Optical properties of chromophoric dissolved organic matter (CDOM) in surface and pore waters adjacent to an oil well in a southern California salt marsh

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Abstract

Chromophoric dissolved organic matter (CDOM) optical properties were measured in surface and pore waters as a function of depth and distance from an oil well in a southern California salt marsh. Higher fluorescence and absorbances in pore vs. surface waters suggest soil pore water is a reservoir of CDOM in the marsh. Protein-like fluorophores in pore waters at distinct depths corresponded to variations in sulfate depletion and Fe(II) concentrations from anaerobic microbial activity. These variations were supported by fluorescence indexes and are consistent with differences in optical molecular weight and aromaticity indicators. Fluorescence indices were consistent with autochthonous material of aquatic origin in surface waters, with more terrestrial, humified allochthonous material in deeper pore waters. CDOM optical properties were consistent with significantly enhanced microbial activity in regions closest to the oil well, along with a three-dimensional excitation/emission matrix fluorescence spectrum peak attributable to oil, suggesting anaerobic microbial degradation of oil.

Keywords: salt marsh, CDOM, optical properties, EEMS, oil

Introduction

Salt marshes play an important role in the sequestration and exchange of organic carbon in coastal aquatic ecosystems (Chmura et al., 2003; Tobias and Neubauer, 2009). Organic carbon in these tidally forced wetlands is primarily a result of inputs from allochthonous terrestrial material (Moran and Hodson, 1994; Scully et al., 2004; Stabenau et al., 2004), and loss processes that include microbial degradation, photodegradation, and export. (Moran and Hodson, 1989; Moran and Zepp, 1997; Miller et al., 2002; Vahatalo and Wetzel, 2008). Dissolved organic matter (DOM) levels and functionality in salt marshes often determines the degree of nutrient uptake, light availability, and overall carbon cycling (McKnight et al., 2001; Gallegos et al., 2005). DOM chemical and physical functionality changes as the material is processed and transformed by both microbial and photochemical processes. These processes vary spatially and temporally and are often linked (Vodacek et al., 1997; Gallegos et al., 2005). Overall, these complex interconnected processes are relatively poorly understood. Even less is known about the exchange of DOM with soils and the transformations in soils in these ecosystems. Export and intertidal mixing of DOM between coastal marine and salt marsh waters are also poorly characterized (de Souza Sierra et al., 1997; Boyd and Osburn, 2004; Coble, 2007). Prior work in this region suggests that salt marshes are the primary source of DOM to Southern California coastal waters in the absence of rain events, with marsh soils being a major reservoir of DOM and the primary source of exported DOM (Clark et al., 2008).

The optical properties of chromophoric dissolved organic matter (CDOM), the UV and visible light-absorbing component of DOM (Coble, 1996; Stedmon et al., 2003), have been used to determine levels and distributions, identify sources, and track transformations of DOM. Optical characterization methods include fluorescence and absorbance intensity measurements, spectral slope, indices based on fluorescence and absorbance data, and three-dimensional excitation and emission matrix (EEMs) fluorescence spectra. EEMs have been used extensively to characterize CDOM (Coble, 1996; Stedmon et al., 2003, 2005; Murphy et al., 2008). Coble (1996) identified five main fluorescent peaks with distinct excitation and emission wavelength regions; more recent parallel factor analysis (PARAFAC) approaches have identified additional components (Stedmon et al. 2003; Stedmon and Markager 2005; Murphy et al. 2008). EEMs have been used to distinguish between different sources in natural waters; for example, fluorescence peak locations were used to differentiate between allochthonous senescent plant material and autochthonous biologically-labile material (Moran and Zepp, 1997; Miller et al., 2002; Tzortziou et al., 2007, 2011). CDOM fluorescence has been used to determine the source and transport of DOM in estuarine and coastal waters (Stedmon et al. 2003). Spectral slope analysis, absorbance and fluorescence-based indices have been used to track the transformation of CDOM (Green and Blough, 1994; Twardowski et al., 2004; Boyd and Osburn, 2004; Del Vecchio and Blough, 2004; Helms et al., 2008). There have been few DOM optical property studies carried out in southern California salt marshes and only one that focused on pore waters (Clark et al., 2014). This used trends with depth in absorption coefficients, EEM peak shifts, spectral slopes and fluorescence intensities and indices to show that marsh soil pore water is a reservoir of CDOM, with organic matter from terrestrial watershed inputs and *in situ* production

from marsh vegetation stored and processed in sediments. Specific depths were observed where changes in optical properties correlated with enhanced microbial activity, suggesting that microbial processing of DOM may play an important role in shaping CDOM optical properties and that optical properties can in turn be used to track microbial processing.

In southern California, intertidal wetlands are often impacted by oil through marine spills, natural seeps, coastal wells, and contaminated storm water runoff (McGenity, 2014). This adds an additional level of complexity to understanding the physical, chemical and biological transformation of DOM in these systems. The degree to which oil products are significant sources of organic carbon is not clear and transformations of oil products in salt marshes are poorly characterized. While a number of literature studies aim to understand the photo and biodegradation of oil compounds in marine environments associated with oil spills (Bugden et al., 2008; Islam et al., 2013; King et al., 2014; Kover et al., 2014), little is known about oil seeps and oil transformations in salt marshes. Understanding the contribution of oil to the DOM pool in salt marshes is important in evaluating the short and long term influence of oil pollution on coastal ecosystems and intertidal water chemistry (McClenachan et al., 2013; Wang et al., 2013; Marton and Roberts, 2014). Understanding oil transformations in these systems would also help assess the potential for microbial remediation (Mills et al., 2004; Garcia-Blanco et al., 2007; Horel et al., 2012). Oil components also undergo photochemical and biological degradation that result in changes in optical properties (Zhou and Guo, 2012). EEMs have been used in prior studies to characterize and monitor oil in the open ocean, including the Deepwater Horizon oil spill in the Gulf of Mexico (Zhou et al., 2013, and references therein). However, to the best of

our knowledge there have been no attempts to characterize oil products in salt marshes using optical properties.

In this study, we sought to examine the distribution and variation of the optical properties of CDOM as a function of depth in salt marsh surface and pore waters around an oil well.

Absorption coefficients, fluorescence intensities, spectral slope, fluorescence indices, and EEMs were compared over a transect away from the well and as a function of depth. Additionally, the study sought to identify the presence of oil in regions in the pore water indicated by higher microbial activity and fluorescence signatures. Iron concentrations and sulfate depletion in pore waters were also measured as indices of anaerobic microbial decomposition.

Experimental Methods

Site description

The study site is a small 0.25 km² salt marsh located adjacent to the Santa Ana River (SAR) outlet in Huntington Beach, Orange County, in southern California (Figure 1). Acquired by the Army Corps of Engineers in 1990 from an oil company, the land still contains functioning oil wells. For the purpose of mitigation for the channelization for flood control of the adjacent SAR, the Army Corps of Engineers restored the land in 1992 by excavating channels and replanting native vegetation. Little freshwater enters the SAR unless a rain event occurs so the SAR outlet is primarily tidally flushed for most of the year, with ocean water flowing in on a flood tide and SAR water out on an ebb tide (Grant et al., 2005). Surface water salinity in the marsh ranges from 30 to 33 PSU (Clark et al., 2008).

Sample Collection

Salt marsh pore water was sampled in the summer of 2012 from 6 to 20 July using pore water equilibrators (peepers, Hesslein 1976). Peepers were constructed from Plexiglass (12 cm x 75 cm) and contained ~30 mL sample chambers spaced at 3 cm intervals. These sample chambers were filled with distilled water and covered on both sides with 0.2 μ m Versapor membrane (Pall Corporation, Port Washington, New York, USA). Once assembled, the peepers were submerged in degassed distilled water and allowed to equilibrate for two weeks prior to field deployment.

Peepers were deployed at three locations along the salt marsh channel adjacent to an oil well. The first peeper was placed in the southeastern bend of the channel before the well at N 33°37.858', W 117°57.244, the second in the mid-channel eastern bend at N 33°37.958', W 117°57.225, and the third in the northeastern shoulder of the channel at N 33°38.011', W 117°57.227 (sites 1, 2, and 3 in Figure 1, respectively). These locations were chosen as a transect of the salt marsh channel from the well to a 4th site used in previous studies (N 33°38.111', W 117°57.298; Clark et al. 2008, 2014). Deployment took place during low tide (<http://www.surflife.com/surflife/tides/getXtideLocation.cfm?alias=huntingtonbeachcam>). To ease the insertion of the peepers, a guide was driven into the exposed marsh soil to a depth of approximately 30 cm below the soil surface. The peepers were then inserted such that there was a sampling chamber approximately 1.5 cm above the soil surface and another -1.5 cm below the soil surface. Sites 1-3 were sampled at 7.5 cm above the surface down to depths of -49.5 cm below the surface. Peepers equilibrated with the surrounding pore water for two weeks in the

field. Over this two-week period, tides ranged from -0.3 m to 1.8 m (<http://www.surflife.com/surflife/tides/getXtideLocation.cfm?alias=huntingtonbeachcam>). While there was no rain in June and August pre- and post-deployment, a single episode of rainfall occurred on 13 July with 0.45 cm (Santa Ana River station).

Following the two-week equilibration, the peepers were extracted and water was removed from each sampling chamber using plastic Luer lock syringes equipped with a 2-way stopcock to minimize oxygen exposure. The sample water was then returned to the laboratory and filtered through a 0.2 μm PVDF filter in an anaerobic glove box (<2% H_2 headspace with a balance of N_2 ; Coy Laboratory Products Inc., Grass Lake, Michigan, USA) to ensure minimal microbial activity. The samples were injected into serum bottles and stored in the dark at 4 °C until optical analysis. Measurements were made for the total of 60 samples collected within two weeks following extraction of the samples.

UV-Visible Spectroscopy

A diode-array UV-visible spectrometer (Agilent 8453) was used to measure absorbance spectra from 200-700 nm in a quartz cell (path length 1 cm) using MilliQ water as a blank. The spectral resolution of the instrument was less than 2 nm and stray light less than 0.03%. The Napierian absorption coefficient (m^{-1}) was calculated from the measured absorbance using Eq. (1) below (Hu et al. 2002):

$$\alpha = [(2.303/\text{Abs})/l] \quad (1)$$

where Abs is the absorbance (at 300 or 350 nm), α is the absorption coefficient, and l is the path length of the quartz cell (0.01 m; Miller et al., 1998).

Spectral slopes (S) were calculated by fitting data to Eq. (2) for S1 (300 to 400 nm), S2 (275 to 295 nm), and S3 (350 to 450 nm) for comparison to our previous work (Clark et al, 2008, 2014). The slope ratio (S_R) is calculated as the ratio of S2 to S3 (Helms et al., 2008):

$$-S = [(\ln \text{Abs}/A_0)/(\lambda - \lambda_0)] \quad (2)$$

where Abs is the absorbance at wavelength λ and A_0 is the absorbance at reference wavelength λ_0 (Green and Blough 1994; Warnock et al. 1999; Moran et al. 2000).

EEM Fluorescence Spectroscopy

Three-dimensional excitation-emission matrix fluorescence spectra (EEMs) were obtained using a scanning fluorometer (Quantamaster, PTI). The excitation wavelengths ranged from 260 to 450 nm in 5 nm increments and the emission from 270 to 650 nm in 5 nm increments. To account for the water Raman peak and Rayleigh scattering, a deionized water blank EEM (Whatman Nanopure Ion Exchanger) was generated daily and subtracted from the sample EEM. Spectra were corrected for instrumental response using the manufacturer's correction file. Fluorescence intensities were given in photons s^{-1} and converted to QSU (quinine sulfate unit; 1 QSU = 1 ppb quinine sulfate in 0.05 M H_2SO_4) using a calibration curve generated prior to analysis (Mopper and Schultz, 1993). Fluorescence/absorbance ratios were determined for Flu1 (Ex 260/Em 450), Flu2 (Ex 340/Em 435), Flu3 (Ex 275/Em 350), Flu4 (Ex 275/Em 300), and Flu5 (Ex 350/Em 450) with absorbance at 300 nm.

Fluorescence Indices

The fluorescence index (McKnight et al., 2001), the humification index (Zsolnay et al., 1999), and the index of recent autochthonous contribution (Huguet et al., 2009) were calculated from EEM measurements. The fluorescence index, the ratio of emission at 450 nm to emission at 500 nm for excitation at 370 nm, can differentiate between microbial and terrestrial sources and is a useful indicator of the aromaticity of the sample. In general, the lower the fluorescence index, the more aromatic the material. The f_{450}/f_{500} value is about 1.9 for aquatic and microbial sources and about 1.3 for terrestrial and soil sources (McKnight et al., 2001; Huguet et al., 2009). The humification index (HIX) is the ratio of emission from 435 to 480 nm to emission from 300 to 345 nm with excitation at 254 nm (Zsolnay et al., 1999; Parlanti et al., 2000; Huguet et al., 2009). This index is a useful indicator of the degree of humification of the sample. Higher HIX values (10-16) are associated with highly humified terrestrial material with high aromaticity and molecular weight. Lower HIX values (<4) are associated with autochthonous material with low aromaticity and low molecular weight (Huguet et al., 2009). The index of recent autochthonous contribution (BIX) is an indicator of recently produced CDOM as a result of biological activity. BIX is calculated at an excitation of 310 nm from the ratio of the emission at 380 nm to 430 nm. These locations correspond to marine humic (Ex310/Em380) and terrestrial humic (Ex310/Em430) material respectively. BIX values increase as contributions from marine humic, as well as fresh production from in situ biological activity, increase (Huguet et al., 2009).

Iron (Fe (II)) and Sulfate depletion

Reduced iron (Fe(II)) concentrations and sulfate depletion were measured in all pore water samples to assess microbial carbon mineralization. Fe (II) concentrations were measured

by absorbance at 562 nm after ferrozine derivatization (Lovley and Phillips, 1986). A 1.0 ml sample of pore water filtered in the anaerobic chamber was immediately added to a buffered ferrozine solution (0.1% ferrozine in HEPES buffer, pH=7.0) for analysis. Portions of pore water were frozen after filtration in the anaerobic chamber for sulfate depletion analysis. Sulfate and chloride concentrations were measured by ion chromatography with an ASRS (anion self-regenerating suppressor, Dionex Corporation, Sunnyvale, California, USA). Thawed samples were diluted and analyzed isocratically using an AG11-HC guard column, an AS11-HC column (Dionex), and a 25 mM NaOH eluent.

Sulfate depletion was then calculated using Eq. 3:

$$\text{SO}_4 \text{ depletion} = [(\text{Cl}^-_{\text{PW}}) \times (\text{R}_{\text{SW}})^{-1}] - \text{SO}_4^{2-}_{\text{PW}} \quad (3)$$

where $(\text{Cl}^-_{\text{PW}})$ is the concentration of Cl^- (mM) in the pore water, $(\text{SO}_4^{2-}_{\text{PW}})$ is the concentration of SO_4^{2-} (mM) in the pore water, and R_{SW} is the constant molar ratio of Cl^- to SO_4^{2-} in surface seawater ($\text{R}_{\text{SW}} = 19.33$; Bianchi, 2006). Positive depletion values represent a net depletion of sulfate compared to the value predicted by the seawater ratio, presumably due to sulfate reduction by the microbial community (Keller et al., 2009).

Results

In general, absorption coefficients increased for both α_{300} and α_{350} from surface waters to pore waters at all sites (Table 1). Average surface water α_{300} values were $3.5 \pm 0.5 \text{ m}^{-1}$, $4.45 \pm 1.0 \text{ m}^{-1}$, and $7.4 \pm 2.2 \text{ m}^{-1}$ at sites 1, 2, and 3 respectively. Average pore water α_{300} values were $31 \pm 24 \text{ m}^{-1}$, $22 \pm 9 \text{ m}^{-1}$, and $22 \pm 7 \text{ m}^{-1}$ at sites 1, 2, and 3 respectively. There were a number of well-defined maxima and minima in α_{300} with depth in pore waters at all three sites, although

the maxima are at slightly different depths at the three sites. At site 1, there were maxima in α_{300} of 29.0 m⁻¹, 86.9 m⁻¹, 20.4 m⁻¹, and 33.4 m⁻¹ at depths of -10.5 to -13.5 cm, -19.5 to -25.5 cm, -34.5 cm and -46.5 cm respectively. At site 2, there were maxima in α_{300} of 24.0 m⁻¹, 35.6 m⁻¹, 39.4 m⁻¹, 28.4 m⁻¹, and 22.1 m⁻¹ at depths of -7.5 cm, -13.5 cm, -22.5 cm, -37.5 cm, and -46.5 cm respectively. For site 3 there were maxima in α_{300} at depths of -4.5 cm, -19.5 cm, -28.5 cm and -46.5 cm. The corresponding absorption coefficient values at site 3 were 29.5 m⁻¹, 31.3 m⁻¹, 34.5 m⁻¹, and 28.9 m⁻¹. The broad maximum in α_{300} at -19.5 to -25.5 cm at site 1 is the dominant feature across all depths and sites.

Across all depths, α_{350} coefficients were consistently lower than α_{300} coefficients. However, the trends in α_{350} with depth were similar to the trends in α_{300} in all three sites (Figure 2). The lower slope in the relationship between α_{350} and α_{300} for site 1 was largely due to data from the dominant absorbance band at a depth of -19.5 to -25.5 cm. When data points from the band at -19.5 to -25.5 cm are excluded, the slope for site 1 increased to a value of 0.50 ($R^2 = 0.93$) and data largely overlies those for sites 2 and 3. This suggests that all three sites contained CDOM of similar composition due to similar source material, except for site 1 at depths of -19.5 to -25.5 where absorbance ratios (300nm/350nm) are noticeably different.

There were no consistent differences between average spectral slopes for surface waters and average values for pore waters for all three wavelength ranges (S1: 300 to 400 nm, S2: 275 to 295 nm, S3: 350-400 nm) at all three sites (Table 1). Spectral slopes generally decreased with depth in surface waters from 7.5 to 1.5 cm and then increased through the transition from surface to pore water from a depth of 1.5 to -1.5 cm. At each site, there are similar oscillatory trends in spectral slope with well-defined maxima and minima as a function of pore water depth for all

three ranges. Site 1 has two well defined minima at depths of -13.5 and -34.5 cm (S1 0.0072 and 0.0091) associated with increases in absorbance. There is a maximum in S, most noticeable in S2, at depths of -22.5 through -25.5 cm, associated with a large maximum in absorbance. At site 2, there are 4 well defined maxima and 4 well defined minima in spectral slope with pore water depth. The minima are aligned with increases in absorbance coefficients and occur at depths of -10.5, -22.5, -37.5 and -46.5 cm (S1 0.0066, 0.0085, 0.0076, and 0.0098). The maxima occur at depths of -4.5, -16.5, -25.5, and -43.5 cm (S1 0.0175, 0.0144, 0.0189, and 0.0147) and are associated with lower absorbance values. At site 3, there are also a number of well-defined minima and maxima in spectral slope with pore water depth; once again the minima are reasonably well aligned with maxima in absorption coefficient. Minima occur at depths of -4.5, -10.5, -19.5, -28.5, -34.5, and -46.5 cm (S1 0.0113, 0.0091, 0.0081, 0.009, 0.0103, and 0.0127). The maxima, at depths of -7.5, -16.5, -31.5 and -37.5cm (S1 0.025, 0.0135, 0.0158, and 0.0177), are associated with lower absorbance values. The maxima at -4.5 and -25.5 cm in S3 are the dominant maxima at site 2, and the maximum in S3 at -7.5 cm is the dominant feature at site 3. Both are associated with minima in absorbance. By contrast, the dominant maximum for Site 1 (S2 at -22.5 to -25.5 cm) is associated with a maximum in absorbance.

For Site 1, average S_R values are 1.00 for surface waters and near 1 for most of the pore waters (Table 1). At sites 2 and 3, average pore water values are lower than average surface water values. The average surface water S_R values are 1.00 ± 0.0 , 2.5 ± 0.5 , and 2.8 ± 2.0 for sites 1, 2, and 3, respectively. The average pore water S_R values are 1.19 ± 0.55 , 1.14 ± 0.46 , and 0.86 ± 0.43 for sites 1, 2, and 3, respectively. In pore waters, there are three well defined maxima with depth at site 1. These maxima are at -10.5, -25.5, and -34.5 cm and have S_R values of 1.19,

2.67, and 1.73, respectively. The three maxima correspond to maxima in absorption coefficient. Site 2 has 2 well defined maxima in S_R . There is a maximum at -10.5 cm of 2.16 and a smaller maximum at -40.5 cm of 1.32. For site 3 there are also 2 well defined maxima, the first once again at -10.5 cm and the second at -34.5 cm. These maxima have values of 1.96 and 1.66 respectively. Oscillations at depth for sites 2 and 3 are less obviously aligned with absorption coefficients.

Fluorescence intensity (Ex 350/Em 450 nm) increases from surface waters to pore waters (Table 1). The average surface water fluorescence is 1.7 ± 0.3 , 5.8 ± 1.5 and 5.8 ± 1.9 QSU at sites 1, 2, and 3, respectively, while the average pore water fluorescence is 93 ± 31 , 85 ± 27 and 97 ± 26 QSU at sites 1, 2, and 3, respectively. At site 1, fluorescence intensity values ranged from 57 to 98 QSU with peaks at depths of -10.5, -22.5, and -46.5 cm in the pore water. These maxima are consistent with absorption maxima. Site 2 showed similar intensity ranges with peaks at depths of -16.5, -25.5, and -49.5 cm. Fluorescence at Site 3 ranges from 75 to 128 QSU with maxima at -7.5, -22.5, and -46.5 cm below the surface. The fluorescence maxima at sites 2 and 3 were associated (aligning with or adjacent to) with maxima observed in absorption.

The 3D excitation-emission matrices (EEMs) were used for identifying specific CDOM sources (Coble, 1996; de Souza Sierra et al. 1997; McKnight et al. 2001). The major peaks identified by EEMS include: 1) peak A, terrestrial humic-like; 2) peak T, tryptophan protein-like; 3) peak B, tyrosine protein-like; 4) peak M, marine humic-like; and 5) peak C, terrestrial humic-like (Table 2). The fluorescence intensities were similar for peaks T and B as well as for peaks C and M. All sites showed increased fluorescence intensity in the transition from surface to pore water (Figure 4). Peak A intensity ranged from 125 to 185 QSU in pore waters with a notable

increase from a depth of -37.5 to -49.5 cm below the surface at site 3 (Figure 4A). Peak T ranged from 35 to 80 QSU in pore waters with notable increases at -7.5 cm for all 3 sites, at -22.5 to -25.5 cm for sites 1 and 3, at -37.5 for sites 1 and 3, and at -46.5 cm for site 1 below the surface (Figure 4B). Peak C intensity ranged from 85 to 165 QSU in pore waters, where sites 1 and 2 had higher values in upper pore water while site 3 showed higher values in lower pore water (Figure 4C). Site 1 showed the highest fluorescence intensities for peak T of 2400 and 3500 QSU at depths of -22.5 and -25.5 cm, respectively (off-scale in Figure 4B). The component in the EEMs for site 1 with excitation between 260 and 280 nm and emission at 320 nm has been previously identified as a component of crude oil (Zhou and Guo, 2012). A similar feature was seen in the surface waters for sites 2 and 3 at similar intensities, and in the pore waters at some depths.

To assess potential differences in pore water microbial processing, we measured dissolved iron and sulfate depletion at the three sites (Figure 5). Fe(II) concentration averaged 0.079 μM , 0.032 μM , and 0.064 μM in surface and upper pore waters (7.5 to -1.5 cm) at sites 1, 2, and 3 respectively and showed significant increases at unique depths for each site. At site 1 (Fig. 5A), the concentration increased at a depth of -13.5 cm to 41.3 μM before dropping back down to 0.3 μM at -19.5 cm. There is a second broad maximum of 5.6 μM across depths from -31.5 to -43.5 cm. At site 2 (Fig. 5B), Fe(II) concentrations were elevated at all depths in the pore water with significant maxima in 3 bands of 17 μM , 17.8 μM , and 26.7 μM at depths of -19.5 to -22.5 cm, -37.5 to -40.5 cm, and -46.5 to -49.5 cm respectively. At site 3 (Fig. 5C), there were elevated Fe(II) concentrations of 12.7 μM , 50.2 μM , 37.1 μM , and 8.0 μM in 4 bands at depths of -4.5cm, -19.5cm, -25.5 to -28.5cm, and -46.5 cm. At all sites, sulfate depletion increased from surface waters to pore waters. Sulfate depletion averaged 0.14, 0.0, and 0.14 mM

in surface waters and shallow pore waters (down to -1.5 cm) and averaged 4.6, 8.3, and 4.7 mM in pore waters at sites 1, 2, and 3 respectively. At site 1, there is a very large maximum of 22.6 mM at a depth centered around -22.5 cm; the maximum is a broad feature from -19.5 cm to -28.5 cm. At site 2, there is a smaller maximum of 7.7 mM at -13.5 to -16.5 cm. There are no noticeable maxima in sulfate depletion at site 3, just a general trend of a slow increase with depth in the pore waters. At site 1, sulfate depletion and Fe(II) concentrations appear anti-correlated; sulfate depletion decreases when the Fe(II) concentration increases at -13.5 cm and Fe(II) concentration decreases when sulfate depletion increases at both -19.5 and -46.5 cm. At sites 2 and 3, bands with increases in Fe(II) overlay a broad increase in sulfate depletion with depth from near zero in surface waters to levels of 5 to 10 mM in the deepest pore waters.

Discussion

General Trends in CDOM Optical Properties in Surface and Pore Waters

An examination of the optical properties of CDOM in salt marsh pore waters provides a way to assess the levels, functionality and sources of the organic matter in these systems. Changes in the magnitude of CDOM fluorescence and absorption are associated with changes in both the functionality and levels of dissolved organic material, whereas variability in parameters like the spectral slope, fluorescence peak indices and fluorescence per unit absorbance ratios reflect changes in CDOM functionality and structure only (McKnight et al., 2001; Tzortziou et al., 2011). The composition and concentration of DOM may change in dynamic salt marsh ecosystems as a result of differences in source material, specifically between allochthonous terrestrial material input from external sources and autochthonous aquatic material produced in

situ. Other factors that affect CDOM composition and concentration are physical processes (like dilution in the water column or absorption onto sediment particles), other abiotic loss processes like photochemical degradation and biotic loss processes like aerobic biological processing in surface waters and anaerobic biological processing at depth in pore waters. The bioavailability of CDOM to biodegradation processes varies based on composition, with more aromatic, higher molecular weight material generally being more resistant to utilization by bacteria (Perdue et al., 2010).

Across all 3 sites for this study in summer 2012, absorption coefficients and fluorescence intensities were lower in the surface waters vs. the pore waters. The higher values in the pore waters may be due to increased concentrations of CDOM or to a shift in the composition of CDOM to more highly absorbing or fluorescing components. However, this is most likely due to higher CDOM levels in pore waters vs. the overlying surface waters due to burial of material in sediments. At all sites, the absorption coefficients (300 and 350 nm) and fluorescence intensities (Ex 350/Em 450 nm) showed similar trends as a function of depth, with increases in bands at depth. The regions at depths where fluorescence intensity increased dramatically were generally associated with a similar increase in absorption coefficient. These regions of higher absorbance and fluorescence occur at depths where there is an increase in sulfate depletion and/or Fe(II) concentration, suggesting that these zones may be due to increased total dissolved organic carbon (DOC) production from microbial degradation processes (Vodacek et al., 1997; Sierra et al., 2001; Burdige et al., 2004; Marchand et al., 2006). Similar results were obtained in a prior study in the same season (summer 2011) at another sampling site in this salt marsh (Clark et al., 2014), with higher absorbance and fluorescence intensities in surface vs. pore waters, and an increase in

both in a band at a depth of -20 cm that occurred where the Fe(II) concentration increased from near 0 to 275 μM .

The spectral slope (S) also provides insight to the chemical characterization of CDOM in pore water. In general, S values increase as photochemical and oxidative processes take place, and decrease as organic matter biodegrades resulting in higher aromaticity and humification (Green and Blough 1994; Vodacek et al. 1997; Boyd and Osburn 2004, Stabenau et al. 2004; Twardowski et al., 2004; Tzortziou et al. 2007). The decrease in slope from 7.5 to 1.5 cm in surface waters at sites 2 and 3 indicates decreasing photochemical degradation and processing has taken place (Green and Blough, 1994; Vodacek et al., 1997; Burdige et al., 2004; Twardowski et al., 2004; Helms et al., 2008). The oscillations of S values with depth at all sites suggest altered degrees of aromaticity and humification throughout the anaerobic region (Stabenau et al., 2004; Tzortziou et al., 2007; Helms et al., 2008). In general, there are minima in S in the bands with higher Fe(II) concentrations and maxima in S in bands with high sulfate depletion; increasing S suggests material with lower aromaticity. The higher S_R values generally observed in the surface waters suggest greater contributions from aquatic material, while the lower values in pore water suggest terrestrial material that is more humified and aromatic in nature (Helms et al., 2008). S_R values generally decrease in Fe(II) bands and increase in sulfate depletion bands; increasing S_R suggests material with lower aromaticity.

The flu:abs ratio is another measure of CDOM composition changes, with decreasing values associated with increasing molecular weight, humification and aromaticity (Belzile and Guo, 2006). Flu:abs ratios were lower in the overlying surface waters (Table 1), averaging 1.3 ± 0.2 , 2.3 ± 0.4 and 1.5 ± 0.5 for sites 1, 2 and 3 respectively, and higher in the pore waters,

averaging 7.7 ± 2.8 , 7.3 ± 3.7 and 9.8 ± 4.0 for sites 1, 2 and 3 respectively. This suggests production of lower molecular weight, fresher and less-humified material is occurring in the pore waters. Like the other optical parameters reported here, ratios also showed oscillations through the soil profile, indicating variable degrees of processing occurring with depth. Minima in flu:abs were generally aligned with maxima in Fe (II) concentrations, consistent with material with higher aromaticity. On the other hand, in bands with high sulfate depletion, flu:abs ratios tend to be a maximum, consistent with material with lower aromaticity. These trends in aromaticity are consistent with those observed in the spectral slopes.

Indicators of Biological Processing

The initial increase in sulfate depletion and Fe(II) concentrations in the pore waters vs. the overlying surface waters (Fig 5) is an indicator of the transition from aerobic to anaerobic processing. Variations in sulfate depletion and Fe(II) concentrations with depth indicate where anaerobic microbial decomposition may be taking place.

The regions where Fe(II) concentrations increase correlate with regions where there is higher aromaticity and humification; regions with increased sulfate depletion correlate with regions with strong autochthonous material and high anaerobic microbial activity (Leslie et al., 1990). These trends suggest that biological processing driven by sulfate reduction is related to less humified, less aromatic material whereas regions associated with iron reduction have material that is more humified and more aromatic. These bands could be due to production of material with lower or higher aromaticity in these regions depending on the type of bacterial population and pathway involved, or due to the fact that bacterial degradation is occurring preferentially on this type of material compared to that in adjacent regions.

The trend of bands where the Fe(II) concentration increases are overlaid over a general trend of increasing sulfate depletion with depth at sites 2 and 3. These trends suggest sulfate reduction is the dominant anaerobic microbial process in the pore waters, resulting in sulfate depletion with respect to the surface waters, except for areas in the pore waters at depths with higher Fe(II) levels, where anaerobic microbial carbon remineralization processes may be occurring via iron rather than sulfate reduction (Megonigal et al., 2004), resulting in increased Fe(II) concentrations.

DOM at these depths was further examined using the results from the EEM spectra at each site. Humic-like peaks, A and C, and protein-like peak T were characterized by depth profiles to analyze the source of humic material and recent autochthonous material, respectively (Yamashita and Tanoue, 2003; Fellman et al., 2008). The fluorescence intensity of peak A and C were highest at site 3, suggesting higher input and retention of allochthonous terrestrial material in the northeastern shoulder of the salt marsh (Moran and Hodson, 1994; Stedmon et al., 2003, 2005; Scully et al., 2004; Stabenau et al., 2004). At site 1, the oscillation of peak T intensity (Figure 6B) and the increased T/C ratio in the -19.5 to -25.5 cm region below the surface (Table 1) support the increased production of protein-like material from microbial activity, since protein-like peaks are associated with amino acids free or bound in proteins and the tryptophan-like peak T indicates recent origin (Yamashita and Tanoue, 2003; Fellman et al., 2008). This is in a region where there is a strong increase in sulfate reduction.

Fluorescence intensity ratios relative to peak C are commonly used to show any oscillation trends due to a wavelength shift (Huguet et al., 2009). The fluorescence intensity ratio of peak A to peak C was consistently between 1.2 and 1.7 in pore water, while reaching as high

as 5.4 in surface waters (Table 1). Due to the association of peak A with recently produced terrestrial humic material and peak C with older terrestrial humic material, this trend in pore and surface water is indicative of higher and lower humified material, respectively. The ratio of peak T to peak C was between 0.3 and 1.0 in pore water, averaged 9.9 in surface water, and increased dramatically at a depth of -22.5 and -25.5 cm at site 1 (Table 1). Higher T/C ratio values in surface water suggest higher primary productivity as a result of recent autochthonous material relative to the lower amount of older humic material in these waters (Huguet et al., 2009, 2010). The increased T/C ratio between -22.5 and -25.5 cm at site 1 signifies a region of higher productivity relative to the other depths.

Aquatic vs. Terrestrial CDOM Sources in Surface vs. Pore Waters

The trend from aquatic material in surface waters to more terrestrial material at depth in the pore waters is supported by the fluorescence indices. The fluorescence index (f_{450}/f_{500}) provides an estimate of the degree of aromaticity; values of 1.9 have been obtained for microbial and aquatic sources and 1.3 for terrestrial and soil sources (McKnight et al., 2001). This index gradually decreased from 1.9 ± 0.6 at a depth of -1.5 cm to 1.31 ± 0.08 at -13.5 cm, indicating a shift from aquatic to terrestrial source material at depth (Figure 6A). Below -13.5 cm, the index remained constant around 1.3 with no significant peaks. The f index averaged 1.4 ± 0.2 for all site pore water samples, 1.3 ± 0.1 for site 1, 1.4 ± 0.3 for site 2, and 1.4 ± 0.1 for site 3. This is consistent with values of 1.2 to 1.3 for pore waters obtained in a prior study at another location in this salt marsh (Clark et al., 2014).

The humification HIX index, a measure of aromaticity and the degree of maturation (Zsolnay et al., 1999), varied among sampling sites and showed unique oscillations with depth in

the pore water (Figure 6B). HIX minima are generally correlated with high Fe(II) concentrations and high sulfate depletion in pore waters. The HIX index for all site surface water samples averaged 0.8 ± 0.3 , indicating a high aquatic biological origin of material. Values were higher in the pore waters, consistent with material of a more terrestrial origin. Site 1 averaged 3.7 ± 2.1 for pore water samples, with maximum values at -10.5, -40.5, and -49.5 cm, suggesting weak humic and strong autochthonous material. Site 2 averaged 6.6 ± 0.3 in upper pore waters and 9.9 ± 1.6 in lower pore waters, indicating a shift from weak to moderate humic characteristics, respectively. At a range of -13.5 to -16.5 cm, site 2 showed the strongest terrigenous humic material contribution at a HIX index of 18 ± 1.9 . The HIX index at site 3 averaged 6.3 ± 1.7 in pore water with maximum values at depths of -16.5 and -49.5 cm. This signifies consistently moderate humic and autochthonous material (Huguet et al., 2009). Based on the HIX index, there is increased terrigenous humic material contribution as depth increased (Huguet et al., 2009). While site 2 and 3 showed similar trends in HIX index values, site 1 showed decreased HIX values in regions where the other sites increased, such as -19.5 to -25.5 cm below the surface. This suggests high aquatic biological origin, as opposed to terrestrial humic material, due to anaerobic microbial activity taking place (Huguet et al., 2009).

The BIX index, a measure of autochthonous biological activity in estuarine and marine environments (Huguet et al., 2010), averaged 0.6 ± 0.2 in surface waters, 0.8 ± 0.04 in upper pore waters, and 0.7 ± 0.1 in lower pore waters (Figure 6C), consistent with values of 0.7 obtained for surface and pore waters in a prior study at this salt marsh site (Clark et al., 2014). This indicates a shift from weaker to stronger to moderate contributions from autochthonous material (Huguet et al., 2009). In general, higher BIX values are associated with maxima in Fe(II) concentrations

and high sulfate depletion. In lower pore waters, site 3 averaged 0.8 ± 0.1 , site 2 averaged 0.7 ± 0.1 , and site 3 averaged 0.7 ± 0.03 . These values are consistent with primarily an allochthonous terrestrial DOM source. Unlike the other sites, however, site 1 showed the highest BIX index value of 1.3 between -22.5 and -25.5 cm, suggesting organic material freshly produced in situ in this region.

Potential Oil Implications

There are a number of unique features at site 1, the area adjacent to the oil well. For example, S_R values and $f(450/500)$ ratios are very low in surface waters at site 1, compared to sites 2 and 3. In addition, in Figure 2, the pore waters at a depth of -19.5 to -25.5 cm do not fall on the same trend line as the points for all the other samples from site 1, and the surface and pore water samples for sites 2 and 3. One important distinctive feature is the appearance of a component in the EEMs with excitation between 260 and 280 nm and emission at 320 nm, which we attribute to a component of crude oil (Zhou and Guo, 2012). The intensity of this peak was low in the surface waters and varied with depth. At site 1, higher intensities were observed at depths of -15.5 through -28.5 cm and again at -46.5 cm. This peak was obscured at the depths of -22.5 and -25.5 by the very high intensity protein peaks. This peak was also observed in the surface water EEMs for sites 2 and 3 at low intensities (40 QSU, similar to site 1), and at lower intensities (compared to site 1) in the pore waters at some depths.

Another unique feature is the very high peak T fluorescence intensities between -22.5 and -25.5 cm, two orders of magnitude higher than typical pore water values. This band was associated with a distinct broad feature of 2- to 4- times higher sulfate depletion levels than observed at the other sites. The BIX index also increased significantly in this region (Fig 6C),

indicating high recent autochthonous contributions. The HIX index showed a similar significant decrease here to near zero values, also indicating a strong contribution of autochthonous material. The significant increase in T peak fluorescence intensity and sulfate depletion trends in the region of -19.5 to -25.5 cm at site 1 suggest specific stratification taking place with high anaerobic microbial activity with sulfate-reducing bacteria. This unique layer at site 1 suggests possible autochthonous biological production is occurring as a result of oil biodegradation, possibly through sulfate-reducing bacteria based on the associated sulfate reduction peak.

Conclusion

Results from this study suggest that soil pore water is a reservoir of CDOM in the salt marsh, based on higher fluorescence and absorbance in the pore water compared to the surface water. Optical characteristics and fluorescence indices are generally consistent with autochthonous material of aquatic origin in the surface waters, with more terrestrial, humified allochthonous material in the deeper pore waters. Tryptophan and tyrosine protein-like fluorophores were observed in pore waters at distinct depths, corresponding to variations in sulfate depletion and Fe(II) concentrations from anaerobic microbial activity. These variations were supported by fluorescence index (f_{450}/f_{500}), humification index (HIX), and index of recent autochthonous contribution (BIX) results, and are consistent with differences in molecular weight and aromaticity indicators from optical properties. These bands at depth with varying optical properties, iron and sulfate depletion peaks and protein fluorescent signatures are attributed to areas where active microbial processing of CDOM is occurring, with the concomitant production of remineralized, less humified material in sulfate depletion bands and

more aromatic material in bands where Fe(II) concentration increases. This activity is strongest at the site adjacent to the oil well, along with a peak in the EEM spectra attributable to oil, suggesting anaerobic microbial degradation of oil may be occurring at depth in the pore waters.

Acknowledgements

CDC and WJD thank the National Science Foundation (OCE grant #072528433) for support. JKK was supported by the National Science Foundation (DEB grant #0816743). The authors thank undergraduate students Brenna McNabb and Paige Aiona for additional sampling support and assistance with peeper preparation and Dr. Kimberly Takagi for assistance with ion chromatography. The authors gratefully acknowledge the assistance of Erin Hardison, staff biologist with the U.S. Army Corps of Engineers, Los Angeles district, for site information, access and sampling permission.

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Table 1. Optical characteristics of CDOM in a salt marsh ecosystem: absorption coefficients (abs; m⁻¹), spectral slopes (*S1* 300-400nm; *S2* 275-295 nm; *S3* 350-450 nm), spectral slope ratio (*S_R*; *S2*÷*S3*), fluorescence intensities (in QSU; Flu $\lambda_{\text{excitation}} = 350 \text{ nm}$, $\lambda_{\text{emission}} = 450 \text{ nm}$), fluorescence intensity ratios (peaks A/C; T/C) and flu/abs ratios (Flu/a₃₅₀).

Sample Location	Depth (cm)	α_{300} (m ⁻¹)	α_{350} (m ⁻¹)	<i>S1</i>	<i>S2</i>	<i>S3</i>	<i>S_R</i>	Flu	A/C	T/C	Flu/abs
<i>Site 1</i>	7.5	3.1	1.4	0.016	0.017	0.017	1.00	1.4	5.4	9.9	1.0
	4.5	4.0	1.2	0.0051	0.021	--	--	1.8	4.3	9.1	1.4
	1.5	3.5	1.4	0.018	0.018	0.018	1.00	2.0	4.5	7.2	1.4
	-1.5	5.0	2.4	0.015	0.015	0.016	0.94	15.5	1.9	1.6	6.5
	-4.5	12.6	5.9	0.016	0.013	0.016	0.84	56.7	1.5	0.70	9.6
	-7.5	16.4	8.1	0.015	0.015	0.016	0.94	80.6	1.5	0.81	10.0
	-10.5	29.0	14.9	0.013	0.015	0.013	1.19	109	1.6	0.57	7.4
	-13.5	26.1	17.9	0.0072	0.0082	0.0085	0.97	75.6	1.6	1.2	4.2
	-16.5	16.4	8.3	0.015	0.014	0.015	0.91	74.5	1.6	1.0	9.0
	-19.5	70.1	28.6	0.014	0.014	0.014	1.02	120	--	1.8	4.2

	-22.5	86.9	33.7	0.016	0.039	0.01 7	2.28	144	--	15.6	4.3
	-25.5	75.1	28.6	0.016	0.042	0.01 6	2.67	139	--	23.3	4.9
	-28.5	44.6	20.8	0.013	0.014	0.01 2	1.10	121	1.2	0.82	5.8
	-31.5	15.3	7.3	0.016	0.014	0.01 6	0.86	82. 9	1.7	0.63	11.3
	-34.5	20.4	12.3	0.009 1	0.009 9	0.00 58	1.72	96. 9	1.6	0.60	7.9
	-37.5	17.3	8.9	0.014	0.014	0.01 4	1.00	85. 4	1.6	0.53	9.5
	-40.5	20.8	10.6	0.015	0.012	0.01 7	0.71	85. 8	1.6	0.47	8.1
	-43.5	18.9	10.1	0.013	0.013	0.01 3	0.99	96. 3	1.7	0.48	9.6
	-46.5	33.4	14.3	0.015	0.016	0.01 7	0.95	104	1.5	1.1	7.3
	-49.5	19.8	9.0	0.018	0.014	--	--	98. 4	1.6	0.4 9	10.9
<hr/>											
<i>Site 2</i>						0.00					1.9
	7.5	5.1	2.5	0.011	0.014	71	1.99	4.9	3.0	3.2	
				0.008		0.00					2.8
	4.5	5.0	2.7	5	0.014	53	2.69	7.6	2.5	3.0	
				0.004	0.001	0.00					2.1
	1.5	3.3	2.4	3	2	04	2.90	5.0	3.3	3.8	
						0.01					2.1
	-1.5	4.9	2.8	0.013	0.013	7	0.79	5.7	2.7	4.7	
						0.02		45.		0.5	10.5
	-4.5	9.3	4.5	0.018	0.012	5	0.47	3	1.6	4	
				0.006	0.008	0.00		75.		0.5	4.5
	-7.5	24.0	16.8	6	3	41	2.02	8	1.5	6	

			0.006	0.008	0.00		73.		0.6	4.7
-10.5	21.8	15.5	3	8	41	2.16	2	1.6	0	
			0.009		0.00				0.3	5.4
-13.5	35.5	20.8	1	0.012	66	1.89	112	1.3	0	
					0.01				0.3	8.8
-16.5	31.4	14.6	0.014	0.014	5	0.94	128	1.3	0	
			0.009	0.007	0.00		86.		0.3	5.1
-19.5	25.8	17.2	0	6	95	0.80	8	1.6	9	
			0.008	0.007	0.00		93.		0.4	3.5
-22.5	39.4	26.2	5	8	79	0.98	0	1.5	1	
					0.02		98.		0.3	16.2
-25.5	14.7	6.1	0.019	0.015	1	0.71	3	1.6	4	
					0.00		90.		0.3	7.8
-28.5	20.8	11.5	0.012	0.011	97	1.09	2	1.7	7	
				0.009	0.00		84.		0.3	6.6
-31.5	21.0	12.7	0.010	2	83	1.11	0	1.7	6	
					0.00		82.		0.3	7.6
-34.5	19.1	10.9	0.011	0.010	89	1.14	9	1.7	9	
			0.007	0.007	0.00		84.		0.3	4.4
-37.5	28.4	19.4	6	6	66	1.14	9	1.6	4	
			0.008	0.009	0.00		88.		0.4	5.9
-40.5	23.8	15.0	9	6	72	1.32	3	1.7	2	
					0.01		97.		0.3	12.2
-43.5	16.2	8.0	0.015	0.013	5	0.88	6	1.7	9	
			0.009	0.009	0.00				0.3	7.6
-46.5	22.1	13.3	8	8	91	1.07	101	1.7	6	
					0.01				0.4	12.4
-49.5	15.9	8.3	0.013	0.013	4	0.98	103	1.7	3	
<hr/>										
Site 3					0.00					2.1
	7.5	4.9	2.1	0.015	0.018	89	2.00	4.4	3.1	3.5

					0.01					1.2
4.5	9.1	4.2	0.012	0.015	1	1.30	5.1	2.9	2.5	
			0.003	0.005	0.00					1.2
1.5	8.1	6.5	7	5	11	5.13	8.0	2.2	2.3	
					0.02		30.			9.4
-1.5	7.1	3.2	0.018	0.015	5	0.59	1	1.5	0.75	
					0.01		83.			4.7
-4.5	29.6	17.9	0.011	0.011	5	0.70	4	1.4	0.67	
					0.03					21.7
-7.5	13.3	4.7	0.025	0.017	6	0.49	101	1.4	0.85	
			0.009	0.009	0.00		76.			8.9
-10.5	14.5	8.6	1	2	47	1.96	5	1.5	0.69	
					0.00		83.			7.9
-13.5	17.8	10.4	0.011	0.012	88	1.33	2	1.5	0.51	
					0.01		88.			7.7
-16.5	21.9	11.5	0.014	0.012	4	0.91	6	1.5	0.47	
			0.008	0.006	0.00		75.			3.4
-19.5	31.3	22.0	1	9	93	0.74	5	1.5	0.49	
					0.01					9.7
-22.5	21.4	10.7	0.015	0.012	6	0.75	104	1.5	0.49	
				0.009	0.01		86.			7.2
-25.5	22.8	12.0	0.014	6	7	0.55	2	1.5	0.48	
			0.009	0.006	0.01		97.			4.1
-28.5	34.4	23.7	0	5	1	0.60	1	1.5	0.63	
					0.01					8.5
-31.5	25.3	12.4	0.016	0.011	9	0.55	105	1.6	0.62	
					0.00					8.9
-34.5	21.6	12.8	0.010	0.011	67	1.66	115	1.6	0.59	
					0.02					14.8
-37.5	18.7	8.6	0.018	0.012	2	0.56	128	1.6	0.57	
					0.02					11.9
-40.5	22.0	9.8	0.017	0.013	2	0.60	117	1.5	0.46	

					0.01					13.6
-43.5	21.8	9.8	0.017	0.014	8	0.81	134	1.6	0.52	
					0.01					8.9
-46.5	28.9	15.2	0.013	0.012	2	1.01	135	1.5	0.43	

Table 2. Major fluorescence bands for natural water EEMs (Coble, 1996).

Peak	Ex _{max} (nm)	Em _{max} (nm)	Specified Peak (Ex/Em)	Component type
C	330 – 350	420 – 480	340/435	Terrestrial, humic-like
A	240 – 260	380 – 460	260/450	Terrestrial, humic-like
M	310 – 320	380 – 420	--	Marine, humic-like
B	270 – 280	300 – 320	275/300	Tyrosine, protein-like
T	270 – 280	320 – 350	275/350	Tryptophan, protein-like

Figure Captions

Figure 1. Diagram of the study site including the Santa Ana River (SAR), sampling locations (Sites 1, 2, and 3), and oil well location in Orange County, California.

Figure 2. Absorption coefficients at 300 nm vs. 350 nm (m^{-1}) for all samples from Sites 1 (■), 2 (○), and 3 (□). Lines shown from linear regression fits to the data (Site 1: $R^2 = 0.96$, slope = 0.38; Site 2: $R^2 = 0.94$, slope = 0.64; Site 3: $R^2 = 0.88$, slope = 0.65).

Figure 3. Contour plots of 3D excitation-emission matrices as a function of depth (cm) for Site 1; x-axis is $\lambda_{\text{excitation}}$ from 260 to 450 nm and y-axis is $\lambda_{\text{emission}}$ from 270 to 650 nm. Contour lines represent intensities ranging from -100 QSU (blue) to 500 QSU (dark red) in increments of 20 QSU. At a depth of -22.5 and -25.5 cm below the surface, contour lines represent intensities ranging from -100 QSU (blue) to 6500 QSU (dark red) in increments of 200 QSU.

Figure 4. Comparison of fluorescence intensity in QSU at A) peak A at $\lambda_{\text{excitation}} = 260$ nm; $\lambda_{\text{emission}} = 450$ nm, B) peak T at $\lambda_{\text{excitation}} = 275$ nm; $\lambda_{\text{emission}} = 350$ nm, and C) peak C at $\lambda_{\text{excitation}} = 340$ nm; $\lambda_{\text{emission}} = 435$ nm, as a function of depth (cm) for Sites 1 (■), 2 (○), and 3 (□).

Figure 5. Iron (II) concentration (μM ○) and SO_4 depletion (mM ■) vs depth (cm) in pore water for Sites 1, 2 and 3 (A, B and C respectively).

Figure 6. A) The fluorescence index (f_{450}/f_{500}) vs. depth (cm), B) the humification index (HIX) vs. depth (cm), and C) the index of recent autochthonous contribution (BIX) vs. depth (cm) for Sites 1 (■), 2 (○), and 3 (□).

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5

Fig. 6.