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1 Lipid biomarkers in suspended particles from a subtropical estuary:

2 Assessment of seasonal changes in sources and transport of organic matter.

3 **Yunping Xu¹ and Rudolf Jaffé***

4 Environmental Geochemistry Group, Southeast Environmental Research Center and Department of
5 Chemistry & Biochemistry, Florida International University, Miami, 33199, USA

6 *Corresponding author: Tel: +1-305-348-3095; fax: +1-305-348-4096

7 *E-mail address:* jaffer@fiu.edu (R. Jaffé)

8 ¹Present address: Department of Physical & Environmental Sciences, S433, University of
9 Toronto, Toronto, ON M1C 1A4, Canada.

10
11 **Abstract**

12 Temporal and spatial variations in the composition of particulate organic matter
13 (POM) from Florida Bay, USA were examined. The predominance of short chain
14 homologues for *n*-alkanes, *n*-alcohols and *n*-fatty acids as well as relatively high abundance
15 of C₂₇ and C₂₈ sterols suggested that an autochthonous/marine source of OM was dominant
16 bay-wide. Several biomarker proxies such as *Paq* [(C₂₃+C₂₅)/(C₂₃+C₂₅+C₂₉+C₃₁) *n*-alkanes],
17 short/long chain *n*-alkanes, (C₂₉+C₃₁) *n*-alkanes and taraxerol indicated a spatial shift in
18 OM sources, where terrestrial OM rapidly decreased while seagrass and microbial OM
19 markedly increased along a northeastern to southwestern transect. Regarding seasonal
20 variations, POM collected during the dry season was enriched in terrestrial constituents
21 relative to the wet season, likely as a result of reduced primary productivity of planktonic
22 species and seagrasses during the dry season. Principal component analysis (PCA)
23 classified the sample set into sub-groups based on PC1 which seemed to be spatially

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

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

30

31 **1. Introduction**

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

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

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

61 While lipids in sediments and soils from south Florida estuaries have been reported
62 (e.g. Hernandez, Mead, Peralba, & Jaffé, 2001; Jaffé et al., 2001; Mead et al., 2005; Neto,
63 Mead, Louda, & Jaffé, 2006; Xu, Jaffé, Wachnicka, & Gaiser, 2006a; Xu, Mead, & Jaffé,
64 2006b), little is known about the sources and transport of particulate organic matter (POM).
65 Here, we assess the spatial and temporal variation in the composition and origin of POM in
66 Florida Bay through the measurement of several classes of lipid biomarkers such as
67 aliphatic hydrocarbons, sterols, aliphatic alcohols, fatty acids, highly branched isoprenoids
68 (HBIs) and terrestrially derived triterpenoids from the Florida Bay estuary, South Florida.

69

70 2. Sampling and methodology

71 2.1 Study area

72 Florida Bay is a large, subtropical body of water with a surface area of ~2200 km²
73 and a mean depth of less than 2m (Corbett, Chanton, Burnett, Dillon, Rutkowski, &
74 Fourqurean, 1999). Florida Bay experiences a warmer wet season from May to October
75 accounting for 75% of the annual precipitation and a cooler dry season from November to
76 April (Fourqurean, & Robbins, 1999). Benthic communities of Florida Bay consist mainly
77 of dense seagrass prairies where *Thalassia testudinum* is the dominant species (Zieman et
78 al., 1989). Mangrove forests dominated by *Rhizophora mangle* (red mangrove) grow along
79 the sea-land interface between the Bay and the Florida Everglades wetlands. In addition,
80 mangrove tree islands are common throughout the northeastern (NE) and central sections of
81 the Bay, but are very sparse in the southwestern (SW) section, and represent an additional
82 source of sedimentary OM to the Bay.

83

84 2.2. Sample collection

85 Water samples were collected during two wet seasons (October of 2003 and 2004)
86 and two dry seasons (March 2004 and April 2005) at five locations corresponding to the
87 Florida Coastal Everglades Long Term Ecological Research project's (FCE-LTER;
88 <http://fcelter.fiu.edu/>) Taylor Slough/Pan Handle sampling transect (TS/Ph 7, 8, 9, 10 and
89 11; Fig. 1). The samples will subsequently be referred to as W1 and W2 for the wet season
90 (October 2003 and 2004, respectively) or D1 and D2 for the dry season (March 2004 and
91 April 2005, respectively) followed by their corresponding site number (7, 8, 9, 10 and 11).
92 For example, W1-7 indicates a sample from TS/Ph 7 during the wet season of 2003. For

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 0.7 μ m nominal pore size (GF/F). The filters with
97 particulate material were freeze-dried at -40°C under the vacuum condition ($<100 \times 10^{-3}$
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 10 μ l 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., 0.25 μ m). The GC oven was programmed from 60 to 180°C at a rate of 6.0°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

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

119

120 **3. Results and discussion**

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

124

125 3.1. Aliphatic hydrocarbons

126 A homologous series of *n*-alkanes ranging from C₁₅ to C₃₃ was observed and
127 displayed a strong odd-over-even carbon number predominance, reflected by their high
128 carbon preference index values (CPI; Fig. 2A and Table 1). Their total concentrations
129 varied from 37 to 349ng/L (Table 1). The C₁₅ and C₁₇ homologues dominated the *n*-alkane
130 distribution accounting for up to 81% of the total *n*-alkanes, while the C₂₉ and C₃₁ *n*-alkanes,
131 indicative of terrestrially derived OM, were only minor components (0~24%). This
132 distribution suggested a primary influence of phytoplankton (Cranwell, Eglinton, &
133 Robinson, 1987). All POM samples except D2-7 featured an average carbon-chain length
134 (ACL) of *n*-alkanes from 16.4 to 21.8, also reflecting strong microbial (planktonic) OM
135 inputs.

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

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

143 Along the NE to SW transect, the percentage of (C₂₉+C₃₁) *n*-alkanes gradually
144 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
145 D2 series, respectively, suggesting a consistent decrease in the source strength of
146 terrestrially-derived OM toward offshore areas. The ratio of long/short (>C₂₀/≤ C₂₀) *n*-
147 alkanes, an indicator of terrestrial vs. marine OM, generally decreased from the NE (site 7
148 and 8) to the central section (site 9) and then increased to the SW bay (site 10, 11), likely as
149 a result of a strong influence of seagrasses in off-shore areas, which are characterized by
150 high amounts of C₂₃ and C₂₅ *n*-alkanes (Jaffé et al., 2001; Mead et al., 2005). This data is
151 consistent with previous reports that planktonic primary productivity is the highest in the
152 central section of the Bay (Philips, Lynch, & Badylak, 1995).

153 The *n*-alkane based *Paq* value, defined as (C₂₃+C₂₅)/(C₂₃ +C₂₅ +C₂₉+C₃₁) *n*-alkanes,
154 was proposed as a means to distinguish between non-emergent and emergent plant derived
155 OM (Ficken, Li, Swain, & Eglinton, 2000). Mead et al. (2005) reported *Paq* values for
156 seagrasses, *Rhizophora mangle* and *Cladium* sp. (sawgrass) as 0.90-1.00, 0.24 and 0.10,
157 respectively. This distinct difference makes the *Paq* a good proxy to estimate seagrass
158 inputs in Florida Bay. The *Paq* value of POM markedly increased from site 7 (as low as
159 0.30) to site 11 (up to 1.0) (Fig. 3), reflecting spatial variations in the strength of seagrass
160 vs. terrestrial (e.g. mangrove) OM. It should be noted that phytoplankton contributions are
161 not reflected in the *Paq* proxy.

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

170 Several C_{20} , C_{25} and C_{30} highly branched isoprenoids (HBIs) were detected in the
171 aliphatic hydrocarbon fractions (Fig. 2A). The C_{20} HBI compounds consisted of the
172 saturated alkane namely 2, 6, 10-trimethyl-7-(3-methylbutyl)dodecane ($C_{20:0}$; Retention
173 index; RI_{DB5} 1693) and its corresponding monounsaturated alkene ($C_{20:1DB5}$ 1685) (Jaffé et
174 al., 2001). The C_{20} HBI was present at concentrations as high as 433ng/L while that of the
175 C_{25} HBIs reached 100ng/L. The C_{30} HBIs, however, were only detectable in the D2 series
176 at a concentration below 10ng/L. Cyanobacteria have been suggested as a potential source
177 for the C_{20} HBIs, but direct evidence for this is still lacking (Jaffé et al., 2001; Kenig,
178 Sinninghe Damsté, Kock-van Dalen, Rijpstra, Huc, & de Leeuw, 1995). In contrast, the
179 biosynthesis of C_{25} HBIs by some diatoms has been firmly established (Sinninghe Damsté,
180 Muyzer, Abbas, Rampen, Massé, & Allard et al. , 2004; Volkman, Barrett, & Dunstan,
181 1994). The C_{30} HBIs are also biosynthesized by some marine diatoms (Sinninghe Damsté et
182 al., 2004; Volkman et al., 1994).

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

185 the mixed contribution of cyanobacterial mats and periphyton mats which are abundant in
186 the NE and central Bay and in the freshwater Everglades, respectively (Jaffé et al., 2001).
187 The C₂₅ HBIs were most abundant in the central Bay POM, as in the surface sediments (Xu
188 et al., 2006b), reflecting autochthonous marine diatom inputs, while the absence of C₃₀
189 HBIs in most POM samples may be a reflection of weak source strengths or fast
190 degradation of those polyunsaturated compounds.

191

192 3.2 Sterols

193 The concentrations of C₂₆-C₃₀ sterols ranged from 91 to 3040ng/L (Fig. 2D and
194 Table 1). Among them, the principal compounds were cholest-5-en-3β-ol (C₂₇Δ⁵; 10-48%),
195 24-methylcholesta-5,22-dien-3β-ol (C₂₈Δ^{5,22}; 2-20%), 24-ethylcholest-5,22-dien-3β-ol
196 (C₂₉Δ^{5,22}; 2-72%) and 24-ethylcholest-5-en-3β-ol (C₂₉Δ⁵; 4-16%). Figure 4 shows the
197 relative abundance of C₂₆-C₃₀ sterols in the POM samples. C₂₇, C₂₈ and C₂₉ sterols were
198 abundant, but the C₂₆ and C₃₀ compounds were minor or undetectable. The only C₂₆ sterol,
199 24-norcholesta-5,22*E*-dien-3β-ol (C₂₆Δ^{5,22}) accounted for < 3% of total sterols. The C₂₇
200 sterols were dominated by C₂₇Δ⁵ (10 to 48%) followed by cholesta-5,22-dien-3β-ol
201 (C₂₇Δ^{5,22}), cholestan-3β-ol (C₂₇Δ⁰) and cholest-22-en-3β-ol (C₂₇Δ²²). C₂₈ sterols were
202 composed of C₂₈Δ^{5,22}, 24-methylcholesta-22*E*-en-3β-ol (C₂₈Δ²²), 24-methylcholesta-
203 5,24(28)-dien-3β-ol (C₂₈Δ^{5,24(28)}), 24-methylcholest-5-en-3β-ol (C₂₈Δ⁵) and 24-
204 methylcholestan-3β-ol (C₂₈Δ⁰). Among them, C₂₈Δ⁵ (2-8%) and C₂₈Δ^{5,22} (2-20%) were the
205 most abundant in most POM samples except for W1-11 which had C₂₈Δ^{5,24(28)} at a
206 concentration of 445ng/L. The percentages of C₂₉ sterols were relatively constant and
207 accounted for ~ 25% of the POM samples, except for the W1 series where this value

208 markedly decreased from site 7 to site 11 (Fig. 4). Several C₃₀ sterols such as 4 α -methyl-
209 24-ethyl-5 α (*H*)-cholest-22(*E*)-en-3 β -ol (C₃₀ Δ^{22}), 4 α ,23,24-trimethyl-5 α (*H*)-cholest-22(*E*)-
210 en-3 β -ol (C₃₀ Δ^{22}), 4 α ,23,24-trimethyl-5 α (*H*)-cholestan-3 β -ol (C₃₀ Δ^0) accounted for 0.2-7%
211 of the total sterols.

212 While the low abundance of C₂₆ sterols may reflect minimal inputs of OM from
213 marine animals (de Leeuw, Rijpstra, Schenck, & Volkman, 1983; Jiang, O'Leary, Volkman,
214 Zhang, Jia, & Yu et al., 1994), the relatively high percentages of C₂₇ Δ^5 (10-48%) suggested
215 an important contribution from zooplankton-derived OM, although an origin from other
216 organisms is possible (Volkman, 1986). C₂₈ sterols were relatively abundant in most POM
217 samples, indicating a significant input from phytoplankton especially diatoms (Volkman,
218 1986), although these sterols have also been found to be abundant in seagrasses (Jaffé et al.,
219 2001).

220 C₂₉ sterols have been widely used as biomarkers of terrestrial OM (Huang, &
221 Meinschein, 1976; 1978), but they are also biosynthesized by some microalgae (Volkman,
222 1986; Volkman, Barrett, Blackburn, Mansour, Sikes, & Gelin, 1998). In Florida Bay, C₂₉ Δ^5
223 in seagrasses accounts for ~ 75% of total sterols (Jaffé et al., 2001). Therefore, the high
224 abundance of C₂₉ sterols does not necessarily reflect a large terrestrially-derived OM input
225 in Florida Bay, which is corroborated by the dominance of short-chain *n*-alkanes and the
226 high *Paq* values (>0.81). The C₂₈ Δ^5 :C₂₉ $\Delta^{5,22}$:C₂₉ Δ^5 ratio of POM fell in the range of
227 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
228 1:1.6:6.6 (Gogou, & Stephanou, 2004; Volkman, 1986). A significantly enhanced
229 abundance of C₂₈ Δ^5 and C₂₉ $\Delta^{5,22}$ relative to C₂₉ Δ^5 in POM suggests an important OM input
230 from marine algae. The relative abundance of the C₂₇ vs. C₂₉ sterols did not show

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

237

238 3.3 Fatty acids

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

251 The relative abundance of monounsaturated fatty acids (MUFAs) varied from 7% to
252 27%, indicating an important microbial contribution to the POM. Compared to the
253 abundance of polyunsaturated fatty acids (PUFAs) in surface sediments (0.7-13%; Table 2;

254 Xu et al., 2006b), the POM samples showed markedly elevated concentrations of these
255 constituents (7-57%), which can be attributed to the preferential degradation of MUFAs
256 and PUFAs relative to their saturated counterparts during early diagenesis (Meyers, 2003).
257 The proportion of branched fatty acids in the POM (0.6-4%) was significantly lower than
258 that in surface sediments (5-15%; Table 2; Xu et al., 2006b), reflecting a more active
259 bacterial reworking at the sediment-water interface (Gogou, & Stephanou, 2004) and a
260 reduced contribution of these compounds from sediment resuspension. Branched fatty acids,
261 principally *iso*- and *anteiso*-C₁₅ and C₁₇, are found to be abundant in bacteria (Budge, &
262 Parrish, 1998). Wakeham and Beier (1991) proposed a bacterial indicator value of 6% to be
263 rather low and not indicative of a large contribution of fatty acids from bacteria.

264 Some fatty acid based proxies can reflect a shift in phytoplankton taxonomic classes
265 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
266 been proposed as indicators of diatoms (Budge, & Parrish, 1998; Ramos, Parrish, Quibuyen,
267 & Abrajano, 2003). For the Florida Bay POM, the ratio of C_{16:1}/C_{16:0} remained below 1.0
268 while the $\Sigma C_{16}/\Sigma C_{18}$ was generally higher than 1.0 and had the maximum value of 3.2
269 (Table 1). This apparent disagreement between the two diatom indicators is most likely
270 attributed to an interference of seagrass derived OM (possibly from epiphytes) in which the
271 C_{16:0} fatty acid is dominant (Jaffé et al., 2001). Therefore, such proxies involve non-source
272 specific biomarkers, and hence their applicability can be limited. The ratio of C_{20:5}/C_{22:6} was
273 as high as 12, indicating an important contribution from diatoms.

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

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

278

279 3.4 *n*-Alkanols

280 The *n*-alkanol distribution exhibited a strong even over odd carbon number
281 predominance with concentrations ranging from 16 to 1220ng/L (Table 1 and Fig. 2C).
282 Terrestrial plants produce long chain *n*-alkanols from C₂₂ to C₃₂ (Sever, & Parker, 1969),
283 while short chain (\leq C₂₀) *n*-alkanols are characteristic of microbial OM inputs (Robinson,
284 Cranwell, Finlay, & Eglinton, 1984). The *n*-alkanol distributions in most POM samples
285 showed maxima at short chain homologues (C₁₂-C₁₈), again consistent with a predominant
286 algal and microbial OM origin. However, a few of the dry season samples (i.e., D1-7, D1-8
287 and D2-7) had significant levels of C₂₈ or C₃₀ *n*-alkanols (Table 1), suggesting important
288 higher plant inputs (Jaffé et al., 2001). This supports the interpretation of the *n*-alkane and
289 fatty acid distributions as having higher relative contributions from terrestrial-higher plant
290 OM in the dry season. The ratio of long chain/short chain *n*-alkanols markedly decreased
291 (Table 1), further confirming a decreasing trend of terrestrial influence toward offshore. In
292 regards to seasonality, the dry season samples had higher values of long/short chain *n*-
293 alkanols (0.2-10) relative to the wet season samples (0.0-1.4), suggesting more terrestrial
294 OM components for the former, while wet season OM sources seem controlled by
295 increased planktonic primary productivity.

296

297 3.5 Higher plant derived pentacyclic triterpenoids

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, Schefuß, 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

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

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

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

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

355

356 **4. Summary**

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

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

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

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

372

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380

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520 **Figure and table captions:**

521

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

523

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

526

527 Fig. 3: The *Paq* distributions in particulate organic matter from Florida Bay.528 $Paq = (C_{23}+C_{25})/(C_{23}+C_{25}+C_{29}+C_{31})$ *n*-alkanes

529

530 Fig. 4: Relative abundance of C₂₆, C₂₇, C₂₈, C₂₉ and C₃₀ sterols in particulate organic matter
531 from Florida Bay

532

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

535

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

538

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

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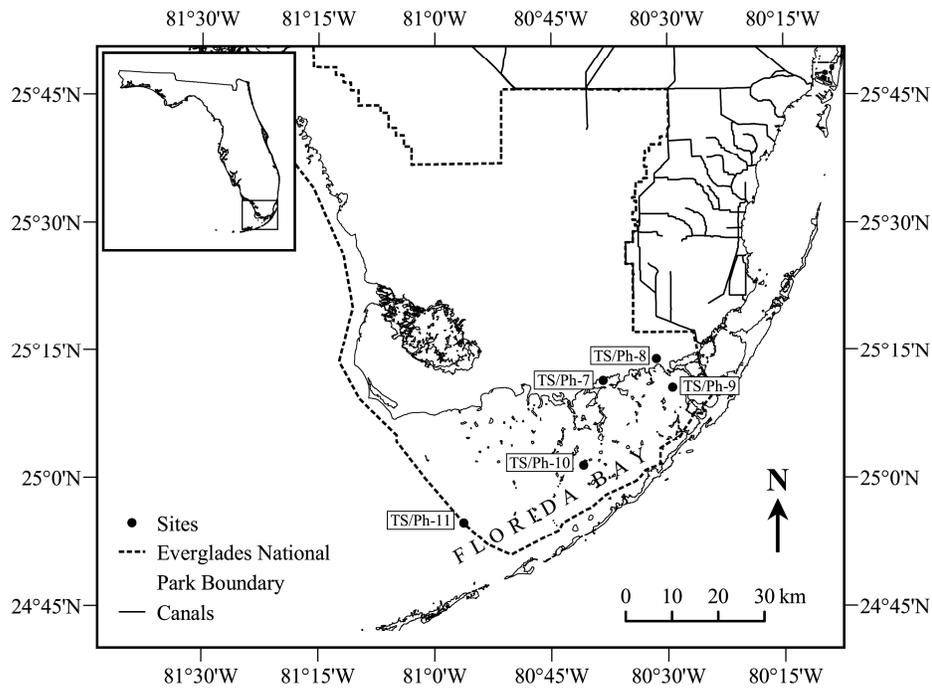
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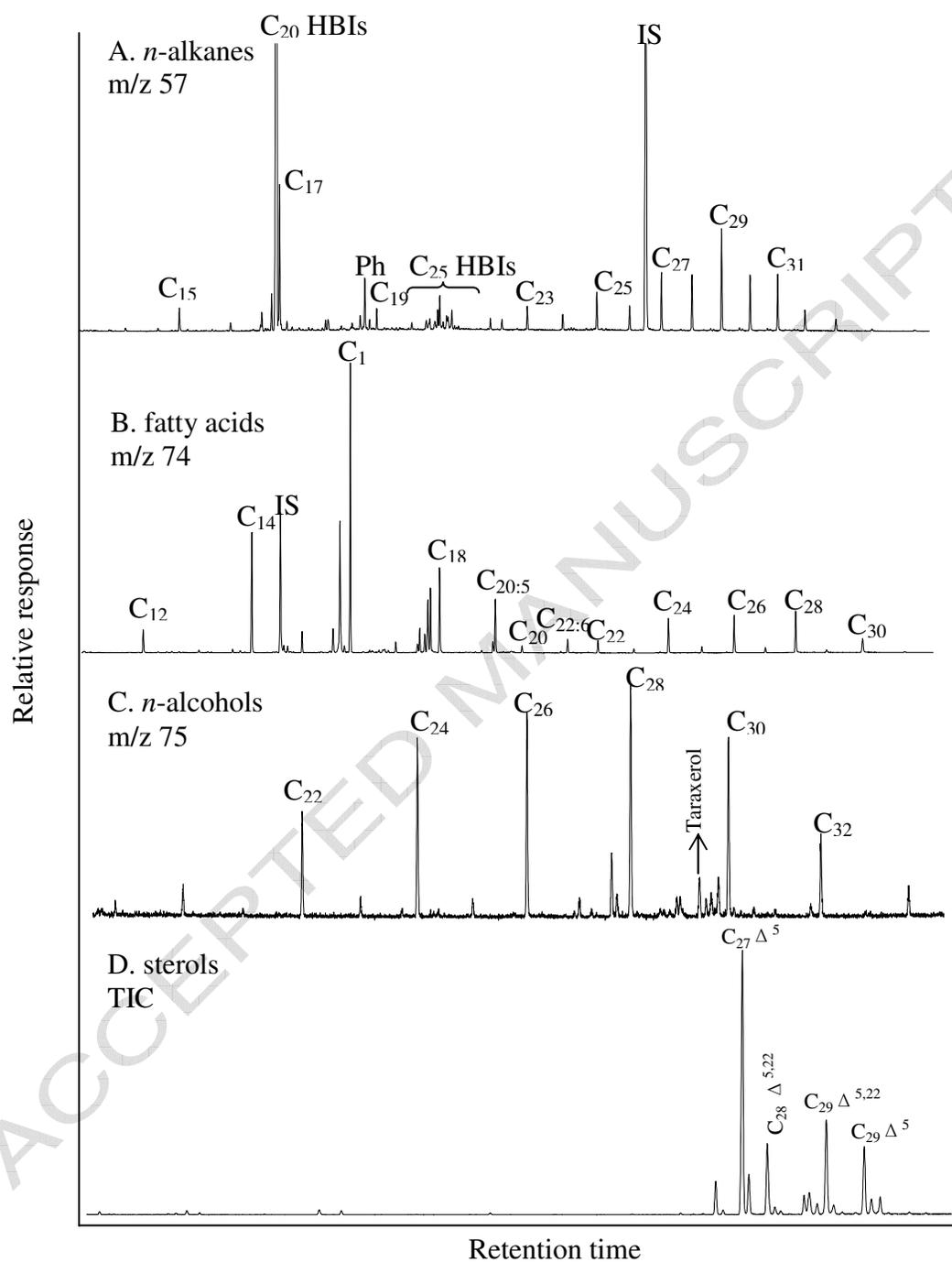
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552 **Figure 1**

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555 Fig. 2

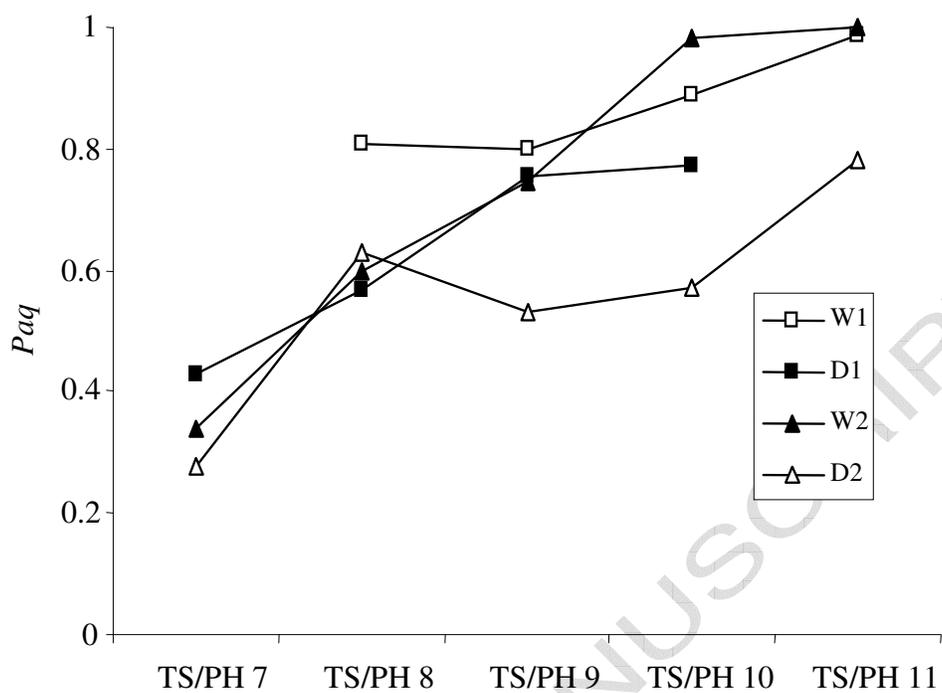


Fig. 3

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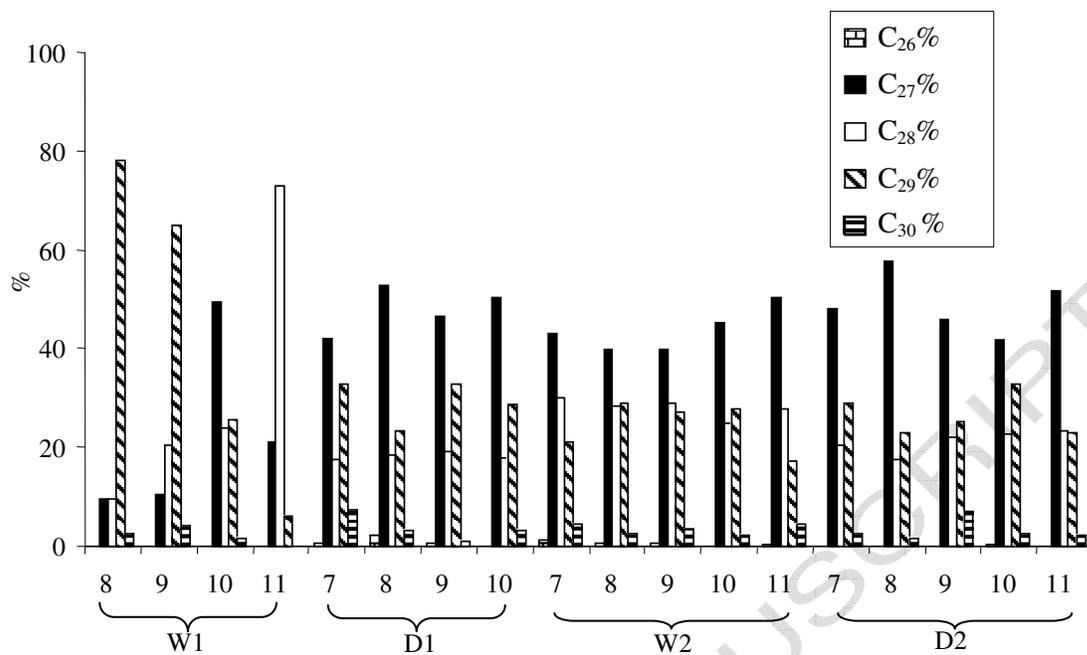


Fig. 4

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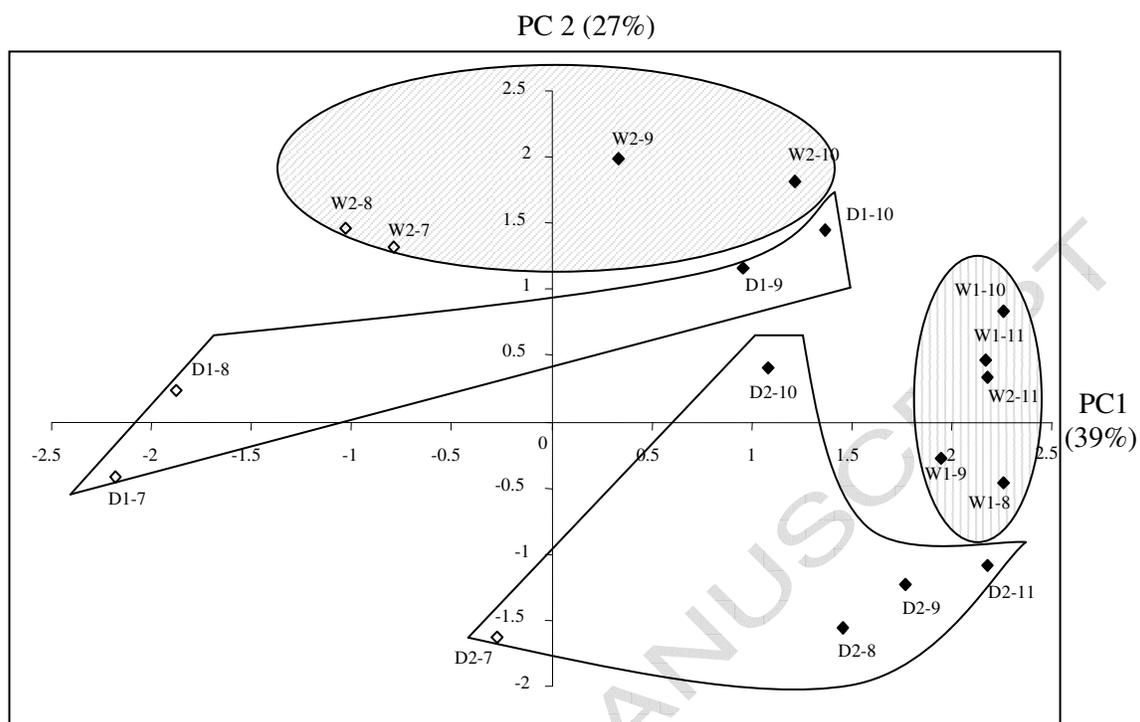


Fig. 5

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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
<i>n</i> -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
<i>Paq</i>	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
<i>Cmax</i>	C ₁₇	C ₁₇	C ₁₅	C ₂₃	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
<i>n</i> -Alkanols																		
Total	16	59	48	29	1220	406	41	63	122	218	80	203	155	143	130	41	177	30
<i>Cmax</i>	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

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. C_{max}: 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-C₁₅ + C₁₇ fatty acids indicative of bacterial contributions. A/B = the ratio of C_{20:5} over C_{22:6} fatty acids. nd = not detected

Table 2

	TS/Ph 7		TS/Ph 8		TS/Ph 9		TS/Ph 10		TS/Ph 11	
<i>n</i> -alkane	POM	Sed.	POM	Sed.	POM	Sed.	POM	Sed.	POM	Sed.
<i>Paq</i>	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
<i>n</i> -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.