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Organic biogeochemistry of detrital flocculent material (floc) in a subtropical, coastal wetland

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Abstract. Flocculent materials (floc), in aquatic systems usually consist of a non-consolidated layer of biogenic, detrital material relatively rich in organic matter which represents an important food-web component for invertebrates and fish. Thus, variations in its composition could impact food webs and change faunal structure. Transport, remineralization rates and deposition of floc may also be important factors in soil/sediment formation. In spite of its relevance and sensitivity to external factors, few chemical studies have been carried out on the biogeochemistry of floc material. In this study, we focused on the molecular characterization of the flocculent organic matter (OM), the assessment of its origin and its environmental fate at five stations along a freshwater to marine ecotone, namely the Taylor Slough, Everglades National Park (ENP), Florida. To tackle this issue, suspended, unconsolidated, detrital floc samples, soils/sediments and plants were analyzed for bulk properties, biomarkers and pigments. Both geochemical proxies and biomass-specific biomarkers were used to assess OM sources and transformations. Our results show that the detrital organic matter of the flocculent material is largely regulated by local vegetation inputs, ranging from periphyton, emergent and submerged plants and terrestrial plants such as mangroves, with molecular evidence of different degrees of diagenetic reworking, including fungal activity. Evidence is presented for both hydrodynamic transport of floc materials, and incorporation of floc OM into soils/sediments. However, some molecular parameters showed a decoupling between floc and underlying soil/sediment OM, suggesting that physical transport, incorporation and degradation/remineralization of OM in floc may be controlled by a combination of a variety of complex biogeochemical variables including hydrodynamic transport, hydroperiod characteristics, primary productivity, nutrient availability, and OM quality among others. Further investigations are needed to better understand the ecological role of floc in freshwater and coastal wetlands.

Introduction

Flocculent materials (floc), according to Droppo (2001), represents a complex matrix of microorganisms (generally bacteria), organic particles (e.g. detritus, extracellular polymers and cellular debris), inorganic particles (e.g. clays and silts) and substantial inter-floc spaces (pores). Floc material is of ecological

importance, since it represents an important environmental component in aquatic ecosystems and may control a variety of biogeochemical processes. Hence, floc can potentially control the fate and effect of particle-associated contaminants as it may alter the hydrodynamic properties of particles in transport (Droppo 2001). Suspended floc materials can quickly respond to nutrient enrichment (Noe et al. 2002) and regulate the overall water quality through physical, chemical and/or biological processes (Droppo et al. 1997) responsible for nutrient transport and cycling via spiraling and microbial activity, respectively (Noe et al. 2001). Detrital flocculent materials are likely to constitute an important component of the detrital food chain in wetland ecosystems, and as such play a crucial biogeochemical role (Moore et al. 2004). In highly oligotrophic environments it may represent an important energy source for aquatic organisms and, therefore a potential source of dissolved organic matter through degradation and re-mineralization processes. Alternatively, it can serve as a source of organic and inorganic materials to wetland soil/sediment formation.

The Florida Everglades is one of most extensive wetland ecosystems in the world (Davis et al. 1994; Holling et al. 1994). It is an oligotrophic fresh water system, which used to cover a large area (10,000 km^2) from Lake Okeechobee (north) to Florida Bay (south; Newman et al. 2001) over a 200 km limestone plate stretch (Holling et al. 1994). Water flow is slow (maximum speed of 36 m/h during floods; Holling et al. 1994), caused by the low difference of elevation (5.3 m) between the northern and southern most points of this system (Gunderson and Loftus 1993). However, urbanization and agricultural activity reduced this area to almost half (Davis and Ogden 1994), altering its hydrology and increasing the levels of nutrients particularly in the Northern section, which is partially responsible for changes in standing stocks of fauna and flora (McIvor 1994). As a consequence of increased awareness of these anthropogenic alterations, a multi-entity effort for the restoration of the system to natural levels has been discussed (Davis and Ogden 1994). In order to assess the effectiveness of such restoration efforts, present day biogeochemistry processes need to be studied and monitored throughout the restoration period. Organic matter (OM) is a key component of the biogeochemical nutrient cycle in this highly oligotrophic system, where most of the nutrient load is in an organic form (Reddy et al. 1999; Noe et al. 2001) and OM is mainly transported in the dissolved (DOM) and flocculent (floc) phase. This flocculent material is most likely derived from local biomass and mainly in the form of organic detrital particles. Flocculation of DOM in the Everglades ecosystem has been reported to be insignificant with the possible exception of the Whitewater Bay area (Jaffé et al. 2004).

Benthic and floating periphyton mats are likely an important source of detrital floc in the Everglades ecosystem, by contributing small, particulate organic matter to this phase. In addition to higher plant vegetation change across the Everglades landscape, variations in periphyton composition, which is very sensitive to nutrient concentration (McCormick et al. 2001; Noe et al.

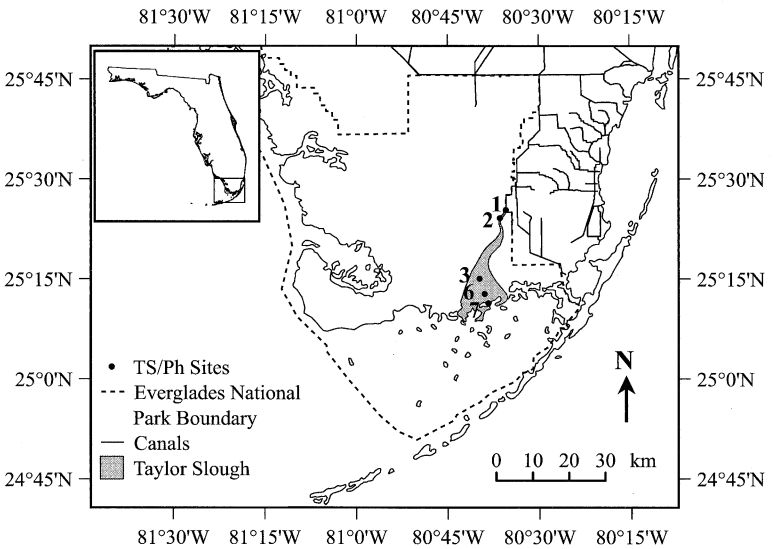

Figure 1. Map of study area and sampling locations.

2001), may result in regional and temporal changes of floc composition (Noe et al. 2002). In spite of its relevance and sensitivity to environmental factors, few chemical studies, other than nutrients, have been carried out on floc material in this system. Floc in the Everglades is believed to consist of higher plant detritus, periphyton, carbonates, and other remains of aquatic organisms found in freshwater and estuarine systems. However, the exact sources of organic matter in floc have not been characterized. Therefore, this study is aimed at characterizing the origin and fate of organic matter present in floc and to assess its potential contribution to the underlying soil/sediment. To address these issues, floc and soil/sediments were collected at five locations along Taylor Slough, ENP (Figure 1) and were analyzed for bulk properties such as %TOC, %TN, C/N, $\%CaCO_3$ and $\delta^{13}C$. In addition to geochemical proxies, biomass-specific molecular markers and pigment-based chemotaxonomy were used in the assessment of floc OM sources. This approach has successfully been used to trace the source and fate of sedimentary organic matter in the Everglades system (Louda et al. 2000; Hernandez et al. 2001; Jaffé et al. 2001).

Materials and methods

Sampling

Floc and soil/sediment samples (8 subsamples pooled) were taken from five sites along Taylor Slough, ENP. The selected sites are part of the on-going Florida Coastal Everglades Long Term Ecological Research (FCE-LTER;

fcelter.fiu.edu) program, and are referred to as TS/Ph sites 1, 2, 3, 6 and 7 (Figure 1). This transect stretches from the *Cladium*/*Eleocharis*/periphyton dominated freshwater marsh sites (FWM 1–3) to the *Rhizophora mangle* dominated estuarine sites (MEST 6 and 7), along the North to South water flow throughout Taylor Slough (see Figure 1) into Florida Bay (Gunderson 1994). Since tidal action is unimportant in NE Florida Bay, only site 7 (and site 6 during the end of the dry period) are influenced by waters from the Bay. While both locations are mainly influenced by mangrove-derived OM inputs, site 7 is exposed to seagrass and planktonic, marine-derived OM inputs, whereas site 6 features aquatic macroalgal growth in its shallow sediments (Jaffé et al. 2001).

Floc and soil/sediment samples were collected using transparent Lexan corers, between November and December of 2000 during the end of the wet season. For the emergent vegetation dominated FWM sites (1–3) the corer had an inner diameter of 3 cm to facilitate sampling between individual plants, while at the MEST sites (6-Taylor River and 7-mouth of Taylor River) the corer had an inner diameter of 7 cm. At each site a core barrel was pushed to 10 cm below the soil/sediment surface. The core was then capped to create suction and retrieved. Intact layers of floc and sediment were visible through the core. Excess water was drained off after placing a foam insert attached to a dowel on top of the floc layer. The foam insert was then removed and a plunger with a slightly smaller diameter to that of the core tube was insert and pushed through the floc layer until it was resting on the surface of the sediment. For the purpose of this sampling protocol, all easily suspended, loose materials, including benthic periphyton, on top of the consolidated sediment/soil layer of the core were considered here as being part of the floc. With the plunger still in place, the core was tilted to decant the floc into a solvent rinsed, clean glass jar with a Teflon lined lid. Once the floc was decanted, the plunger was removed, the soil core was extruded and the top 2 cm surface soil/sediment was sampled and placed into a clean, solvent-rinsed glass jar with a Teflon lid. This process was performed a total of eight times at each site, to yield one floc and one soil/sediment composite sample. Floc and soil/sediment samples were placed on ice in the field and once in the laboratory, they were kept frozen until processing for analysis (Jaffé et al. 2001).

Bulk parameters and biomarker analyses

The %TOC, %TN and $\delta^{13}C$ were analyzed as previously described by Jaffé et al. (2001). For lipid analyses, aliquots of freeze-dried floc and soil/sediments (0.3–1.5 g) were extracted three consecutive times in dichloromethane (60 ml) by sonication, each for 15 min. The combined extracts were treated and analyzed as previously described (Jaffé et al. 2001). Briefly, the extracts were separated into acid and neutral fractions via saponification, fractionated by column chromatography, and the acid and alcohol fractions derivatized with

diazomethane and BSTFA, respectively. The fractions were then analyzed by GC/MS using a HP-5993 system. GC and MS conditions have been previously described (Jaffé et al. 2001).

Pigment analysis

Freeze-dried floc and sediment/soil samples (0.2–0.5 g) were extracted using 3.00 ml of a mixture of acetone/methanol/dimethylformamide/water (30:30:30:10, v/v/v/v; Hagerthey et al. 2003) in a pre-chilled Potter-Elvehjem tissue grinder (Stainless steel/Teflon pestle in a glass mortar: Wheaton #385039) at ice bath temperatures with steeping for 2–3 h. The UV/Vis of the clarified extract was recorded on a Perkin–Elmer Lambda-2 spectrometer (330–800 nm) for an initial assessment of total pigment yield (cf. Jeffrey et al. 1997).

Lipophilic pigments, chlorophylls and carotenoids, were separated by reverse-phase HPLC coupled to full-spectral (190–800 nm) photodiode array (PDA) detection as detailed in Loudas et al. (2002). The equation which was used for the estimation of algal division contributions (cyanobacteria/chlorophyta/diatoms/dinoflagelates/cryptophytes) to the flocculent materials on the sediment surface and the underlying sediments in the Taylor Slough system is

$$\sum \mathrm{CHL}a = ([1.1 \times \mathrm{ZEA}*] + [11.1 \times \mathrm{ECH}]) + (2.4 \times \mathrm{CHL}b) + (1.2 \times \mathrm{FUCO}) + (1.5 \times \mathrm{PERI}) + (3.8 \times \mathrm{ALLO})$$

where 'ZEA*' equates to the amount of zeaxanthin corrected for ZEA contributions (=[ZEA]–[ECH]) from echinenone ECH containing cyanobacteria. We estimate this on a 1:1 molar basis. CHL*b*, chlorophyll *b* (chlorophytes); FUCO, fucoxanthin (chrysophytes, esp. diatoms); PERI, peridinin (dinoflagellates); and ALLO, alloxanthin (cryptophytes). The analytical variability of the % *a*-derivs and the % taxonomic assignments were in all cases below 5%.

Results and discussion

Bulk measurements

The bulk measurements for all samples are shown in Table 1 where average values for FWM and MEST sites are shown as well. The %TOC in sediments was 20–50% lower than in floc and may represent the degradation of labile organic material (probably mostly the labile plankton-derived OM) before incorporation into the sediments resulting in an enrichment of carbonates in the soils. In agreement, FWM sites 1–3 contain abundant periphyton biomass. This difference in the %TOC is much smaller at the MEST sites 6 and 7, probably due to the presence of more recalcitrant mangrove-derived OM.

Mangrove forests dominate the vegetation at these sites, and thus cutin, tannins and other biomacromolecules, which are present in leaves of many vascular plants, including mangroves (Killops and Frewin 1994), may add more refractory characteristics to floc samples here. The more pronounced difference between floc and sediment at site 6 in contrast to the more similar values for site 7 (Table 1), is likely to be caused by a higher abundance of aquatic macroalgae-derived OM at site 6 (Jaffé et al. 2001), and thus is more prone to degradation (i.e. lower TOC in sediments).

The percentage of total nitrogen content (%TN) in both floc and sediments had similar patterns to those of %TOC in all sites, except for site 1, which had sediments with higher %TN content than floc. The higher content of %TOC and %TN at site 2 (Table 1) relatively to the other sites may have been caused by a high accumulation of OM as a result of reduced $CaCO_3$ accumulation at the longer hydroperiod sites (Gleason and Spackman 1974). This is further evidenced by lipid and pigment data shown below. On average the FWM site's TN was higher compared to the MEST sites, probably as a result of higher inputs of N-fixing cyanobacteria-derived OM at the former.

As expected, the percentage of calcium carbonate ($\%CaCO_{3)}$ had an inverse trend to those of %TOC and %TN, with higher values in sediments, except for site 7, where the value for floc was about equal to that of sediments (Table 1). The high amount of $CaCO_3$ in soils/sediments is not surprising, as surficial Taylor Slough soils have been classified as marl (Gleason and Stone 1994) and are presumably formed due to periphyton-derived calcareous inputs, particularly at the shorter hydroperiod sites.

Molar carbon to nitrogen ratio (C/N) increased steadily in sediments from 4.30 at site 1 to about 18 at site 7. This trend was not observed for floc, which had higher C/N ratios than sediments at sites 1 and 2, lower at sites 3 and 6,

Table 1. Bulk composition data of floc and sediments from Taylor Slough.

Site	Type	Material	%TOC	TN (%)	$\%CaCO_3$	Molar C/N	$\delta^{13}C$
1	FWM[a]	FLOC	4.07	0.37	88.54	12.83	−24.74
1	FWM	SED	2.90	0.79	90.44	4.30	−22.68
2	FWM	FLOC	18.45	1.30	63.23	16.58	−28.21
2	FWM	SED	10.97	1.16	72.91	11.06	−27.55
3	FWM	FLOC	6.84	0.73	83.69	10.87	−27.77
3	FWM	SED	4.99	0.47	90.67	12.44	−26.82
Average	FWM	FLOC	9.79	0.80	78.49	13.43	−26.91
Average	FWM	SED	6.29	0.81	84.67	9.27	−25.68
6	MEST[b]	FLOC	7.96	0.66	80.00	14.11	−27.00
6	MEST	SED	5.05	0.33	87.22	17.88	−25.78
7	MEST	FLOC	5.12	0.33	83.69	18.22	−25.44
7	MEST	SED	5.15	0.33	78.21	18.39	−24.50
Average	MEST	FLOC	6.54	0.50	81.85	16.17	−26.22
Average	MEST	SED	5.10	0.33	82.72	18.14	−25.14

[a]Freshwater marsh.
[b]Mangrove estuary.

and about equal at site 7 (Table 1). For comparison, higher plant and microbial OM have C/N values >20 (~80 for *Cladium*; Rubio and Childers, personal communication) and <10, respectively. Thus the general increasing pattern from site 1 to site 7, particularly in sediments, could be explained by the higher abundance of N-fixing cyanobacteria-containing periphyton (Vymazal and Richardson 1995) at the most northern part of the FWM transect (sites 1 and 2), while sites 6 and 7 are dominated by mangroves, suggesting a predominant input of this vegetation in sediment and in floc at sites 6 and 7. Overall, C/N ratios observed along this transect (except for sediments at site 1) showed values that were intermediate between the terrestrial and microbial end-members, suggesting a mixed source of OM. However, the difference of C/N between floc and sediments at site 1 suggests a decoupling between them. It seems that C in soil/sediments is being re-mineralized quicker than N, compared to floc OM.

Carbon stable isotope ratios ($\delta^{13}C$) ranged from −27.55 to −22.68‰ in soil/sediments whereas they fluctuated between −27.77 and −24.74‰ in floc (Table 1). The differences of $\delta^{13}C$ values between floc and sediments along this transect were generally less than 2.2‰, with floc being consistently slightly more $\delta^{13}C$-depleted. This observed difference may be the result of a higher degree of OM reworking in the sediments compared to the floc. It may be noted that the MEST sites 6 and 7, show slightly more enriched $\delta^{13}C$ values (Table 1) than mangrove leaves (−27 to −32‰, Jaffé et al. 2001), which suggests that mangrove litter is an important, but not the sole input of OM in floc and sediments at these sites. This seems to be in agreement with prior biomarker-based assessments in this area (Jaffé et al. 2001).

Pigments

The premise of pigment-based chemotaxonomy is based on the fact that as algae and higher plants evolved, they selected for photosynthetic accessory pigments and photoprotectorants in taxon-specific ways (Millie et al. 1993). Thus, in addition to chlorophyll *a* which is present in all oxygenic photoautotrophs, green algae and higher plants have chlorophyll *b* and lutein, cyanobacteria have zeaxanthin and/or echinenone, diatoms and other chrysophytes have fucoxanthin, dinoflagellates have peridinin or gyroxanthin diester, and cryptophytes have alloxanthin plus large amounts of α-carotene. Certain other pigment mixtures allow chemotaxonomic discrimination to various class levels (see Jeffrey et al. 1997 and references therein).

Table 2 shows total CHL*a* yields, percent pheopigments, chemotaxonomic estimations made according to the formula given above and an indication as to the importance of the UVA sunscreen scytonemin, an indicator of high light environments (Garcia-Pichel et al. 1992). The value 'CHL*a*μg/g-sed' refers to the sum of chlorophyll *a* chromophoric species ($\sum$CHL*a* = CHL*a* + CHL*a*-allomer + CHL*a*-epimer + chlorophyllide *a* + pyrochlorophyllide *a*) per

Table 2. Summarized pigment data of floc and sediments from Taylor Slough (see nomenclature in text).

Site	Type	Sample	CHL*a* (μg/g dry sediment)	% *a*-derivs	Scytonemin	% Cyano	% Chloro	% Diats	% Dinos	% Cryptos
1	FWM[a]	FLOC	56	26.9	+	79	0	21	0	0
1	FWM	SED	1.3	0[b]	+	0	0	100	0	0
2	FWM	FLOC	32.3	58	+	77	10	13	0	0
2	FWM	SED	16.1	60.4	+	76	14	10	0	0
3	FWM	FLOC	16.2	25.5	+	91	0	9	0	0
3	FWM	SED	2.7	45.5	+	86	0	14	0	0
Average	FWM	FLOC	34.8	36.8	+	82.3	3.3	14.3	0	0
Average	FWM	SED	6.7	35.3	+	54	4.7	41.3	0	0
6	MEST[c]	FLOC	36.4	20.1	–	85	1	14	0	0
6	MEST	SED	1.1	0	–	100	0	0	0	0
7	MEST	FLOC	33.5	30	–	52	33	15	0	0
7	MEST	SED	0[d]	100	–	98	0	2	0	0
Average	MEST	FLOC	35	25.1	–	68.5	17.0	14.5	0	0
Average	MEST	SED	0.6	50	–	99	0	1.0	0	0

+ and – represent the presence or absence of scytonemin, respectively.
[a]Freshwater marsh.
[b]Very low yield, S/N was low. Traces of phaeopigments indicated.
[c]Mangrove estuary.
[d]0.7 μg/g sed as phaeopigments.

gram DW of floc or sediment. On the other hand, percent '*a*-derivs' (= CHL*a*-derivatives) refers to the percentage of the sum of all identifiable CHL*a* derivatives, mainly the phaeopigments but including certain other pigments, such as cyclopyropheophrbide-*a* (Louda et al. 2000) and purpurin-18-phytyl ester (Louda et al. 1998, 2002), compared to the total yield of all CHL*a*-derived species (%*a*-derivs = ([$\sum$ *a*-derivs]/[$\sum$CHL*a* + $\sum$*a*-derivs]) × 100).

CHL*a* in suspended matter is commonly used as an indicator of primary productivity. However, due to the degradability of chlorophyll, in floc and sediments the CHL*a* levels are more indicative of recent planktonic OM inputs. Thus, its concentration showed that floc at site 1 had a higher, recent microalgal input (almost 2-fold higher than floc at the other sites, Table 2). Interestingly, CHL*a* levels in floc at site 2 do not correlate with the elevated %TOC and TN, suggesting that microalgae were not solely responsible for the high concentration of OM at this site, or that chlorophyll has undergone more extensive diagenetic reworking at this site. In agreement with the latter, the % *a*-derivs (see below) at site 2 is the highest among the analyzed samples in this study (Table 2), indicating a higher degradation state of OM at this site. The elevated CHL*a* for the sediments at site 2 suggests an early incorporation of floc (and associated periphyton) into the sediments at this site.

The % *a*-derivs and CHL*a* at site 3 were the lowest and second lowest for floc, respectively (Table 2), suggesting a relatively low input of periphyton-derived microalgae at this site. Floc at sites 6 and 7 showed the same level of CHL*a* as that of site 2, however, with a significantly lower (by a factor of two) degree of degradation (% *a*-derivs), suggesting that microalgal inputs, possibly in part in the form of epiphytic growth on the macroalgae, are relatively 'fresh' at the MEST sites.

All sediments had very low CHL*a*, except at site 2, where its concentration was similar to that found in floc (Table 2). This suggests that a rapid incorporation of floc into sediment at that site, probably as a result of water column depth and therefore, longer hydroperiods. Such sites should not be subject to seasonal drying and as such avoid open air oxidation of the floc layer.

The pigment-based chemotaxonomic classification of microalgae, reveals that inputs to floc and sediments were dominated by cyanobacteria and diatoms, with small proportions of chlorophyta. The only exception was site 7, where the chlorophytes were the second most abundant taxonomic group after cyanobacteria, followed by diatoms (Table 2 and Figure 2b). In floc, the content of cyanobacteria, diatoms and chlorophyta ranged from 52 to 98, 9 to 21, and 0 to 33% respectively. These values were much more variable in sediments, likely reflecting the inherently low signal-to-noise problems associated with low yields.

Based on the divisional makeup of the surficial floc and underlying sediments at sites 2 and 3 (Table 2 and Figure 2), these sites have an apparent strong compositional linkage between the recent (floc) and older (sediment) materials. Site 1, on the other hand, has a highly elevated total CHL*a* value for floc and, relative to its underlying sediment, a greatly increased presence of cyanobacteria

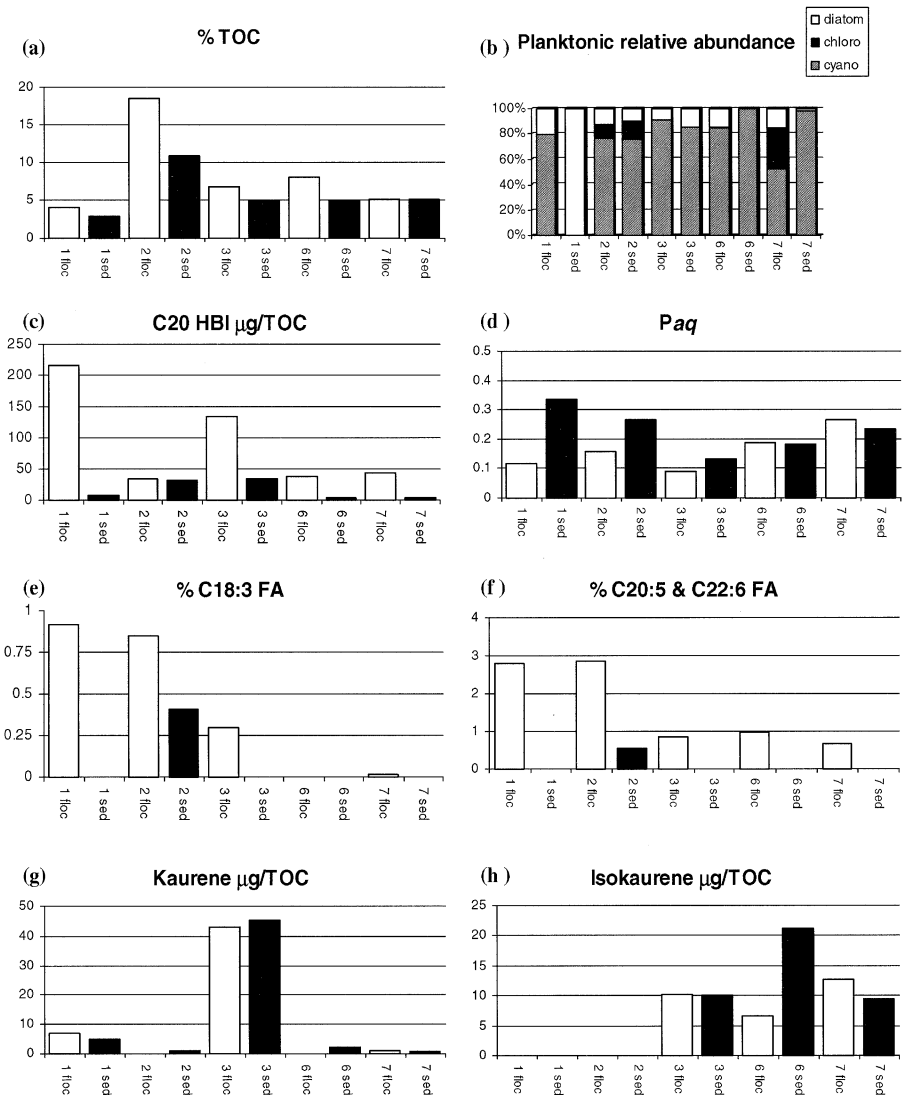

Figure 2. Geochemical parameters or proxies for floc (white bars) and soils/sediments (black bars) along the Taylor Slough transect: (a) TOC as %; (b) planktonic composition as %; (c) concentration of HBI C_{20} in µg/g TOC; (d) P_{aq}; (e) $\%C_{18:3}$ of total fatty acids; (f) $\%C_{20:5} + C_{22:6}$ of total fatty acids; (g) Kaurene concentration in µg/g TOC; (h) Isokaurene concentration in µg/g TOC.

(Table 2). In spite of the fact that the diatom signal (fucoxanthin) is more labile than that (zeaxanthin/echinenone) from the cyanobacteria (Louda et al. 2000), it appears that the level of growth of cyanobacteria at site 1 is a recent phenomenon, based on CHL*a* contents in the floc from the FWM sites (Table 2).

This decoupling between floc and sediment at site 1 agrees with lipid results (HBI C_{20}, $\%C_{18:3}$ and $\%C_{20:5} + C_{22:6}$, discussed below).

Comparing floc with the underlying sediments at the MEST sites, reveals that either the green algae/plant (viz. chlorophyll *b*) and diatom (viz. fucoxanthin) signals were indeed lost with age (as in Louda et al. 2000; Baker and Louda 2002), or there was a change in surface production. The former is more likely with the more stable cyanobacterial pigment (zeaxanthin) surviving.

Table 2 also gives an indication as to the presence or absence of scytonemin, a dimeric indole–phenol sunscreen in the sheaths of certain cyanobacteria when growing in high UVA (λ = 320–400 nm) light (Garcia-Pichel et al. 1992). Immediately obvious is the fact that the FWM sites are higher light environments compared to the MEST sites mainly due to the shade effect by the mangroves in the latter. Additionally, the presence of scytonemin in the soil/sediments at the FWM sites indicate that, at least for the time span during their accumulation, high light conditions existed during OM deposition. This is expected since these sites are shallow (1–2 feet), open areas typical of Everglades freshwater marshes. In contrast, while the MEST sites are also fairly shallow, they are dominated by dense mangrove forests where direct light may be partially blocked. It seems clear that photoexposure is more important at the FWM sites compared to the MEST sites.

Lipid biomarkers

Compounds from several lipid classes were identified in both sediment and flocculent material, including alkanes, alcohols, fatty acids, terpenoids and others. Many of these compounds have been reported before in sedimentary organic matter in Taylor Slough (Jaffé et al. 2001). These authors identified several biomass-specific biomarkers, which in conjunction with other molecular markers were used in the assessment of OM sources and fate of flocculent material in this study.

The highly branched isoprenoid (HBI), C_{20}, tentatively identified in our samples as 2,6,10-trimethyl-7-(3-methylbutyl)-dodecane (Jaffé et al. 2001) has been suggested to be a biomarker for periphyton in ENP freshwater marsh areas (Jaffé et al. 2001). While this compound has been frequently reported in the literature (Gearing et al. 1976; Rowland and Robson 1990; Jaffé et al. 2001), its exact origin has not been established, although a diatom origin has been suggested (Rowland and Robson 1990) due to the structural similarity with the corresponding C_{25} HBIs. Based on its highly depleted $\delta^{13}C$ isotopic composition (Jaffé et al. 2001) it may be a biosynthetic product from cyanobacteria. Such organisms are quite abundant in Everglades' periphyton mats (Gleason and Spackman 1974).

The concentration profile of the C_{20} HBI along the Taylor Slough transect is shown in Figure 2c. Concentrations of this compound were highly variable, with maximum values at FWM sites 1 and 3 for floc (215 and 134 μg/g TOC,

Table 3. *n*-Alkane proxy values (P_{aq}) for plants from the Taylor Slough.

Plants	*n*-Alkane proxy
Terrestrial	
Laguncularia racemosa	0.15(0.07)
Avicennia germinans	0.15(0.04)
Rhizophora mangle[b]	0.24(0.03)
Emergent	
Eleocharis cellulosa[b]	0.51(0.02)
Cladium jamaicenses[b]	0.13(0.02)
Submerged freshwater	
Chara sp.[b]	0.89(0.06)
Utricularia foliosa	0.93(0.01)
Utricularia purpurea[b]	0.85[a]
Ruppia maritime[b]	0.67(0.09)
Periphyton[b]	0.45[a]

Standard deviations are between brackets (n = 3–5).
[a]Individual sample.
[b]From Mead et al. (2004).

respectively). Floc at sites 2, 6 and 7, and sediments at sites 2 and 3 showed similar values (33–45 μg/g TOC). Sediments at sites 1, 6 and 7 had the lowest concentrations of HBI C_{20} (4.26–4.89 μg/gTOC; Figure 2c). The high concentration in floc at sites 1 and 3 could be explained by the fact that periphyton is more abundant relative to other biomass, in these sites. Interestingly, floc in site 2, showed similar concentration to sites 6 and 7, areas dominated by mangrove forests. This suggests that floc at site 2 had a lower relative input of periphyton, particularly cyanobacteria. The chemotaxonomic assessment at this site also suggests that the relative abundances of diatoms and green algae were higher compared to floc at sites 1 and 3. This reinforces the suggestion that cyanobacteria are the source of the C_{20} HBI rather than diatoms. The relatively lower concentration of C_{20} HBI at the MEST sites may be the result of physical transport of periphyton from the freshwater marshes to these sites (see also Jaffé et al. 2001) or a low relative abundance of epiphytic cyanobacteria at these sites.

The *n*-alkane proxy (P_{aq}) is the ratio between the concentration of the *n*-alkanes C_{23} + C_{25} and C_{23} + C_{25} + C_{29} + C_{31} and has been proposed by Ficken et al. (2000) to differentiate sedimentary input of submerged/floating and emergent plants. Table 3 shows the P_{aq} values for the predominant plants along Taylor Slough. Clearly, this proxy can aid in distinguishing the main vegetation groups, namely terrestrial/emergent higher plants and submerged plants. These differed by ranging between 0.13 and 0.51 vs. 0.45 and 0.89, respectively (Mead et al. 2005; in this context periphyton is considered as a submerged plant). P_{aq} values of floc and sediments are presented in Figure 2d and for the FWM sites the sediments consistently show higher values than the associated floc, while these were about equal for the MEST sites.

On a site-by-site basis, site 1 showed P_{aq} values in sediments above 0.3, while floc values were only about 0.1. The elevated P_{aq} value for the sediments suggests OM inputs dominated by, or as a result of a combination of, periphyton, spikerush and/or utricularia, while the floc seems to be influenced by OM derived from sawgrass. For site 2 the sediment P_{aq} continues to be more elevated than the floc, but lower than at site 1. In contrast, the floc values at site 2 are a bit higher than those at site 1. This distribution change suggests a relative increment in the abundance of periphyton-derived OM in the floc and of sawgrass in the sediment compared to site 1. At site 3 the dominant OM in both floc and sediment seem to be sawgrass. At the MEST sites the P_{aq} values were quite similar and close to the value of red mangrove (Figure 2d and Table 3), which is the dominant vegetation at these sites. The P_{aq} at site 6 is, however, lower than at site 7, and below typical red mangrove values suggesting either transport of sawgrass-derived OM and/or the influence of aquatic macroalgae-derived OM at this site, and/or the presence of seagrass-derived OM at site 7 (Jaffé et al. 2001).

One of the most predominant fatty acids in cyanobacteria is the polyunsaturated fatty acid (PUFA) $C_{18:3}$ (up to 35% of total fatty acids; Vargas et al. 1998), which has not been detected in any other biomass studied here, apart from periphyton, known to be dominated by cyanobacteria during the wet season (Vymazal and Richardson 1995). Thus, this compound will be used here to trace this source. For comparative purposes, we are reporting the percentage of this compound in relation to total fatty acids ($\%C_{18:3}$) in order to assess the relative abundances of cyanobacterial OM along the Taylor Slough transect. Although the $\%C_{18:3}$ is relatively low, a decreasing trend from north to south was observed along the transect (Figure 2e) suggesting a decrease in the relative contribution of cyanobacteria to the floc/sediment OM fraction.

The $C_{20:5}$ and $C_{22:6}$ PUFAs, known to be very abundant in diatoms (Volkman et al. 1989; Skerratt et al. 1995), were also present in these samples and their relative abundance along this transect is depicted in Figure 2f. The observed pattern was similar to that of the $\%C_{18:3}$, with high concentration in the northern sites but with the difference that the $C_{20:5}$ and $C_{22:6}$ PUFAs were also present in low abundance at sites 6 and 7. In floc, the $\%C_{20:5} + C_{22:6}$ was higher at sites 1 and 2 (2.78 and 2.86%, respectively) and less so at sites 3, 6 and 7 (0.66–0.98%). This suggests a higher relative input of diatoms (and cyanobacteria; see above) at the northern sites which is likely linked to their importance as components of periphyton (Vymazal and Richardson 1995). The presence of $C_{20:5}$ and $C_{22:6}$ at sites 6 and 7 suggests either transport of diatom-rich periphyton from the freshwater marshes and/or the presence of autochtonous diatoms at the estuarine sites, possibly associated with epiphytic growth on macroalgae which are abundant particularly at site 6.

In contrast to floc, PUFAs were not observed in the soil/sediment samples, with the exception of site 2. The absence of these compounds in sediments is expected because these fatty acids are highly unsaturated (rich in energy),

Table 4. The concentration μg/g TOC of the mangrove-derived compounds and its possible degradation products.

Sites	Type	Material	Taraxerol	β-Amyrin	Taraxer-14-ene	Taraxera-2,14-diene	Taraxeranone	β-Amyrenone	Olean-18-en-3-one	Lupenone	β-Amyrin + taraxerol/taraxer-14-ene
1	FWM[a]	Sed	–	–	–	–	–	–	–	–	
1	FWM	Floc	–	–	–	–	–	–	–	–	
2	FWM	Sed	–	–	–	–	–	–	–	–	
2	FWM	Floc	–	24.1	–	–	–	–	–	–	
3	FWM	Sed	–	–	–	–	–	–	–	–	
3	FWM	Floc	–	–	–	–	–	–	–	–	
6	FWM	Sed	191	12.1	0.75	0.5	14.1	0.36	–	–	271
6	FWM	Floc	2590	246	3.8	3.4	147	33.6	–	7.0	754
7	MEST[b]	Sed	696	8.2	2.6	2.6	35.1	2.7	–	–	272
7	MEST	Floc	1300	93	2.9	4.1	–	123	18	24.7	483
AVG	MEST	Sed	444	10.2	1.7	1.6	24.6	1.5	–	–	272
AVG	MEST	Floc	1950	170	3.4	3.8	74	78	9	15.9	619

–, Not detected; AVG, average.
[a]Freshwater marsh.
[b]Mangrove estuary.

making them prone to quick degradation by microorganisms and/or by photoxydation processes (Canuel and Martens 1996). However, their relatively high abundance at site 2 in sediments suggests again, the incorporation and preservation of fresh planktonic OM at that site.

Figure 2g and h shows the abundance of two diterpenoids, kaurene and isokaurene, in our samples. Isokaurene was tentatively identified based on its mass spectrum. Kaurene and its isomer phyllocladene have very similar mass spectra and gas chromatographic retention times, and cannot easily be differentiated by mass spectrometry. However, their source in the environment is quite different. While phyllocladene is mainly found in gymnosperms in the southern hemisphere (Thomas 1970; Noble et al. 1985) and is not detected or is present in very low concentrations in conifers from the north hemisphere (Simoneit, personal communication), kaurene, as well as isokaurene are found in fungi (Fraga et al. 1987; Fernández-Martín et al. 2000). The latter is the reason for which we suspected that our unknown is in fact kaurene. To test this hypothesis, we analyzed some fungi-infected and non-infected sawgrass leaves. The kaurene like compound was detected only on the leaves infected by fungi and had an identical spectrum and chromatographic retention time to those found in floc and sediments, confirming the presence of kaurene and not its isomer phyllocladene. Therefore, we are using, kaurene and isokaurene, as indicators of fungal activity.

Candau et al. (1992) and Fernández-Martín et al. (2000) showed that fungi can biosynthesize kaurene instead of ergosterol, which has been frequently used as a biomarker for fungi under nitrogen limiting conditions (e.g. Newell 2003; Nikolcheva et al. 2003). In fact, ergosterol was not observed in these samples. Although nitrogen is not known to be a limiting nutrient in the Everglades, phosphorus limitations in this oligotrophic ecosystem (Davis and Ogden 1994; Gaiser et al. 2004) may induce fungi to produce kaurene. Figure 2g shows a higher abundance of kauarene in both sediments and floc at site 3 (~20-folder higher than the other sites), indicating high fungal activity in this site (note that the concentration of pore-water TN is at the same order of magnitude at all sites; Childers, personal communication). Taking kaurene concentrations as a fungal OM proxy, such materials seem to be present at about equal amounts (at sites 1, 3 and 7) in floc and sediments. Kaurene was particularly abundant at site 3, known to contain primarily sawgrass-derived OM.

It is interesting to note that isokaurene distributions did not correlate with those of kaurene. The isokaurene distributions (Figure 2h) show that this fungal marker is more abundant at sites 3, 6 and 7, particularly the latter two which are dominated by mangrove derived OM. As in the case of kaurene, the concentrations in floc and soil/sediments are about equal, except for site 6 where the sediments had a higher abundance (factor of about 3). While the reasons for the observed difference in the distribution of these fungal biomarkers are presently unclear, they may be controlled by organic matter type and quality, nutrient levels, salinity and other parameters of biogeochemical

importance. While fungi may play an important role in the cycling of OM in this oligotrophic system, little is known about this process.

In order to assess the input of mangrove-derived OM to samples from sites 6 and 7, biomarkers characteristic for this plant were determined, namely taraxerol and β-amyrin (see also Killops and Frewin 1994; Versteegh et al. 2004), their corresponding ketones, as well as some early diagenetic derivatives of these (Table 4). All of these biomarkers were found in abundance at sites 6 and 7 only. β-Amyrin was also observed but at very low levels in floc at site 2. This compound has also been detected in Everglades tree island soils (Jaffé, unpublished results), which could explain its presence at site 2. In contrast, β-amyrin was not observed in samples from sites 1 and 3, dominated by sawgrass. Taraxerol and β-amyrin were very abundant, reaching concentrations of 1300 and 246 μg/g TOC in floc at sites 6 and 7, respectively (Table 4). The high concentration of mangrove-derived OM in floc and in sediments at sites 6 and 7 indicates that detritus from this kind of vegetation is an important component of floc in the estuarine areas.

The concentration of taraxerol and β-amyrin and their degradation products (taraxer-14-ene, taraxera-2,14-diene) are illustrated in Table 4. Note that these degradation products occur in much lower concentrations than their precursors, taraxerol and β-amyrin. Taraxer-14-ene and olean-12-ene are early diagenesis products of taraxerol and β-amyrin (Figure 3; Ten Haven and Rullkotter 1988; Ekweozor and Telnaes 1990). The presence of the former in floc and sediments at sites 6 and 7 could be indicative that the mangrove-derived OM is prone to early diagenetic transformations. The proposed intermediate in this reaction, olean-12-ene, was not detected in our samples, suggesting that this compound is unstable and rapidly transformed to taraxer-14-ene. Thus, the ratio of the concentrations of the sum of taraxerol and β-amyrin to the concentration of taraxer-14-ene was used as a proxy to compare the relative degree of OM degradation between floc and sediment samples from sites 6 and 7 (Table 4). As expected sediment samples were more degraded (lower ratio) than floc by a factor of 2–3 based on this parameter. This observation is in agreement with the lower CHL*a* levels, $\delta^{13}C$ values, C/N ratios and PUFA abundances observed in sediments compared to floc.

In order to statistically assess the similarities and/or differences between floc and soil/sediment OM for the freshwater marsh and mangrove estuarine environments studied here, Hierarchial Clustering using the Ward method was applied using all determined bulk and molecular parameters. The clustering results are shown in Figure 4. For ease of discussion we have color coded the cluster into freshwater marsh (FWM – white) and mangrove estuarine (MEST – shaded) and further subdivided the overall cluster into five subsets (a–e). The cluster arrangement depicts a clear decoupling between OM in floc and soils/sediments for some sites, and coupling for others. Clearly, the MEST sites (6 and 7) the sediments are differentiated from their corresponding floc as shown in subsets b and e, as well as for the FWN site 1 and its corresponding floc for subsets a and d.

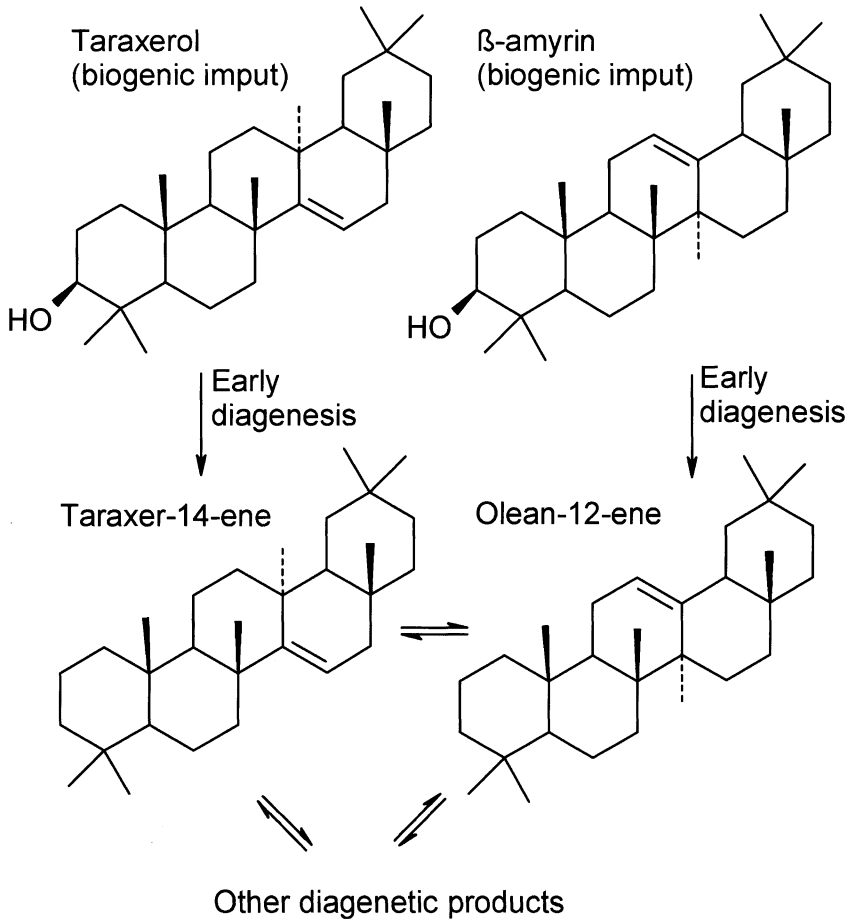

Figure 3. Formation of taraxer-14-ene through diagenesis of taraxerol and β-amyrin, common components of mangroves (after Ten Haven and Rullkotter 1988; Ekweozor and Telnaes 1990).

Floc at site 1, showed a high periphyton input based on elevated HBI C_{20}, $\%C_{18:3}$, $\%C_{20:5} + C_{22:6}$ and CHL*a*(=total microalgae) abundance. On the other hand, the corresponding sediments showed different (lower) values for these proxies and a different pigment-based taxonomic composition (100% diatoms), suggesting a combination of higher degradation of labile, microalgal-derived molecular proxies in the sediments, or recent periphyton inputs to the floc layer and, therefore, a decoupling between floc and soil/sediment OM for some geochemical parameters. In contrast, samples from the MEST sites 6 and 7 were highly influenced by mangrove-derived OM based on taraxerol and β-amyrin concentrations, indicating that mangrove litter is an important part of OM in floc and sediments. Whilst coupling based on several geochemical proxies was observed for the MEST floc/sediment pairs,

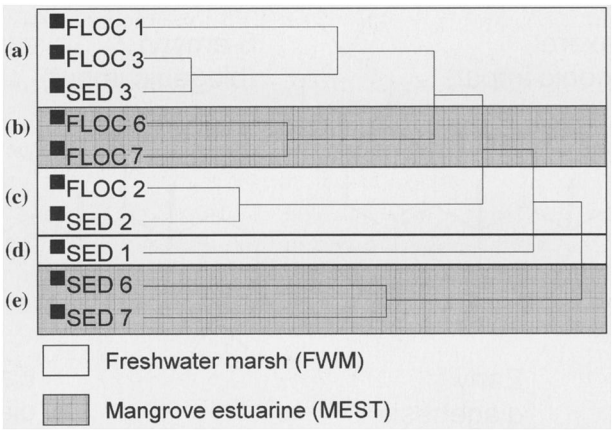

Figure 4. Hierarchical clustering using the Ward method for bulk and molecular parameters in floc and soil/sediment samples by site. The cluster was divided into five subclusters (a–e) where mangrove estuarine sites are indicated by light gray shading.

the significant changes in OM preservation (based on pigments, PUFAS and taraxerol degradation products) leads to an overall decoupling of these matrices at the MEST sites.

In contrast, floc and soils for FWM sites 2 and 3 are clustered in subsets c and a, respectively. Soils and floc samples at these FWM sites had similar taxonomic compositions. In addition, highly degradable compounds such as PUFAs, which were observed in floc at all sites, were present in sediments at this site 2 only, indicating a rapid incorporation of floc into soils. Sediment at site 3 showed low values of CHL*a* and other planktonic-proxies indicating a low algal production at this site, while P_{aq} values seem to point to important OM inputs from *Cladium jamaicense* for both floc and soils. The high concentration of kaur-16-ene at this site indicates a high fungal activity or fungal remains in both floc and soils.

Conclusions

This study shows that OM composition of floc and its underlying sediment/soil is highly variable among sites and seemingly controlled by local vegetation inputs and early diagenetic transformations. OM in Everglades' floc is mainly derived from the dominant vegetation at a particular location, and likely generated *in situ* (e.g. plant litter, cyanobacteria, fungi, etc.). While the biomarker data suggest that soil OM is more degraded compared to floc, some evidence for OM degradation in the floc layer was obtained as well. Although our data suggest some incorporation of floc OM into soils/sediments, the decoupling of some of the molecular parameters indicates that this process may depend on OM type, floc re-mineralization rates, hydrological

conditions and the geomorphology of the location. Incorporation of floc into soils/sediments may occur through consolidation during the dry periods in the short hydroperiod freshwater marshes, where dry-down conditions may result in the rapid oxidation of floc materials during the dry season. In contrast, sedimentation and reduced re-mineralization may become important processes during the wet season and in long hydroperiod marshes (e.g. FWM site 2). The presence of dense populations of aquatic macrophytes might also control the floc transport rate, increasing its residence time and possibilities for physical deposition and incorporation into soils. However, the processes controlling floc incorporation to freshwater wetland soils remain largely unknown.

For the estuarine, mangrove-influenced areas (MEST), hydrological transport from the freshwater marshes (during the wet season) and from the marine end-member (during the dry season; see Jaffé et al. 2001) may also play a role in controlling the origin of floc. Benthic vegetation, in the form of macroalgae such as *Utricularia* sp., *Chara* and *Rupia*, may act as traps for floc, and in fact reduce bottom transport of such materials. The benthic vegetation itself may influence the floc and soil/sediment OM composition in conjunction with mangrove-derived detrital particles and hydrologically transported materials as described above.

Ultimately, the low water discharge rates, nutrient limitations and relatively high primary productivity of submerged and emergent vegetation in the Florida Coastal Everglades may be the main drivers for the production and limited transport of floc materials in this system. Due to the oligotrophic nature of the Everglades, floc may in fact be the most bioavailable OM substrate to the detrital food chain, and become reworked and re-mineralized to a large extend during transport. Such processes could limit its incorporation into soils/sediments as suggested by the decoupling described above. While this study provides, to our best knowledge, the first detailed organic matter characterization of floc along a freshwater to marine ecotone, still little is known about the biogeochemistry of floc and further investigations are needed to better understand the ecological role of this important biogeochemical component in freshwater and coastal wetlands.

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