass occurs. The f_{450}/f_{500} of such 'fresh' mangrove-derived DOM was observed to be 1.68 in this study, and therefore higher than expected for a terrestrial end-member. However, over time, photobleaching may transform the f_{450}/f_{500} into values similar to the proposed terrestrial end-member. In fact, after 48 and 72 h of simulated sunlight exposure, the f_{450}/f_{500} changed to $1.50 (\pm 0.012; n=3)$ and $1.51 (\pm 0.013; n=3)$, respectively. That said, we believe the fluorescence index still is a very useful indicator of changes in DOM quality in the Florida

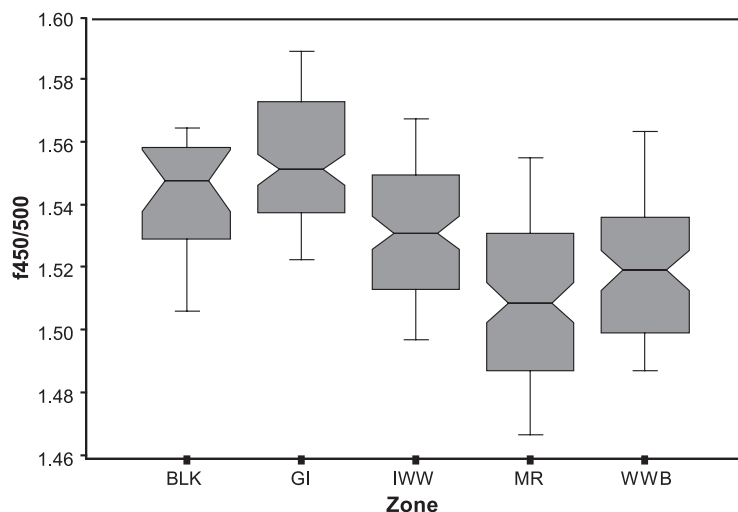


Fig. 6. Box-and-whisker plot of the fluorescence index ($f_{450/500}$) in distinct water quality zones.

coastal Everglades. To that end, it is important to notice that the $f_{450/500}$ index was developed for the source assessment of humic substances (particularly fulvic acids), and may not be as effective in samples that contain significant amounts of non-humic substances (McKnight et al., 2001).

3.5. Synchronous fluorescence spectra

While fluorescence emission spectra were reported to lack observable differences among DOM samples originating from different sources, synchronous fluorescence spectra can provide useful composition and source information on fluorophores of natural DOM (De Souza Sierra et al., 1994; Lombardi and Jardim, 1999; Lu and Jaffé, 2001; Lu et al., 2003). Four peaks at wavelength 274–286 nm (Peak I), 350 nm (Peak II), 385 nm (Peak III), and 460 nm (Peak IV) were observed for these samples (Fig. 7A). Those synchronous spectral features of the water samples can be used to compare general molecular characteristic of the DOM in the area studied. The signal of Peak I has been suggested to indicate the presence of dissolved proteins (e.g. Coble et al., 1990; Ferrari and Mingazzini, 1995; Lu et al., 2003) since it is related to microbial primary productivity (De Souza Sierra et al., 1994; Lombardi and Jardim, 1999). In confirmation of this assertion, our analysis of a solution of protein (bovine serum albumin—BSA) showed a

single intense peak at about 285 nm. Peaks II, III, and IV are indicative of humic substances (Miano and Senesi, 1992; Pullin and Cabaniss, 1995). De Souza Sierra et al. (1994) reported that such peaks were more common in estuarine and coastal waters compared to the less terrestrially influenced marine waters. According to Miano and Senesi (1992), peaks which appear at shorter wavelength, represent fulvic acid fraction with the lower degree of aromaticity, while peaks which appear at longer wavelength are associated with polycondensation of phenolic aromatic units such as humic acids. Photobleaching experiments showed little effect on the %Peak I for mangrove-derived DOM (about 2% over a 72-h period).

The relative intensity of Peak I to total fluorescence of Peaks I to IV in the synchronous spectra (%Peak I) was used to compare DOM quality among the subregions. Synchronous fluorescence spectra of the surface water samples showed large spatial variability in %Peak I (Fig. 7B). As with the $f_{450/500}$ distribution, %Peak I values showed a general decreasing trend from the strongly marine-influenced regions (BLK and GI) to the more terrestrially influenced regions (IWW, MR and WWB). Again, the WWB region presented somewhat more elevated mean values compared to the MR region, possibly due to the accumulation of less degraded mangrove-derived DOM inputs at WWB. Although Peak I has been reported to be derived from marine microorganisms (De Souza

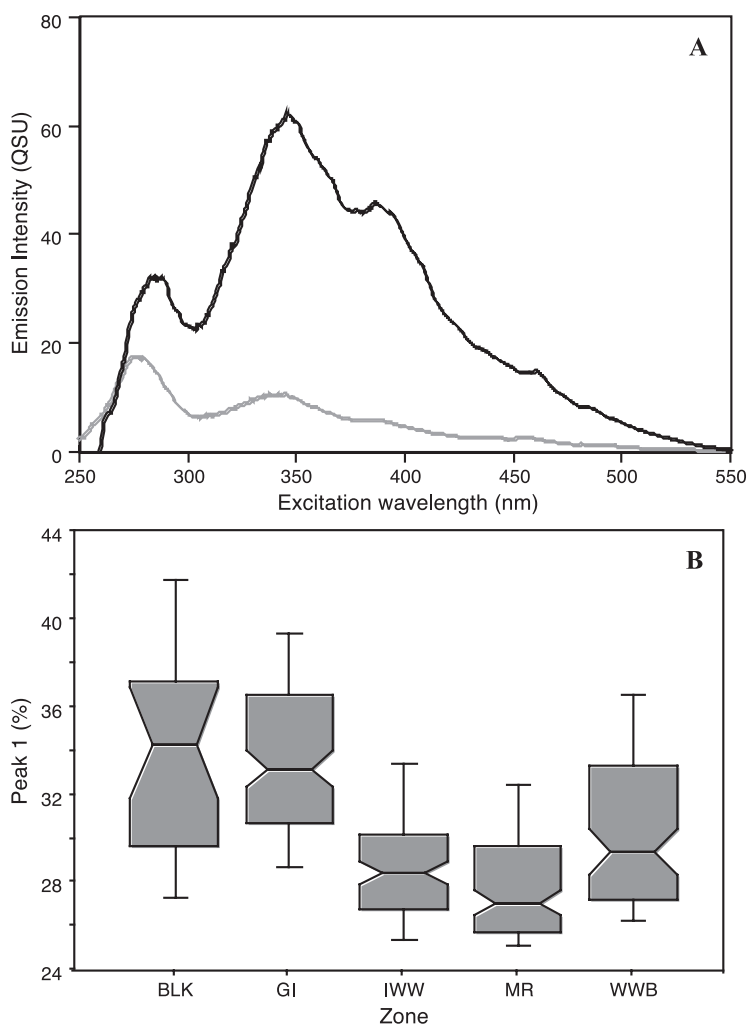


Fig. 7. (A) Synchronous fluorescence spectra of water samples collected from representative MR (solid line) and IW (dotted line) sites. (B) Box-and-whisker plot of synchronous fluorescence results showing relative intensity of Peak I to total fluorescence of the synchronous spectra (%) in the different water quality zones.

Sierra et al., 1994), it is also present in DOM freshly leached from mangrove leaves, sawgrass, and periphyton (Lu and Jaffé, 2001). Overall, the %Peak I seems to be a good parameter to assess DOM sources and quality in estuaries of the Florida West coast.

4. Summary

This study presents a preliminary evaluation of the concentrations, sources, and degradation of DOM in

the Florida coastal Everglades using UV–visible and fluorescence techniques. Our data suggest that the main sources of DOM are from freshwater marsh biomass, mangrove forests, and marine organisms. The DOM concentrations in the area studied were not only influenced by source strength but also by the hydrology and geomorphology of five subregions within the southwest Florida estuarine area of Everglades National Park. Mangroves provided a significant input of DOM to the mesohaline region that was structurally and functionally distinct from upstream

terrestrial sources. DOM was not significantly removed by the processes of flocculation and particulate adsorption in the estuarine and coastal areas, with the possible exception of WWB, but was more consistent with conservative mixing of fresh and marine waters. An attempt to monitor DOM sources and degree of degradation, using the fluorescence emission index ($f_{450/500}$) and a synchronous fluorescence index (%Peak I) was successful, and showed clear differences in DOM optical characteristics between the five subregions. While both fluorescence parameters were in good agreement regarding DOM source changes, the a_{254}/a_{436} index was found to be too variable for DOM source assessments in these estuaries. This was most likely caused by potential interference in the absolute values of the a_{254}/a_{436} index by the presence of freshly leached DOM from local higher plant biomass, and the susceptibility of this index to photo-bleaching. Although terrestrially derived, bulk DOM underwent conservative mixing in the estuaries of the Florida Everglades; at salinities ≥ 30 , there was a clear switch from allochthonous to autochthonous DOM (from fluorescence characterizations) indicating a change in the nature and origin of the dominant DOM, and not a simple dilution of terrestrial DOM.

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