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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  $\mu\text{g m}^{-2} \text{yr}^{-1}$ , 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 and *n*-fatty acids predominated over long-chain *n*-alkanes. Cross-shelf changes in proportions of *n*-fatty acids and *n*-alkanols relative to *n*-alkanes point to an increased degradation of terrigenous 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  $\mu\text{g m}^{-2} \text{yr}^{-1}$ , 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.

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

	Eutrophic site		Mesotrophic site		Oligotrophic site				
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>				
<i>Bottom currents</i>									
Mean speed (cm s <sup>-1</sup> ) <sup>c,d</sup>	20		5		3				
Max speed (cm s <sup>-1</sup> ) <sup>c,d</sup>	40		15		10				
<i>Sediment dynamics and characteristics</i>									
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>				
	(homogeneous layer)		(homogeneous layer)		(sediment depth 0–2 cm)				
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>c</sup> ; 45 <sup>i</sup>		62 <sup>c</sup> ; 65 <sup>i</sup>		72 <sup>c</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									
Sample name	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			
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			
Depth (m)	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 nitrogen (mg g <sup>-1</sup> )	0.83	1.56	0.42	0.33	0.32	0.29	0.32	0.29	
C/N weight ratio (relative units)	21.1	16.3	8.1	12.4	7.6	8.5	7.6	8.5	
ΣFree 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., 1994.

<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).

planktonic foraminifers and of pelagic gastropods can be used to identify palaeoupwelling occurrence and extension (Thiede and Jünger, 1992). Specific algal lipids, including long-chain alkenones, *n*-alkane diols, highly branched hydrocarbons and phytosterols are biomarkers of marine phytoplankton and are another tool increasingly used to reconstruct marine palaeoproductivity (Hinrichs et al., 1999; Menzel et al., 2003; Álvarez et al., 2005; Zhao et al., 2006; Xu et al., 2006). The value of these biomarkers as palaeoproxies of productivity depends on our knowledge of the response of sedimentary biomarkers to environmental parameters. The pelagic–benthic coupling and the different resistance of molecular biomarkers to early diagenesis have an intrinsic influence on this response. These relationships can only be assessed in present-day oceanic conditions, where driving factors can be characterized. Studies relating lipids to marine productivity and wind systems in present-day marine sediments are however scarce (Prah et al., 2000), while a critical need for such documentation is shown by the increasing number of studies using lipid biomarkers to understand past palaeoproductivity and land changes.

In the frame of the French JGOFS program, EUMELI, three sites, defined by their markedly different productivity regime (Eutrophic, MEsotrophic and oLIgotrophic) (Table 1), were studied in the North Eastern Atlantic. The selected sites covered a cross-shelf productivity gradient from upwelling conditions to an oligotrophic regime. Together with the information on sedimentary redox parameters and benthic fauna they provide a framework to explore how lipid biomarkers record primary productivity and vascular plant inputs. The objective of the present paper is to provide fundamental knowledge for implementing the interpretation of the following proxies: long-chain *n*-alkanes, *n*-alcohols, *n*-fatty acids, as proxies for terrigenous inputs; *n*-alkyl diols, hydroxy ketones and sterols as indicators of phytoproductivity in the inter-tropical ocean. Besides these selected compounds, labile (polyunsaturated fatty acids, phospholipids) and bacterial lipids were also studied to assess the freshness of the sedimentary matter.

### 1.1. Regional settings and study site location

The major wind regimes driving the Eastern inter-tropical Atlantic climate are the low troposphere North East Trades (500–1500 m), stronger in winter, and the mid-tropospheric Saharian Air Layer (SAL, ca 3000 m), strongest in summer (Fig. 1). Even though dust inputs are episodic, they can account for important inputs of materials derived from the semi-arid and desert lands of Northern Africa, particularly during dust storms that are frequently observed over the ocean (e.g. 28 February 2000, <http://seawifs.gsfc.nasa.gov/SEAWIFS/HTML/dust.html>). The mid-tropospheric SAL, yielding the African Easterly Jet at its summer maximum, is another possible source of dust and pollen at the continental margin (Hooghiemstra, 1988). It blows seawards from the heart of the Sahara and is deflected to the Northwest above the trade wind layer. The Inter-Tropical Convergence Zone (ITCZ) is the boundary between the north-east trades and the Southerly trades and acts as a barrier against the N–S transport of dust and pollen grains. The main pollen production is from July to September during the local humid period (Hooghiemstra and Agwu, 1986), when the SAL reaches its maximum intensity and the ITCZ is at its northernmost position (Dupont, 1991).

The North East Trades establish a permanent coastal upwelling located between 14°N and 24°N, as indicated by low temperatures and high particulate organic carbon concentrations (Bishop, 1989). The hydrology of the Mauritanian upwelling area is influenced by the Canary Current which carries cool surface waters southwards to the coastal upwelling (Bricaud et al., 1987). The

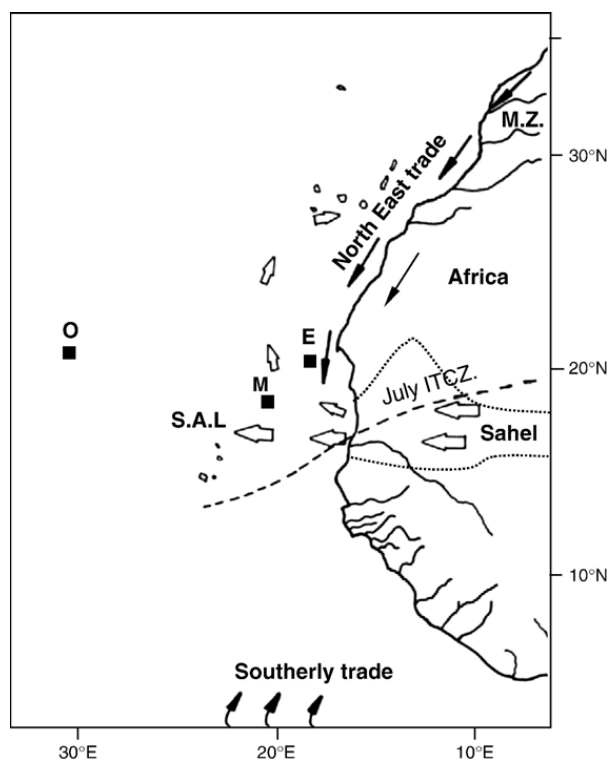


Fig. 1. Coring sites: E = eutrophic zone, M = mesotrophic zone, O = oligotrophic zone, M.Z. = Mediterranean zone. The dominant winds and kinds of vegetation are indicated: M.Z. = Mediterranean zone. The northernmost position of the Inter-tropical Convergence Zone (ITCZ) occurs in July–August. Its position in winter is close to the equator.

eutrophic site lies directly beneath one of the zones of major coastal upwelling, the mesotrophic site is located outside the upwelling area but in its vicinity, and the open marine oligotrophic site is on the abyssal plain, well away from the region of enhanced production. Primary productivity decreases four fold from the Eutrophic to the Oligotrophic site (Auffret et al., 1992; Morel 1996).

The study sites are located off the northeast African coast (Fig. 1). The eutrophic site lies on the continental slope at about 110 km west of Cape Blanc and covers depths from 1000 to 2030 m (Table 1). The mesotrophic site lies on the Cape Verde Terrace at about 500 km from the coast and is about 3100 m deep. The oligotrophic site is located on the Cape Verde abyssal plain, at 1650 km from the coast (A1 SM). Sedimentary characteristics are detailed in Cosson et al. (1997) at 4590 m depth.

## 2. Material and methods

### 2.1. Total organic carbon and nitrogen

The carbon and nitrogen content of sediments were determined by high temperature oxidation using a Shimadzu TOC 5000 analyzer. Carbonates were removed with phosphoric acid (10 M) prior to analysis to achieve full removal of carbonate from the carbonaceous ooze from the mesotrophic and oligotrophic sites. The detection limit of the measurement was 0.4  $\mu\text{MC}$  and the accuracy  $\pm 2\%$ .

### 2.2. Sampling, extraction and analysis

Two cores from each EUMELI site were collected from separate drops. Two drops at the Eutrophic site were carried out at distinct locations and distinct depths: 1069 and 2030 m (Table 1) to cover the variability of the site. The samples will be designed by ES and ED for Eutrophic shallow and Eutrophic deep (Table 1). At the mesotrophic and oligotrophic sites, two drops were carried out at close distance and similar depths, and can be considered as replicates for the area (Table 1). The cores were collected with a SMBA multicorer (Barnett et al., 1984) that provided cores with an undisturbed sediment/water interface (Legeleux et al., 1994) and with a modified 50  $\times$  50 cm USNEL boxcorer (Hessler and Jumars, 1974), equipped with large top-flaps to minimize the bow-wave effect. The first half-centimeter of each core were sliced and macro- and megafauna, if present, was removed. The sediment slices were immediately stored frozen at  $-70^\circ\text{C}$  until the laboratory, where they were frozen-dried and homogenized by short-term grinding and stored under argon at  $-20^\circ\text{C}$  until analysis.

Lipids were extracted according to a modified one-phase method (Bligh and Dyer, 1959), using dichloromethane. A blank was run to check the total extraction procedure and no noticeable contaminants were observed. The details of ana-

lytical procedure used for the lipid extraction and analysis were described in Laureillard et al. (1997) and Pinturier-Geiss et al. (2001). Total lipid extracts were analyzed for lipid classes by thin layer chromatography with flame ionization detection (TLC-FID) using an Iatroscan MK-5 analyzer (Iatron, Japan). Quantitation was carried out by external calibration for each lipid class. Aliquots of the total lipid extracts spiked with the internal standards (tricosanoic acid, perdeuterated *n*-tetracosane, and androstanol) were converted into methyl esters using toluene- $\text{BF}_3$  (14%) in methanol (1:2, v:v) under nitrogen (1 h,  $65^\circ\text{C}$ ). After extraction and drying, the lipid extracts were separated into three fractions using a small column (5 mm i.d.) filled with 2 g of 10% deactivated silica gel 40 (Merck, mesh size 0.063–0.200). The first fraction, eluted with 7 mL of hexane, contained hydrocarbons. The second fraction, eluted with 5 mL of hexane–diethyl ether (9:1, v:v), contained fatty acid methyl esters (FAME) and long-chain alkenones. The third fraction, eluted with 10 mL of hexane–diethyl ether (1:1, v:v), contained alcohols, sterols, *n*-alkyl diols and hydroxy ketones. This latter fraction was transformed into the corresponding TMS ether derivatives by treatment ( $80^\circ\text{C}$ , 1 h) with a mixture of bis(trimethylsilyl)-trifluoroacetamide and trimethylchlorosilane (99:1, Silyl-99, Macherey-Nagel, Germany). The hydrocarbons were analyzed using a Hewlett-Packard HP5890 gas chromatograph (GC) fitted with a CPSil 8 (Chrompack) column (50 m, 0.32 mm i.d., 0.25  $\mu\text{m}$  film thickness). The oven temperature was programmed from  $60^\circ\text{C}$  (3 min, isothermal) to  $100^\circ\text{C}$   $25^\circ\text{C min}^{-1}$ , then to  $300^\circ\text{C}$  at  $3^\circ\text{C min}^{-1}$  (80 min hold time), namely:  $60^\circ(3')/25^\circ\text{min}^{-1}/100^\circ/3^\circ\text{min}^{-1}/300^\circ(80')$ . FAMES were analyzed on a polar BPX70 column (SGE, 30 m, 0.22 mm, 0.25  $\mu\text{m}$ ) on a Varian 3300 chromatograph, using the following oven temperature program:  $60^\circ(3')/25^\circ\text{min}^{-1}/100^\circ/1^\circ\text{min}^{-1}/180^\circ/2^\circ\text{min}^{-1}/195^\circ/3^\circ\text{min}^{-1}/260^\circ(>60')$ . The FAMES were also analyzed on a non-polar DB5 (J&W, 30 m, 0.25 mm, 0.25  $\mu\text{m}$ ) column for confirmation of identity and for the quantitation of long-chain FAMES. The temperature program of the chromatograph (HP 5890) oven was as follows:  $60^\circ/25^\circ\text{min}^{-1}/100^\circ/2^\circ\text{min}^{-1}/300^\circ(>60\text{ min})$ . Long-chain ketones were analyzed using a non-polar column (HP5, 50 m, 0.32 mm, 0.17  $\mu\text{m}$ ) and a Hewlett-Packard HP5890 chromatograph, with the oven temperature rising from  $60^\circ\text{C}$  to  $100^\circ\text{C}$  at  $25^\circ\text{C min}^{-1}$ , then to  $220^\circ\text{C}$  at  $5^\circ\text{min}^{-1}$  and to  $300^\circ\text{C}$  at  $10^\circ\text{min}^{-1}$ , followed by a temperature hold of 30 min. Alcohols, sterols, alkyl diols and hydroxy alkenones were analyzed on a non-polar column (DB5, 50 m, 0.32 mm, 0.25  $\mu\text{m}$ ) and a Carlo-Erba 5300HR chromatograph, using the following oven temperature program:  $60^\circ(1\text{ min})/25^\circ\text{min}^{-1}/100^\circ/15^\circ\text{min}^{-1}/150^\circ/3^\circ\text{min}^{-1}/300^\circ(>60\text{ min})$ . All the GC were equipped with an on-column injector and a FID detector at  $320^\circ\text{C}$  and helium was used as carrier gas. Based on replicate analyses on other samples (Laureillard, unpublished data), the repeatability of results expressed in concentrations was  $\pm 10\%$ .

GC coupled to mass spectrometry (MS) and co-injection with authentic compounds of known structures confirmed the

identities of the major components. GC/MS analyses of lipids were performed on a Varian 3400GC coupled to a Varian Saturn ion trap mass spectrometer. MS operating conditions were: ion source temperature of 140 °C, electron impact energy of 70 eV, the scanned mass range was 40–600 amu at 0.6 scan s<sup>-1</sup>. The chromatographic columns used were DB5 or BPX70 with oven programs as previously described.

### 2.3. Nomenclature

Aliphatic hydrocarbons are designated by C<sub>x</sub> where *x* is the number of C atoms of the chain. Aliphatic alcohols are labelled C<sub>x</sub>OH, with *x* being the total number of C atoms. The nomenclature used for fatty acids is illustrated by 22:6*n*-3, where 22 is the total number of carbon atoms, 6 is the number of double bonds and 3 is the position of the double bond nearest the methyl end, and the others are regularly spaced by methylene groups.

### 2.4. Calculation of molecular compositional parameters

Molecular composition of *n*-alkanes, *n*-alkanols and *n*-alkanoic acids are appraised by the Carbon Preference Index (CPI) and Average Chain Length (ACL). The formulae used for calculation of these indices, as well as for computing the diol index, the keto-ol index and the alkanol preservation index are discussed and given in Annex 1 (Supplementary materials).

### 2.5. Calculation of mass accumulation rates

The EUMELI program (JGOFS-France) characterized the sampled sediments by a consortium of physical, chemical and biological core data (PROOF database, [http://www.obsvlf.fr/cd\\_rom\\_dmtt/eu\\_main.htm](http://www.obsvlf.fr/cd_rom_dmtt/eu_main.htm)). The organic carbon (OC) and

nitrogen fluxes at the water–sediment interface were calculated for each site using a one-dimensional model. The model balances particulate organic carbon accumulation in the sediment with electron acceptor profiles, their diffusion in the pore water and their advective fluxes (Rabouille et al., 1993). The computed organic carbon accumulations at each site reflect the differences in organic carbon fluxes measured 25 m above to the sea bed (Khrpounoff et al., 1998). Knowing OC fluxes of each surface sediment and their OC concentration at each site makes it possible to compute the mass accumulation rate for each surface sediment, which in turn allows conversion of biomarker concentrations (C<sub>i</sub> being the concentration in the first centimeter of surface sediment in µg of compounds per g of dry sediment weight) into mass accumulation rates (MAR<sub>i</sub> in µg of compounds per m<sup>2</sup> and per year) according to:

$$\text{MAR}_i = \frac{C_i \times \text{OC flux}}{\text{OC concentration}}.$$

## 3. Results

### 3.1. Bulk characteristics

The highest TOC values (17.5–25.4 mg g<sup>-1</sup>) were measured at the upwelling site while TOC concentrations fell at the mesotrophic, and further so, at the oligotrophic site (Table 1). Organic carbon contents of sediments from the oligotrophic site, 2.42–2.46 mg g<sup>-1</sup>, are in the typical range of open-ocean surface sediments (Santos et al., 1994; Schefuß et al., 2004; Gogou and Stephanou, 2004). The location of the eutrophic site sediments, under the upwelling, favors the sedimentation of fresh marine material. Typical C/N ratios of marine material rich in amino acids are 5.0–7.7 (Jasper and Gagosian, 1989; Westerhausen et al., 1993). This location also receives an important input of aeolian terrigenous material

Table 2

Concentrations of lipid classes in µg per g of dry weight (µg gdw<sup>-1</sup>), and relative composition in percent

	Eutrophic (ED)		Mesotrophic (M2)		Oligotrophic (O2)	
	(µg gdw <sup>-1</sup> )	(%)	(µg gdw <sup>-1</sup> )	(%)	(µg gdw <sup>-1</sup> )	(%)
Hydrocarbons	21	2.0	7.0	3.2	5.0	6.0
Wax esters	6.0	1.0	n.d.	n.d.	n.d.	n.d.
Methyl esters	4.0	n.d.	n.d.	n.d.	n.d.	n.d.
Free fatty acids (FFA)	46	5.0	20	9.0	8.0	9.0
Triacylglycero-esters	6.0	1.0	3.0	1.4	2.0	2.0
Aliphatic alcohols	6.0	1.0	4.0	1.8	n.d.	n.d.
Sterols	9.0	1.0	4.0	1.8	1.0	1.0
DiAcylGlycero-esters (DAG)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MonoAcylGlycero-esters (MAG)	n.d.	n.d.	10	4.5	7.0	8.0
Glycolipids and phospholipids	734	84	167	76	62	69
Chlorophylls	46	5.0	6.0	2.7	5.0	6.0
ΣLipids	878	3.0	221	3.2	90	2.0
ΣDegr=Σ(FFA+DAG+MAG)	46	5.0	30	13.5	15	17.0
ΣDeg/PL (%)		6.3		18		24
LI (%)		7.0		20		23

LI: Lipolysis Index (Goutx et al., 2003). LI=(Aliphatic alcohols+FFA+MAG+DAG)/(Triacylglycero-esters+Wax esters+Glycolipids+Phospholipids).

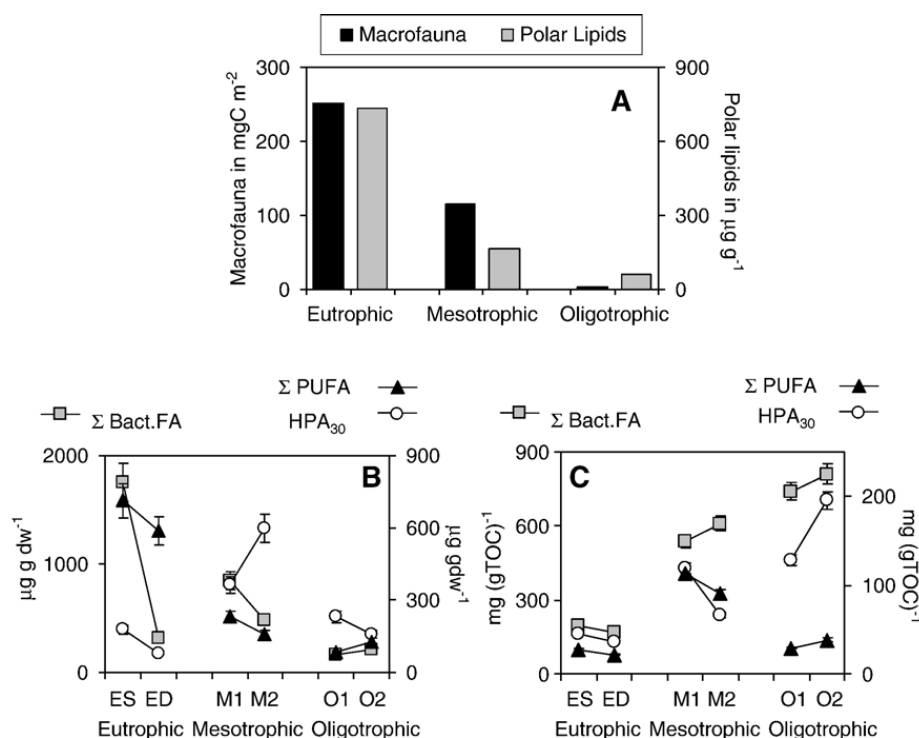


Fig. 2. Relationships of biomarkers related to the living benthic fauna at the three sites. A: concentration of summed phospholipids in mg (g of dry weight)<sup>-1</sup> and mean macrofauna concentration in mg of C per 10 cm<sup>-2</sup>, from Gáleron et al., 2000. B: concentrations of C<sub>30</sub> hopanoic acid (HPA<sub>30</sub>), summed polyunsaturated acids (ΣPUFA) and summed bacterial fatty acids (ΣBactFA = branched and cyclopentanoic acids + 18:1-*n*7 + 16:1-*n*5) in mg (g of dry weight)<sup>-1</sup>. C: same concentrations normalized to organic carbon (OC) and expressed as mg per g of OC. Error bars correspond to the analytical error.

(Hooghiemstra, 1988), of higher C/N value (20–100, Jasper and Gagosian, 1989). The C/N weight ratios of sediments from the eutrophic site, 21.1 and 16.3, are on the higher range of the literature values from productive sites (Uchida et al., 2005; Niggemann and Schubert, 2006) and takes decreasing values off coast (Table 1).

### 3.2. Lipid classes

Total lipid concentrations spanned a large concentration range and reflect the trophic gradient of the sites (Table 2). The polar lipids, phospholipids and glycolipids, are representative of living organisms whereas di-, and monoacylglycerol esters and free fatty acids are produced by the hydrolysis of the glyceride lipid classes and are rather associated to degradation (Goutx et al., 2003). Polar lipids largely dominated over other lipid classes in sediments from all studied trophic regimes (Table 2). The highest concentrations and percentages of polar lipids, involved in biomembrane structures, were observed in the eutrophic site and decreased at the oligotrophic site (Table 2). Concentrations of polar lipids displayed the same trend than faunal biomass over the trophic regime gradient (Fig. 2). Triacylglycerides and wax esters are animal lipids used for long-term energy storage; wax esters could also originate from higher plants and triacylglycerol-esters from algae. In sediments of the three sites, the Lipolysis Index (LI) proposed by Goutx et al. (2003) have much lower values

(Table 2) than those observed in decaying algal detritus, which vary from ca 0.05 to 0.85 (Goutx et al., 2003). This shift in both types of values is rather due to the different nature of both types of matrices than to a degradation signal. The sum of degradation components (di- and monoacylglycerides and free fatty acids) followed the general concentration trend and decreased from the eutrophic to the oligotrophic site. In contrast, their contribution to total lipids gradually rose versus decreasing trophic regime, from 5% at the eutrophic site to 17% at the oligotrophic site, indicating that the organic matter becomes more degraded offshore (Table 2).

### 3.3. Hydrocarbons

The aliphatic hydrocarbon fraction consists of several families of resolved compounds: *n*-alkanes, phytadienes and highly branched isoprenoid (HBI) polyenes. The contribution of land plant-derived hydrocarbons is indicated by the odd homologue preference of the C<sub>24</sub>–C<sub>35</sub> *n*-alkanes (Table 3). In samples from the eutrophic site, HBI and phytadienes related to autochthonous primary production dominated over long-chain *n*-alkanes originating from allochthonous terrestrial inputs (Fig. 3). In contrast, hydrocarbon profiles from the meso- and oligotrophic sites are dominated by the long-chain *n*-alkanes. The different families of hydrocarbons displayed distinct concentrations along the trophic gradient. Total hydrocarbon concentration, quantified by Iatroscan, decreased four fold from

Table 3  
Lipid characteristics of surficial sediments from sites E, M and O

	Eutrophic		Mesotrophic		Oligotrophic	
	ES	ED2	M1	M2	O1	O2
<b>Hydrocarbons</b>						
$\Sigma n$ -Alkanes $\geq C_{25}$ in $\mu\text{g gdw}^{-1}$	0.52	0.34	0.69	1.36	1.40	0.98
$C_{\text{max}}$	C31	C29	C31	C29–31	C31	C31
$\text{CPI}_{24-35}$	4.6	1.5	4.4	1.9	2.6	2.9
ACL	29.9	29.1	29.6	29.4	29.6	29.6
HBI in $\mu\text{g g}^{-1}$	1.21	0.505	0.072	0.095	0.021	0.033
Phytadienes in $\mu\text{g gdw}^{-1}$	1.08	0.27	0.11	0.045	0.015	0.012
<b>Fatty acids</b>						
$\Sigma$ Long-chain FA $\geq C_{24}$ in $\mu\text{g gdw}^{-1}$	5.1	1.4	1.6	1.1	1.0	1.3
$C_{\text{max}}$	C24–26	C24	C24–26	C24	C26	C26
$\text{CPI}_{21-31}$	6.0	7.6	3.3	4.8	3.4	3.2
16:1- <i>n</i> /16:0 (RU)	0.41	1.11	0.78	0.57	0.84	1.06
$\Sigma$ PUFA in $\mu\text{g gdw}^{-1}$	0.48	0.55	0.39	0.37	0.071	0.094
Bacterial FA <sup>a</sup> in $\mu\text{g gdw}^{-1}$	3.45	4.24	1.85	2.49	1.79	1.99
$C_{30}$ HPA in $\mu\text{g gdw}^{-1}$	0.8	0.91	0.41	0.27	0.31	0.48
<b><i>n</i>-Alkanols</b>						
$\Sigma n$ -Alkanols $\geq C_{24}$ in $\mu\text{g g}^{-1}$	2.1	2.5	0.44	0.37	0.50	0.79
$C_{\text{max}}$	C28	C28	C28	C28	C28	C28
$\text{CPI}_{23-32}$		7.5		5.3		5.0
<b>Sterol concentrations in <math>\mu\text{g gdw}^{-1}</math> and percent of total sterols in brackets</b>						
Sitosterol	0.86 (19%)	2.2 (31%)	0.37 (39%)	0.33 (36%)	0.12 (29%)	0.26 (54%)
Cholesterol	0.74 (17%)	1.5 (21%)	0.20 (21%)	0.18 (20%)	0.081 (20%)	0.088 (19%)
Dinosterol	0.93 (21%)	1.13 (24%)	0.087 (9%)	0.094 (10%)	0.043 (11%)	0.036 (8%)
Brassicasterol	1.07 (24%)	1.33 (12%)	0.170 (18%)	0.115 (13%)	0.080 (20%)	0.062 (13%)
Dehydrocholesterol	0.54 (12%)	0.73 (10%)	0.089 (9%)	0.074 (8%)	0.048 (12%)	0.032 (7%)
24-Methylenecholesterol	0.29 (7%)	0.26 (4%)	0.038 (4%)	0.11 (12%)	0.031 (8%)	n.d.
Sum of sterols	4.4	7.2	0.96	0.90	0.40	0.47
<b>Alkyl diols and hydroxy alkenones</b>						
$\Sigma$ Diols in $\mu\text{g gdw}^{-1}$	1.05	1.28	0.197	0.079	0.070	0.126
$\Sigma$ Ketols in $\mu\text{g gdw}^{-1}$	0.98	1.29	0.172	0.145	0.045	0.124
I-diols (RU)	83	84	87	86	95	94
I-ketols (RU)	58	62	81	66	85	87
<b>Alkenones</b>						
$\Sigma C_{37}$ alkenones in $\mu\text{g gdw}^{-1}$	2.75	6.62	0.690	0.565	0.057	0.118
Uk'37 (RU)	0.742	0.722	0.899	0.867	0.869	0.870
Temperature estimates <sup>b</sup>	20.4 °C	19.8 °C	25.2 °C	24.2 °C	24.2 °C	24.3 °C

Concentrations are given in  $\mu\text{g per g}$  of dry weight ( $\mu\text{g gdw}^{-1}$ ). RU: relative units.

<sup>a</sup>  $\Sigma$ Bacterial fatty acids=branched and cyclic FAMES+18:1*n*-7+16:1*n*-5.

<sup>b</sup> Temperatures estimated from Uk'37 and the [Prahl et al.'s \(1988\)](#) equation.

the eutrophic to the oligotrophic site (Table 2). Concentrations of hydrocarbons related to primary productivity, phytadienes and HBI, also followed this seaward decrease (Table 3). In contrast, long-chain *n*-alkane concentrations are lower at the eutrophic site and in one of the samples from the mesotrophic site.

The long-chain *n*-alkanes exhibited varying odd-to-even carbon number predominance. Most of the alkane patterns are characterized by maxima at  $C_{31}$  with an  $\text{ACL} \geq 29.4$  and  $\text{CPI}_{24-34} \geq 2.7$  (Table 1). CPI values showed a strong heterogeneity within sites with the highest values observed at one of the E and one of the M sites. Lower CPI (1.5–1.9) concurred with higher contribution of  $C_{29}$  relative to  $C_{31}$ . This signature

(samples ED and M2) could indicate the contribution of petroleum possibly from European/Mediterranean air brought by NE trade winds. However, other molecular fingerprints of petroleum contribution (hopane signature, unresolved complex material and phytane) could not be detected. Furthermore long-chain *n*-alkane concentrations in ED was lower than in the ES collected at the same site (Annex 2 in Supplementary Materials), which does not match the hypothesis of a petroleum contamination overprinting natural background alkanes. *n*-Alkane patterns of ED and M2 show similarities to those observed in aerosols transported by North East Trade winds to the EUMELI latitude (northernmost sample D1 in [Schefuß et al., 2003](#)), with respect to CPI (ca 2.4 in D1, 1.5 and

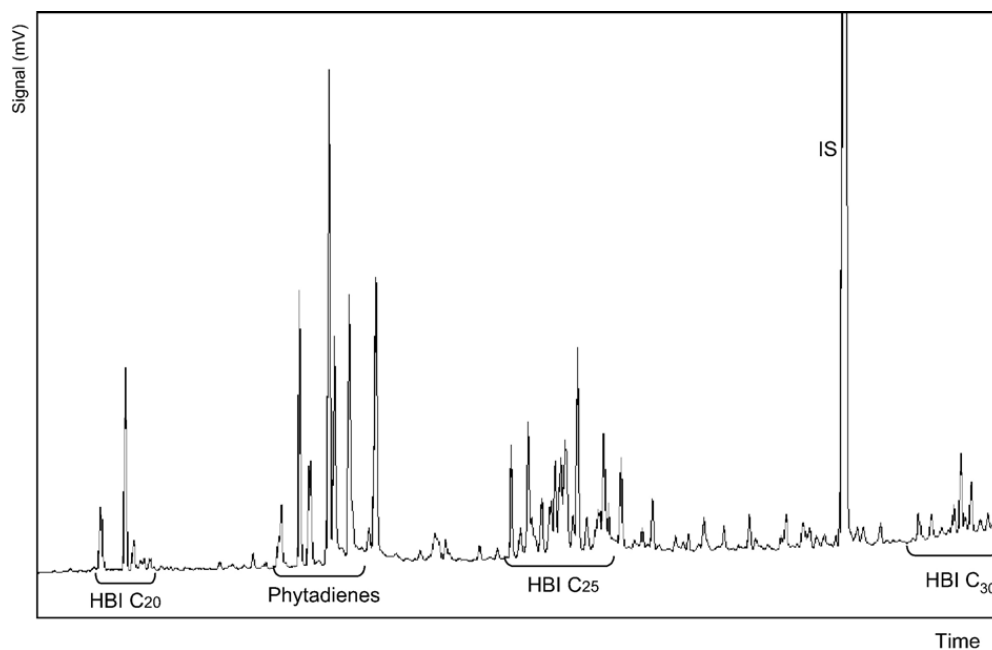


Fig. 3. Partial GC/MS spectra of hydrocarbons from the KGS 37 sample, at the eutrophic site.

1.9 in ED and M2) and  $C_{31}/C_{31}+C_{29}$  ratio (ca 0.48 in D1, 0.46 and 0.52 in ED and M2).

Phytadienes were identified by their characteristic ions in GC/MS ( $m/z$  68+82+123+278). They are degradation products of the phytol chain of chlorophylls, produced during herbivorous foraging or algal decay. Phytol dehydration leading to phytadiene is promoted by sample treatment at low pH values ( $\leq 4$ ), such as during transmethylation with  $BF_3$  (Grossi et al., 1996). When the same derivatization method as the one we used was applied to estuarine particles, the phytadienes produced were shown to be artefacts (from 0.012 to 1.08  $\mu g\ g^{-1}$ , Sadouni, 2002). Therefore phytadienes occurring in the sediments studied here are rather related to chlorophyll reaching the seafloor than to herbivory. Concentrations of phytadienes and of chlorophylls followed the same trend in the samples where both concentrations were determined (Tables 2 and 3).

HBI polyenes and HBI alkanes are widespread compounds of various sedimentary settings (Rowland and Robson, 1990) and occurred at the three studied sites. The only confirmed producers of HBI are diatoms, though some herbivorous zooplanktons have been suggested as other possible source (Cripps, 1995a). The first identified producer for  $C_{25}$  HBI was *Haslea ostrearia* (Volkman et al., 1994), but *Rhizosolenia setigera* was later assumed to be the main source for  $C_{25}$  and  $C_{30}$  HBI among diatoms (Schouten et al., 2000). The latter also synthesizes  $C_{35}$  HBI (Hoefs et al., 1995; Schouten et al., 2000). Abundant  $C_{20}$ ,  $C_{25}$  and  $C_{30}$  HBI polyenes obtained at the more coastal station reflected the important contribution of diatoms to these organic-rich sediments. All diatoms do not synthesize HBI, therefore the sum of HBI expresses the contribution of HBI-producing diatoms. Numerous isomers of HBI were observed in the eutrophic site: six  $C_{20:1}$  monoene

isomers and the saturated homologue  $C_{20:0}$ , 4 dienes, 5 trienes, 2 tetraenes in the  $C_{25}$  series, and 5 pentaenes and 1 hexaene in the  $C_{30}$  series. At the mesotrophic site the distribution was less diverse: 1 monoene and 4 trienes in the  $C_{30}$  series, 1 tetraene in the  $C_{25}$  series and 3 pentaenes in the  $C_{30}$  series. At the oligotrophic site, the isomer profile was devoid of polyunsaturated homologues. HBI concentrations were high in organic-rich sediments at the eutrophic site, low at the mesotrophic site and only at trace level in the open-sea oligotrophic site (Table 3).

### 3.4. Fatty acids

Fatty acids ranged from 14 to 36 carbons in chain length and showed bimodal distributions at all stations. They maximized predominantly at  $C_{16}$  while the long-chain homologues were present in lower amounts, as in most abyssal sediments (Santos et al., 1994; Uchida et al., 2005; Niggemann and Schubert, 2006). In all samples saturated homologues dominated with palmitic (16:0) being the most abundant compound. Monounsaturated fatty acids, ascribed to marine sources including bacteria and diatoms (Volkman et al., 1980), accounted for about 40% of total fatty acids. In addition, high concentrations of branched and cyclic fatty acids indicated a significant bacterial contribution to all the sediments (Fig. 2). Their concentrations were higher at the E site than at the M and O sites where they fall in the same range, a trend also followed by the  $C_{30}$  hopanoic acid, of bacterial origin. Polyunsaturated fatty acids were present only in trace amounts, the highest contribution being from the algal biomarker 20:5n-3, accounting only to 0.01% of total fatty acids. The highest concentrations of polyunsaturated fatty acids were measured in the eutrophic sediment ED (3% of

total fatty acids), as well as the highest monounsaturated fatty acids levels (44%). Long-chain *n*-fatty acids maximized at either C<sub>24</sub> or C<sub>26</sub>, with strong even-to-odd carbon predominance indicative of possible higher-plant origin (Table 3), as in sediments under the Chilean upwelling (Niggemann and Schubert, 2006). Their concentrations varied in a narrow range at all stations except the shallower of the eutrophic sites, where they are four fold higher, underlining a marked heterogeneity (Table 3). A similar cross-shelf decrease in concentration was observed off Crete (Gogou and Stephanou, 2004). The carbon number preference of alkanolic acids decreased from the coast seawards. As for aliphatic hydro-

carbons, the stations ED and M2 showed molecular profiles distinct from ES and M1, respectively, with a stronger even carbon number predominance and a shift towards lower ACL (C<sub>24</sub> more abundant than C<sub>26</sub>) (Annex 3 in Supplementary Materials).

### 3.5. Long-chain alkenones

All sediments contained relatively high amounts of C<sub>37</sub> and C<sub>38</sub> unsaturated methyl and ethyl alkenones (Table 3). These compounds are synthesized by haptophytes, in particular the worldwide distributed coccolithophores *Emiliania huxleyi* and

Table 4

Concentrations of TOC, long-chain alkenones ( $\Sigma$ LCK), *n*-alkyl diols ( $\Sigma$ diols) and of hydroxy alkenones ( $\Sigma$ OH-alkenones), in modern surficial sediments of different areas

Sites	TOC <sup>a</sup> in%	$\Sigma$ LCK in $\mu\text{g gdw}^{-1}$	$\Sigma$ Diols in $\mu\text{g gdw}^{-1}$	$\Sigma$ OH-alkenones in $\mu\text{g gdw}^{-1}$	References
<b>Very productive sites</b>					
E site — (20°32N, 18°32W)	1.75–2.54	2.8–6.6	1.05–1.28	0.98–1.29	This study
Angola Basin	0.67–4.35	2.6	4.3	2.7 <sup>b</sup>	Hinrichs et al. (1999)
Cape Basin — Walvis Bay	0.41–3.16	1.8	2.4	0.8 <sup>b</sup>	
Cape Basin — Walvis Bay (0.4–0.5 m)		2.1 <sup>c</sup>			Volkman et al. (1980)
Angola basin (max values)	17.6	56			Schefuß et al. (2004)
Peruvian upwelling (surface $\mu$ core)	12	68.8			McCaffrey et al. (1990)
Black Sea — deep basin	3.2	93			Freeman and Wakeham, 1992
Black Sea — deep basin	2	149.2	2.9 <sup>d</sup>	24	Sadouni, 2002
Black Sea			50 <sup>d</sup>	15 <sup>b</sup>	de Leeuw et al. (1981)
Santa Catalina Basin — California		4.07	2 <sup>d</sup>	1.09 <sup>b</sup>	Shaw and Johns, 1986
Santa Barbara Basin — California		3			Kennedy and Brassell, 1991
St Laurent estuary — gulf		2.3 <sup>c</sup>		1 <sup>b</sup>	Nichols and Johns, 1986
St Laurent estuary — offshore reaches		0.2 <sup>c</sup>		0.55 <sup>b</sup>	
North Sea (0–0.9 m)		0.65 <sup>c</sup>			Volkman et al. (1980)
Brunnefjord — Norway (surface)	2.2		n.d.	n.d.	Pinturier-Geiss et al. (2002)
Brunnefjord — 1976	5.6		0.425(max)		
Brunnefjord — 1963	5.4			0.28(max)	
Oman Margin — Arabian Sea	1.4–5.7		0–22.9	0–3.3	Smallwood and Wolff, 2000
<b>Sites of intermediate productivity</b>					
M sites (18°30 N, 21°W)	0.34–0.41	0.6–0.7	0.08–0.2	0.15–0.17	This study
NE Atlantic Sea (59°N, 20°W)	0.38	1.25 <sup>e</sup>			Conte et al. (1992)
(47°N, 20°W)	0.36	1 <sup>e</sup>			
Okinawa Trough — China	0.76		0.29	0.15	Shanchun et al. (1994)
Mediterranean sapropel	0.5–3		0.48–0.6 <sup>d</sup>	0.08–0.15 <sup>b</sup>	Ferreira et al. (2002)
<b>Oligotrophic sites</b>					
O site — (21°N, 31°W)	0.24–0.25	0.06–0.12	0.07–0.13	0.05–0.12	This study
Cretan Sea, Cross-shelf gradient	0.3–0.82	0.013–0.154 <sup>c</sup>	0.010–0.116 <sup>f</sup>		Gogou and Stephanou, 2004
Equatorial Atlantic Sea	0.25	0.46			Sikes and Keigwin, 1994
NE Atlantic Sea (48°N, 25°W)	0.18	0.3 <sup>e</sup>			Madureira et al. (1997)
SE Atlantic Sea (2–22°S, 2–14°E)	0.1–0.2	0.21–0.48			Schefuß et al. (2004)
Mediterranean sapropels (surface)	0.3–0.4		<0.04 <sup>d</sup>	<0.01 <sup>b</sup>	Ferreira et al. (2001)
<b>Sinking particles</b>					
NW Mediterranean Sea (200 m)	10	5–63			Ternois et al. (1997)

<sup>a</sup> When reported for these samples.

<sup>b</sup> C<sub>30</sub> hydroxy alkenones.

<sup>c</sup>  $\Sigma$ C<sub>37–39</sub> alkenones.

<sup>d</sup> C<sub>30</sub> alkyl diol.

<sup>e</sup>  $\Sigma$ C<sub>37–39</sub> alkenones + alkyl alkenoates.

<sup>f</sup> Sum of alkyl diols and hydroxy alkenones.

*Gephyrocapsa oceanica* (Conte et al., 1992). The levels are in the same range as in other modern sediments of comparable productivity (Table 4). The unsaturation index Uk'37 were converted into sea surface temperatures (SST) using the Prahl et al.'s (1988) calibration. Temperature estimated from Uk'37 represents temperature integrated over the growth period of haptophytes. SST estimates at the eutrophic site were 4 °C colder than estimates at the mesotrophic and oligotrophic sites, clearly indicating the influence of the upwelling (Table 3). Owing to the strong coastal currents and the occurrence of eddies and upwelling filaments (Van Camp et al., 1991), it should be borne in mind that SST estimates reflect a surface water temperature not necessarily located above the sediment but rather integrating SST over surface waters upstream. However, the SST estimated from Uk'37 correspond well to the average annual Uk'37, 20 °C, 23 °C and 24 °C at the eutrophic site, mesotrophic and oligotrophic site, respectively (NOAA climatology <http://www.nodc.noaa.gov/cgi-bin/OC5/WOA05F/woa05f.pl>).

### 3.6. Long-chain *n*-alkanols

*n*-Alkanol distributions in the different studied sites were essentially identical. Long-chain *n*-alkanols exhibited a maximum at C<sub>28</sub>OH, with a strong even-to-odd carbon number predominance (CPI<sub>23–32</sub> = 5.0–7.5), a pattern consistent with a higher-plant wax origin (Eglinton et al., 2002). *n*-Alkanol concentrations were four fold higher at both stations of the E site, suggesting that their source is more abundant at the coast.

### 3.7. Sterols

Information on palaeoproductivity may be derived from phytosterols sourced by marine algae. Besides, river and aerosol inputs can be documented by sterols synthesized by higher plants. In most of the sediments of the three sites, 24-ethylcholest-5-en-3 $\beta$ -ol (sitosterol) was the dominant sterol (Table 3). Cholesta-5,22-dien-3 $\beta$ -ol (dehydrocholesterol), cholest-5-en-3 $\beta$ -ol (cholesterol), 24-methylcholest-5-en-3 $\beta$ -ol (campesterol), 24-methylcholesta-5,22-dien-3 $\beta$ -ol (brassicasterol), 24-methylcholesta-5,24(28)-dien-3 $\beta$ -ol (24-methylencholesterol), 24-ethylcholesta-5,22-dien-3 $\beta$ -ol (stigmasterol) and 4 $\alpha$ ,23,24-trimethyl-5 $\alpha$ -cholest-22-en-3 $\beta$ -ol (dinosterol) were also present in all the studied sediments. Sitosterol, campesterol and stigmasterol are common in vascular plants and therefore, have often been ascribed to a terrigenous source. However, a possible algal source for these sterols is now also well documented (Volkman, 1986; Volkman et al., 1998). Sterol concentrations declined along the trophic gradient (Table 3). The concentrations of potential higher-plant sterols, such as 24-ethylcholesterol showed parallel pattern to those of cholest-5-en-3 $\beta$ -ol and long-chain alkenones, unequivocal biomarkers of zooplankton and algae. Consequently, 24-ethylcholesterol cannot be ascribed to higher plants only and a dual source should be considered. Dehydrocholesterol and 24-methylencholesterol, representative of diatoms, dinosterol, associated to dinoflagellates and brassicasterol, sourced by both diatoms

and prymnesiophytes, were much more abundant at the eutrophic site than at the other stations. The concentration of these phytosterols showed a similar pattern as the other sterols. The shallowest eutrophic station had a different distribution of phytosterols, brassicasterol and dinosterol being dominant (Table 3).

### 3.8. Long-chain alkyl diols and hydroxy alkanones

Since their identification in the Black Sea sediments (de Leeuw et al., 1981), these compounds have been found in high abundance in different marine settings. Owing to the stability of their proportions, they are most often reported in palaeostudies, although concentrations in surface sediments are not always indicated (Table 4). *n*-Alkyl diols and hydroxy mid-chain *n*-alkanones occurred in comparable amount (Table 3). Alkyl diol concentrations exceeded that of hydroxy alkanones in most sediments. Eustigmatophytes are the most common source of C<sub>26</sub> to C<sub>36</sub> alkyl diols and they also comprise hydroxy alkanones in minute amounts (Méjanelle et al., 2003). In sediments, hydroxy alkanones often occur at considerably higher levels than in living cells and they are most probably formed by oxidation of *n*-alkyl diols or by hydrolysis of complex mid-chain functionalized polymers (Gelin et al., 1997; Xu et al., 2007). C<sub>30</sub> homologues were prominent members for both alkyl diols and hydroxy alkanones. Mass spectra showed various positional isomers of the mid-chain hydroxyl co-eluting in composite peaks for each given chain length. According to fragment ion intensities, the 1,15-( $\omega$ 16)C<sub>30</sub> diol largely dominated over 1,12, 1,13 and 1,14 isomers. Hydroxyl positions of C<sub>32</sub> diol isomers were 1,13, 1,14, 1,16 and 1,17, whereas the isomers 1,15, 1,16, 1,17 and 1,18 were encountered for the C<sub>33</sub> homologue. The 1,15 isomer was generally the only hydroxy mid-chain alkanone observed. However, at ED and M2 stations where hydroxy alkanones dominated over alkyl diols, four isomers (1,16, 1,17, 1,18 and 1,19) of the C<sub>34</sub> hydroxy alkanone were identified. The relative proportion of selected alkyl diols and hydroxy alkanones, termed the “diol index” (DI) and the “keto-ol index” (KI), were showed to vary according to the productivity. DI values for the eutrophic site were 83 and 84 (Table 1), higher than the range originally defined as typical of upwelling regime (68  $\leq$  DI  $\leq$  79, Versteegh et al., 1997). DI values increased at the mesotrophic site and further at the oligotrophic site, in agreement with the expected values of DI in low productivity areas. C<sub>28</sub> *n*-alkyl diols, synthesized by some diatoms (Sinninghe Damsté et al., 2003), were absent.

## 4. Discussion

Palaeoceanographic reconstructions rely on our ability to extract reliable information from the sedimentary record. The relationship between target environmental parameters (temperature, productivity, terrigenous inputs,...) and the sedimentary record of molecular biomarkers is uncertain (Wefer et al., 1999). The present

study takes the opportunity to examine empirical trends between terrigenous inputs and marine productivity in one hand, and biomarker signatures in sediments, in the other.

#### 4.1. Transport and diagenetic processes affecting all biomarker records

Trends between sedimentary signals recorded at the three EUMELI sites and sea surface parameters most likely integrate some lateral transport effects, through advective transport of particles across the water column, through sediment focusing, resuspension, cross-margin transport through canyons, etc. The significance of advective transport cannot easily be deconvoluted and therefore is integrated in the trends examined in the discussion. It should be underlined that the studied sites were selected for their bathymetric and sedimentary characteristics after a preliminary study: they show a steady state regime of sedimentation without large physical disturbances such as turbidites or terrigenous inputs (Auffret et al., 1992), even though nepheloid resuspension occurred at the oligotrophic site (Vangriestheim et al., 1993).

Lipid biomarkers are degraded by heterotrophs during the sinking of particles and during sediment accretion (Lee et al., 1983). The intensity of degradation

impacts the concentrations as well as the relative proportions of biomarkers, reflecting their various stabilities (Sun et al., 2000). Therefore the faunal abundance and the freshness of the organic matter were assessed at the three study sites. As it is shown in Fig. 2, the abundance of benthic heterotrophs, responsible for organic matter degradation, followed the trophic conditions and maximized at the eutrophic site (Cosson et al., 1997). Polar lipids (phospho- and glycolipids), very labile constituents of the living heterotrophic fauna inhabiting the sediments, closely followed the benthic meiofauna and macrofauna (Galéron et al., 2000) which validates their value as biomass indicators. Total lipids, triacylglycerol-esters and cholesterol also followed the same trend, but they are contributed to by detrital matter as well as by living biomass and thus have a less specific significance. Fatty acids specific to bacteria indicated that bacterial remains were most abundant at the eutrophic site, and equivalent at both the meso- and oligotrophic sites. In addition they showed that the biomass of microorganisms relative to available organic matter gradually increased offshore (Fig. 2C, TOC-normalized concentrations). Along the trophic gradient, the organic matter was enriched in bacterial markers and refractory biomarkers (*n*-alkanes, Fig. 4C) on the one hand, and impoverished in labile biomarkers, such as polyenoic HBI (Fig. 6C) on the other hand. Particles are

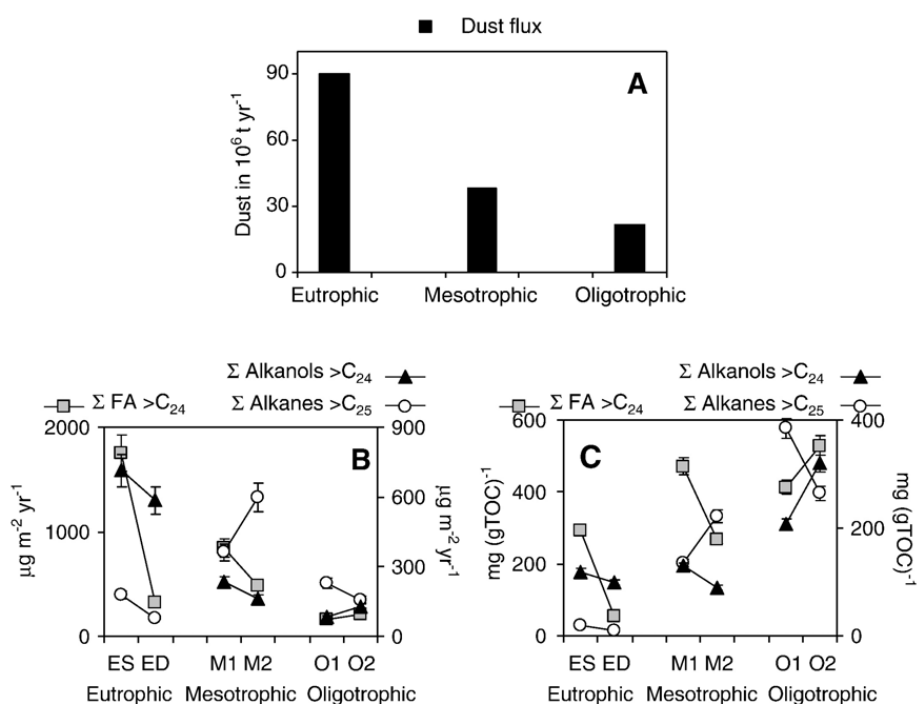


Fig. 4. Relationships of terrigenous biomarker records to dust flux at the three sites. A: annual dust flux transported over the Atlantic between 15 and 24°N in the NE trade wind zone in  $10^6 \text{ t yr}^{-1}$ , from Schütz et al. (1981). B: mass accumulation rate of long-chain *n*-fatty acids ( $\Sigma \text{FA} > \text{C}_{24}$ ), *n*-alkanols ( $\Sigma \text{Alkanols} > \text{C}_{24}$ ) and *n*-alkanes ( $\Sigma \text{Alkanols} > \text{C}_{25}$ ) in  $\mu\text{g m}^{-2} \text{ yr}^{-1}$ . C: concentrations of the same biomarkers, normalized to organic carbon (OC) and expressed as mg per g of OC. Error bars correspond to the analytical error.

more exposed to degradation during sinking to deeper water and more degraded during sediment accretion when accumulation rates are small. Accordingly, the degradation becomes gradually more intense from the eutrophic site to the oligotrophic site. At the oligotrophic site, only 0.3% of the primary productivity reaches the sea floor (Khripounoff et al., 1998).

Reconstructing past oceanic productivity and terrigenous inputs has to consider drivers of pelagic–benthic coupling, such as water column depth and indicators of mega-, macro-, and meiofaunal biomass.

#### 4.2. Terrigenous inputs recorded at the three sites

The high C/N values at the three sites suggest an important contribution of terrigenous matter (Stein et al., 1994), decreasing seawards. C/N of 11.4 was measured in a dust sample collected off Sahel at a latitude of 17°58N (Eglinton et al., 2002), while C/N of up to 35 in old sediments located close to the eutrophic site were ascribed to Saharan inputs (658 site, Stein, 1991) and C/N of up to 28 with dust deposition in modern Arctic sediments (Schubert and Stein, 1997). In addition to this, high C/N values can also reflect denitrification (Meyers, 2006). The EUMELI surface sediments were oxic, however low oxygen concentration and nitrate peaks in the top 0–0.7 cm of the eutrophic site sediments (Rabouille et al., 1993) suggested that the C/N values of eutrophic site may signal denitrification and that bulk parameters do not reflect the input of higher-plant derived material. In palaeoceanographic studies, higher-plant inputs associated with changes in wind regime are commonly addressed through one class of long-chain lipids, either the *n*-alkanes along with their <sup>13</sup>C value, *n*-alkanols or *n*-alkanoic acids. The area of study is not under the influence of direct river discharge (Cosson et al., 1997) and terrigenous inputs are mostly related to dust fallout, that decreases with distance from the coast (Schütz et al., 1981). Chenopodiaceae–Amaranthaceae pollen, from both Sahelian and Saharan regions, together with Gramineae and Cyperaceae pollens transported from Sahel by the SAL constitute an important terrigenous inputs to sediments between 19° and 22°N (Melia, 1984; Hooghiemstra and Agwu, 1986; Hooghiemstra, 1988). *n*-Alkane concentrations compare well with values of older sediments from the same area, which are interpreted as dust record proxies (Zhao et al., 2000). Bulk organic contents of the sediments varied at the 3 study sites (Annex 1 in Supplementary materials); these differences were integrated as part of the variation in concentrations expressed as ng of alkanes per g of dry sediments.

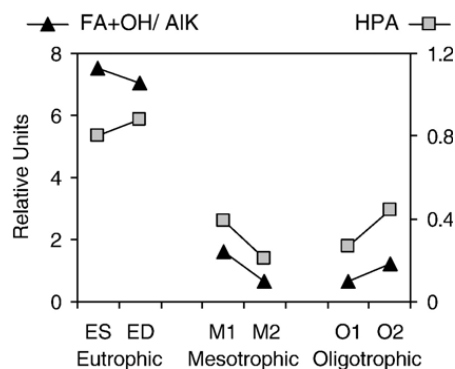


Fig. 5. Change in proportions of long-chain terrigenous biomarkers along the cross-shelf gradient. FA+OH/Alk stands for the ratio value  $C_{24-32}$  *n*-fatty acids +  $C_{22-32}$  *n*-alkanols/ $C_{21-36}$  *n*-alkanes and HPA is the alkanol preservation index defined as  $HPA = \frac{\sum(C_{24-OH} + C_{26-OH} + C_{28-OH})}{\sum(C_{24-OH} + C_{26-OH} + C_{28-OH}) + \sum(C_{27} + C_{29} + C_{31})}$  (Santos et al., 1994).

Biomarker records were more pertinently expressed as mass accumulation rates. Mass accumulation rates of long-chain *n*-alkanes described a pattern unlike that of dust fallout, whereas those of *n*-alkanols and *n*-alkanoic acids were in good agreement with dust fallout (Fig. 4). In aerosols *n*-alkanols and *n*-alkanoic acids dominate over *n*-alkanes (Gagosian et al., 1981; Poynter et al., 1989; Prahl et al., 1989; Stephanou, 1992), whereas deep sediments are very poor in these compounds, presumably as the functionalized compounds are more labile than the hydrocarbons (Poynter et al., 1989; Prahl et al., 1989; Madureira et al., 1995). The degradation effect would be likely to be greater the deeper the water column and the slower the sedimentation accumulation rate. Indeed, as it is shown in Fig. 5, the ratio of concentrations of the long-chain *n*-alkanoic acids and *n*-alkanols to the long-chain *n*-alkanes ( $C_{24-32}$  FA +  $C_{22-32}$  OH/ $C_{21-36}$  ALK) decreased from the coast to the open sea. This ratio takes into account long-chain *n*-alkanoic acids which the alkanol preservation index does not, and we propose that it characterizes the “freshness” of higher-plant derived waxes (Fig. 5).

The contrasting intra-site variation of CPI of *n*-alkanoic acids and *n*-alkanes opens the question of a source other than higher plants for these biomarkers. The relevance of long-chain *n*-alkanes as a terrigenous proxy has been questioned in the Arctic, the Antarctic, the Pakistan margin and the Peruvian upwelling where they are thought to have had a marine origin (Zegouagh et al., 1998; Hayakawa et al., 1996; Schulte et al., 2000; McCaffrey et al., 1991). No predominance (CPI close to 1) has been related to bacterial reworking and degraded organic matter (Kennicut et al., 1987). The sources of these compounds remained uncertain even if a bacterial production or biomass

were supposed. Krill faeces also show low CPI whereas the *n*-alkane composition of the phytoplanktonic organisms from which they are fed, exhibited an odd predominance (Cripps, 1995b), also suggesting that enteric bacterial contribution would lower *n*-alkane CPI. Therefore, the ED and M2 *n*-alkane profiles could also suggest higher bacterial contribution. However, comparable CPI and modal distributions of *n*-alkanes in the EUMELI sediments and in dust collected at the same latitude does support the premise that long-chain *n*-alkanes record dust

inputs (Schefuß et al., 2003). Finally, similarities between *n*-alkanes from sediments and dust underpin the implementation of the  $C_{31}/C_{31+29}$  ratio as a proxy for aridity (Schefuß et al., 2003).

#### 4.3. Productivity record at the three sites

TOC, TON and chlorophylls concentration in coastal sediments are likely to reflect the occurrence of coastal upwelling (Köster et al., 1997). Phytadienes, derived

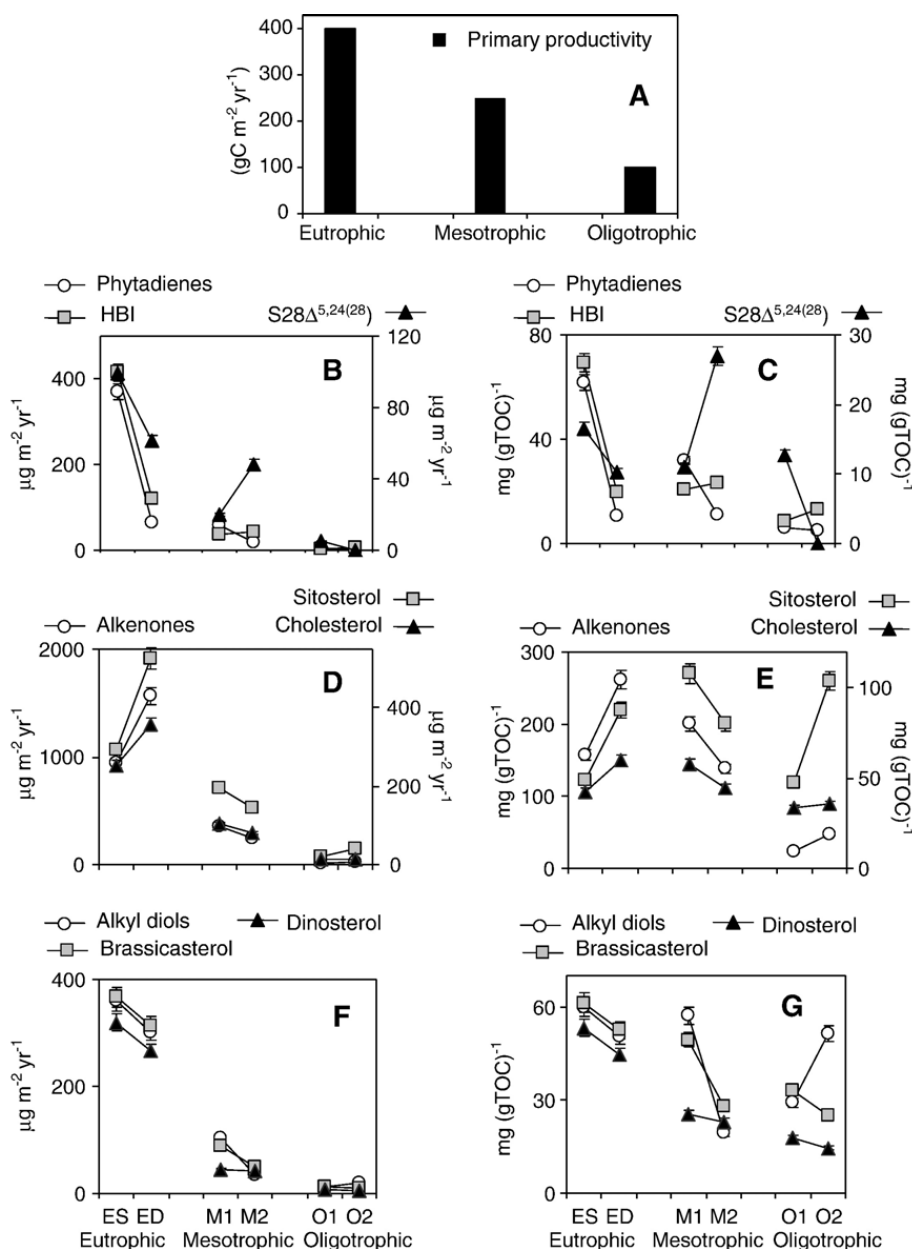


Fig. 6. Relationships of phytoplanktonic biomarker records to primary productivity at the three sites. A: primary productivity in  $\text{gC m}^{-2} \text{yr}^{-1}$ , from Morel (1996). B: mass accumulation rate of the sum of phytadienes, the sum of HBI and 24-methylenecholesta-5-en-3 $\beta$ -ol, ( $S28\Delta^{5,24(28)}$ ) in  $\mu\text{g m}^{-2} \text{yr}^{-1}$ . C: concentrations of the same biomarkers, normalized to organic carbon (OC) and expressed as mg per g of OC. D: mass accumulation rate of the sum of  $C_{37}$  alkenones, sitosterol and cholesterol in  $\mu\text{g m}^{-2} \text{yr}^{-1}$ . E: concentrations of the same biomarkers, normalized to organic carbon (OC) and expressed as mg per g of OC. F: mass accumulation rate of the sum of the sum of *n*-alkyl diols, brassicasterol and dinosterol in  $\mu\text{g m}^{-2} \text{yr}^{-1}$ . G: concentrations of the same biomarkers, normalized to organic carbon (OC) and expressed as mg per g of OC. Error bars correspond to the analytical error.

from chlorophyll, are also general indicators of primary producers. Over the trophic gradient from the eutrophic to the oligotrophic site, TOC, TON, chlorophyll and phytadiene concentrations do not match the productivity trend, as they fail to register any difference between the mesotrophic and oligotrophic sites (Tables 1 and 3). Accumulation rates show a better agreement with primary production (Table 1, Fig. 6A and B), in the same way as long-chain lipid mass accumulation rates better reflect dust inputs than do their concentrations. Molecular biomarkers specific to groups of algae can be expected to record the corresponding phytoplanktonic communities. Mass accumulation rate of biomarkers of various types of phytoplankton inferred a marked decrease in productivity of all targeted algal groups from the eutrophic to the oligotrophic sites (Fig. 6). The decrease of nanoplankton, particularly the haptophytes along the trophic gradient is on good agreement with the strong representation of coccolithophores and particularly *E. huxleyi* in the surface assemblages of the productive site (Giraudeau and Bailey, 1995; Kinkel et al., 2000).  $\text{CaCO}_3$  and alkenone concentrations showed opposing cross-shelf variation (Table 1). Organic carbon mineralization results in acidification of sediment pore waters that promotes  $\text{CaCO}_3$  dissolution at the more productive site. Complex interplay between productivity and benthic processes give rise to difficulties in using  $\text{CaCO}_3$  as a proxy for haptophyte productivity in highly productive areas, while alkenones have no particular sensitivity to reducing conditions and constitute a good alternative and complementary proxy. Accumulation rates of diatom molecular biomarkers and dissolved  $\text{SiO}_2$  concentration in sediment pore waters (Table 1) were in agreement with the observed higher abundance of diatoms in the coastal upwelling area (Lange et al., 1998). The accumulation rate of HBIs, produced by diatoms of the *Haslea* genus, closely tracks that of chlorophyll and phytadienes, suggesting that the contribution of *Haslea*-type diatoms to the phytoplanktonic community was comparable along the trophic gradient (Fig. 6B,C). This trend is confirmed by the mass accumulation of 24-methylenecholest-5-en-3 $\beta$ -ol, a diatom biomarker, not restricted to the *Haslea* genus, except at the M2 station where the higher accumulation of 24-methylenecholest-5-en-3 $\beta$ -ol suggested an increase of non-*Haslea* diatoms (Fig. 6B).

In addition to the onshore–offshore decrease, the record of biomarkers of diatoms, coccolithophorids, dinoflagellates and eustigmatophytes are much different at both stations of the E site. Accumulation of diatom, eustigmatophyte and dinoflagellate biomarkers maximized at the shallowest station, whereas haptophyte

biomarkers (alkenones) peaked at the other eutrophic station (Fig. 6B,D and F). Both stations are located 1000 m apart another. At the shallower coastal station, the duration of particle sinking to the sea-bed depth is short and the organic matter is likely better preserved. HBIs are labile biomarkers, as shown by their occurrence in a trap moored at 2200 m in the Arabian Sea but their absence in surface sediments beneath the trap at 3974 m depth (Prah et al., 2000). During burial in anoxic sediments, they may also react with elementary sulphur (Sinninghe Damsté and Rijpstra, 1993; Sinninghe Damsté et al., 1999). Owing to the sensitivity of HBIs to degradation, the heterogeneity in HBI accumulation rates at the eutrophic site can be explained both by the higher abundance of *Haslea*-type diatoms at the shallower station, or by less intense degradation. Despite of the limited number of samples, the results show that a better knowledge on the pelagic–benthic coupling, encompassing characterization of phytoplankton assemblages and of sediment heterogeneity (Smallwood and Wolff, 2000) would improve the information on phytoplankton community appraised by molecular proxies. An abundant literature documents concentrations of biomarkers, allowing a comparison of the studied sites with respect to others of analogous productivity (Table 4). However biomarker mass accumulation rates are better proxies of primary productivity than concentrations, and existing data on accumulation rates are rather scarce. The way for improving molecular proxies of phytoplanktonic assemblages lies in addressing both sedimentary mass accumulation rates of biomarkers and microalgal communities in the present ocean. Literature describing phytoplanktonic abundance in the studied area shows maximum abundances of algae of all size classes in the nutrient-rich surface waters of upwelling areas: picoplanktonic *Synechococcus*, nanoplanktonic coccolithophores and microplanktonic diatoms (Zubkov et al., 1998; Giraudeau and Bailey, 1995; Kinkel et al., 2000; Lange et al., 1998). Unfortunately, these papers do not provide a synoptic view of the phytoplanktonic assemblages along the trophic gradient which impede to relate the sedimentary record of phytobiomarkers to changes in the phytoplanktonic assemblages.

## 5. Conclusions

The higher molecular diversity and the occurrence of labile unsaturated biomarkers at the eutrophic site reflect the high preservation efficiency, resulting from the relatively shallow water depths and the fast organic carbon accumulation. Cross-shelf biomarker accumulation trends integrated both productivity decline and an

increase in degradation. Cross-shelf changes in the pelagic–benthic coupling were apparent from indicators of living biomass. In particular, phospholipid concentrations reflect decreasing heterotrophic benthic faunal abundance while microbial biomarkers represent an increasing fraction of the organic carbon. Despite the limited data, molecular proxies showed recognizable trends over the distance from the coast and the productivity gradient. Mass accumulation rates of long-chain alkanolic acids and *n*-alkanols were in good agreement with dust inputs. Mass accumulation rates of biomarkers from all types of targeted phytoplanktonic groups declined along with primary productivity, which holds great promise for the development of molecular proxies of palaeoproductivity. Pertinent data for dust inputs and for productivity palaeoreconstruction should be based on mass accumulation rates rather than concentrations. Unfortunately modern sediment studies yield profuse data as biomarker concentrations, but seldom as accumulation rates and the data available for developing productivity-biomarkers relationships need to be extended. In addition, progress is still needed to quantify degradation effects. All proxies would certainly be improved by better understanding of processes delivering carrier particles to the sediment, and of degradation occurring at the sea bed and during burial.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.marchem.2007.10.002](https://doi.org/10.1016/j.marchem.2007.10.002).

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