



Origin and distribution of terrestrial organic matter in the NW Mediterranean (Gulf of Lions): Exploring the newly developed BIT index

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[1] The Branched and Isoprenoid Tetraether (BIT) index is based on the relative abundance of nonisoprenoidal glycerol dialkyl glycerol tetraethers (GDGTs) derived from organisms living in terrestrial environments versus a structurally related isoprenoid GDGT “crenarchaeol” produced by marine Crenarchaeota. The BIT index varies between 0 and 1, representing marine and terrestrial organic matter (OM) end-members, respectively (Hopmans et al., *Earth Planet. Sci. Lett.*, 224, 107–116, 2004). In this study, the applicability of the BIT index to trace terrestrial OM is tested in combination with other organic parameters (TOC, C/N ratio, $\delta^{13}\text{C}_{\text{org}}$, total lipid, and *n*-alkane) in the Gulf of Lions, a river-dominated continental margin of the western Mediterranean. We analyzed a variety of soils and riverbed sediments from the continent as well as surface sediments from the shelf and canyons. The BIT index in soils and riverbed sediments shows high values (>0.9), while it varies between 0.02 and 0.83 in marine sediments, decreasing seaward from the inner shelf to the slope. For marine surface sediments, high BIT values are associated with lower $\delta^{13}\text{C}_{\text{org}}$ values as well as higher TOC contents and higher *n*-alkane concentrations. Our results confirm that the BIT index can be applied in coastal marine environments in order to characterize terrestrial OM as proposed by Hopmans et al. (2004). Therefore the BIT index is a useful addition to the proxies presently available for studying the origin and distribution of OM in continental margins and especially valuable in multiproxy studies.

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1. Introduction

[2] One of the major issues in studying sedimentary organic matter (OM) on continental margins is to make accurate estimates of the relative contributions of terrestrial and marine OM. Detailed information of the origin of OM will considerably improve our knowledge on the sedimentary processes ruling the transport of sediments from the continent to the deep-sea and therefore improve the estimate of the global carbon budgets. Furthermore, as the natural particulate OM fraction has the potential to adsorb organic micropollutants and heavy metals, the understanding of the fate of the terrestrial OM in the coastal environment is of utmost importance to determine the impact of anthropogenic activities and to establish efficient strategies to protect the coastal zones.

[3] The stable carbon isotope composition ($\delta^{13}\text{C}_{\text{org}}$) and the C/N ratio have been widely used to trace sources of particulate OM [e.g., Meyers, 1994; Middelburg and Nieuwenhuize, 1998; Kerhervé et al., 2001]. However, interpretation of these proxies is often complicated by the fact that bulk material represents mixtures from several sources, and thus their isotope ratios are weighted averages. Furthermore, selective degradation of OM components during early diagenesis can substantially alter C/N ratios. Organic compounds in sediments that have a demonstrable origin from certain living organisms are termed biological markers or biomarkers [e.g., Brassell, 1993]. Many organic compounds, particularly lipid biomarkers, are relatively resistant to degradation, and can be well preserved in sediments. Identification and quantification of major lipid biomarkers as well as measuring the isotopic compositions of individual lipid biomarkers showed great potential of providing less equivocal proxies for the sources of OM. A large range of marine and terrestrial lipid

biomarkers (e.g., alkenones, taraxerol, long-chain *n*-alkanes, *n*-alcohols, and fatty acids) is available [e.g., Brassell, 1993; Meyers, 1997]. However, quantification of the relative input of terrestrial OM is still complicated due to large variations in concentrations of compounds in the different plant materials and different degradation rates of terrestrial and marine organic compounds [e.g., Sinninghe Damsté et al., 2002a].

[4] An alternative approach to reconstruct the relative amounts of terrestrial and marine OM is to use the newly developed proxy, the Branched and Isoprenoid Tetraether (BIT) index [Hopmans et al., 2004]. This index is based on a group of nonisoprenoidal glycerol dialkyl glycerol tetraethers (GDGTs) derived from anaerobic bacteria thriving in terrestrial environments [Weijers et al., 2006a] and a structurally related isoprenoid GDGT “crenarchaeol” predominantly produced by marine planktonic Crenarchaeota [Sinninghe Damsté et al., 2002b]. The BIT index varies between 0 and 1, representing marine and terrestrial OM end-members, respectively [Hopmans et al., 2004]. There are several advantages to the use of the BIT index compared to other molecular and bulk proxies. First, the terrestrial and marine GDGTs have a similar chemical structure and are therefore likely to be degraded at similar rates during sediment diagenesis. As a result, the BIT index is less sensitive to diagenetic effects compared to individual lipid compounds and other conventional organic carbon tracers. Second, the branched GDGTs are derived from seemingly ubiquitous anaerobic bacteria living in terrestrial environments, mostly soils and peats [Schouten et al., 2000; Hopmans et al., 2004; Weijers et al., 2006a]. Therefore they are not specific for particular vegetation types but for terrestrial vegetation in general. Third, the BIT index is easily measured in a single GDGT analysis of lipid extracts and

does not require specific chemical degradation procedures. Fourth, the BIT index is fully related to fluvial input of terrestrial OM and not to eolian transport [Hopmans *et al.*, 2004; Weijers *et al.*, 2006b]. Therefore the BIT index has a great potential to estimate the relative amount of fluvial terrestrial OM input. However, the BIT index has not been widely tested yet and its use as a robust proxy for terrestrial OM input still has to be validated in various coastal settings.

[5] The main goals of this study are thus (1) to test the general applicability of the newly developed BIT index in combination with other organic parameters and (2) to better understand the origin and distribution of OM in coastal zones. We choose the Gulf of Lions to conduct this study as it is a river dominated continental margin where during flood events large amounts of terrestrial matter are delivered to the coastal zone via rivers. Furthermore, physical, biological as well as sedimentological processes have been widely studied in the Gulf of Lions [e.g., Buscail and Germain, 1997; Durrieu de Madron *et al.*, 1999; Monaco *et al.*, 1999; Lique *et al.*, 2004]. This area combines therefore the necessary conditions to study and validate the newly developed BIT index as a proxy for continental versus marine OM input.

2. Study Area

[6] The Gulf of Lions is located in the northwestern Mediterranean basin between 42N-3E and 43N-6E. Its continental shelf is crescent shaped and fairly broad (up to 20 miles) and its continental slope is incised by numerous submarine canyons (Figure 1a). From a hydrodynamic point of view, the Gulf of Lions is a complex region where several intense and highly variable phenomena such as the energetic general circulation along the continental slope (the “courant liguro-provençal”), the cascading of dense water both on the shelf and offshore, the mesoscale circulation (eddies, filaments, etc.), the internal waves (mainly in the near-inertial band), the seasonal variation of stratification, and the extreme meteorological events interact. The major physical forcings in the Gulf of Lions are the strong winds (both from land and sea), the general circulation and the fresh water discharge from rivers. The Northern Current flowing along the continental slope is part of the cyclonic circulation of the western Mediterranean basin (Figure 1a). The core of this geostrophic current is about several hundreds meters thick and primarily composed of Modified Atlantic Water (upper 150 m) and Levantine

Intermediate Water (deeper down) [Millot, 1990, 1991]. It constrains the shelf circulation and influences the shelf-slope exchanges. Furthermore, it forms a density front that separates the continental influenced fresh shelf water and the more saline open ocean water.

[7] Several sources of particulate matter feed the continental shelf in the Gulf of Lions: fluvial and atmospheric (primarily Saharan dust deposition) input of continental material, biological production, and resuspended coastal sediment. Riverine inputs of water and sediments in the Gulf of Lions originate mainly from the Rhône River, which is, since the damming of the Nile at Aswan, the largest Mediterranean river in terms of its freshwater discharge [Ludwig *et al.*, 2003]. Also the smaller coastal rivers (e.g., the Têt, Orb, Aude, and Hérault Rivers) can significantly contribute to the sediment budgets in this environment. Although on average much lower than the Rhône discharges, the particulate inputs by these rivers arrive almost exclusively via the occurrence of short and violent flash-floods [Serrat, 1999; Serrat *et al.*, 2001], thereby providing important pulses of terrestrial matter injections into the marine environment.

[8] The Rhône River has a catchment's area of 97,800 km² [Pont *et al.*, 2002] and discharges on average about 1,700 m³/s [Thill *et al.*, 2001] of freshwater into the Gulf of Lions. Its discharge regime is rather constant, but during floods peak discharges greater than 10,000 m³/s can be measured (e.g., in December 2003 [Arnau *et al.*, 2004]). The Rhône River has high mean sediment discharge of about 7–10 10⁶ tons/yr [Sempéré *et al.*, 2000; Pont *et al.*, 2002], accounting for ~80% of the riverine inputs to the Gulf of Lions [Durrieu de Madron *et al.*, 2000]. The formation of the Rhône prodelta is centered at ~30 m water depth with high sediment accumulation rates of >20 cm/yr [Radakovitch *et al.*, 1999].

[9] The Têt River has a catchment's area of about 1,400 km² [Ludwig *et al.*, 2004]. It delivers water and suspended materials into the southwestern part of the Gulf of Lions where these sediments built a prodeltaic deposit on the inner shelf [Buscail *et al.*, 1990, 1995; Courp and Monaco, 1990; Guidi-Guilvard and Buscail, 1995]. The average water discharge of the river is close to 10 m³/s, but it can increase by more than two orders of magnitude during major floods [Ludwig *et al.*, 2004]. Serrat *et al.* [2001] estimated the annual mean sediment discharge to 53,000 ± 16,000 tons/yr for the reference period of 1980–1999. Also here, this

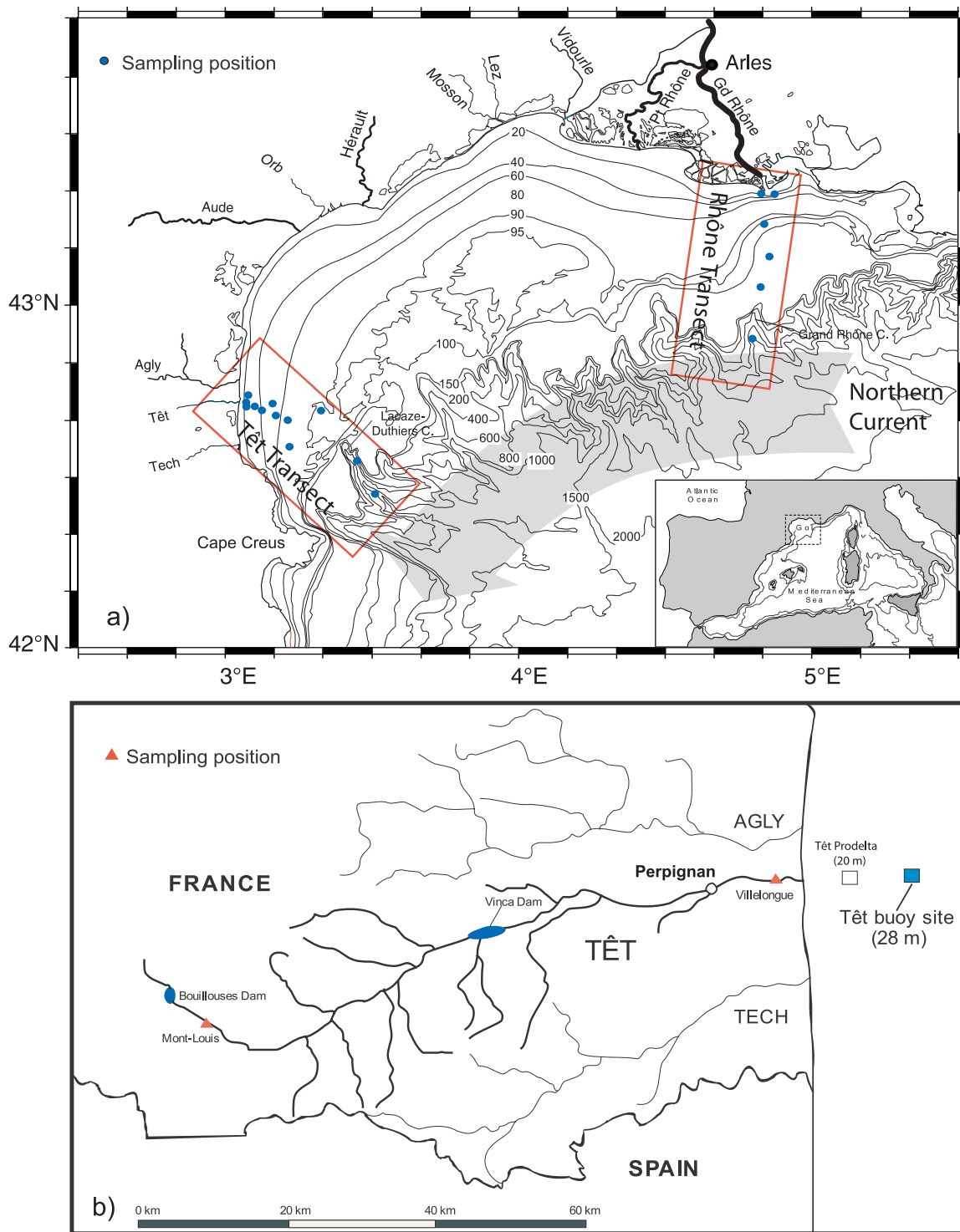


Figure 1. Map of the study area showing (a) the Gulf of Lions with main rivers and submarine canyons and (b) the detailed catchment area of the Têt River and sampling stations. Blue dots in Figure 1a indicate the sampling positions of Rhône and Têt transects. Red triangles in Figure 1b show the sampling positions along the Têt River. The Têt buoy site is located off Têt River mouth in 28 m water depth.

value is accompanied by a very high interannual and seasonal variability, since in some years, about 2–3 times of this amount was discharged during only three days (e.g., 1996 [see *Serrat et al.*, 2001]).

3. Material and Methods

3.1. Soil and Sediment Sampling

[10] In this study, soils and riverbed sediments from the land as well as surface sediments from the shelf and canyons were investigated (Table 1 and Figure 1b). Detailed sample information is summarized in Table 1. Four soil samples were taken near the Bouillouses dam situated at an altitude of 2000 m. Soil samples SO-LB1 were taken a few meters from the shore of the Bouillouses dam, representing a histosol with the vegetation essentially composed of pasture grass. Soil samples SO-LB2 were collected downstream a few hundred meters from the dam and a few meters from the Têt River shore in a wetland (peat-like) where the vegetation is essentially made of furze and carex. The surrounding forest is mainly composed of beech trees, Douglas and Laricio pine trees. One Têt riverbed sediment sample was taken in Mont-Louis (RBS-ST1). This muddy-sand sediment was dry-sieved ($<63\ \mu\text{m}$) for chemical analyses.

[11] The core tops of fifteen sediment cores recovered from October 2003 to July 2005 from the Têt buoy site (42.7041N, 3.0668E) were analyzed, giving a time series of about 21 months. This site is located 2 km off the Têt River mouth at 28 m water depth and is part of the POEM-L2R (Observation Platform of the Mediterranean Environment of the Littoral of Languedoc-Roussillon) station maintained by the CEFREM since 2003. One additional core top of the sediment core recovered closer to the Têt River mouth (20 m water depth, 42.7092N, 3.0541E) on the 28 April 2004 was also analyzed. Sediment cores were sliced at 1 cm interval, frozen and freeze-dried in the laboratory a few hours after core sub-sampling. Additionally, to provide a picture of the offshore extent of terrestrial OM inputs, surface sediments were collected along two transects located off the Rhône and Têt river mouths. The two transects span from the prodelta to depths of almost one thousand meter (Table 1) into the submarine canyons incising the slope (Figure 1a). The sediment cores were recovered using a box corer during the REMORA 3 cruise in November 2002 [*Roussiez*

et al., 2005]. The cores were sliced and immediately deep-frozen on board. Soils and sediment samples were freeze-dried and homogenized prior to analysis.

3.2. Chemical Analyses

3.2.1. Bulk Sediment Analyses

[12] Bulk chemical parameters were analyzed using milled, freeze-dried sediment sub-samples. Total nitrogen, total and organic carbon concentrations (TN, TC and TOC, respectively) were measured on homogenized, precisely weighed samples in an automatic CN-analyzer LECO 2000 at CEFREM. TOC values were obtained after acidification with 2N HCl (overnight, at 50°C) in order to remove carbonates prior to the analyses. The analyses are performed by dry combustion in a furnace and the CO_2 and N_2 formed are quantitatively measured by infra-red adsorption for TC and TOC, and thermal conduction for TN [*Cauwet et al.*, 1990]. Extensive testing and application at CEFREM showed long-term precisions for TOC and TN of about 2% and for TC of 0.3%. To calculate C/N ratio, we used TOC and organic nitrogen that corresponds to the difference between TN and mineral nitrogen ($\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-$). *Delille et al.* [1990] found that mineral nitrogen corresponds to about 10% of TN in the surface sediments of 3 stations located on the NW Mediterranean continental shelf and slope and sampled monthly during 2 years (March 1984 to April 1986, 78 samples). We therefore corrected TN to obtain organic nitrogen according to *Delille et al.* [1990].

[13] After acidification of the samples with 2 M HCl, the stable carbon isotopic composition of TOC ($\delta^{13}\text{C}_{\text{org}}$) was determined using a Flash EA 1112 Elemental Analyser interfaced with a ThermoFinnigan Delta^{Plus} mass spectrometer at NIOZ. Isotope values were calibrated to a benzoic acid standard ($\delta^{13}\text{C}_{\text{org}} = -27.8\text{‰}$ with respect to Vienna Pee Dee Belemnite (VPDB) calibrated on NBS-22 and corrected for blank contribution. The $\delta^{13}\text{C}_{\text{org}}$ values are reported in the standard delta notation relative to VPDB standard. The analyses were done at least in duplicate. The analytical error was usually smaller than $\pm 0.2\text{‰}$.

3.2.2. Lipid Analyses

3.2.2.1. Total Lipid Analysis

[14] Total lipid contents of sediments were measured at CEFREM using a colorimetric method

Table 1. Detailed Information on Samples, Including Sampling Dates and Sample Positions

Sample Type	Sample Code	Geological Setting	Cruise	Station	Core Type	Date, dd/mm/yy	Core Depth, cm	Longitude, E	Latitude, N	Water Depth, m	Distance From the River Mouth, km
Soils	SO-LB1-T	Meadow				22/06/2005	5–15				
	SO-LB1-B	Meadow				22/06/2005	25–30				
	SO-LB2-T	Wetland				22/06/2005	5–10				
	SO-LB2-B	Wetland				22/06/2005	15–25				
Têt riverbed sediment	RBS-ST1	Têt River		Mont-Louis		22/06/2005					
Marine surface sediment											
	TB-10/10/2003	Têt Prodelta		POEM-L2R	Scuba Diving Hand Core	10/10/2003	0–1	3.0668	42.7041	28	2.5
	TB-26/11/2003	Têt Prodelta		POEM-L2R	Scuba Diving Hand Core	26/11/2003	0–1	3.0668	42.7041	28	2.5
	TB-12/12/2003	Têt Prodelta		POEM-L2R	Scuba Diving Hand Core	12/12/2003	0–1	3.0668	42.7041	28	2.5
	TB-11/02/2004	Têt Prodelta		POEM-L2R	Scuba Diving Hand Core	11/02/2004	0–1	3.0668	42.7041	28	2.5
	TB-15/03/2004	Têt Prodelta		POEM-L2R	Scuba Diving Hand Core	15/03/2004	0–1	3.0668	42.7041	28	2.5
	TB-18/04/2004	Têt Prodelta		POEM-L2R	Scuba Diving Hand Core	18/04/2004	0–1	3.0668	42.7041	28	2.5
	TB-28/04/2004	Têt Prodelta		POEM-L2R	Scuba Diving Hand Core	28/04/2004	0–1	3.0668	42.7041	28	2.5
	TB-26/05/2004	Têt Prodelta		POEM-L2R	Scuba Diving Hand Core	26/05/2004	0–1	3.0668	42.7041	28	2.5
	TB-23/06/2004	Têt Prodelta		POEM-L2R	Scuba Diving Hand Core	23/06/2004	0–1	3.0668	42.7041	28	2.5
	TB-28/07/2004	Têt Prodelta		POEM-L2R	Scuba Diving Hand Core	28/07/2004	0–1	3.0668	42.7041	28	2.5
	TB-30/09/2004	Têt Prodelta		POEM-L2R	Scuba Diving Hand Core	30/09/2004	0–1	3.0668	42.7041	28	2.5
	TB-13/12/2004	Têt Prodelta		POEM-L2R	Scuba Diving Hand Core	13/12/2004	0–1	3.0668	42.7041	28	2.5
	TB-15/03/2005	Têt Prodelta		POEM-L2R	Scuba Diving Hand Core	15/03/2005	0–1	3.0668	42.7041	28	2.5
Têt prodelta (20 m)	TB-20/05/2005	Têt Prodelta		POEM-L2R	Scuba Diving Hand Core	20/05/2005	0–1	3.0668	42.7041	28	2.5
	TB-06/07/2005	Têt Prodelta		POEM-L2R	Scuba Diving Hand Core	06/07/2005	0–1	3.0668	42.7041	28	2.5
Têt transect	TP-28/04/2004	Têt Prodelta			Scuba Diving Hand Core	28/04/2004	0–1	3.0541	42.7092	20	1.4
	SS-35	Têt Prodelta	REMORA 3	35	Multitube	22/10/2002	1–2	3.0652	42.7155	27	2.2
	SS-352	Têt Prodelta	REMORA 3	352	Multitube	22/10/2002	1–2	3.0639	42.7282	27	2.3
	SS-351bis	Shelf	REMORA 3	351bis	Multitube	22/10/2002	1–2	3.0900	42.6988	33	5.0
	SS-353	Shelf	REMORA 3	353	Multitube	22/10/2002	1–2	3.1524	42.7121	51	9.4
	SS-37bis	Shelf	REMORA 3	37bis	Multitube	23/10/2002	1–2	3.2062	42.5825	81	20.5
	SS-34bis	Shelf	REMORA 3	34bis	Multitube	23/10/2002	1–2	3.3256	42.6920	91	23.7
	SS-38bis	Lacaze-Duthiers Canyon	REMORA 3	38bis	Multitube	24/10/2002	1–2	3.4395	42.5418	603	38.4
	SS-39bis	Lacaze-Duthiers Canyon	REMORA 3	39bis	Multitube	23/10/2002	1–2	3.5112	42.4489	783	49.0

Table 1. (continued)

Sample Type	Sample Code	Geological Setting	Cruise	Station	Core Type	Date, dd/mm/yy	Core Depth, cm	Longitude, E	Latitude, N	Water Depth, m	Distance From the River Mouth, km
Rhône transect	SS-KB16	Rhône Prodelta	REMORA 3	KB16	Multitube	03/11/2002	1–2	4.8239	43.3203	15	1.5
	SS-KB4	Rhône Prodelta	REMORA 3	KB4	Multitube	03/11/2002	1–2	4.8678	43.3181	26.6	2.3
	SS-9X	Shelf	REMORA 3	9X	Multitube	02/11/2002	1–2	4.8324	43.2328	95	10.4
	SS-2	Shelf	REMORA 3	2	Multitube	14/10/2002	1–2	4.8547	43.1393	105	21.3
	SS-3	Shelf	REMORA 3	3	Multitube	14/10/2003	1–2	4.8217	43.0481	112	31.4
	SS-4	Grand Rhône Canyon	REMORA 3	4	Multitube	02/11/2002	1–2	4.7969	42.9007	781	48.0

[Barnes and Blackstock, 1973] after extraction with a mixture of chloroform:methanol (MeOH) (2:1 v/v). Absorption of the products was measured at 520 nm with a Beckman spectrophotometer.

3.2.2.2. Lipid Extraction and Purification Procedure

[15] Hydrocarbon and GDGT analyses were conducted at NIOZ. Soil and sediment samples (1–12 g) for hydrocarbon and GDGT analyses were either ultrasonically extracted with MeOH (3×), MeOH:dichloromethane (DCM) (1:1 v/v; 3×), and DCM (3×) or extracted with an Accelerated Solvent Extractor (DIONEX ASE 200) using a mixture of DCM:MeOH (9:1 v/v) at a temperature of 100°C and a pressure of 7.6×10^6 Pa. The supernatants were combined, the solvents were removed by rotary evaporation, and the extracts were taken up in DCM and dried over anhydrous Na_2SO_4 . Afterward, activated copper was added and stirred overnight for removal of elemental sulfur. The extracts were cleaned over MgSO_4 column with DCM and separated into three fractions over an Al_2O_3 column (activated for 2 h at 150°C) using hexane:DCM (9:1 v/v), hexane:DCM (1:1 v/v), and DCM:MeOH (1:1 v/v), respectively.

3.2.2.3. Aliphatic Hydrocarbon Analysis

[16] For aliphatic hydrocarbon (*n*-alkane) analysis, the hexane:DCM, 9:1 v/v fractions of the total lipid extract were further purified over a AgNO_3 impregnated silica gel column using hexane. A known amount of standard, perdeutero-*n*- C_{24} alkane was added and used as reference for quantification of each compound. Analyses were performed on a Hewlett Packard 5890 series II gas chromatograph equipped with an on-column injector and fitted with a fused-silica capillary column (25 m \times 0.32 mm) coated with CP Sil 5 (film thickness 0.12 μm). Helium was used as carrier gas. The GC oven was heated from 70°C to 130°C at 20°C/min, followed by 4°C/min to 320°C (10 min holding time). Effluents were detected using flame ionization (FID). To identify compounds in selected samples, GC-MS analyses were performed with a ThermoFinnigan TRACE gas chromatograph using the GC conditions described above. The column was directly inserted into the electron impact ion source of a ThermoFinnigan DSQ quadrupole mass spectrometer, scanning a mass range of m/z 50–800 at 3 scans per second and an ionization energy of 70 eV. Compound identifications are based on comparison of relative GC retention times and mass spectra published in the literature. Quantification of com-

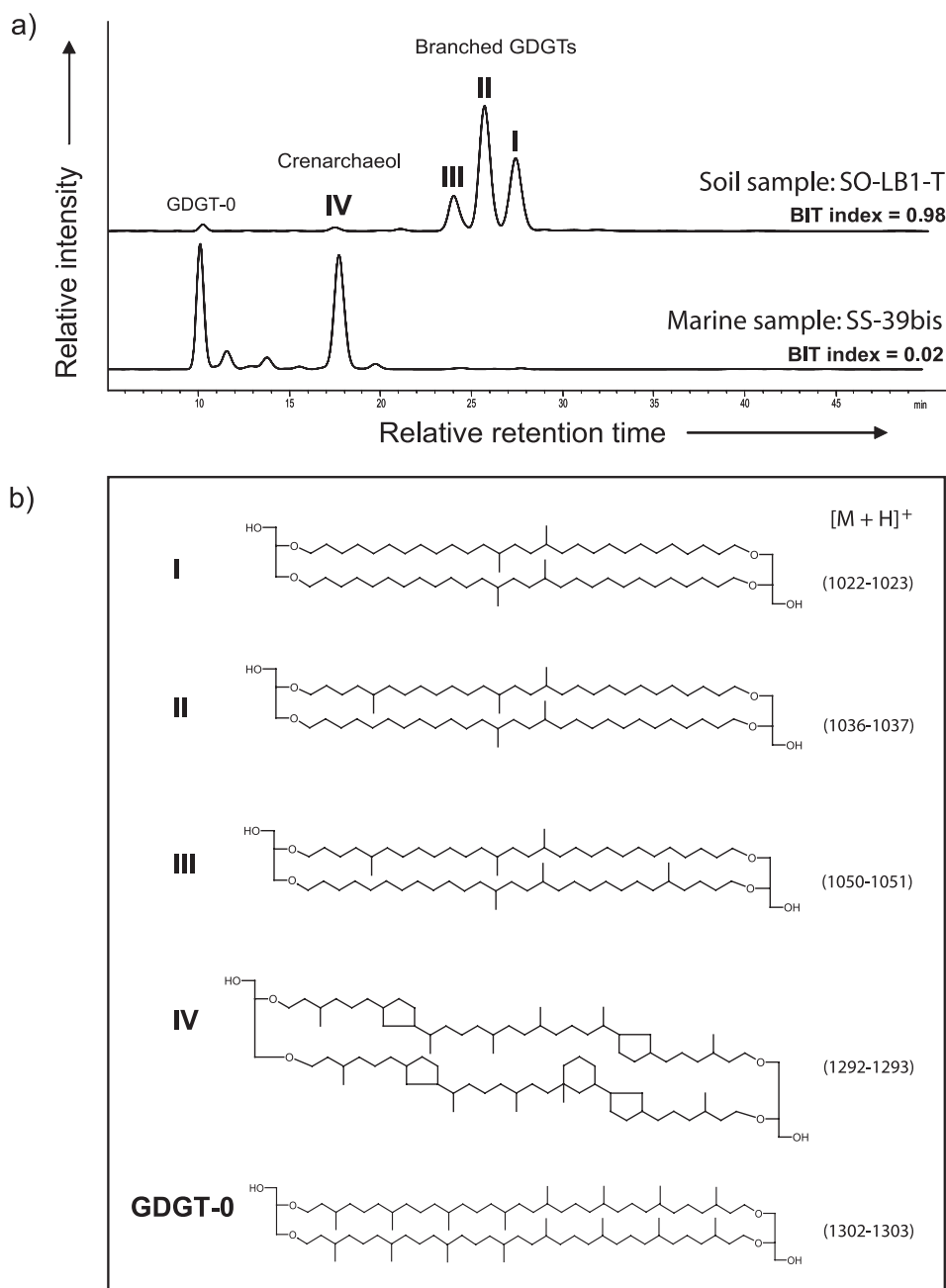


Figure 2. (a) HPLC/APCI-MS base peak chromatograms of GDGT lipids in a soil (SO-LB1-T) and a marine sediment (SS-39bis) and (b) GDGT structures: I, II, and III indicate the branched GDGTs, and IV is crenarchaeol.

pounds was performed by peak area integration in FID chromatograms. Data were acquired and integrated using ATLAS analytical software.

3.2.2.4. GDGT Analysis

[17] The polar fractions (DCM:MeOH, 1:1; v/v) were analyzed for GDGTs according to the procedure described by *Hopmans et al.* [2000, 2004]. Aliquots of polar fractions were blown down under

a stream of nitrogen, redissolved by sonication (5 min) in hexane:propanol (99:1 v/v), and filtered through 0.45 μ m PTFE filters. The samples were analyzed with a high performance liquid chromatography/atmospheric pressure positive ion chemical ionization mass spectrometry (HPLC/APCI-MS). Analyses were performed on an HP (Palo Alto, CA, USA) 1100 series LC-MS, equipped with auto-injector and Chemstation chro-



Table 2. Results of Bulk OM, Total Lipid, *n*-Alkane, and GDGT Analyses^a

Sample Type	Sample Code	TOC, wt. %	C/N Ratio	$\delta^{13}\text{C}_{\text{org}}$, ‰ VPDB	Terr. TOC, %	Total Lipids, mg/g _{sed}	CPI ₂₇₋₃₁	C _{max}	31/(29+31)	ACL ₂₇₋₃₁	ΣALK_{27-31} , $\mu\text{g/g}_{\text{TOC}}$	BIT Index	Branched GDGTs, $\mu\text{g/g}_{\text{TOC}}$	Crenarchaeol, $\mu\text{g/g}_{\text{TOC}}$	Terr. TOC, %
Soils	SO-LB1-T	7.8	12.8	-25.8	n.d.	n.d.	8.6	31	0.6	29.9	410	0.98	27.3	0.5	n.d.
	SO-LB1-B	6.2	13.7	-25.7	n.d.	n.d.	16.2	31	0.6	29.8	200	0.99	21.5	0.2	n.d.
	SO-LB2-T	16.1	56.2	-28.7	n.d.	n.d.	15.9	31	0.5	29.7	3200	1.00	183.8	0.2	n.d.
	SO-LB2-B	4.4	15.8	-27.2	n.d.	n.d.	8.9	31	0.6	29.9	760	0.98	36.0	0.7	n.d.
Têt riverbed sediment	RBS-ST1	4.2	10.5	-27.0	n.d.	n.d.	9.2	29	0.4	28.9	670	0.99	105.7	1.4	n.d.
Marine surface sediment															
Têt buoy site (28 m)	TB-10/10/2003	0.6	12.4	-23.9	56	0.2	7.2	29	0.4	29.2	130	0.21	1.8	7.2	20
	TB-26/11/2003	0.3	13.2	-23.3	46	0.1	5.5	29	0.5	29.1	120	0.19	2.4	10.3	18
	TB-12/12/2003	1.7	5.9	-26.0	86	1.6	7.9	29	0.4	28.9	660	0.52	9.1	9.8	52
	TB-11/02/2004	1.5	11.9	-25.1	73	0.9	10.0	29	0.4	28.9	410	0.37	10.0	16.9	36
	TB-15/03/2004	0.4	17.7	-23.4	48	0.1	6.3	31	0.5	29.4	170	0.13	0.9	5.9	11
	TB-18/04/2004	0.2	12.4	-22.8	40	0.1	4.2	29	0.5	29.2	120	0.15	0.6	3.8	13
	TB-28/04/2004	0.3	13.8	-23.1	45	0.1	6.2	29	0.5	29.4	150	0.19	1.6	7.4	17
	TB-26/05/2004	0.4	14.5	-23.4	49	0.1	7.8	29	0.5	29.3	170	0.22	1.8	6.8	21
	TB-23/06/2004	0.5	9.9	-23.1	44	0.1	7.9	31	0.5	29.5	270	0.13	1.4	9.6	11
	TB-28/07/2004	0.5	20.6	-23.3	48	0.2	6.6	29	0.5	29.2	90	0.15	0.5	3.0	13
	TB-30/09/2004	0.4	16.5	-22.8	40	0.1	3.0	29	0.4	29.1	110	0.18	1.6	7.3	17
	TB-13/12/2004	0.5	21.6	-23.7	53	0.2	7.0	29	0.4	29.1	110	0.19	2.6	12.4	17
	TB-15/03/2005	0.5	12.3	-24.3	61	0.1	5.2	29	0.4	29.1	50	0.20	0.03	0.1	18
	TB-20/05/2005	0.5	12.5	-23.5	49	0.1	3.8	29	0.4	29.1	60	0.17	0.04	0.2	16
	TB-06/07/2005	0.5	16.2	-23.4	48	0.1	8.4	29	0.4	29.0	70	0.12	0.02	0.1	10
Têt prodelta (20 m)	TP-28/04/2004	1.4	18.4	-25.7	82	1.1	8.1	29	0.4	28.9	470	0.55	6.1	7.4	55
Têt transect															
	SS-35	0.7	24.8	-24.4	63	n.d.	5.9	29	0.4	29.1	70	0.26	5.2	14.6	25
	SS-352	0.6	19.8	-23.9	56	n.d.	7.9	29	0.4	29.2	90	0.27	7.6	20.6	26
	SS-351bis	0.6	13.4	-23.7	53	n.d.	9.3	29	0.4	29.1	70	0.20	7.6	29.8	19
	SS-353	1.0	12.2	-23.4	49	n.d.	5.0	29	0.5	29.3	60	0.12	10.9	83.5	10
	SS-37bis	0.9	12.7	-23.3	48	n.d.	6.1	29	0.5	29.4	60	0.09	7.5	74.5	7
	SS-34bis	0.3	10.5	-22.5	35	n.d.	4.7	29	0.5	29.4	60	0.05	1.7	36.6	3
	SS-38bis	0.9	11.9	-22.4	35	n.d.	5.2	31	0.5	29.5	50	0.02	1.6	94.5	0
	SS-39bis	0.7	10.4	-22.4	34	n.d.	3.1	31	0.5	29.6	70	0.02	1.4	62.4	0

Table 2. (continued)

Sample Type	Sample Code	TOC, wt. %	C/N Ratio	$\delta^{13}\text{C}_{\text{org}}$, ‰ VPDB	Terr. TOC, b_0 %	Total Lipids, mg/g _{sed}	CPI_{27-31}	C_{max}	$31/(29+31)$	ACL_{27-31}	ΣALK_{27-31} , $\mu\text{g/g}_{\text{TOC}}$	BIT Index	Branched GDGTs, $\mu\text{g/g}_{\text{TOC}}$	Crenarchaeol, $\mu\text{g/g}_{\text{TOC}}$	Terr. TOC, b_0 %
Rhône	SS-KB16	1.8	13.0	-25.9	84	n.d.	8.2	29	0.4	29.0	270	0.83	15.0	3.1	83
Transect	SS-KB4	1.7	14.8	-25.5	79	n.d.	8.8	29	0.4	29.0	270	0.80	9.8	2.5	80
	SS-9X	1.0	12.1	-24.4	63	n.d.	4.2	29	0.5	29.3	110	0.12	3.4	26.6	10
	SS-2	0.8	11.3	-23.3	47	n.d.	3.8	31	0.5	29.4	120	0.06	3.1	54.2	4
	SS-3	0.3	7.8	-22.7	39	n.d.	3.4	31	0.5	29.4	110	0.05	2.5	53.3	3
	SS-4	0.7	10.1	-22.5	36	n.d.	3.5	31	0.5	29.6	110	0.02	0.6	25.8	0

^aNotes: n.d., not determined; C_{max} , carbon number of the homologue with highest abundance; $31/(29+31)$, ratio of the $n\text{-C}_{31}$ to the sum of the $n\text{-C}_{29}$ and $n\text{-C}_{31}$ alkane; ACL (average chain length), $\text{ACL}_{27-31} = (\Sigma[\text{C}_i] \times i) / \Sigma[\text{C}_i]$, where i is the range of carbon numbers and C_i is the relative concentration of the alkane containing i carbon atoms; CPI (Carbon Preference Index), $\text{CPI}_{27-31} = 1/2 \times (\Sigma\text{odd } \text{C}_{27\text{to-C}_{31}} / \Sigma\text{even } \text{C}_{26\text{to-C}_{30}} + 1/2 \times (\Sigma\text{odd } \text{C}_{27\text{to-C}_{31}} / \Sigma\text{even } \text{C}_{28\text{to-C}_{32}})$.
^bTerr. TOC indicates the calculated terrestrial TOC content based on $\delta^{13}\text{C}_{\text{org}}$ and BIT index, respectively (see text).

matography manager software. Separation was achieved on a Prevail Cyano column (2.1×150 mm, $3 \mu\text{m}$; Alltech, Deerfield, IL, USA), maintained at 30°C . Flow rate of the hexane:propanol (99:1 v/v) eluent was 0.2 ml/min, isocratically for the first 5 min, thereafter with a linear gradient to 1.8% propanol in 45 min. After each analysis, the column was cleaned by back-flushing hexane/propanol (90:10, v/v) at 0.2 ml/min for 10 min. Detection was achieved using APCI-MS of the eluent. Conditions for APCI-MS were as follows: nebulizer pressure 60 psi, vaporizer temperature 400°C , drying gas (N_2) flow 6 l/min and temperature 200°C , capillary voltage -3 kV, corona $5 \mu\text{A}$ (~ 3.2 kV). GDGTs were detected by single ion monitoring of their $[\text{M} + \text{H}]^+$ ions and quantification of the GDGT compounds was achieved by integrating the peak areas and comparing these to a standard curve prepared with known amounts of GDGT-0 which contains no cyclopentane ring (see Figure 2 for the structure).

[18] Values of BIT index were calculated according to Hopmans *et al.* [2004]:

$$\text{BIT index} = [\text{I} + \text{II} + \text{III}] / [\text{I} + \text{II} + \text{III} + \text{IV}]$$

The roman numerals refer to the GDGTs indicated in Figure 2. I, II, and III are branched GDGTs and are tracers for terrestrial OM and IV the isoprenoid GDGT, “crenarchaeol”, a tracer for marine OM [Hopmans *et al.*, 2004]. The analyses were done at least in duplicate and mean concentrations and BIT values are reported.

4. Results

4.1. Soils and Riverbed Sediments

[19] The TOC contents of the soils were relatively high (4.4 to 16.1 wt.%; see Table 2). The C/N ratios varied between 12.8 and 56.2 and the $\delta^{13}\text{C}_{\text{org}}$ values ranged from -25.7 to -28.7 ‰. For the Têt River bed sediment, the TOC content was lower than in the soils but remained relatively high (4.2 wt.%; see Table 2). The C/N ratio was 10.5 and the $\delta^{13}\text{C}_{\text{org}}$ value -27 ‰.

[20] In all soils and sediments a homologous series of n -alkanes ($n\text{-C}_{21}$ to $n\text{-C}_{35}$) was detected. The distributions of n -alkanes showed a strong odd-over-even carbon number predominance in the range of $\text{C}_{27}\text{--}\text{C}_{31}$ n -alkanes with the carbon preference index (CPI_{27-31} [Kolattukudy, 1976]) varying between 8 and 16 (Table 2). $n\text{-C}_{31}$ was the major n -alkane in the soils, while the Têt River bed

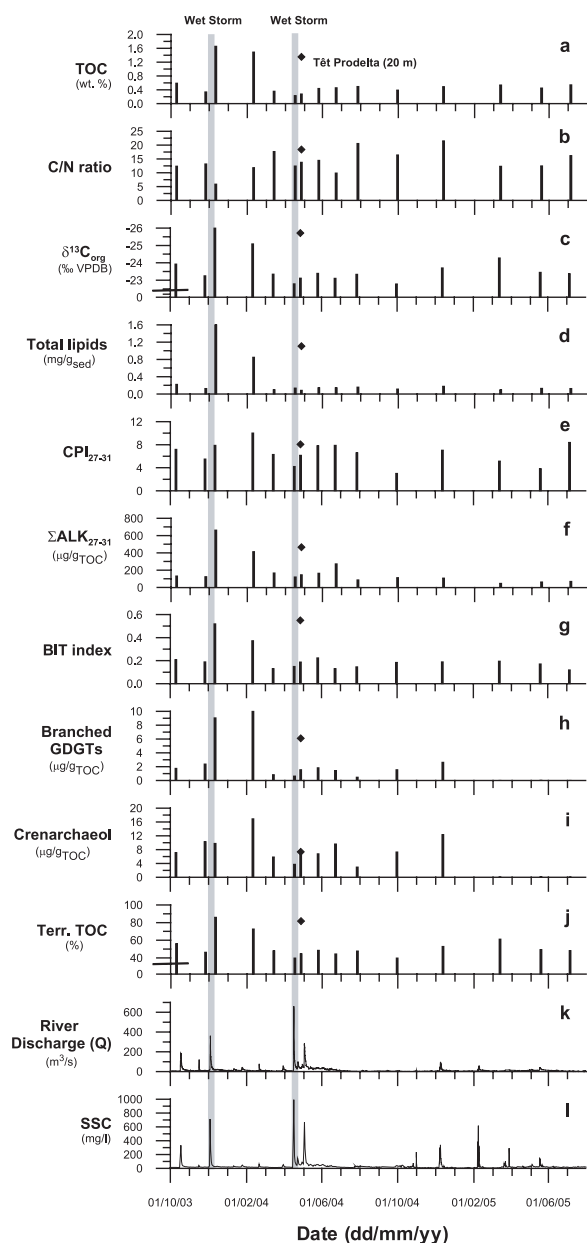


Figure 3. Results of bulk sediment and lipid analyses from Têt buoy site surface sediments: (a) TOC contents in wt.%, (b) C/N ratio, (c) $\delta^{13}\text{C}_{\text{org}}$ in ‰, (d) total lipids in mg/g_{sed} , (e) CPI_{27-31} , (f) ΣALK_{27-31} in $\mu\text{g/g}_{\text{TOC}}$, (g) BIT index, (h) sum of branched GDGTs concentration in $\mu\text{g/g}_{\text{TOC}}$, (i) crenarchaeol concentration in $\mu\text{g/g}_{\text{TOC}}$, (j) calculated terrestrial TOC (terr. TOC) based on $\delta^{13}\text{C}_{\text{org}}$ in ‰, (k) river discharge (Q) in m^3/s , and (l) suspended sediment concentration (SSC) in mg/l . The hourly data of Têt River discharge are the sum of the water discharge at the “Joffre” hydrologic station (code Y047030) and the Basse River, a small affluent (code Y0475610) obtained from the “HYDRO” data bank hosted at the French Ministry of Environment. Filled diamonds indicate the data for the core top sample taken in the Têt prodelta at 20 m water depth on 28 April 2004. Note that the y axis of $\delta^{13}\text{C}_{\text{org}}$ is inverted.

sediment was dominated by $n\text{-C}_{29}$. The average chain-length of the range of $\text{C}_{27}\text{--C}_{31}n$ -alkanes (ACL_{27-31}) showed quite stable values of around 29. The summed C_{27} to $\text{C}_{31}n$ -alkane concentrations (ΣALK_{27-31}) varied between 200 and $3200 \mu\text{g/g}_{\text{TOC}}$.

[21] As expected, the BIT index from these soils and the riverbed sediment were close to 1 (Table 2 and Figure 2a). The concentrations of branched GDGTs ranged between 22 and $184 \mu\text{g/g}_{\text{TOC}}$, while the concentrations of crenarchaeol varied between 0.2 and $1.4 \mu\text{g/g}_{\text{TOC}}$.

4.2. Time Series of Têt Prodelt Surface Sediments

[22] The TOC contents of the surface sediments at the Têt buoy site were relatively low between 0.2 and 0.6 wt.% (Figure 3a). However, substantially higher TOC contents were observed in the sediments sampled in December 2003 and February 2004, containing 1.7 and 1.5 wt.% of TOC, respectively. In contrast to TOC, the C/N ratios of surface sediments strongly fluctuated between 5.9 and 21.6 (Figure 3b). Interestingly, the sediments with enhanced TOC had lower C/N ratios compared to those from other periods. The $\delta^{13}\text{C}_{\text{org}}$ values ranged from -26.0 to -22.8‰ , with the ^{13}C depleted values in the TOC-rich sediments (Figure 3c).

[23] The total lipid concentrations of the surface sediments varied between 0.1 and $1.6 \text{ mg/g}_{\text{sed}}$, with the highest concentration in the TOC-rich sediment taken in December 2003 (Figure 3d). The CPI_{27-31} of the n -alkanes ranged from 3 and 10 (Figure 3e). Two sediments sampled in March and June 2004 had the $n\text{-C}_{31}$ as the most dominant n -alkane, whereas distributions in all other samples were dominated by the $n\text{-C}_{29}$ (Table 2). However, the differences in the abundances of $n\text{-C}_{31}$ and $n\text{-C}_{29}$ in the surface sediments where $n\text{-C}_{31}$ was dominating were very small. This was reflected in the ratio of the $n\text{-C}_{31}$ to the $n\text{-C}_{29}$ alkane ($31/(29+31)$), which showed no substantial changes over time (Table 2). The ACL_{27-31} showed quite stable values of around 29 (Table 2). The ΣALK_{27-31} varied between 50 and $660 \mu\text{g/g}_{\text{TOC}}$ (Figure 3f).

[24] The BIT index for the surface sediments from the Têt buoy site varied between 0.12 and 0.52, showing higher values in the TOC-rich sediments obtained in December 2003 and February 2004 (Figure 3g). The concentration of branched GDGTs ranged between 0.02 and $10 \mu\text{g/g}_{\text{TOC}}$ (Figure 3h),

while that of crenarchaeol varied between 0.1 and 17 $\mu\text{g/g}_{\text{TOC}}$ (Figure 3i). Branched GDGTs were strongly enhanced in the TOC-rich sediments sampled in December 2003 and February 2004. Clear systematic seasonal patterns were not observed in the BIT index as well as in the concentrations of crenarchaeol and branched GDGTs.

4.3. Têt and Rhône Transects

4.3.1. Têt Transect

[25] The TOC contents of the surface sediments from the Têt transect generally varied between 0.3 and 1.0 wt.% (Figure 4a), with higher values offshore than around the prodelta (except at station 34bis). The C/N ratios fluctuated between 10.4 and 24.8, with the highest value in the Têt prodelta (Figure 4b). The $\delta^{13}\text{C}_{\text{org}}$ values generally increased seaward from -24.4 to -22.4‰ (Figure 4c).

[26] The CPI_{27-31} ranged from 3.1 to 9.3 and decreased substantially with increasing distance from the coast (Figure 4d). $n\text{-C}_{29}$ was the most abundant sedimentary n -alkanes in the prodelta and shelf sediments, whereas in the canyon samples $n\text{-C}_{31}$ was slightly more abundant (Table 2). This was reflected in the $31/(29+31)$ ratio, showing slightly increased values with increasing distances from the coast. The ACL_{27-31} showed quite stable values between 29 and 30 with perhaps a slight seaward increase. The ΣALK_{27-31} in the Têt transect remained fairly constant between 50 and 90 $\mu\text{g/g}_{\text{TOC}}$ (Figure 4e).

[27] The BIT index varied between 0.02 and 0.27, showing a decreasing trend from the Têt prodelta to the Lacaze–Duthiers Canyon (Figure 4f). The concentrations of branched GDGTs ranged between 1.4 and 11 $\mu\text{g/g}_{\text{TOC}}$ and, in contrast to the BIT index, showed a less clear trend (Figure 4g). The concentrations of crenarchaeol varied more widely between 15 and 95 $\mu\text{g/g}_{\text{TOC}}$ but again with no particular trend (Figure 4h).

4.3.2. Rhône Transect

[28] The TOC contents of the surface sediments of the Rhône transect abruptly decreased seaward, ranging from 1.8 wt.% in the Rhône prodelta to 0.7 wt.% in the Grand Rhône Canyon (Figure 4j). The C/N ratios showed the same pattern, decreasing from 14.8 to 10.1 toward the Grand Rhône Canyon (Figure 4k) as well as the $\delta^{13}\text{C}_{\text{org}}$ values which increased from -25.9 to -22.5‰ (Figure 4l).

[29] The CPI_{27-31} sharply decreased from 8.8 to 3.4 with increasing water depths (Figure 4m). The $31/(29+31)$ ratio and the ACL_{27-31} increased slightly seaward similar to what was observed for the Têt transect (Table 2). The ΣALK_{27-31} in the Rhône transect showed an abrupt shift from the prodelta area (270 $\mu\text{g/g}_{\text{TOC}}$) to the Grand Rhône Canyon (110 $\mu\text{g/g}_{\text{TOC}}$) (Figure 4n).

[30] The BIT index ranged from 0.83 to 0.02, with a substantial decrease from the Rhône prodelta to the Grand Rhône Canyon (Figure 4o). The concentrations of branched GDGTs ranged between 0.6 and 15 $\mu\text{g/g}_{\text{TOC}}$, with the highest concentration in the prodelta (Figure 4p). The concentrations of crenarchaeol showed an opposite pattern compared to that of branched GDGTs, i.e., with low concentrations in the sediments of the prodelta (~ 2.8 $\mu\text{g/g}_{\text{TOC}}$) and higher concentrations offshore (54 $\mu\text{g/g}_{\text{TOC}}$; Figure 4q).

5. Discussion

5.1. Bulk Proxies for Transport of Terrestrial OM to the Marine Environment

[31] Higher plant-derived OM is characterized by a higher C/N ratio (e.g., >20 [Meyers and Ishiwatari, 1993]) than that of OM derived from marine organisms (6 to 9 [Müller, 1977]) as terrestrial OM contains a higher percentage of nonprotein materials. Due to humification and mineralization of plant litter in soils, C/N ratios of soil OM are typically lower compared to vascular plants, varying between 8 and 20 [e.g., Hedges and Oades, 1997]. The C/N ratios of the investigated soils are well within the range cited above except the sample SO-LB2-T. The relatively high C/N ratio (56.2) of the sample SO-LB2-T can be attributed to the high abundance of nondegraded plant roots. The $\delta^{13}\text{C}_{\text{org}}$ of higher plants that use the Calvin-Benson cycle of carbon fixation (i.e., so-called C_3 plants) ranges from -29.3 to -25.5‰ , with an average value of about -27‰ [e.g., Fry and Sherr, 1984; Tyson, 1995; Meyers, 1997]. The $\delta^{13}\text{C}_{\text{org}}$ values (-28.7 to -25.7‰) of the investigated soils near the Têt River are typical of C_3 vegetation. Consequently, our data indicate that soil OM was primarily derived from C_3 plants, and it is thus likely that C_3 -derived soil OM is the dominant OM contribution to fine fractions (<63 μm) of riverbed sediments. Indeed, the riverbed sample RBS-ST1 showed low C/N ratio (10.5) and low $\delta^{13}\text{C}_{\text{org}}$ (-27‰).

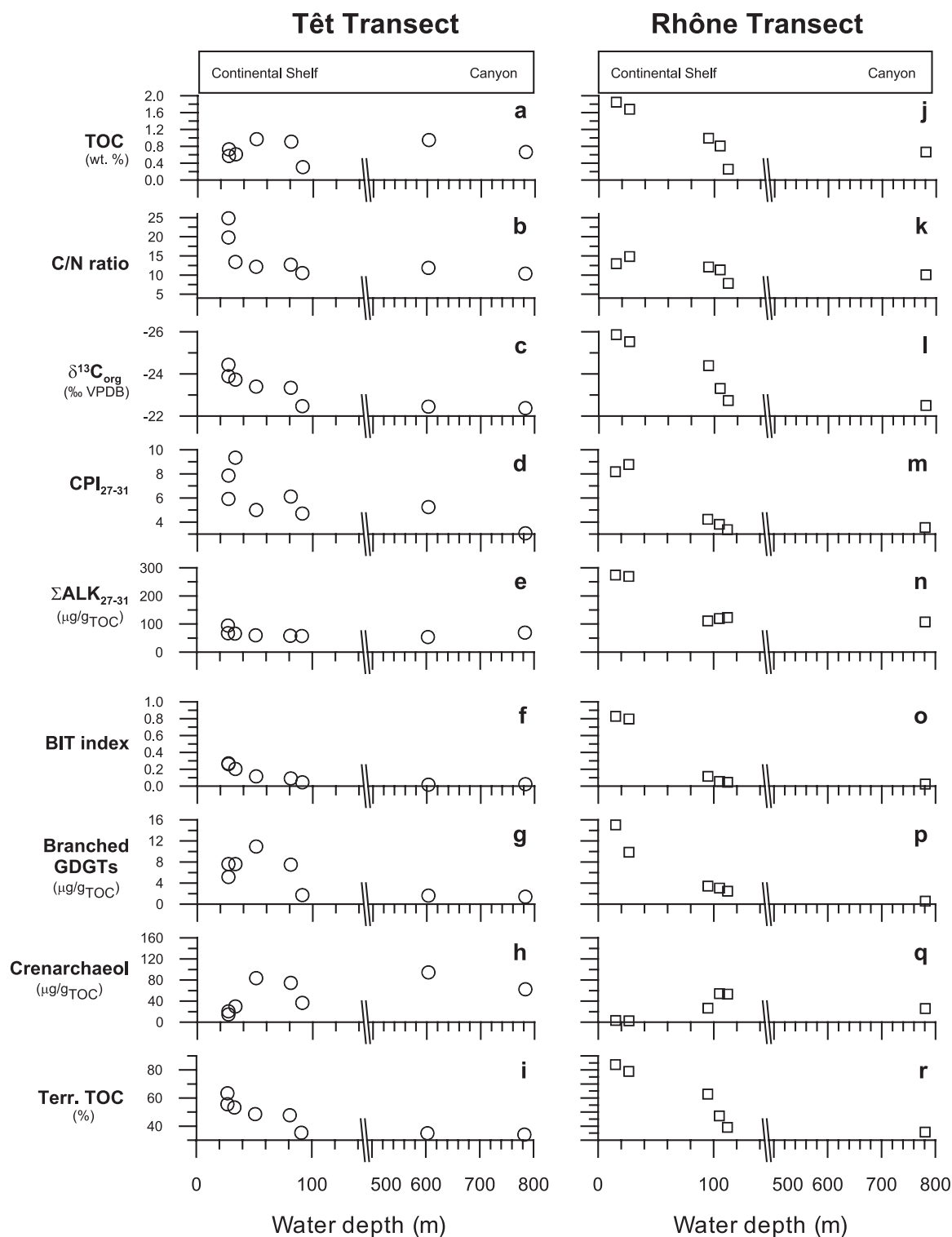


Figure 4. Results of bulk sediment and lipid analyses from transect surface sediments: (a) TOC contents in wt.%, (b) C/N ratio, (c) $\delta^{13}\text{C}_{\text{org}}$ in ‰, (d) CPI_{27-31} , (e) ΣALK_{27-31} in $\mu\text{g/g}_{\text{TOC}}$, (f) BIT index, (g) sum of branched GDGTs concentration in $\mu\text{g/g}_{\text{TOC}}$, (h) crenarchaeol concentration in $\mu\text{g/g}_{\text{TOC}}$, and (i) calculated terrestrial TOC (terr. TOC) based on $\delta^{13}\text{C}_{\text{org}}$ in ‰ are for the Têt transect, while (j) TOC contents in wt.%, (k) C/N ratio, (l) $\delta^{13}\text{C}_{\text{org}}$ in ‰, (m) CPI_{27-31} , (n) ΣALK_{27-31} in $\mu\text{g/g}_{\text{TOC}}$, (o) BIT index, (p) sum of branched GDGTs concentration in $\mu\text{g/g}_{\text{TOC}}$, (q) crenarchaeol concentration in $\mu\text{g/g}_{\text{TOC}}$, and (r) calculated terrestrial TOC based on $\delta^{13}\text{C}_{\text{org}}$ in ‰ are for the Rhône transect. Note that the y axis of $\delta^{13}\text{C}_{\text{org}}$ is inverted.

[32] At the Têt buoy site, the significant enhancements of TOC content and total lipid concentration in the sediments sampled in December 2003 and February 2004 (Figure 3) corresponds to lower C/N ratios (5.9 and 11.9) as well as lower $\delta^{13}\text{C}_{\text{org}}$ values (-26.0 and -25.1‰). The C/N ratio is closer to a marine value than most other samples from this time series, suggesting an increased marine OM input. However, the $\delta^{13}\text{C}_{\text{org}}$ value indicates the opposite. Considering that soil OM can have similar a C/N ratio as marine OM and C/N ratios around 10–12 are commonly found in total suspended solids of the Têt River during floods (Ludwig, unpublished results), our data suggest that terrestrial OM input was enhanced and soil OM was dominant rather than vascular plant detritus. On the basis of the $\delta^{13}\text{C}_{\text{org}}$ values (Table 2), the TOC contents of surface sediments were separated into a marine and terrestrial portion. We estimated the portions of marine and terrestrial OM with a simple binary mixing model, assuming terrestrial ($\delta^{13}\text{C}_{\text{terr}} = -27\text{‰}$) and marine ($\delta^{13}\text{C}_{\text{mar}} = -20\text{‰}$) OM end-members [e.g., Meyers, 1994, 1997]:

$$\text{TOC} = \text{OM}_{\text{mar}} + \text{OM}_{\text{terr}}$$

$$\delta^{13}\text{C}_{\text{org}} * \text{TOC} = \delta^{13}\text{C}_{\text{mar}} * \text{OM}_{\text{mar}} + \delta^{13}\text{C}_{\text{terr}} * \text{OM}_{\text{terr}}$$

where OM_{mar} and OM_{terr} are the contents of marine and terrestrial OM, and $\delta^{13}\text{C}_{\text{mar}}$ and $\delta^{13}\text{C}_{\text{terr}}$ are the isotopic compositions of marine and terrestrial OM, respectively. The estimated contribution of terrestrial OM was much higher for the TOC-rich sediments sampled in December 2003 and February 2004, corresponding to 86% and 73% of TOC, respectively (Figure 3j), while TOC was estimated to contain 50% terrestrial OM on average during the other periods.

[33] The prodelta sediments from the Têt transect (Figure 4) showed similar TOC contents, C/N ratios, and $\delta^{13}\text{C}_{\text{org}}$ values as those from the Têt prodelta time series during “low TOC” periods (i.e., all samples except those taken in December 2003 and February 2004; Figure 3). Interestingly, the TOC contents were slightly higher in the mid shelf than in the prodelta across the Têt transect, while the estimated terrestrial OM, based on $\delta^{13}\text{C}_{\text{org}}$, remained more or less at the same level (Figure 4i). The canyon sediments showed similar TOC contents, and C/N ratios, compared to those from the prodelta, but lower $\delta^{13}\text{C}_{\text{org}}$ values and thus lower estimated terrestrial OM portions. This

suggests that contribution of marine OM is enhanced in the mid shelf and the canyon.

[34] All bulk parameters from the Rhône transect showed a distinctive difference between the prodelta and the mid shelf as well as the canyon (Figure 4). OM in the Rhône prodelta sediments showed C/N ratios >13 and $\delta^{13}\text{C}_{\text{org}}$ values of approximately -26.0‰ . This indicates a substantial contribution of soil OM originating from C_3 plants as illustrated in a scatterplot for the C/N ratio and the $\delta^{13}\text{C}_{\text{org}}$ (Figure 5a). The calculated contribution of terrestrial OM based on the two end-member isotopic mixing model corresponds to 79–84% (Figure 4r). The estimated terrestrial TOC portions of the mid shelf and canyon sediments were much lower than those in the prodelta, decreasing from 63% to 36% offshore. This suggests that terrestrial OM in the mid shelf and the canyon is substantially diluted by increased marine OM contributions or that less soil OM reaches the mid shelf to the canyon.

5.2. Molecular Proxies for Transport of Terrestrial OM to the Marine Environment

[35] The presence of C_{27} , C_{29} , and $\text{C}_{31}n$ -alkanes is evidence for an origin of predominantly epicuticular waxes of higher plants [Eglinton and Hamilton, 1967], whereas aquatic algal and photosynthetic bacterial contributions are indicated by the presence of $n\text{-C}_{17}$ alkane [e.g., Cranwell et al., 1987]. Epicuticular waxes derived from higher plants generally have high (>5) CPI values [e.g., Eglinton and Hamilton, 1963; Mazurek and Simoneit, 1984], while marine- and petroleum-derived n -alkanes have a CPI of 1 [Simoneit, 1984]. Therefore the predominance of C_{27} , C_{29} , and $\text{C}_{31}n$ -alkanes and the high CPI values in the terrestrial samples (CPI > 8) as well as in the marine sediments of the Gulf of Lions (CPI > 3) indicate that n -alkanes are predominantly derived from terrestrial sources, i.e., land-plant epicuticular waxes. This is consistent with previous results by Bouloubassi et al. [1997]. Small variations in $31/(29+31)$ and ACL_{27-31} through the whole sample series investigated imply no significant changes in terrestrial OM sources. Terrestrial n -alkanes in marine sediments can be derived from either contemporary vascular plant leaves or n -alkanes from soils [e.g., Eglinton et al., 1997; Pearson and Eglinton, 2000]. In our data set, the enhanced n -alkane concentrations in the Rhône prodelta were accompanied by depleted $\delta^{13}\text{C}_{\text{org}}$ values and low

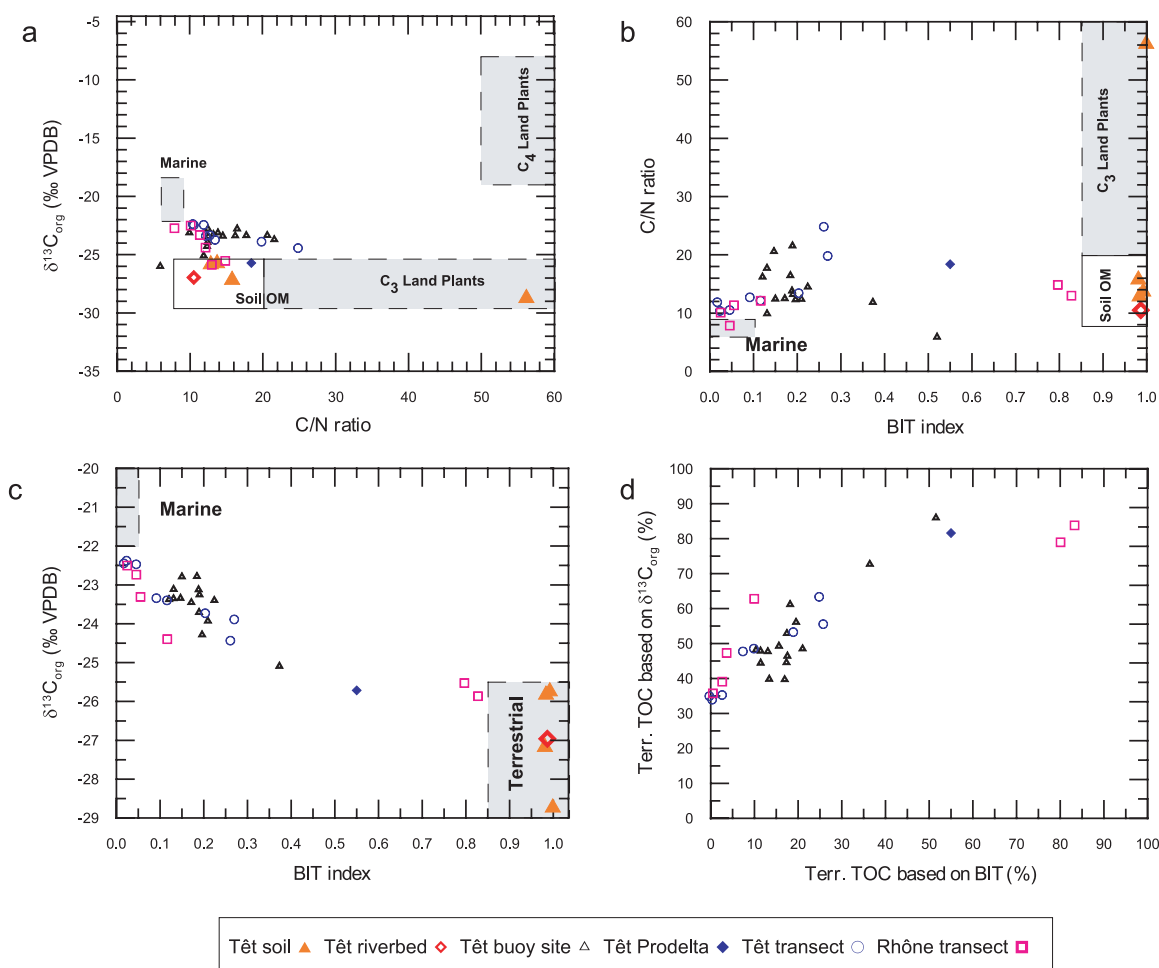


Figure 5. Scatterplots for (a) $\delta^{13}C_{org}$ and C/N ratio (boundaries of major OM sources are according to Müller [1977], Sackett [1989], Meyers and Ishiwatari [1993], Meyers [1994], Tyson [1995], and Hedges and Oades [1997]), (b) BIT index and C/N ratio, (c) BIT index and $\delta^{13}C_{org}$, and (d) calculated terrestrial TOC percentages based on $\delta^{13}C_{org}$ and BIT index.

C/N ratios (<20). This suggests that the contribution of *n*-alkanes derived from soils is more important than from contemporary vascular plant leaves in the Gulf of Lions, which could be dispersed by wind over much larger distances [e.g., Pancost and Boot, 2004].

[36] As expected [cf. Hopmans *et al.*, 2004], high abundances of branched GDGTs were measured in the soils and the riverbed sediment and thus the BIT indices showed values close to 1 (Table 2). Interestingly, crenarchaeol was also found in those samples, although its concentration was much lower than that of branched GDGTs (Table 2). Crenarchaeol was initially considered to be exclusively produced by nonthermophilic marine planktonic Crenarchaeota [Sinninghe Damsté *et al.*, 2002b], but it was also recently found in lake sediments [Powers *et al.*, 2004], peats [Weijers *et al.*, 2004], soils [Weijers *et al.*, 2006b], and river water [Herfort *et al.*, 2006] albeit in relatively low concentrations. Crenarchaeol was also identified in Nevada hot springs having pHs between 6.0 and 9.2 and temperatures between 40 and 84°C [Pearson *et al.*, 2004]. Accordingly, our results along with the previous observations imply that crenarchaeol is not a biomarker exclusively produced in marine environments. The identification of crenarchaeol in terrestrial environments is consistent with molecular ecological work showing that nonthermophilic crenarchaeota are present in soils [e.g., Buckley *et al.*, 1998], lake systems [e.g., Keough *et al.*, 2003], and rivers [e.g., Abreu *et al.*, 2001; Wells *et al.*, 2006]. However, compared to marine environments [e.g., Karner *et al.*, 2001], the amounts of Crenarchaeota found on land are relatively low [e.g., Buckley *et al.*, 1998]. Therefore we may

al., 2004], soils [Weijers *et al.*, 2006b], and river water [Herfort *et al.*, 2006] albeit in relatively low concentrations. Crenarchaeol was also identified in Nevada hot springs having pHs between 6.0 and 9.2 and temperatures between 40 and 84°C [Pearson *et al.*, 2004]. Accordingly, our results along with the previous observations imply that crenarchaeol is not a biomarker exclusively produced in marine environments. The identification of crenarchaeol in terrestrial environments is consistent with molecular ecological work showing that nonthermophilic crenarchaeota are present in soils [e.g., Buckley *et al.*, 1998], lake systems [e.g., Keough *et al.*, 2003], and rivers [e.g., Abreu *et al.*, 2001; Wells *et al.*, 2006]. However, compared to marine environments [e.g., Karner *et al.*, 2001], the amounts of Crenarchaeota found on land are relatively low [e.g., Buckley *et al.*, 1998]. Therefore we may

expect the amount of crenarchaeol produced by terrestrial Crenarchaeota to be much lower than that by marine Crenarchaeota. However, the concentrations of crenarchaeol from the terrestrial samples (0.2 to 1.4 $\mu\text{g/g}_{\text{TOC}}$) investigated in this study were in some cases higher than those from marine samples (0.1 to 95 $\mu\text{g/g}_{\text{TOC}}$). In contrast, the concentrations of branched GDGTs in the soils from the Têt River catchments were much higher (22 to 184 $\mu\text{g/g}_{\text{TOC}}$) than that from marine environments (0.16 to 15 $\mu\text{g/g}_{\text{TOC}}$). Consequently, the BIT values were well below 1 in marine environments and usually much lower than in terrestrial environments. One concern related to the lower concentrations of crenarchaeol in the time series of Têt prodelta surface sediments compared to the terrestrial samples (only in some cases) is that possible selective degradations of branched GDGTs after entering into marine environments may bias the BIT index, causing lower values and thus misleading as higher marine OM input. A recent study by Schouten *et al.* [2004] showed that the different isoprenoidal GDGT isomers degraded at similar rates. Therefore we expect that crenarchaeol and branched GDGTs which have a similarly functionalized chemical structure are likely to be degraded at similar rates during sediment diagenesis [Hopmans *et al.*, 2004]. Nevertheless, degradation impacts on the BIT index should be tested in near future to better assess the robustness of this index.

[37] The BIT index was compared with the C/N ratio and the $\delta^{13}\text{C}_{\text{org}}$, widely used bulk proxies to trace sources of OM in marine sediments (Figures 5b and 5c). The C/N ratios and the BIT values do not show a linear relationship (Figure 5b). This may be attributed to the fact that the C/N ratio can be strongly affected by diagenesis and that it characterizes not just two end-members (marine versus terrestrial) in our study area. Indeed, different terrestrial OM sources (e.g., higher land plant detritus and soils) complicate the interpretation of this proxy as C/N ratios from soils can be similar to those from marine sources (see Figure 5a). When all the BIT values generated in this study are compared with $\delta^{13}\text{C}_{\text{org}}$ values, a strong correlation is visible (Figure 5c). $\delta^{13}\text{C}_{\text{org}}$ values of soil OM depend on the soil sources of C_3 or C_4 plants and are generally higher compared to those of vascular plants due to humification and mineralization of plant litter in soils [e.g., Mariotti and Peterschmitt, 1994]. The $\delta^{13}\text{C}_{\text{org}}$ values of the investigated soils lie well within the range representative of C_3 vegetation (Figure 5a). The $\delta^{13}\text{C}$ values of the

n-alkanes in the soils and the marine sediments varied between -30 and -35‰ (unpublished data), supporting a predominant origin from C_3 plants for the terrestrial OM. Accordingly, $\delta^{13}\text{C}_{\text{org}}$ in marine sediments in the Gulf of Lions is affected by mixing of marine OM with C_3 -plant derived terrestrial OM originating from or higher land plants or soil OM. The good correlation between $\delta^{13}\text{C}_{\text{org}}$ and BIT index, a proxy of soil-derived terrestrial OM input, is probably due to the high proportion of soil OM in marine sediments.

[38] Similar to the calculation of terrestrial OM based on the $\delta^{13}\text{C}_{\text{org}}$ values, we estimated the portions of marine and terrestrial OM, assuming terrestrial ($\text{BIT}_{\text{terr}} = 0.99$) and marine ($\text{BIT}_{\text{mar}} = 0.02$) OM end-members (Table 2). The estimated contributions of terrestrial OM based on the BIT indices ranged from 0 to 83%, showing generally lower percentages compared to those based on the $\delta^{13}\text{C}_{\text{org}}$ values (Figure 5d). Part of this discrepancy may lie in the assumed end-member values for $\delta^{13}\text{C}_{\text{org}}$. For example, if we assume that the marine end-member is -21‰ instead of -20‰ then this will substantially lower the terrestrial OC estimates. Nevertheless, both methods showed the same trends and a strong positive correlation to each other. This strongly suggests that the $\delta^{13}\text{C}_{\text{org}}$ and the BIT index are overall better proxies than the C/N ratio to assess terrestrial OM input into the Gulf of Lions. Furthermore, this study shows that the BIT index, in combination with other proxies, provides a good constraint for the relative estimation of soil-derived terrestrial OM amount in marine surface sediments.

[39] The elevated *n*-alkane concentrations in our data set were positively correlated with higher BIT values. In general, *n*-alkanes are transported by river runoff or by wind to marine environments and are therefore less specific for fluvial OM inputs [e.g., Pancost and Boot, 2004]. Nevertheless, the sharp increase of ΣALK_{27-31} in the Têt prodelta time series (Figure 3) and an abrupt shift of ΣALK_{27-31} in the Rhône transect (Figure 4) indicate that in this coastal setting fluvial transports of *n*-alkanes seem to be much more important than aeolian *n*-alkane inputs. A positive relationship between the *n*-alkane concentrations and the BIT values further supports the fluvial input of *n*-alkanes to TOC in marine sediments in the Gulf of Lions. Moreover, the rather stable 31/(29+31) ratio and ACL values suggest a similar constant terrestrial OM sources. Saharan dust is a major source of atmospheric particulate input in the

Mediterranean Sea [Löye-Pilot and Martin, 1996]. In the sparse vegetation of the Sahara, C₄ plants (e.g., halophytes and other herbs) are dominant [e.g., Ehleringer *et al.*, 1977]. Therefore C₄ plant signals (*n*-alkane $\delta^{13}\text{C}$: -17 to -24% [e.g., Schefuß *et al.*, 2003; Bendle *et al.*, 2006]) are representative as atmospheric terrestrial OM inputs from the African continent. Our preliminary *n*-alkane $\delta^{13}\text{C}$ results (-30 to -35%) suggest that terrestrial OMs were predominantly transported by rivers into the Gulf of Lions.

5.3. Origin and Distribution of OM in the Gulf of Lions

[40] River floods and storm waves are major processes for the deposition and dispersal of terrestrial OM in modern, river-dominated coastal oceans. A “wet storm” is connected to a flood with a high river discharge, while a “dry storm” is without significant river runoff [Ogston *et al.*, 2000]. During wet storms, enhanced riverine suspended materials can form a fine-grained flood deposit on continental shelves [Mullenbach and Nittrouer, 2000].

[41] In the Têt prodelta surface sediment time series, the highest BIT values were obtained in the TOC-rich sediments sampled in December 2003 and February 2004. This was accompanied by lower $\delta^{13}\text{C}_{\text{org}}$ and by higher *n*-alkane and branched GDGT concentrations. Therefore all bulk and molecular proxies (Figure 3) suggest that terrestrial OM proportions were enhanced in the sediments sampled in December 2003 and February 2004. The increased terrestrial OM signals in the Têt prodelta surface sediment time series correspond well to the high Têt River discharge ($Q = \sim 400 \text{ m}^3/\text{s}$, Figure 3k) and high suspended sediment concentration ($\text{SSC} = \sim 700 \text{ mg/l}$; Figure 3l) during the December wet storm in 2003 [Guillen *et al.*, 2006]. It is likely that this event resulted in significant soil erosion, transporting soil OM including soil-derived branched GDGTs via the Têt River to the Têt prodelta.

[42] The wet storm in April 2004 was accompanied by the highest Têt River discharge ($660 \text{ m}^3/\text{s}$) and the highest SSC (1000 mg/l) within the time frame of this study (Figure 3). Interestingly, the surface sediments recovered after this wet storm did not show enhanced terrestrial OM signal. In contrast, the core collected at 20 m water depth on the 28 April 2004 near to the Têt buoy site did show an increased TOC content ($1.4 \text{ wt}\%$), lower $\delta^{13}\text{C}_{\text{org}}$ value (-25.7%), and higher ΣALK_{27-31} ($470 \mu\text{g/l}$

g_{TOC}) and BIT (0.55) values, all suggesting an increased terrestrial OM deposit (Table 2 and Figure 3). This suggests that the Têt River flood plume in April 2004 did not reach the Têt buoy site (28 m water depth) but was limited to the nearshore (at least up to 20 m water depth) and further propagated along the coast. This further implies that, besides river discharge amounts, hydrodynamics processes are foremost important for the transport and deposition of river-derived OM in the coastal zones.

[43] In the sediments of the cross-shelf transects, higher BIT values were recorded in the Rhône prodelta, accompanied by higher TOC contents, lower $\delta^{13}\text{C}_{\text{org}}$, and higher *n*-alkane concentration. Accordingly, higher BIT values in marine sediments are in accordance with other bulk parameters, suggesting enhanced terrestrial OM inputs to marine environments. The BIT values from the Rhône prodelta are higher compared to those from the Têt prodelta. This is probably due to much larger water discharge, resulting from its much larger drainage basin and thus high mean sediment input from the Rhône River to the shelf. This is in agreement with the particularly high sediment accumulation rates ($>20 \text{ cm/yr}$) in the Rhône prodelta [Radakovitch *et al.*, 1999]. The low BIT values of the surface sediments in the canyons, along with enhanced $\delta^{13}\text{C}_{\text{org}}$, indicate that terrestrial OM was not deposited there or only temporarily. This supports the idea that upper canyons (300–800 m water depth) are by-pass conduits rather than terrestrial OM accumulation zones [e.g., Monaco *et al.*, 1990; Durrieu de Madron, 1994; Buscail and Germain, 1997].

[44] This study thus suggests that the BIT index is a useful proxy to trace floods and storm events in river dominated continental margins. Further work is necessary to better constrain different origins of terrestrial OM deposited in the Gulf of Lions and thus to better understand sediment depositional and transport processes from the rivers across canyons to open oceans.

6. Conclusions

[45] Branched GDGTs as well as crenarchaeol were detected in all soil samples surveyed in this study. The BIT index from terrestrial samples shows high values (>0.9), while it varies between 0.02 and 0.83 in marine environments, decreasing seaward from the inner shelf to the slope. For marine surface sediments, higher BIT values are

associated with lower $\delta^{13}\text{C}_{\text{org}}$ values as well as higher TOC contents and higher *n*-alkane concentrations, suggesting higher portion of terrestrial OM in sediments. These results support the idea that the BIT index can be applied in marine environments in order to characterize terrestrial OM as proposed by Hopmans *et al.* [2004] and hence to estimate the relative terrestrial OM amount in marine sediments. Furthermore, our study shows that soil OM along with contemporary vascular land plant detritus has an important contribution to TOC in marine sediments in the Gulf of Lions. The BIT index along with the concentration of branched GDGTs can serve as indicators for soil-derived terrestrial OM input to continental margins.

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