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## Lipid biomarker record in surface sediments at three sites of contrasting productivity in the tropical North Eastern Atlantic

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## Abstract

Selected lipid biomarkers were analyzed in modern aerobic surface sediments from the tropical NE Atlantic off the Mauritanian coast, in the frame of the JGOFS EUMELI program. This paper explores how sedimentary molecular proxies record productivity and vascular plant inputs. Dry weight-normalized concentrations and TOC-normalized concentrations of biomarkers poorly matched the gradient of higher-plant inputs and of primary productivity. In contrast, mass accumulation rates of long-chain *n*-alkanols and *n*-fatty acids (80–710 and 210–1750  $\mu$ g m<sup>-2</sup> yr<sup>-1</sup>, respectively) showed good agreement with dust inputs transported between 15 and 24°N by NE trade winds, whereas long-chain *n*-alkanes showed a distinct pattern. At the coastal site, *n*-alkanols relative to *n*-alkanes point to an increased degradation of terrigeneous waxes when going offshore. The cross-shelf C/N ratio poorly registered vascular plant inputs, most probably because denitrification influenced C/N values at the eutrophic site.

Mass accumulation rates of phytoplanktonic biomarkers declined from the eutrophic to the oligotrophic site, reflecting the primary productivity variation. Mass accumulation rates of highly branched isoprenoid hydrocarbons, C37 *n*-alkenones, *n*-alkyl diols and dinosterol varied from 3 to 410, 9 to 1600, 12 to 360 and 7 to 320  $\mu$ g m<sup>-2</sup> yr<sup>-1</sup>, respectively. They target the productivity of *Haslea*-type diatoms, coccolithophorids, eustigmatophytes and dinoflagellates. While the results encourage the development of molecular proxies of palaeoproductivity and of palaeophytocommunities, progress is still needed to deconvolute the impact of degradation on mass accumulation rates and to move towards quantitative calibrations. © 2007 Elsevier B.V. All rights reserved.

Keywords: North Eastern tropical Atlantic; Hydrocarbons; n-Alkenones; n-Alkanols; n-Alkyl diols; Sterols; Higher plants; Primary productivity

## 1. Introduction

Marine sediments are sinks for organic carbon produced by marine phytoplankton and land plants, the latter by aeolian and river transport. Lipid biomarkers in marine sediments can be used to infer past variation of important drivers of the climate system. For instance, higher-plant cuticles contain waxes, corresponding to long-chain *n*-alkanes, *n*-alcohols and *n*-fatty acids, which are transported over remote ocean areas by aerosols (Simoneit, 1977; Simoneit et al., 1991, 1977). These lipids preserved in sediments have helped to reconstruct past variations of land vegetation coverage combined with wind direction and intensities (Simoneit and Eglinton, 1977; Poynter et al., 1989; Sicre et al., 2000; Pancost and Boot, 2004). Community structure of

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 $<sup>0304\</sup>text{-}4203/\$$  - see front matter @ 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.marchem.2007.10.002

## Table 1 Benthic characteristics and bulk composition of the studied sediments at the three EUMELI sites

Primary productivity (mg C m <sup>-2</sup> yr <sup>-1</sup> ) $47^{a}$ ; 100 <sup>b</sup> $125^{a}$ ; 250 <sup>b</sup> $47^{a}$ ; 100 <sup>b</sup> Bottom currents       20       5       3         Mean speed (cm s <sup>-1</sup> ) <sup>c.d</sup> 20       5       3         Sediment dynamics and characteristics       40       15       10         Sediment dynamics and characteristics       0.5       0.5         Measured <sup>1-1</sup> / <sub>2</sub> b <sup>-1</sup> b <sup>-1</sup> 0.5       0.68         Bioturbation rates (cm <sup>2</sup> s <sup>-1</sup> ) <sup>g</sup> (50–200) 10 <sup>-9</sup> (30–70) 10 <sup>-9</sup> (0.3–0.6) 10 <sup>-9</sup> Mixing layer thickness (cm <sup>0</sup> s <sup>-1</sup> ) <sup>g</sup> 12–15       8–9       2         Annual OC flux at the sediment interface (g C m <sup>-2</sup> yr <sup>-1</sup> ) <sup>h</sup> 6       1.8       0.4         CaCO3, (%)       12–15       8–9       2         Dissolved SiO <sub>2</sub> in interstitial waters at 30 cm depth (mmol L <sup>-1</sup> ) <sup>g</sup> 350       250       80         Sample location and bulk content       E       ED       M1       M2       O1       O2         EUMELI Sample code       KGS37       KTB9       KGS11       KTB6       KTB10       KTB3         Latitude       20°28.42'N       20°31.97'N       18°30.17'N       18°31.96'N       21°0.51'N       21°0.61'N         Loggin carbon (mg g <sup>-1</sup> )		Eutrophic site			Mesotrophic site			Oligotrophic site				
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Primary productivity (mg C m <sup>-2</sup> yr <sup>-1</sup> )		47 <sup>a</sup> ; 100 <sup>b</sup>			125 <sup>a</sup> ; 250 <sup>b</sup>			47 <sup>a</sup> ; 100 <sup>b</sup>			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Bottom currents											
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Mean speed (cm $s^{-1}$ ) <sup>c, d</sup>		20			5				3		
Sediment dynamics and characteristics         Accumulation rates (cm/1000 yr) <sup>e</sup> 4.4       1.5       0.5         Measured <sup>210</sup> Pb vertical fluxes/expected flux near the sea floor <sup>f</sup> $5.3-6.3$ 1.18       0.68         Bioturbation rates (cm <sup>2</sup> s <sup>-1</sup> ) <sup>g</sup> (50-200) 10 <sup>-9</sup> (30-70) 10 <sup>-9</sup> (0.3-0.6) 10 <sup>-9</sup> Mixing layer thickness (cm) <sup>g</sup> 12-15       8-9       2         Annual OC flux at the sediment interface (g C m <sup>-2</sup> yr <sup>-1</sup> ) <sup>h</sup> 6       1.8       0.4         CaCO <sub>3</sub> (%)       40 <sup>e</sup> ; 45 <sup>i</sup> 62 <sup>e</sup> ; 65 <sup>i</sup> 72 <sup>e</sup> Dissolved SiO <sub>2</sub> in interstitial waters at 30 cm depth (mmol L <sup>-1</sup> ) <sup>g</sup> 350       250       80         Sample location and bulk content       EU       KGS37       KTB9       KGS11       KTB6       KTB10       KTB10         Latitude       20°28.42′N       18°30.17′N       18°30.17′N       18°31.07′N       21°02.51′N       21°00.61′N         Longitude       1069       2030       3124       3121       4593       4589         Organic carbon (mg g <sup>-1</sup> )       0.83       1.56       0.42       0.33       0.32       0.32       2.33-2.69 <sup>d</sup> CN weight ratio (relative units)       21.1       16.3       8.1       12.4       4.6-8.9<	Max speed (cm s <sup><math>-1</math></sup> ) <sup>c, d</sup>		40			15				10		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Sediment dynamics and characteristics											
$\begin{array}{l c c c c c c c c c c c c c c c c c c c$	Accumulation rates (cm/1000 yr) <sup>e</sup>		4.4			1.5				0.5		
Bioturbation rates (cm <sup>2</sup> s <sup>-1</sup> ) <sup>g</sup> (50–200) 10 <sup>-9</sup> (30–70) 10 <sup>-9</sup> (0.3–0.6) 10 <sup>-9</sup> Mixing layer thickness (cm) <sup>g</sup> (homogeneous layer)       (homogeneous layer)       (sediment depth 0–2 cm)         Annual OC flux at the sediment interface (g C m <sup>-2</sup> yr <sup>-1</sup> ) <sup>h</sup> 6       1.8       0.4         CaCO <sub>3</sub> (%)       40 <sup>e</sup> ; 45 <sup>i</sup> 62 <sup>e</sup> ; 65 <sup>i</sup> 72 <sup>e</sup> Dissolved SiO <sub>2</sub> in interstitial waters at 30 cm depth (mmol L <sup>-1</sup> ) <sup>g</sup> 350       250       80         Sample location and bulk content       ES       ED       M1       M2       O1       O2         EUMELI Sample code       KGS37       KTB9       KGS11       KTB6       KTB10       KTB3         Latitude       20 <sup>-2</sup> 28.42 <sup>·</sup> N       20 <sup>o</sup> 31.97 <sup>·</sup> N       18 <sup>o</sup> 30.17 <sup>·</sup> N       18 <sup>o</sup> 31.96 <sup>·</sup> N       21 <sup>o</sup> 02.51 <sup>·</sup> N       1 <sup>o</sup> 13.75 <sup>·</sup> V         Depth (m)       1069       2030       3124       3121       4593       4589         Organic carbon (mg <sup>-1</sup> )       0.83       1.56       0.42       0.33       0.32       0.29         C/N weight ratio (relative units)       21.1       16.3       8.1       12.4       7.6       8.5         Epree lipids/TOC (%) <sup>k</sup> 3.5       5.4       4.6–8.9       3.7       3.46–9.96     <	Measured <sup>210</sup> Pb vertical fluxes/expected flux near the sea floor <sup>f</sup>		5.3-6.3			1.18				0.68		
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Bioturbation rates $(cm^2 s^{-1})^g$	$(50-200) 10^{-9}$			$(30-70) \ 10^{-9}$			$(0.3-0.6) 10^{-9}$				
Mixing layer thickness (cm) <sup>g</sup> 12–15       8–9       2         Annual OC flux at the sediment interface (g C m <sup>-2</sup> yr <sup>-1</sup> ) <sup>h</sup> 6       1.8       0.4         CaCO <sub>3</sub> (%)       40°; 45 <sup>i</sup> 62°; 65 <sup>i</sup> 72°         Dissolved SiO <sub>2</sub> in interstitial waters at 30 cm depth (mmol L <sup>-1</sup> ) <sup>g</sup> 350       250       80         Sample location and bulk content       ES       ED       M1       M2       O1       O2         EUMELI Sample code       KGS37       KTB9       KGS11       KTB6       KTB10       KTB3         Latitude       20°28.42'N       20°31.97'N       18°30.17'N       18°31.96'N       21°02.51'N       21°0.061'N         Longitude       1069       2030       3124       3121       4593       4589       Organic carbon (mg g <sup>-1</sup> )       17.48       25.36       27.0 <sup>j</sup> 3.44       4.09       3.73–4.29 <sup>d</sup> 2.0 <sup>j</sup> 2.42       2.46       2.33–2.69 <sup>d</sup> Organic carbon (mg g <sup>-1</sup> )       0.83       1.56       0.42       0.33       0.32       0.29       2.0 <sup>j</sup> C/N weight ratio (relative units)       21.1       16.3       8.1       12.4       7.6       8.5         E/Free lipids/TOC (%) <sup>k</sup> 3.5       5.4       4.6–8.9		(h	(homogeneous layer)			(homogeneous layer)			(sediment depth $0-2$ cm)			
Annual OC flux at the sediment interface (g C m <sup>-2</sup> yr <sup>-1</sup> ) <sup>h</sup> 6       1.8       0.4         CaCO <sub>3</sub> (%)       40°; 45°       62°; 65°       72°         Dissolved SiO <sub>2</sub> in interstitial waters at 30 cm depth (mmol L <sup>-1</sup> ) <sup>g</sup> 350       250       80         Sample location and bulk content       ES       ED       M1       M2       O1       O2         EUMELI Sample code       KGS37       KTB9       KGS11       KTB6       KTB10       KTB3         Latitude       20°28.42'N       20°31.97'N       18°30.17'N       18°31.96'N       21°02.51'N       21°00.61'N         Logitude       18°04.61'W       18°35.90'W       20°59.71'W       21°03.12'W       31°11.39'W       31°13.75'W         Depth (m)       1069       2030       3124       3121       4593       4589         Organic carbon (mg g <sup>-1</sup> )       0.83       1.56       0.42       0.33       0.32       0.29         C/N weight ratio (relative units)       21.1       16.3       8.1       12.4       7.6       8.5 <u>∑</u> Free lipids/TOC (%) <sup>k</sup> 3.5       5.4       4.6–8.9       3.7       3.46–9.96	Mixing layer thickness (cm) <sup>g</sup>	<sup>*</sup>	12–15			8-9			2			
CaCO3 (%) Dissolved SiO2 in interstitial waters at 30 cm depth (mmol $L^{-1}$ )g $40^{e}$ ; $45^{i}$ $350$ $62^{e}$ ; $65^{i}$ $250$ $72^{e}$ $80$ Sample location and bulk contentSample location and bulk contentESEDM1M2O1O2EUMELI Sample codeKGS37KTB9KGS11KTB6KTB10KTB3Latitude $20^{\circ}28.42'N$ $20^{\circ}31.97'N$ $18^{\circ}30.17'N$ $18^{\circ}31.96'N$ $21^{\circ}02.51'N$ $21^{\circ}00.61'N$ Longitude $18^{\circ}04.61'W$ $18^{\circ}35.90'W$ $20^{\circ}59.71'W$ $21^{\circ}02.51'N$ $21^{\circ}00.61'N$ Longitude $1069$ $2030$ $3124$ $3121$ $4593$ $4589$ Organic carbon (mg g^{-1}) $17.48$ $25.36$ $27.0^{i}$ $3.44$ $4.09$ $3.73-4.29^{d}$ $2.0^{j}$ $2.42$ $2.46$ $2.33-2.69^{d}$ Organic nitrogen (mg g^{-1}) $0.83$ $1.56$ $0.42$ $0.33$ $0.32$ $0.29$ C/N weight ratio (relative units) $21.1$ $16.3$ $8.1$ $12.4$ $7.6$ $8.5$ $\Sigma$ Free lipids/TOC (%) k $3.5$ $5.4$ $4.6-8.9$ $3.7$ $3.46-9.96$	Annual OC flux at the sediment interface $(g C m^{-2} yr^{-1})^h$		6			1.8				0.4		
Dissolved SiO2 in interstitial waters at 30 cm depth $(mmol L^{-1})^g$ 35025080Sample location and bulk contentESEDM1M2O1O2EUMELI Sample codeKGS37KTB9KGS11KTB6KTB10KTB3Latitude20°28.42'N20°31.97'N18°30.17'N18°31.96'N21°02.51'N21°00.61'NLongitude18°04.61'W18°35.90'W20°59.71'W21°03.12'W31°11.39'W31°13.75'WDepth (m)106920303124312145934589Organic carbon (mg g <sup>-1</sup> )17.4825.3627.0 <sup>j</sup> 3.444.093.73-4.29 <sup>d</sup> 2.0 <sup>j</sup> 2.422.462.33-2.69 <sup>d</sup> C/N weight ratio (relative units)21.116.38.112.47.68.52.544.6-8.93.73.46-9.96 $\Sigma$ Free lipids/TOC (%) k3.55.44.6-8.93.73.46-9.963.73.46-9.96	CaCO <sub>3</sub> (%)		40°; 45 <sup>i</sup>			62°; 65 <sup>i</sup>				72 °		
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Sample nameESEDM1M2O1O2EUMELI Sample codeKGS37KTB9KGS11KTB6KTB10KTB3Latitude $20^{\circ}28.42'N$ $20^{\circ}31.97'N$ $18^{\circ}30.17'N$ $18^{\circ}31.96'N$ $21^{\circ}02.51'N$ $21^{\circ}00.61'N$ Longitude $18^{\circ}04.61'W$ $18^{\circ}35.90'W$ $20^{\circ}59.71'W$ $21^{\circ}03.12'W$ $31^{\circ}11.39'W$ $31^{\circ}13.75'W$ Depth (m) $1069$ $2030$ $3124$ $3121$ $4593$ $4589$ Organic carbon (mg g <sup>-1</sup> ) $17.48$ $25.36$ $27.0^{j}$ $3.44$ $4.09$ $3.73-4.29^{d}$ $2.0^{j}$ $2.42$ $2.46$ $2.33-2.69^{d}$ Organic nitrogen (mg g <sup>-1</sup> ) $0.83$ $1.56$ $0.42$ $0.33$ $0.32$ $0.29$ C/N weight ratio (relative units) $21.1$ $16.3$ $8.1$ $12.4$ $7.6$ $8.5$ $\Sigma$ Free lipids/TOC (%) <sup>k</sup> $3.5$ $5.4$ $4.6-8.9$ $3.7$ $3.46-9.96$	Sample location and bulk content											
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Latitude $20^{\circ}28.42'N$ $20^{\circ}31.97'N$ $18^{\circ}31.17'N$ $18^{\circ}31.96'N$ $21^{\circ}02.51'N$ $21^{\circ}00.61'N$ Longitude $18^{\circ}04.61'W$ $18^{\circ}35.90'W$ $20^{\circ}59.71'W$ $21^{\circ}03.12'W$ $31^{\circ}11.39'W$ $31^{\circ}13.75'W$ Depth (m) $1069$ $2030$ $3124$ $3121$ $4593$ $4589$ Organic carbon (mg g <sup>-1</sup> ) $17.48$ $25.36$ $27.0^{j}$ $3.44$ $4.09$ $3.73-4.29^{d}$ $2.0^{j}$ $2.42$ $2.46$ $2.33-2.69^{d}$ Organic nitrogen (mg g <sup>-1</sup> ) $0.83$ $1.56$ $0.42$ $0.33$ $0.32$ $0.29$ C/N weight ratio (relative units) $21.1$ $16.3$ $8.1$ $12.4$ $7.6$ $8.5$ $\Sigma$ Free lipids/TOC (%)^k $3.5$ $5.4$ $4.6-8.9$ $3.7$ $3.46-9.96$	EUMELI Sample code	KGS37	KTB9		KGS11	KTB6			KTB10	KTB3		
Longitude $18^{\circ}04.61'W$ $18^{\circ}35.90'W$ $20^{\circ}59.71'W$ $21^{\circ}03.12'W$ $31^{\circ}11.39'W$ $31^{\circ}13.75'W$ Depth (m) $1069$ $2030$ $3124$ $3121$ $4593$ $4589$ Organic carbon (mg g <sup>-1</sup> ) $17.48$ $25.36$ $27.0^{\text{ j}}$ $3.44$ $4.09$ $3.73-4.29^{\text{ d}}$ $2.0^{\text{ j}}$ $2.42$ $2.46$ $2.33-2.69^{\text{ d}}$ Organic nitrogen (mg g <sup>-1</sup> ) $0.83$ $1.56$ $0.42$ $0.33$ $0.32$ $0.29$ C/N weight ratio (relative units) $21.1$ $16.3$ $8.1$ $12.4$ $7.6$ $8.5$ $\Sigma$ Free lipids/TOC (%) k $3.5$ $5.4$ $4.6-8.9$ $3.7$ $3.46-9.96$	Latitude	20°28.42′N	20°31.97′N		18°30.17′N	18°31.96′N			21°02.51′N	21°00.61′N		
Depth (m)106920303124312145934589Organic carbon (mg $g^{-1}$ )17.4825.3627.0 j3.444.09 $3.73-4.29^{d}$ $2.0^{j}$ $2.42$ $2.46$ $2.33-2.69^{d}$ Organic nitrogen (mg $g^{-1}$ )0.831.560.420.330.320.29C/N weight ratio (relative units)21.116.38.112.47.68.5 $\Sigma$ Free lipids/TOC (%) k3.55.44.6-8.93.73.46-9.96	Longitude	18°04.61′W	18°35.90'W		20°59.71′W	21°03.12′W			31°11.39′W	31°13.75′W		
Organic carbon (mg $g^{-1}$ )17.4825.3627.0 j3.444.09 $3.73-4.29^{d}$ $2.0 j$ $2.42$ $2.46$ $2.33-2.69^{d}$ Organic nitrogen (mg $g^{-1}$ )0.831.560.420.330.320.29C/N weight ratio (relative units)21.116.38.112.47.68.5 $\Sigma$ Free lipids/TOC (%) k3.55.44.6-8.93.73.46-9.96	Depth (m)	1069	2030		3124	3121			4593	4589		
Organic nitrogen (mg $g^{-1}$ )       0.83       1.56       0.42       0.33       0.32       0.29         C/N weight ratio (relative units)       21.1       16.3       8.1       12.4       7.6       8.5 $\Sigma$ Free lipids/TOC (%) k       3.5       5.4       4.6–8.9       3.7       3.46–9.96	Organic carbon (mg $g^{-1}$ )	17.48	25.36	27.0 <sup>j</sup>	3.44	4.09	$3.73 - 4.29^{d}$	2.0 <sup>j</sup>	2.42	2.46	2.33-2.69 <sup>d</sup>	
C/N weight ratio (relative units)       21.1       16.3       8.1       12.4       7.6       8.5 $\Sigma$ Free lipids/TOC (%) <sup>k</sup> 3.5       5.4       4.6–8.9       3.7       3.46–9.96	Organic nitrogen (mg $g^{-1}$ )	0.83	1.56		0.42	0.33			0.32	0.29		
∑Free lipids/TOC (%) <sup>k</sup> 3.5         5.4         4.6-8.9         3.7         3.46-9.96	C/N weight ratio (relative units)	21.1	16.3		8.1	12.4			7.6	8.5		
	$\sum$ Free lipids/TOC (%) <sup>k</sup>		3.5			5.4	4.6-8.9			3.7	3.46-9.96	

<sup>a</sup> Auffret et al., 1992.

<sup>b</sup> Morel, 1996.

<sup>c</sup> Cosson et al., 1997.

<sup>d</sup> Galéron et al., 2000.

<sup>e</sup> Auffret et al., 1992.

<sup>f</sup> Legeleux et al., 1996.

<sup>g</sup> Legeleux et al., 1990. <sup>h</sup> Modelled by Rabouille et al., 1993. <sup>i</sup> Stein, 1991.

<sup>j</sup> Stein, 1991 (surface values). <sup>k</sup> From Relexans et al., 1996 (0–1 cm).

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