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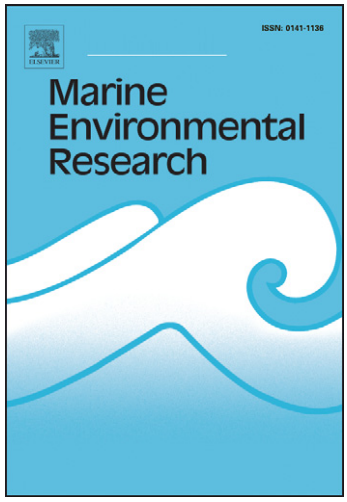

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Lipid biomarkers in suspended particles from a subtropical estuary: Assessment of seasonal changes in sources and transport of organic matter.

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Abstract

Temporal and spatial variations in the composition of particulate organic matter (POM) from Florida Bay, USA were examined. The predominance of short chain homologues for *n*-alkanes, *n*-alcohols and *n*-fatty acids as well as relatively high abundance of C_{27} and C_{28} sterols suggested that an autochthonous/marine source of OM was dominant bay-wide. Several biomarker proxies such as *Paq* [$(C_{23}+C_{25})/(C_{23}+C_{25}+C_{29}+C_{31})$ *n*-alkanes], short/long chain *n*-alkanes, $(C_{29}+C_{31})$ *n*-alkanes and taraxerol indicated a spatial shift in OM sources, where terrestrial OM rapidly decreased while seagrass and microbial OM markedly increased along a northeastern to southwestern transect. Regarding seasonal variations, POM collected during the dry season was enriched in terrestrial constituents relative to the wet season, likely as a result of reduced primary productivity of planktonic species and seagrasses during the dry season. Principal component analysis (PCA) classified the sample set into sub-groups based on PC1 which seemed to be spatially

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controlled by OM origin (terrestrial-mangrove vs. marine-planktonic/seagrass). The PC2 seemed to be more seasonally controlled suggesting that hydrological fluctuations and seasonal primary productivity are the drivers controlling the POM composition in Florida Bay.

Key words: suspended particulate organic matter, Florida Bay, lipid biomarkers, seagrass, mangroves

1. Introduction

Relative to open oceans, coastal areas are highly vulnerable to environmental change due to their small size and location close to urban areas (Canuel, Cloern, Ringelberg, Guckert, & Rau, 1995). Coastal areas serve as sites of organic material exchange between land and oceans and are also active zones where OM is produced by higher plants, phytoplankton, benthic algae and bacteria (e.g. Jaffé, Mead, Hernandez, Peralba, & DiGuida, 2001; Jaffé, Boyer, Lu, Maie, Yang, & Scully et al., 2004; McCallister, Bauer, Ducklow, & Canuel, 2006). Additionally, aquatic vegetation is often abundant in coastal wetlands and estuarine areas and also serves as a significant source of OM (e.g. Campbell, & Miller, 2002;Jaffé et al., 2001; Paula, Fidalgo Ecosta, Martins, & Gove, 2001). This is the case of Florida Bay, where dense seagrass prairies dominate the benthic communities (Zieman, Fourqurean, & Iverson, 1989). The strength of each OM source can vary spatially as well as temporally on seasonal to tidal cycle time scales.

Various methods have been employed to characterize OM in aquatic environments. Among them, lipid tracers or biomarkers are particularly useful because they can reveal valuable information on OM sources at the molecular level (Meyers, 2003). Previous

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studies have successfully used this approach to assess sedimentary OM sources in coastal areas, estuaries, rivers and lakes (e.g. Bianchi, Mitra, & McKee, 2002; Jaffé et al., 2001; Mead, Xu, Chong, & Jaffé, 2005; Prartono, & Wolff, 1998; Volkman, Rohjans, Rullkotter, Scholz-Bottcher, & Liebezeit, 2000). However, OM preserved in sediments may not always accurately reflect original inputs. In fact over 90% of organic material produced by the source organisms is degraded or consumed before reaching the sediments (Eadie, Chambers, Gardner, & Bell, 1984), and the preferential degradation of more labile plankton derived OM enhanced the apparent importance of terrestrial contributions which contain more resistant constituents (Meyers, 2003). In aquatic environments, suspended particles serve as an important vehicle in the transfer of OM from sources to sediments. Thus through the comparison of OM composition between sediments and suspended particles, early degradation processes of OM can be assessed (Canuel et al., 1995; Jaffé, Cabrera, Hajje, & Carvajal-Chitty, 1996; Saliot, Mejanelle, Scribe, Fillaux, Pepe, & Jabaud et al. , 2001), allowing for a better source strength interpretation of sedimentary OM.

While lipids in sediments and soils from south Florida estuaries have been reported (e.g. Hernandez, Mead, Peralba, & Jaffé, 2001; Jaffé et al., 2001; Mead et al., 2005; Neto, Mead, Louda, & Jaffé, 2006; Xu, Jaffé, Wachnicka, & Gaiser, 2006a; Xu, Mead, & Jaffé, 2006b), little is known about the sources and transport of particulate organic matter (POM). Here, we assess the spatial and temporal variation in the composition and origin of POM in Florida Bay through the measurement of several classes of lipid biomarkers such as aliphatic hydrocarbons, sterols, aliphatic alcohols, fatty acids, highly branched isoprenoids (HBIs) and terrestrially derived triterpenoids from the Florida Bay estuary, South Florida.

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2. Sampling and methodology

2.1 Study area

Florida Bay is a large, subtropical body of water with a surface area of ~2200 km^2 and a mean depth of less than 2m (Corbett, Chanton, Burnett, Dillon, Rutkowski, & Fourqurean, 1999). Florida Bay experiences a warmer wet season from May to October accounting for 75% of the annual precipitation and a cooler dry season from November to April (Fourqurean, & Robbins, 1999). Benthic communities of Florida Bay consist mainly of dense seagrass prairies where *Thalassia testudinum* is the dominant species (Zieman et al., 1989). Mangrove forests dominated by *Rhizophora mangle* (red mangrove) grow along the sea-land interface between the Bay and the Florida Everglades wetlands. In addition, mangrove tree islands are common throughout the northeastern (NE) and central sections of the Bay, but are very sparse in the southwestern (SW) section, and represent an additional source of sedimentary OM to the Bay.

2.2. Sample collection

Water samples were collected during two wet seasons (October of 2003 and 2004) and two dry seasons (March 2004 and April 2005) at five locations corresponding to the Florida Coastal Everglades Long Term Ecological Research project's (FCE-LTER; http://fcelter.fiu.edu/) Taylor Slough/Pan Handle sampling transect (TS/Ph 7, 8, 9, 10 and 11; Fig. 1). The samples will subsequently be referred to as W1 and W2 for the wet season (October 2003 and 2004, respectively) or D1 and D2 for the dry season (March 2004 and April 2005, respectively) followed by their corresponding site number (7, 8, 9, 10 and 11). For example, W1-7 indicates a sample from TS/Ph 7 during the wet season of 2003. For

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93 each sample, 50 liters of waters were collected at 20cm depth and kept in clean
94 polycarbonate bottles (Nalgene) until transport to the laboratory (within 8 hours of
95 collection). Samples were kept on ice and immediately vacuum filtered through pre-
96 combusted glass-fiber filters with 0.7µm nominal pore size (GF/F). The filters with
97 particulate material were freeze-dried at -40°C under the vacuum condition (<100x10^{-3}
98 mBar). After that, dried samples were kept at -20°C until analysis.
99
100 2.3. Chemical analysis
101 The analytical procedure used in this study has been described by Jaffé et al. (2001).
102 Briefly, dried filters were Soxhlet extracted with pure methylene chloride (Optima, Fisher,
103 USA) for 24 hours. Activated copper was added to remove any elemental sulfur from the
104 organic extracts. Total extractable organics were saponified with 1.0N KOH and separated
105 into neutral and acid fractions. The neutral fraction was further separated by silica gel
106 adsorption chromatography. Known amounts of squalane and per D phenanthrene were
107 added as internal standards for aliphatic hydrocarbons and other fractions, respectively. The
108 % error of the compound quantifications was of the order of 5-8%. Prior to analysis by GC-
109 MS, the acid fraction was derivatized with freshly distilled diazomethane and the aliphatic
110 alcohol and sterol fractions were derivatized with bis(trimethylsilyl)trifluoroacetamide
111 (BSTFA) after addition of 10µl pyridine.
112 A HP 5973 GC-MS system was used for the analysis and operated in electron
113 impact (EI) ionization mode at 70eV. The capillary column was a DB5 MS (30m, 0.25mm
114 i.d., 0.25µm). The GC oven was programmed from 60 to 180°C at a rate of 6.0^{o}C/min after
115 1 min at the initial temperature; then increased to 315°C at a rate of 3°C/min and kept at the

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maximum temperature for 15 min. The identification of individual compounds was performed by comparison of chromatographic retention time and mass spectra of authentic standards and those previously reported in the literature.

3. Results and discussion

Several lipid compound classes such as *n*-alkanes, sterols, fatty acids and aliphatic *n*-alcohols as well as highly branched isoprenoids (HBIs) and pentacyclic triterpenoids were examined. All concentrations are expressed in ng per liter (ng/L).

3.1. Aliphatic hydrocarbons

A homologous series of *n*-alkanes ranging from C_{15} to C_{33} was observed and displayed a strong odd-over-even carbon number predominance, reflected by their high carbon preference index values (CPI; Fig. 2A and Table 1). Their total concentrations varied from 37 to 349ng/L (Table 1). The C_{15} and C_{17} homologues dominated the *n*-alkane distribution accounting for up to 81% of the total *n*-alkanes, while the C_{29} and C_{31} *n*-alkanes, indicative of terrestrially derived OM, were only minor components (0~24%). This distribution suggested a primary influence of phytoplankton (Cranwell, Eglinton, & Robinson, 1987). All POM samples except D2-7 featured an average carbon-chain length (ACL) of *n*-alkanes from 16.4 to 21.8, also reflecting strong microbial (planktonic) OM inputs.

Whereas surface sediments have a seagrass-derived lipid signature (Table 2; Xu et al., 2006b), POM was characterized by predominant phytoplankton-derived compounds. This difference may reflect (1) the preferential degradation of short-chain (microbial and

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algal) *n*-alkanes relative to mid- (seagrasses) and long-chain (mangrove) counterparts during early diagenesis of POM and surface sediment OM; and (2) an unimportant contribution of seagrass- and mangrove-derived in resuspended OM relative to planktonic POM in the water column.

Along the NE to SW transect, the percentage of (C_{29}+C_{31}) *n*-alkanes gradually decreased from 1.5 to 0.3%, 13 to 2.7%, 8.2 to 0% and 24 to 2.7% for the W1, D1, W2 and D2 series, respectively, suggesting a consistent decrease in the source strength of terrestrially-derived OM toward offshore areas. The ratio of long/short (>C_{20}/≤ C_{20}) *n*-alkanes, an indicator of terrestrial vs. marine OM, generally decreased from the NE (site 7 and 8) to the central section (site 9) and then increased to the SW bay (site 10, 11), likely as a result of a strong influence of seagrasses in off-shore areas, which are characterized by high amounts of C_{23} and C_{25} *n*-alkanes (Jaffé et al., 2001; Mead et al., 2005). This data is consistent with previous reports that planktonic primary productivity is the highest in the central section of the Bay (Philips, Lynch, & Badylak, 1995).

The *n*-alkane based *Paq* value, defined as (C_{23}+C_{25})/(C_{23} +C_{25} +C_{29}+C_{31}) *n*-alkanes, was proposed as a means to distinguish between non-emergent and emergent plant derived OM (Ficken, Li, Swain, & Eglinton, 2000). Mead et al. (2005) reported *Paq* values for seagrasses, *Rhizophora mangle* and *Cladium* sp. (sawgrass) as 0.90-1.00, 0.24 and 0.10, respectively. This distinct difference makes the *Paq* a good proxy to estimate seagrass inputs in Florida Bay. The *Paq* value of POM markedly increased from site 7 (as low as 0.30) to site 11 (up to 1.0) (Fig. 3), reflecting spatial variations in the strength of seagrass vs. terrestrial (e.g. mangrove) OM. It should be noted that phytoplankton contributions are not reflected in the *Paq* proxy.

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The POM samples from the dry season (D1 and D2) were enriched in terrestrial components relative to those from the wet season (W1 and W2), as reflected by several *n*-alkane based proxies. The percentage of high molecular weight *n*-alkanes (C_{29}+C_{31}) ranged from 3 to 24% during the dry season *vs*. 0 to 8% during the wet season. The sample D2-7 showed the lowest *Paq* value (0.3), the highest ACL value (25.0) and the most abundant long-chain *n*-alkanes (24%). The terrestrial "background" signal is apparently suppressed by the higher autochthonous primary production in the summer months in Florida Bay (wet season).

Several C_{20}, C_{25} and C_{30} highly branched isoprenoids (HBIs) were detected in the aliphatic hydrocarbon fractions (Fig. 2A). The C_{20} HBI compounds consisted of the saturated alkane namely 2, 6, 10-trimethyl-7-(3-methylbutyl)dodecane ($C_{20:0}$; Retention index; RI_{DB5} 1693) and its corresponding monounsaturated alkene ($C20{:}1_{DB5}$ 1685) (Jaffé et al., 2001). The C_{20} HBI was present at concentrations as high as 433ng/L while that of the C_{25} HBIs reached 100ng/L. The C_{30} HBIs, however, were only detectable in the D2 series at a concentration below 10ng/L. Cyanobacteria have been suggested as a potential source for the C_{20} HBIs, but direct evidence for this is still lacking (Jaffé et al., 2001; Kenig, Sinninghe Damsté, Kock-van Dalen, Rijpstra, Huc, & de Leeuw, 1995). In contrast, the biosynthesis of C_{25} HBIs by some diatoms has been firmly established (Sinninghe Damsté, Muyzer, Abbas, Rampen, Massé, & Allard et al. , 2004; Volkman, Barrett, & Dunstan, 1994). The C_{30} HBIs are also biosynthesized by some marine diatoms (Sinninghe Damsté et al., 2004; Volkman et al., 1994).

Regarding the spatial distribution, C_{20} HBIs were generally more abundant at the NE and central Bay relative to the SW Bay especially at TS/Ph 11. This distribution reflects

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the mixed contribution of cyanobacterial mats and periphyton mats which are abundant in the NE and central Bay and in the freshwater Everglades, respectively (Jaffé et al., 2001). The C_{25} HBIs were most abundant in the central Bay POM, as in the surface sediments (Xu et al., 2006b), reflecting autochthonous marine diatom inputs, while the absence of C_{30} HBIs in most POM samples may be a reflection of weak source strengths or fast degradation of those polyunsaturated compounds.

3.2 Sterols

The concentrations of C_{26}-C_{30} sterols ranged from 91 to 3040ng/L (Fig. 2D and Table 1). Among them, the principal compounds were cholest-5-en-3β-ol ($C_{27}\Delta^{5}$; 10-48%), 24-methylcholesta-5,22-dien-3β-ol ($C_{28}\Delta^{5,22}$; 2-20%), 24-ethylcholest-5,22-dien-3β-ol ($C_{29}\Delta^{5,22}$; 2-72%) and 24-ethylcholest-5-en-3β-ol ($C_{29}\Delta^{5}$; 4-16%). Figure 4 shows the relative abundance of C_{26}-C_{30} sterols in the POM samples. C_{27}, C_{28} and C_{29} sterols were abundant, but the C_{26} and C_{30} compounds were minor or undetectable. The only C_{26} sterol, 24-norcholesta-5,22*E*-dien-3β-ol ($C_{26}\Delta^{5,22}$) accounted for < 3% of total sterols. The C_{27} sterols were dominated by $C_{27}\Delta^{5}$ (10 to 48%) followed by cholesta-5,22-dien-3β-ol ($C_{27}\Delta^{5,22}$), cholestan-3β-ol ($C_{27}\Delta^{0}$) and cholest-22-en-3β-ol ($C_{27}\Delta^{22}$). C_{28} sterols were composed of $C_{28}\Delta^{5,22}$, 24-methylcholesta-22*E*-en-3β-ol ($C_{28}\Delta^{22}$), 24-methylcholesta-5,24(28)-dien-3β-ol ($C_{28}\Delta^{5,24(28)}$), 24-methylcholest-5-en-3β-ol ($C_{28}\Delta^{5}$) and 24-methylcholestan-3β-ol ($C_{28}\Delta^{0}$). Among them, $C_{28}\Delta^{5}$ (2-8%) and $C_{28}\Delta^{5,22}$ (2-20%) were the most abundant in most POM samples except for W1-11 which had $C_{28}\Delta^{5,24(28)}$ at a concentration of 445ng/L. The percentages of C_{29} sterols were relatively constant and accounted for ~ 25% of the POM samples, except for the W1 series where this value

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markedly decreased from site 7 to site 11 (Fig. 4). Several C_{30} sterols such as 4α-methyl-24-ethyl-5α(*H*)-cholest-22(*E*)-en-3β-ol ($C_{30}\Delta^{22}$), 4α,23,24-trimethyl-5α(*H*)-cholest-22(*E*)-en-3β-ol ($C_{30}\Delta^{22}$), 4α,23,24-trimethyl-5α(*H*)-cholestan-3β-ol ($C_{30}\Delta^{0}$) accounted for 0.2-7% of the total sterols.

While the low abundance of C_{26} sterols may reflect minimal inputs of OM from marine animals (de Leeuw, Rijpstra, Schenck, & Volkman, 1983; Jiang, O'Leary, Volkman, Zhang, Jia, & Yu et al., 1994), the relatively high percentages of $C_{27}\Delta^{5}$ (10-48%) suggested an important contribution from zooplankton-derived OM, although an origin from other organisms is possible (Volkman, 1986). C_{28} sterols were relatively abundant in most POM samples, indicating a significant input from phytoplankton especially diatoms (Volkman, 1986), although these sterols have also been found to be abundant in seagrasses (Jaffé et al., 2001).

C_{29} sterols have been widely used as biomarkers of terrestrial OM (Huang, & Meinschein, 1976; 1978), but they are also biosynthesized by some microalage (Volkman, 1986; Volkman, Barrett, Blackburn, Mansour, Sikes, & Gelin, 1998). In Florida Bay, $C_{29}\Delta^{5}$ in seagrasses accounts for ~ 75% of total sterols (Jaffé et al., 2001). Therefore, the high abundance of C_{29} sterols does not necessarily reflect a large terrestrially-derived OM input in Florida Bay, which is corroborated by the dominance of short-chain *n*-alkanes and the high *Paq* values (>0.81). The $C_{28}\Delta^{5}$:$C_{29}\Delta^{5,22}$:$C_{29}\Delta^{5}$ ratio of POM fell in the range of 1:0.76:1.24 to 1:9.93:0.90, while higher plants have this value in the order of 1:1.4:4.0 to 1:1.6:6.6 (Gogou, & Stephanou, 2004; Volkman, 1986). A significantly enhanced abundance of $C_{28}\Delta^{5}$ and $C_{29}\Delta^{5,22}$ relative to $C_{29}\Delta^{5}$ in POM suggests an important OM input from marine algae. The relative abundance of the C_{27} *vs.* C_{29} sterols did not show

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pronounced variations along the NE to SW transect for D1, W2 and D2 series (1 to 3), again suggesting seagrass as an important POM source. As a biomarker for dinoflagellates (de Leeuw et al., 1983), $C_{30}\Delta^{22}$ (dinosterol) remained at low abundance in the POM, suggesting only minor contributions from these organisms. The presence of only minor amounts of stanols in the POM samples suggests that this OM is fairly fresh and has not undergone significant degradation (Jaffé et al., 1996; Wakeham, & Lee, 1989).

3.3 Fatty acids

The concentration of fatty acids was as high as 2580ng/L (Table 1). The *n*-fatty acid homologues displayed a strong even-over-odd carbon predominance (Fig. 2B). Short-chain fatty acids (SCFAs; $\leq C_{20}$) are mainly derived from planktonic and microbial organisms, while long-chain fatty acids (LCFAs; $>C_{20}$) are produced by higher plants including seagrasses (Jaffé et al., 2001). Therefore, the high SCFAs/LCFAs values observed for POM (up to 47) suggest a primary marine planktonic influence, in agreement with the data from *n*-alkanes. However, seagrasses, commonly covered by epiphytic organisms, cannot be excluded as an important source as they have a strong predominance at C_{16} followed by C_{24} in their fatty acids distributions (Jaffé et al., 2001). The long chain fatty acids observed here are most likely derived from mixed inputs of seagrasses and mangroves. Fatty acid homologues maximized at n-C_{14} (300ng/l) for W1-11, a distribution typical of phytoplankton.

The relative abundance of monounsaturated fatty acids (MUFAs) varied from 7% to 27%, indicating an important microbial contribution to the POM. Compared to the abundance of polyunsaturated fatty acids (PUFAs) in surface sediments (0.7-13%; Table 2;

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Xu et al., 2006b), the POM samples showed markedly elevated concentrations of these constituents (7-57%), which can be attributed to the preferential degradation of MUFAs and PUFAs relative to their saturated counterparts during early diagenesis (Meyers, 2003). The proportion of branched fatty acids in the POM (0.6-4%) was significantly lower than that in surface sediments (5-15%; Table 2; Xu et al., 2006b), reflecting a more active bacterial reworking at the sediment-water interface (Gogou, & Stephanou, 2004) and a reduced contribution of these compounds from sediment resuspension. Branched fatty acids, principally *iso*- and *anteiso*-C_{15} and C_{17}, are found to be abundant in bacteria (Budge, & Parrish, 1998). Wakeham and Beier (1991) proposed a bacterial indicator value of 6% to be rather low and not indicative of a large contribution of fatty acids from bacteria.

Some fatty acid based proxies can reflect a shift in phytoplankton taxonomic classes such as diatoms and dinoflagellates. The ratios of $C_{16:1}/C_{16:0}$, $\Sigma C_{16}/\Sigma C_{18}$ and $C_{20:5}/C_{22:6}$ have been proposed as indicators of diatoms (Budge, & Parrish, 1998; Ramos, Parrish, Quibuyen, & Abrajano, 2003). For the Florida Bay POM, the ratio of $C_{16:1}/C_{16:0}$ remained below 1.0 while the $\Sigma C_{16}/\Sigma C_{18}$ was generally higher than 1.0 and had the maximum value of 3.2 (Table 1). This apparent disagreement between the two diatom indicators is most likely attributed to an interference of seagrass derived OM (possibly from epiphytes) in which the $C_{16:0}$ fatty acid is dominant (Jaffé et al., 2001). Therefore, such proxies involve non-source specific biomarkers, and hence their applicability can be limited. The ratio of $C_{20:5}/C_{22:6}$ was as high as 12, indicating an important contribution from diatoms.

Seasonally, the percentages of (MUFAs+PUFAs) in the POM remained at relatively constant, high levels, suggesting consistently important contributions of phytoplankton

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derived OM. The fatty acids also showed higher percentages of long-chain homologues during the dry season, as did the *n*-alkanes.

3.4 *n*-Alkanols

The *n*-alkanol distribution exhibited a strong even over odd carbon number predominance with concentrations ranging from 16 to 1220ng/L (Table 1 and Fig. 2C). Terrestrial plants produce long chain *n*-alkanols from C_{22} to C_{32} (Sever, & Parker, 1969), while short chain ($\leq C_{20}$) *n*-alkanols are characteristic of microbial OM inputs (Robinson, Cranwell, Finlay, & Eglinton, 1984). The *n*-alkanol distributions in most POM samples showed maxima at short chain homologues (C_{12}-C_{18}), again consistent with a predominant algal and microbial OM origin. However, a few of the dry season samples (i.e., D1-7, D1-8 and D2-7) had significant levels of C_{28} or C_{30} *n*-alkanols (Table 1), suggesting important higher plant inputs (Jaffé et al., 2001). This supports the interpretation of the *n*-alkane and fatty acid distributions as having higher relative contributions from terrestrial-higher plant OM in the dry season. The ratio of long chain/short chain *n*-alkanols markedly decreased (Table 1), further confirming a decreasing trend of terrestrial influence toward offshore. In regards to seasonality, the dry season samples had higher values of long/short chain *n*-alkanols (0.2-10) relative to the wet season samples (0.0-1.4), suggesting more terrestrial OM components for the former, while wet season OM sources seem controlled by increased planktonic primary productivity.

3.5 Higher plant derived pentacyclic triterpenoids

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298 Pentacyclic triterpenoids such as taraxerol, β-amyrin and lupeol are widely found in
299 higher plants, especially in trees, but rarely in other organisms. Hence they are often used
300 as biomarkers of terrestrial inputs (Brassell, Eglinton, & Maxwell, 1983; ten Haven, &
301 Rullkotter, 1988; Versteegh, Schefuβ, Dupont, Marret, Sinninghe Damsté, & Jansen, 2004).
302 Previous studies have reported taraxerol concentration of up to 1.4 mg/g in mangrove
303 leaves (Versteegh et al., 2004) but it is absent in the other two main higher plant biomass
304 components of the Everglades ecosystem, namely seagrass and sawgrass (Xu et al., 2006b).
305 Several pentacyclic triterpenoids such as taraxerol, β-amyrin, germanicol and lupeol were
306 detected in the POM. Overall, their concentrations rapidly decreased from site 7 to 11
307 (Table 1), suggesting reduced transport from the NE mangrove fringe to the Bay and/or the
308 sparse distribution of mangrove tree islands in SW Florida Bay. The abundance of these
309 triterpenoids was found to be higher during the dry season (D1 and D2) relative to the wet
310 season (W1 and W2). For example, taraxerol, a specific biomarker of mangroves
311 (Versteegh et al., 2004), was as high as 1210ng/L for the D1 series and 109ng/L for the D2
312 series, but only 19ng/L for the W1 series and 102ng/L for the W2 (Table 1). These results
313 are in agreement with data on source variations for dissolved organic matter (DOM) in
314 Florida Bay (Maie, Boyer, Yang, & Jaffé, 2006).
315
316 3.6 Principal components analysis (PCA)
317 PCA is a multivariate statistical technique, useful in extracting information from
318 complex organic geochemical data (e.g. Hernandez et al., 2001; Mead et al., 2005; Mudge,
319 East, Bebianno, & Barreira, 1998). Figure 5 shows the PCA score plot for POM in Florida
320 Bay where the first principal component (PC 1) accounted for 39% and the second principal

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component (PC 2) accounted for 27% of the variance. The biomarker concentration data and indices used in this analysis were for the taraxerol, sterols, *Paq*, *n*-alkanes and fatty acid distributions.

The variability among the samples seems to be controlled mainly by OM source and season, and neither the PCs properly define these variables independently. However, PC1 seems to more strongly control the special variables separating the POM samples into two groups, namely near-shore (empty diamonds) and offshore areas (filled diamonds) with the exception of samples W1-8 and D2-8. In contrast, PC2 seems to control the seasonal component and roughly separates the D and W series along its axis (with some exceptions). However, analyzing the sample clusters in more detail, one can observe that the W1 samples are clearly distinct from W2 samples, except for samples from site 11 which both fall in the W1 cluster. Even sample W1-8 falls into the W1 cluster with a high positive correlation with PC1 although station 8 is assumed to contain high relative contributions from terrestrial sources. The main difference between the W1 and W2 sampling is that rainfall for the W1 season was about twice that for the W2 season. The average daily precipitation at the Flamingo Ranger Station close to Florida Bay was 0.81mm during October 2003 (W1) and 0.39mm during October 2004 (W2); (see http://fcelter.fiu.edu). Based on this, it seems that higher rainfall resulted in increased planktonic/seagrass primary productivity probably due to atmospheric phosphorus inputs into this highly P-limited environment (Sutula, Perez, Reyes, Childers, Davis, & Day et al., 2003). This result also suggests that potential seasonal variations in POC composition are not primarily driven by hydrology (POM transport) but by primary productivity. Samples W1-11 and W2-11 were

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co-located in the PCA plot since this site experiences active P-exchange with waters from the Gulf of Mexico and as such is less sensitive to atmospheric P-inputs.

With regards to the D samples, the drier D1 season compared to D2 (0.04mm during March 2004 (D1) and 0.22mm during April 2005 (D2)) was more controlled by hydrology (POM transport from terrestrial environments) compared to D2. And a consistent shift from more terrestrial (negative correlation with PC1) to more marine (positive correlation with PC1) was observed for the nearshore sites (7, 8 and 9), but as expected not for sites 10 and 11. These data again suggest that POM in Florida Bay is primarily derived from marine (planktonic/seagrass) OM where primary productivity during the wet season is an important ecological driver. In contrast, the dry season exerts a stronger terrestrial OM influence on the nearshore sites, probably as a result of a relative increase in terrestrial (mangrove) OM transport in comparison with marine biomass primary productivity.

4. Summary

Autochthonous/marine sources were the principal contributors to POM in Florida Bay, while allochthonous/terrestrial OM, although minor, played a more important role mostly in the NE, nearshore sites and during the dry season. Multi-biomarker proxies indicated a shift in OM sources along the NE to SW transect from mangrove influenced to plankton/seagrass dominated marine OM inputs. The higher relative abundance of terrestrially derived POM during the dry season relative to the wet season is most likely an indirect consequence of the seasonal primary productivity changes in the Bay.

Higher percentages of mono- and poly-unsaturated fatty acids and lower proportions of branched fatty acids in the POM samples relative to surface sediments reflect a

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preferential degradation of unsaturated compounds during sedimentation and active microbial reworking at the water-sediment interface.

PCA analyses classified the POM samples into two groups according to PC1, namely a nearshore and a more marine influenced group, while PC2 separated the POM samples according to seasonality (hydrology/primary productivity). This study is the first to report seasonal variations in suspended POM compositions in Florida Bay.

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Figure and table captions:

Fig. 1: Geographic locations of particulate organic matter sampling sites in Florida Bay

Fig. 2: Representative GC/MS chromatograms of (A) *n*-alkanes, (B) fatty acids, (C) *n*-alcohols and (D) sterols in particulate organic matter from Florida Bay

Fig. 3: The *Paq* distributions in particulate organic matter from Florida Bay.
Paq = $(C_{23}+C_{25})/(C_{23}+C_{25}+C_{29}+C_{31})$ *n*-alkanes

Fig. 4: Relative abundance of C_{26}, C_{27}, C_{28}, C_{29} and C_{30} sterols in particulate organic matter from Florida Bay

Fig. 5: Biomarker-based score plot of the first two principal components (PC-1 and PC-2) for suspended particles from Florida Bay

Table 1: Concentration of *n*-alkanes, *n*-alkanols, triterpenoids, fatty acids, HBIs and sterols in Florida Bay suspended particles during dry season (D) and wet season (W)

Table 2: Comparison of biomarker proxies between POM and surface sediments in Florida Bay

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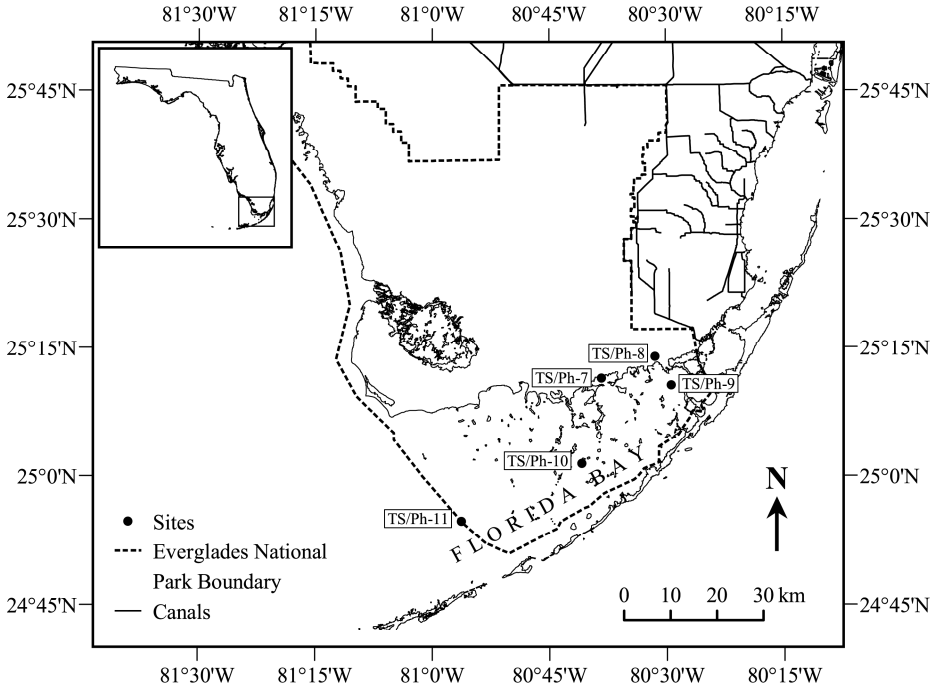

Figure 1

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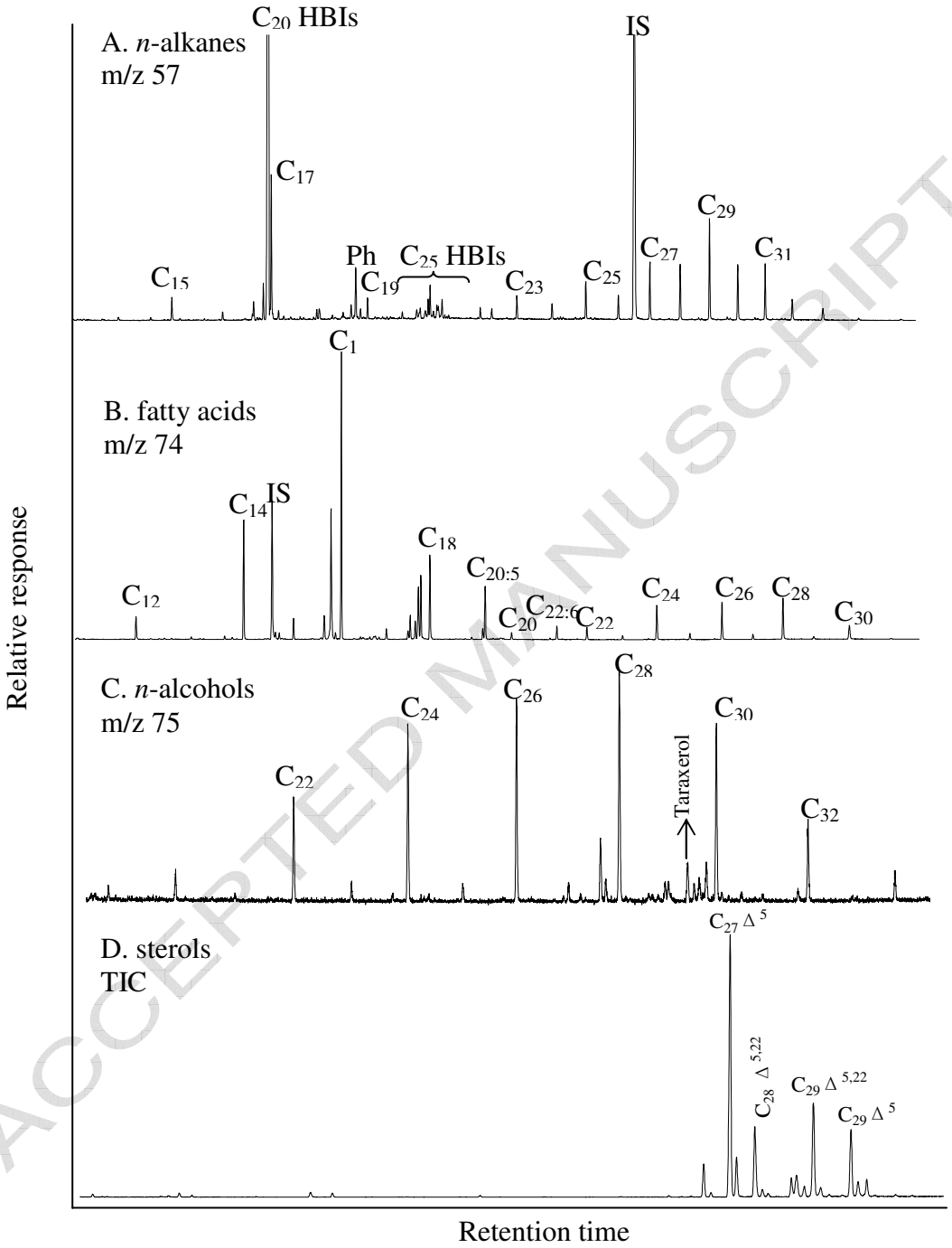

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555 Fig. 2

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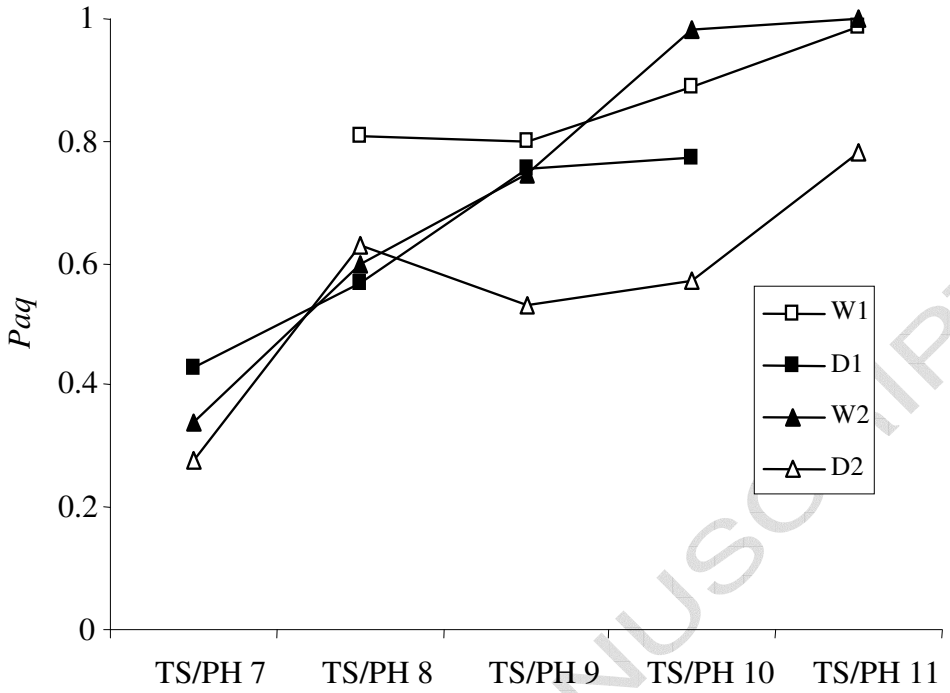

Fig. 3

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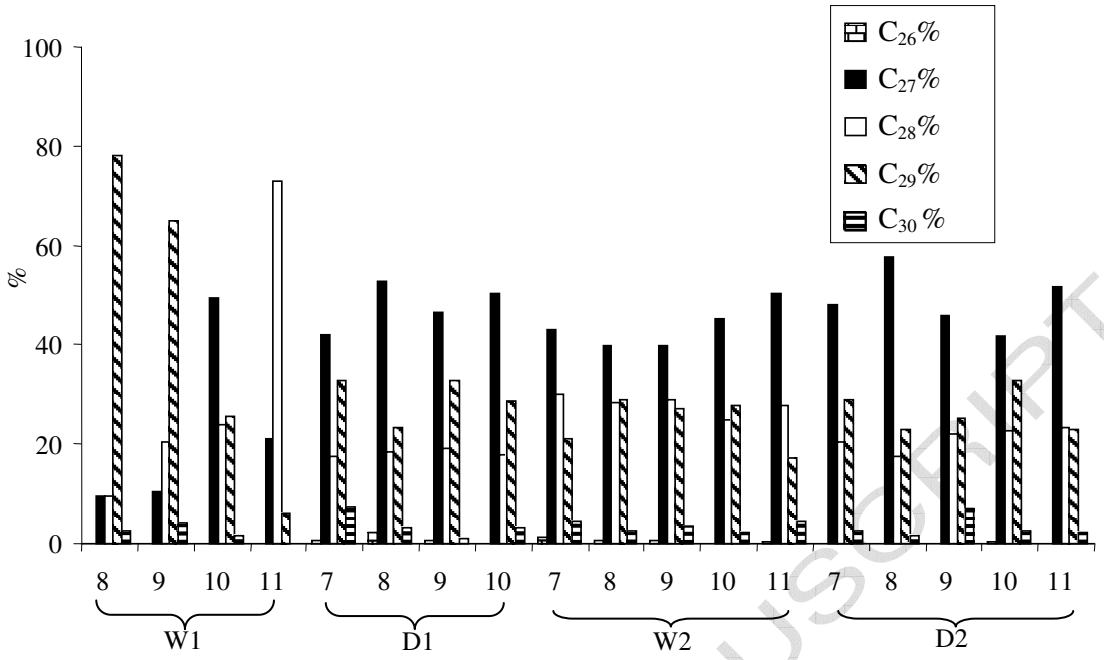

Fig. 4

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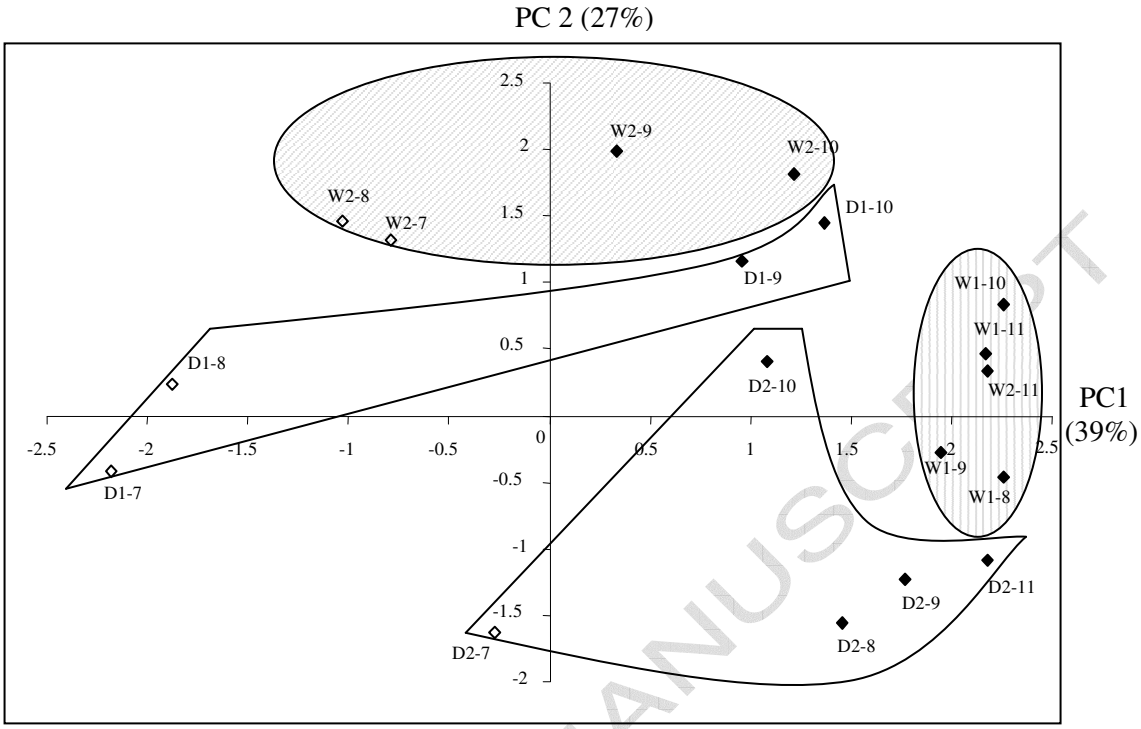

Fig. 5

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Table 1 Concentration of *n*-alkanes, *n*-alkanols, triterpenoids, fatty acids, HBIs and sterols in Florida Bay suspended particulates during dry season (D) and wet season (W)

	W1				D1				W2					D2				
	8	9	10	11	7	8	9	10	7	8	9	10	11	7	8	9	10	11
n-Alkanes																		
Total	119	338	349	281	316	266	37	95	43	163	76	75	38	128	95	73.7	214	60
$C_{29}+C_{31}$	1.8	3	1	1	41	12	1	3	4	10	2	0.2	0	29	8	5	6	4
Paq	0.8	0.8	0.9	1.0	0.4	0.6	0.8	0.8	0.3	0.6	0.7	1.0	1.0	0.3	0.6	0.5	0.6	0.8
Cmax	C_{17}	C_{17}	C_{15}	C_{23}	C_{15}	C_{15}	C_{15}	C_{15}	C_{15}	C_{15}	C_{15}	C_{21}	C_{15}	C_{17}	C_{17}	C_{15}	C_{15}	C_{15}
Short	96	293	326	140	195	212	22	63	33	103	51	50	21	34	45	50	177	23
Long	23	46	23	141	121	55	15	33	10	60	26	54	17	86	50	23	36	35
Long/short	4.1	6.3	14	1.0	1.6	3.8	1.5	1.9	3.2	1.7	2.0	0.9	1.2	0.4	0.9	2.2	5	0.7
ACL	18.5	17.9	16.5	20.6	20.1	17.5	19.7	20.6	18.2	19.6	19.4	20.5	19.4	25	21.8	19.3	17.6	21.5
CPI	7.1	3.4	5.4	1.6	7.8	10.9	2.1	1.9	7.1	3.0	1.6	1.9	2.2	2.4	1.4	5.1	11.3	3.8
$\%(C_{15}+C_{17})$	69	61	76	11	57	75	32	31	68	41	33	12	31	24	15	63	81	33
$\%(C_{29}+C_{31})$	1.5	0.9	0.3	0.3	13	4.7	3.2	2.7	8.1	6.0	2.8	0.2	0.0	24	8.8	6.2	2.7	6.8
n-Alkanols																		
Total	16	59	48	29	1220	406	41	63	122	218	80	203	155	143	130	41	177	30
Cmax	C_{14}	C_{12}	C_{18}	C_{12}	C_{30}	C_{28}	C_{18}	C_{18}	C_{18}	C_{12}	C_{12}	C_{12}	C_{12}	C_{28}	C_{14}	C_{18}	C_{18}	C_{18}
Long/short	0.3	0.3	0.0	0.0	10	7.8	1.5	0.2	0.0	1.4	0.1	0.1	0.0	3.9	0.9	1.0	0.5	0.5
Triterpenoids																		
Taraxerol	7	19	0.0	0.0	1210	181	9	8.4	102	30	0.0	0.0	0.0	109	21	2	1	0.0
β-amyrin	0.0	9.9	0.0	0.0	518	97	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4	5	0.0	0.0	0.0
Germanicol	0.0	0.0	0.0	0.0	131	29	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.6	0.0	0.0	0.0
Lupeol	7.0	0.0	0.0	0.0	231	39	0.0	0.0	18	7.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

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Table 1 continued

Fatty acids																		
Total	153	40	165	601	2580	1063	1230	1980	598	214	270	535	454	1370	1824	1800	3411	1130
Short	149	40	162	587	2000	832	1180	1800	543	161	246	495	436	662	752	869	1140	577
Long	3.7	0.0	3.4	14	577	231	44	184	55	53	24	41	18	202	185	174	223	72
Short/long	39.8	nd	47.4	41.1	3.5	3.6	26.7	9.7	10.0	3.0	10.5	12.2	23.9	3.3	4.1	5.0	5.1	8.0
MUFAs (%)	26	21	27	16	20	18	23	23	15	7.0	11	17	20	11	16	18	23	24
PUFAs (%)	10	0.9	7.5	11	6.5	8.6	9.6	9.0	3.3	0.2	0.9	1.5	1.2	22	21	20	35	16
Br-FAs (%)	3.5	2.3	1.7	1.2	2.1	1.2	1.1	1.5	0.8	0.6	0.7	2.0	1.7	3.9	3.1	3.5	2.3	3.0
C16:1/C16:0	0.6	0.3	0.3	0.8	0.3	0.3	0.4	0.5	0.2	0.1	0.1	0.2	0.2	0.5	0.4	0.5	0.7	0.3
C16/C18	2.1	3.2	2.0	2.8	1.6	1.7	1.9	1.7	2.2	2.0	1.7	2.1	2.3	2.0	1.9	1.7	0.9	1.0
A/B	8.7	nd	3.1	0.6	3.9	3.2	5.5	7.0	4.1	nd	nd	nd	nd	4.1	5.4	11.9	2.8	1.3
HBIs																		
C_{20} HBIs	154	282	148	7.1	404	191	58	133	40	52	77	17	1.1	410	71	145	433	4.3
C_{25} HBIs	13	41	91	0.0	35	22	14	56	3.0	16	24	0.0	0.0	56	33	9.8	100	0.0
C_{30} HBIs	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	10.3	nd	nd	nd	nd
Sterols																		
Total	180	91	526	800	3040	2290	1137	1090	1380	1460	1040	1180	161	596	451	430	1500	309

All concentrations are expressed in ng/L. Cmax: the maximum compounds in homologues.
Short: total concentrations of short-chain homologues ($\leq C_{20}$). Long: total concentrations of long-chain homologues ($>C_{20}$). ACL = average chain length of the homologues. CPI = carbon preference index. MUFAs = mono-unsaturated fatty acids. PUFAs = poly-unsaturated fatty acids. Br-FAs- = branched-C_{15} +C_{17} fatty acids indicative of bacterial contributions. A/B = the ratio of $C_{20:5}$ over $C_{22:6}$ fatty acids. nd = not detected

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Table 2

	TS/Ph 7		TS/Ph 8		TS/Ph 9		TS/Ph 10		TS/Ph 11	
n-alkane	POM	Sed.	POM	Sed.	POM	Sed.	POM	Sed.	POM	Sed.
Paq	0.33	0.44	0.65	na	0.7	0.53	0.83	0.63	0.94	0.83
Cmax	C_{15}	C_{29}	C_{15}	na	C_{15}	C_{25}	C_{15}	C_{25}	C_{23}	C_{25}
ACL	21.1	26.6	19.4	na	19.1	25.7	18.8	24.5	20.5	21.4
%(C_{15}+C_{17})	50	2.6	67	na	47	7.4	50	9.7	25	13
%(C_{29}+C_{31})	16	29	5.3	na	3.3	23	1.5	10	2.4	4.6
Fatty acids										
PUFA%	11	0.7	10	na	8	4.4	13	8.2	9.2	13
MUFA%	15	4.9	17	na	18	6.4	23	11	20	37
BrFA%	2.3	7.3	2.1	na	1.9	5.2	1.9	8	2	15
Sterol										
C_{27}%	44	19	40	na	36	37	47	38	41	42
C_{28}%	23	17	18	na	23	17	22	19	41	22
C_{29}%	28	64	38	na	38	46	29	43	15	36
n-alkanol										
Long/short	4.6	10	2.6	na	0.7	50	0.2	6.3	0.1	1.8

na = not analyzed

*The data on sediments are from Xu et al., 2006b while data on POM are the average values from this study.

ACCEPTED MANUSCRIPT