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Aliphatic hydrocarbons and triterpenes of the Congo deep sea fan

Laurence Méjanelle^{(1)*}, Béatrice Rivière⁽¹⁾, Laurence Pinturier⁽²⁾, Alexis Khripounoff⁽³⁾, François Baudin⁽⁴⁾ and Jordi Dachs⁽⁵⁾

(1) Sorbonne Universités, UPMC-Univ. Paris 06, CNRS, Laboratoire d'ECObiogéochimie Benthique, UMR 8222, 18 Avenue du Fontaulé, 66650 Banyuls Sur Mer, France (corresponding author: laurence.mejanelle@upmc.fr)

(2) Total E&P, Norge AS, Finnestadveien 44, 4029 Stavanger, Norway

(3) Ifremer Centre Bretagne, Institut Carnot-Ifremer-EDROME, Laboratoire Environnement Profond, (REM-EEP-LEP), 29280 Plouzané, France

(4) Sorbonne Universités, UPMC-Univ. Paris 06, CNRS, Institut des Sciences de la Terre de Paris, 4 place Jussieu, 75005 Paris, France

(5) Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Catalonia, Spain.

Abstract :

Hydrocarbons were analyzed in sediments from the Congo River deep-sea fan, from the Congo River, and in sinking particles collected by sediment traps 40 m above the sediment. Studied sites encompassed three lobes of decreasing age of formation along the canyon: sites A, F and C and a another lobe system, disconnected from the active channel since 4 ka, Site E. Terrestrial long-chain odd *n*-alkanes were dominant in all sediments of the lobe system. Unsaturated terpenoids sourced by higher plants, such as gammacerene, lupene, ursene and oleanene, were also detected. At site C, characterized by high accumulation rates (10–20 cm yr⁻¹), the organic matter spends less time in the oxic layer than at other sites and high phytadiene concentrations (10–17 µg g_{OC}⁻¹) evidenced recent terrestrial and phytoplanktonic remains reworked in anaerobic conditions. In these sediments, organic carbon-normalized concentrations of terrestrial alkanes and terpenoids were several fold higher than in the lobe sediments with lower accumulation rates (sites A and F), arguing for a more rapid degradation of terrestrial hydrocarbons than bulk organic carbon in the first steps of pre-diagenesis. Ample variations in the contributions of biomarkers from higher plants, ferns, bacteria and angiosperms, indicate an heterogeneous contribution of the soil and vegetation detritus delivered to the Congo lobe sediments. Lower concentrations in terrestrial hydrocarbons at site E, 45 km away from the active canyon, indicated that river particles are still admixed to the dominant marine organic matter. Diploptene and hop-7(21)-ene have a dual origin, from terrestrial and marine microorganisms. Scatter in their relationship to gammacerene argues for a contribution of marine microorganisms, in addition to soils-sourced microorganisms. The close distribution patterns of diploptene, hop-21-ene, hop-7(21)ene and neohop-13(18)-ene is in line with the hypothesis of sequential clay-catalyzed isomerisation of bacterial hopenes. Terrestrial biomarker accumulation fluxes at site C are one order of magnitude higher than vertical pelagic flux, demonstrating the magnitude of the inputs delivered through turbiditic transport in the submarine canyon. Crude oil contamination was evidenced at the disconnected site E (UCM, C₂₁ to C₂₆ tricyclic diterpanes, CPI) and, in smaller amounts, in some sediments from sites A and C. It may be related to marine crude oil extraction and transport. A short-chain mode of alkanes with an even predominance is evidenced in sediments of the lobe complex and likely sources, crude oil, microorganisms and ferns, are discussed.

Keywords : Congo fan, hydrocarbons, NAH, hopanes, hopenes, sediments, turbidite system.

1. Introduction

The effort to quantitatively understand and predict the carbon cycle includes the assessment of the inventory of marine reservoirs of organic carbon and the prediction of its oxidation and transfer back to atmospheric CO₂. However part of the terrestrial organic carbon escapes degradation and is buried in sedimentary horizons where no more oxidation occurs. Marine sediments are among the largest sinks of organic carbon, and half of this organic carbon reservoir is sourced by terrestrial plants and organisms (Blair and Aller, 2012; Burdige, 2005, 2007). This preserved organic carbon accounts for less than half the rivers inputs (Burdige, 2007 and references therein) which pictures the ocean margins as efficient in both remineralizing terrestrial organic matter and sequestering it (Middelburg et al., 1993). The organic carbon budget bridges processes on different times scales. The water column biogeochemical cycling and early diagenesis processes integrate annual to decadal time scales. In contrast, the cycle of organic carbon that is ultimately preserved in marine sediments as geopolymers, kerogen or source rocks eroded from the continent, may exert feedbacks on atmospheric CO₂ over thousand years to geologic time scale, with enhanced carbon burial during low sea level glacial ages (Cartapanis et al., 2016).

The Congo River (ex-Zaire) has a large intertropical watershed mainly covered by C3 rain forest vegetation. It delivers a large flux of higher plant debris and fine particles eroded from soils to the Atlantic Ocean, while it carries a minor contribution of riverine planktonic organic matter (Spencer et al., 2012). The particulate organic carbon exported to the Atlantic Ocean by the Congo River accounts for an input of 2 Tg organic carbon per year (Coynel et al., 2005). The Congo River is connected to a sinuous submarine canyon that starts within the river mouth, deeply incises in the shelf and slope and further extends in the deep basin through an active channel-levees-lobe system. The active terminal lobe complex is located at 4750 m depth, 760 km away from the river mouth (Savoie et al., 2009; Vangriesheim et al., 2009).

Overload of river sediments and sliding of sediment at the canyon head can initiate energetic gravity currents that transport most of the river particles to the terminal lobe complex. Besides terrestrial organic matter, sediments of the Congo-Angola margin also comprise a remarkable contribution of marine organic matter sourced by the coastal upwelling North and South the Congo River plume and within the plume itself (Schefuß et al., 2004). As a result, the gravity currents may transport an admixture of organic carbon sourced by this coastal autochthonous production together with the river inputs. Times series studies have captured very energetic turbidity events upstream the terminal lobe complex (Khripounoff et al., 2003; Vangriesheim et al., 2009). For example, a turbiditic event in 2001 caused a massive particle flux within the canyon but also spilled over its edge thereby yielding a high pulse of terrestrial clay on the levee, 18 km away from the canyon channel, in an area otherwise characterized by marine pelagic particle flux (Khripounoff et al., 2003). In 2004, two intense events were recorded by intense peaks in turbidity and in particle flux, and by mooring breaking (Vangriesheim et al., 2009). When reaching the terminal lobe system, even though the current loses velocity, it can still deliver intense particle flux (Vangriesheim et al., 2009). Besides turbiditic currents smaller pulses in particle flux with no current increase were also recorded, and indicate local sliding of sediment accumulated on the walls or terraces on the sides of the channel (Vangriesheim et al., 2009).

The Congolobe project aims at studying the geology, geochemistry and ecology of the Congo terminal deep-sea fan system (Rabouille et al., 2017), a hotspot of terrestrial carbon burial (Baudin et al., 2017b). The sediments of the lobe complex are organic-rich silts and silty-clays, their C/N and $\delta^{13}\text{C}$ values indicated that 70–80% of the OM was terrestrial in origin (Baudin et al., 2010; Stetten et al., 2015), and was mostly composed by river particles conveyed from the Congo mouth by turbiditic currents. Sediment palynofacies

revealed predominant well preserved particles derived from plant structures. In addition, amorphous organic matter was relatively more abundant in the studied levee whereas the denser well preserved wood fragments and transparent intact phytoclasts were enriched in the channel sediment, suggesting a general sorting of particles according to the density of particle (Schnyder et al., 2017). Palynofacies also evidenced a vertical gradient in the upper 20 cm of the cores. Amorphous organic matter is relatively enriched upcore with respect to denser terrestrial components, which further supports hydraulic sorting of particles in the turbiditic deposits.

Molecular geochemistry brings complementary views to bulk geochemical information. Terrestrial molecular biomarkers fall into extractable lipids or non extractable macromolecules. Typical terrestrial biomarkers such as lignin phenols for instance, have revealed selective sorting of higher plant debris and soil particles (Cathalot et al., 2013; Gordon and Goñi, 2004; Rezende et al., 2010). Branched glycerol dialkyl glycerol tetraethers (DGDG) are used to trace soil inputs to aquatic sediments (Kim et al., 2012; Lopes dos Santos and Vane, 2016). Even if lipids comprise less than 1% of the bulk terrestrial organic pool, terrestrial lipid biomarkers are routinely used to detect variations in terrestrial inputs and in their preservation in sediments. Odd long-chained (C₂₅-C₃₅) alkanes are higher plant biomarkers resistant to degradation and are commonly used as vascular plant proxy, in present day environments as well as in paleoreconstruction studies (Castañeda et al., 2011; Gogou et al., 2000; Mangelsdorf et al., 2000; Romero-Viana et al., 2012). A 3 year survey of *n*-alkanes in suspended particles from the Congo River showed that they integrate the catchment signal with minimal seasonality (Hemingway et al., 2016).

The present contribution examines the hydrocarbon composition of sediments of the lobe complex, of Congo River sediments and of sediment traps in order to complement bulk proxies and palynofacies evidences. It aims at bringing information on the source of the organic matter preserved in the lobe sediments and questions whether the spatial distribution of terrestrial hydrocarbon biomarkers reflects the variability evidenced by palynofacies. Concentrations of both aliphatic and terpenic hydrocarbons in recent marine sediments are very seldom reported in the literature and concentrations of both aliphatic and terpenic hydrocarbons presented here provides original reference data for this region, displaying uncommon terpene abundances. In addition, fluxes have seldom been reported previously. Comparing sedimentary mass accumulation rates and water column fluxes of aliphatic and terpenic hydrocarbons brings new understanding of the importance of terrestrial hydrocarbon inputs.

Five sites representative of an upstream-downstream gradient in the lobe complex, including both the active lobe system and an abandoned lobe, and a site in the Congo River were selected for sedimentary hydrocarbon molecular study. This sample set has been previously characterized for grain size, organic carbon concentration (OC), $\delta^{13}\text{C}$, C/N ratio, Rock-Eval and other geochemical approaches (Baudin et al., 2017a; Stetten et al., 2015; Schnyder et al., 2017). Particles collected by sediment trap moored 40 m above the lobe sediment beds were also analyzed to understand the contribution of sinking particles.

2. Material and methods

2.1 Sampling strategy

The samples were collected during two cruises that took place in 2011 on the RV *Pourquoi Pas?* The first one, WACS (Olu, 2011) was conducted in February 2011 and the second one, Congolobe, was performed between

December 2011 and January 2012 (Rabouille et al., 2009). The objectives of the Congolobe project, the sampling rationale and geological and geochemical characteristics of the studied sites are detailed in Rabouille et al. (2017). The distal lobe complex of the active canyon is the area where the canyon depth progressively decreases and the sediments accumulate, as shown by the maxima in sediment accumulation rates (Rabouille et al., 2017). The lobe complex comprises 5 prograding lobes partly stacked one over the other and having increasing age of formation, from ca 4 ka for the most upstream and oldest lobe (numbered lobe 1, Fig. 1) to present time for the most distal and youngest lobe (numbered lobe 5, Fig. 1) (Bonnel, 2005; Dennielou et al., 2017; Rabouille et al., 2017). In addition, the high resolution bathymetric study showed an abandoned channel that led to the lobe complex in the past, on the northern levee. This presently inactive channel departs from the active one upstream from site A. Close to the area where both channels depart one from another, the presently inactive one is 25 m deep and 1000 m wide and it extends to lobe 3. The channel that is currently active is 45 m deep and 1400 m wide and connects to the more recent lobe 5. When turbidite particles spill over the levees of the active channel, they may fill the inactive channel, and create the smoothed morphology of that canyon while filling it. The morphology of this canyon may also allow some particle transport to lobe 3.

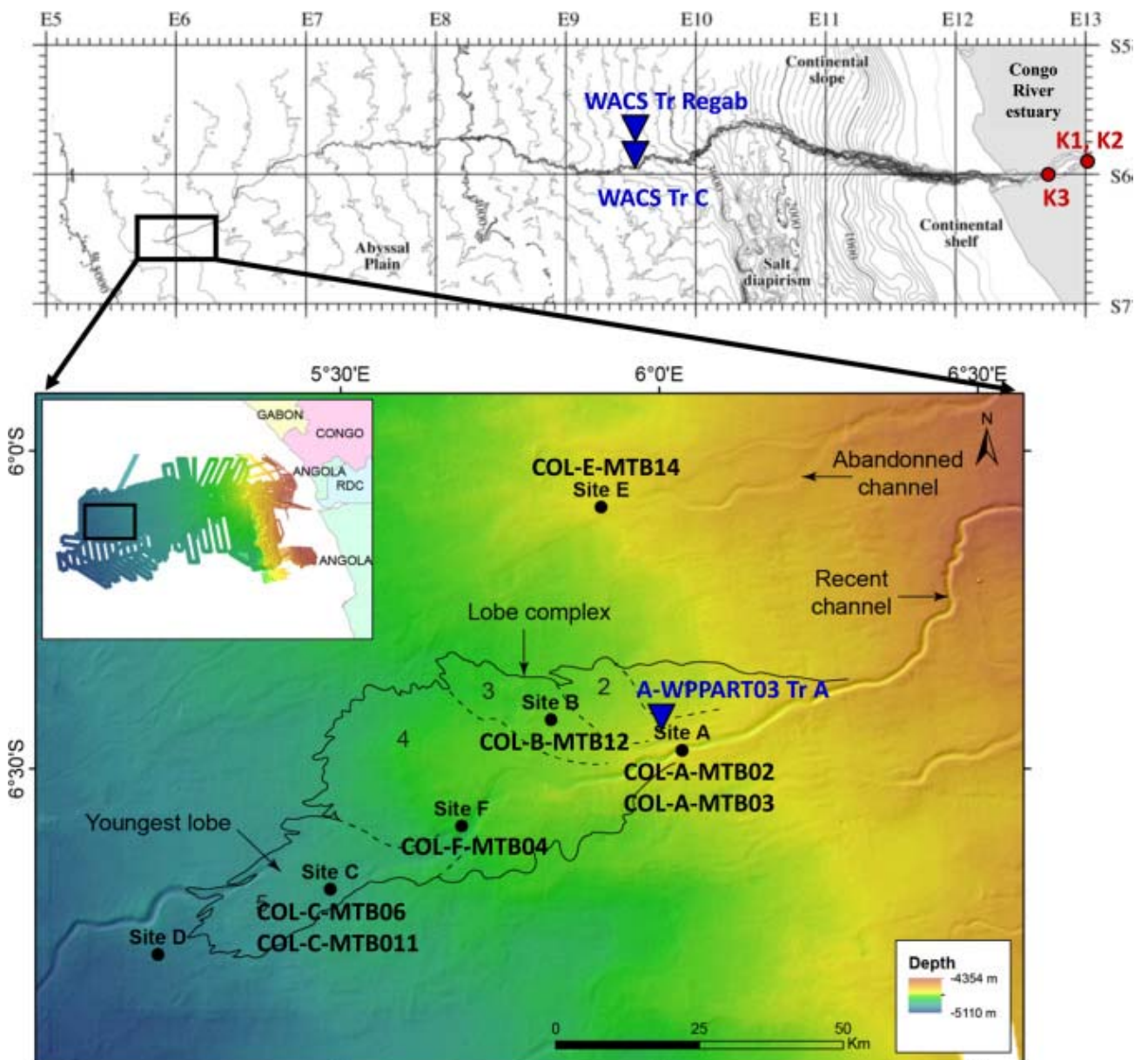


Fig. 1. Study area. Red dots on the top figure shows the locations of the Congo River sediments K1, K2 and K3, at the entrance to the Malebo Pool. Sediment trap moorings at the Regab site (Tr R1 and Tr R2) at the site WACS Tr C (Tr C1, Tr C2 and Tr C4) are indicated by blue triangles. The lower panel shows the general bathymetric map of the Congo River deep-sea fan. The boundaries of the terminal lobe complex are outlined by a black line, while dotted lines outline distinct lobes, from the older lobe 1 to the youngest lobe 5. The presently active channel feeds the lobe 5. The locations of coring sites are indicated by black dots. The Site E is located at the end of the abandoned channel. The location of the sediment trap mooring at site A (A-WPPART03) is indicated by a blue triangle.

Table 1 reports the locations and depths of the analyzed sample set. Sites A, F and C are located along an upstream – downstream gradient along the active southern channel. Site A is located in lobe 2 (A), where the canyon is a 45 m deep channel in which the sediment core CoL-A-MTB03 was recovered. This core was collected on the southern levee displaying gentle flanks (Rabouille et al., 2017). Site F is located at the onset of lobe 4, 40 km downstream of site A and the sediment core CoL-F-MTB-04 was collected on the northern levee of this site. At site F, the canyon is a 45 m deep and 2500 m wide channel. Site C is located 25 km downstream of site F, at the distal part of the lobe 5, where the canyon structure fades into a 11 m deep channel, as a result of the accumulation of recent particle deposits. At this site, the sediment core CoL-C-MTB-06 was collected on the levee and CoL-C-MTB-11 on the channel. CoL-B-MTB-12 was sampled on lobe 3 at site B, located on the northern levee in the vicinity of the inactive channel. At the coring location the presently inactive channel leading to lobe 3 is only a few meters deep. Site E characterizes an abandoned northern lobe complex, 45 km north of the active channel that receives little turbiditic matter since at least 4 ka BP (Rabouille et al., 2017; Stetten et al., 2015). This site refers to conditions where mainly pelagic inputs build up the sediments, as opposed to the other sites where turbidites are the main deposit types. The sediment core CoL-E-MTB-14 was collected at this site.

In order to characterize the Congo River particulate inputs, sediments from the river floodplain were analyzed (Table 1). They were collected at three sites at the Malebo Pool, permanently flooded, inundated during high discharge months, and recently exposed, and were donated from H. Talbot and R. Spencer (Talbot et al., 2014, Supplementary Table 2). At these sites the particulate organic carbon composition compares well to that in the estuary and these 3 river sediments are considered as representative of the Congo particulate export to the Atlantic (Spencer et al., 2012).

In order to characterize the vertical rain of pelagic particles, a limited set of sediment trap samples from 3 sites were considered (Table 1). Two sediment traps were located at a mid distance between the canyon head and the lobe complex, one is located 10 km north of the canyon channel and is located above a large cold seep pockmark (samples TrR1 and TrR2), the other is above the canyon itself (TrC1, TrC2 and TrC4). The third trap was moored at the entrance of the lobe complex above the site A (TrA1 and TrA2).

2.2 Hydrocarbon molecular analyses

Known amounts of C₂₄D₅₀ were added to the lyophilised samples prior to extraction as a surrogate for non aromatic hydrocarbons. The lyophilised sediment samples (ca. 0.2 to 6 g d.w.) were extracted using accelerated solvent extraction. The samples were homogenised with diatomaceous powder previously combusted at 450°C and sequentially extracted using accelerated solvent extraction (Dionex ASE 350). The first extraction, with acetone at 100°C and 1500psi for 1 static cycle of 5 min. and 60% of flush, was followed by 3 static cycles of 5 min. with acetone/dichloromethane (1:1) at 100°C and under a pressure of 140 bars. The sequence was previously optimized using coastal sediments to ensure no cross-contamination. The lipid extracts were treated with acid-activated copper to remove elemental sulfur. The extracts were concentrated using rotary evaporation, solvent exchanged to *iso*-octane and concentrated down to 200 µl. They were purified into different fractions on a dual silica/alumina column made of 5g of silica deactivated at 5% and 3 g of alumina deactivated at 3%. The first fraction, eluded by 25 ml of hexane, contained the aliphatic and cyclic hydrocarbons.

This fraction was first analyzed for aliphatic compounds by gas chromatography (GC) coupled to a flame ionization detector (FID) equipped with a DB-5MS capillary column (J&W, 30m x 0.249 mm i.d. x 0.25 µm thick phase film). The carrier gas was helium at a pressure of 110 kPa. The oven temperature, initially at 60°C was brought to 100°C at a rate of 25°C/min, then to 310°C at a rate of 2°C/min. The final isotherm of 310°C was held for 60 minutes. The FID was kept at 330°C. Aliphatic hydrocarbons were quantified relatively to the internal standard added prior to extraction. For river and trap samples the quantity of available material (0.2 to 1g) did not allow a proper quantification by GC-FID. These samples were quantified by GC-Mass Spectrometry (GC-MS) on an Agilent 6890 Series GC system coupled to an Agilent 5973 Network Mass Selective Detector. A DB-5MS capillary column (Agilent DB5, 30m x 0.25 mm i.d. x 0.25 µm thick phase film) was used. The carrier gas was helium at a flow of 1.2 ml/min. The initial oven temperature of 60°C was held for 5 minutes, then brought from 60°C to 160°C at a rate of 25°C/min, then increased to 310°C at a rate of 3°C/min with a final isotherm of 10 minutes. Full acquisition program scan (from 40 to 600 amu) under electron impact ionization at 70eV was used. Individual hydrocarbons were quantified relatively to the surrogate (C₂₄D₅₀) and corrected with relative response factors (RRFs). Calibration solutions containing 25 target *n*-alkanes (prepared from Alkane mix 10, Dr Erhenstorfer GmD), chosen to bracket the sample concentrations, were used to derive the RRFs of the analytes. Carbon Preference Index (CPI) was calculated as:

$$\text{CPI}_{24-34} = \frac{1}{2} \times \left(\frac{(C_{25} + C_{27} + C_{29} + C_{31} + C_{33} + C_{35})}{(C_{24} + C_{26} + C_{28} + C_{30} + C_{32} + C_{34})} + \frac{(C_{25} + C_{27} + C_{29} + C_{31} + C_{33} + C_{35})}{(C_{26} + C_{28} + C_{30} + C_{32} + C_{34} + C_{36})} \right)$$

Hopanes and other triterpenes were semi-quantified by integrating peaks on the ion current at m/z 191. The major hopanoid, hop-17(21)-ene, was quantified by GC-FID, and the other triterpene abundances were calculated by relating their area to that of the hop-17(21)-ene. In a few samples, hop-17(21)-ene could not be quantified on the GC-FID trace. In those few samples, the hopane abundances were calculated by relating their area to that of the n-C₃₁ *n*-alkane, and correcting with response factors determined from the samples where both n-C₃₁ and hop-17(21)-ene were unequivocally quantified by GC-FID responses.

Procedural blanks were processed and analyzed. They were clear of contamination. The method was also tested for reproducibility and repeatability. The disparity was less than 5%.

Sedimentary accumulation fluxes of the given hydrocarbons were calculated as :

$$\Phi_{\text{alk}} = C_{\text{alk}} \times \text{AR} \times d \times (1 - p) \times 10^4$$

With Φ_{alk} the mass accumulation rate of the hydrocarbon in $\text{ng m}^{-2} \text{yr}^{-1}$, C_{alk} the concentration of a given hydrocarbon in ng.g^{-1} of dry weight, AR the sediment accumulation rate in cm yr^{-1} , d the sediment density in g cm^{-3} , p the sediment porosity.

3. Results

3.1 *n*-alkanes molecular profiles and concentrations

A total of 31 *n*-alkanes ranging from C_{10} to C_{40} , and 8 isoprenoid hydrocarbons were identified and quantified in the samples. The dominant biomarkers in most sediments of the lobe complex sediments are a suite of *n*-alkanes dominated by high-MW compounds ($> C_{24}$) with predominance of odd over even carbon chain alkanes (CPI values from 4.0 to 9.6) (Fig. 2, Table S1 Supplementary material, p. 40-47). They derive from higher plant waxes (Table 2). Their concentrations in the lobe sediments varied from 50 to 6070 $\text{ng g}_{\text{DW}}^{-1}$, from 320 to 1150 $\text{ng g}_{\text{DW}}^{-1}$ in Congo River banks and from 470 to 2040 $\text{ng g}_{\text{DW}}^{-1}$ in sediment traps. Their range compares well with other river deltas (Table 3).

Table 2. Source assignment of hydrocarbon biomarkers detected in the present study.

Biomarker	Source organisms	Source environment	References
C ₂₅ -C ₃₅ odd alkanes	waxes of higher plants	terrestrial inputs	Eglinton et al., 1962; Eglinton and Hamilton, 1967
C ₁₇	phytoplankton	marine	Clark and Blumer, 1967
C ₁₆ , C ₁₈	bacteria	marine	Grimalt and Albaigés, 1987; Nishimura and Baker, 1986
grass		terrestrial	Kuhn et al., 2010
sedimentary rocks		terrestrial	Tao et al., 2016
petroleum		oil input	Tao et al., 2016
Phytadienes	reducing environment	marine	Grossi et al., 1998
UCM	petroleum	oil input	Broman et al., 1987
Gammacerene Banta et al. 2015	ciliates, ferns, bacteria	terrestrial, marine	Bravo et al., 2001; Hamed et al., 2014; Kleemann et al., 1990,

Oleanene, ursene	angiosperms		terrestrial	Peters et al., 2005
Ferrenes	ferns		terrestrial	Ageta and Arai 1983; Paull et al., 1998
anaerobic bacteria		Marine		Volkman et al., 1986; Marynowski et al., 2007b
bacteria				Brassel and Eglinton 1893
Diploptene and	bacteria		marine	Rohmer et al., 1984; Talbot et al., 2014, Banta et al., 2015
hop-21-ene	soil bacteria		terrestrial	Prahl et al., 1992
Hop-17(21)-ene	ferns		terrestrial	Patitucci et al., 1995; Shiojima and Ageta, 1990
Neohop-13(18)enes	diagenetic products of diploptene		terrestrial, marine	Sinninghe-Damsté et al., 2016

Table 3. Concentration levels ($\text{ng g}_{\text{dw}}^{-1}$ and $\text{ng}_{\text{oc}}^{-1}$) and fluxes ($\mu\text{g m}^{-2} \text{yr}^{-1}$) of terrestrial alkanes, Short-chain alkanes, UCM and terpenoids in marine, lacustrine and continental sediments in comparison with sediments from the terminal Congo lobe system.

Study location	Terrestrial alkanes			Short-Chain alkanes C16 + C18			UCM		Terpenoids				Reference	
	$\text{ng g}_{\text{dw}}^{-1}$	$\mu\text{g g}_{\text{oc}}^{-1}$	$\mu\text{g m}^{-2} \text{yr}^{-1}$	$\text{ng g}_{\text{dw}}^{-1}$	$\mu\text{g g}_{\text{oc}}^{-1}$	$\mu\text{g m}^{-2} \text{yr}^{-1}$	$\text{ng g}_{\text{dw}}^{-1}$	$\mu\text{g m}^{-2} \text{yr}^{-1}$	$\text{ng g}_{\text{dw}}^{-1}$	$\mu\text{g g}_{\text{oc}}^{-1}$	$\mu\text{g m}^{-2} \text{yr}^{-1}$	$\mu\text{g m}^{-2} \text{yr}^{-1}$		
<i>Atlantic Ocean</i>														
SE margin, including Congo fan	C27-C33 odd		20 - 290	nc				nc		nc			Rommerkirshen et al., 2003	
SE margin, including Congo fan	C25-35 odd	460 - 39 000	6 000	nc				nc		nc			Schefuss 2004	
Congo River particles	C23-35		66.0 - 207.1										Hemingway et al., 2016	
Congo deep sea fan	C25-35odd	30 - 2 050	2.2 - 56.4	0.23 - 2 702	nd-350	nd-16.4	nd-651	nd - 10 470	nd-2 050	Neohopene	nd-69	nd-2.85	nd - 68	This study
Congo deep sea fan										Diploptene	nd-303	nd-7.34	nd - 249	This study
Southwest African coast C25-33		2 000 - 31 000			nc				nc		nc			Hermann et al., 2016
Washington Coast C25-31 odd		600 - 2 500			nc				nc	Diploptene	30-500			Prahl et al., 1992
Amazon estuary	C29+C31	46- 424			nc				nc		nc			Haggi et al., 2016
Brazilian estuary-shelf transition	C21-C35	100 - 4 900			nc				nc		nc			Maciel et al., 2016
Brazilian Coast	Sum Alkanes	1 560 - 104 750						nd - 189 100						Venturini et al., 2004
Pacific Ocean														
Californian margin	C25-C35 odd		40 - 150	100 - 500	nc				nc		nc			Mangelsdorf et al., 2000.
<i>Mediterranean Sea</i>														
Rhone prodelta Sum alkanes		830 - 1699			nc			1 798 - 13340	39 - 205		nc			Tolosa et al., 1996
Ebro prodelta		458 - 854			nc			1 072 - 12 056	29 - 295		nc			Tolosa et al., 1996
Cretan margin	C25-C35 odd	94 - 417						343 - 4 800						Gogou et al., 2000
Black Sea sapropels	C29+C31	7500 - 83 600	140-350							Diploptene	2 300-9 900	40- 180		Wakeham et al., 1995
<i>Pacific Ocean</i>														
Yangtze estuary	C15-38	160-1880								Hopanes		ca 2-11		Bouloubassi et al., 2001
Yellow Sea	C15-35	240-1340	6 - 47											Liu et al., 2012
China Sea	C15-35	140-1680	2.5 - 27											
Chinese marginal Sea C15-C33	C29+C31		40 - 300			2- 200			nc		nc			Tao et al., 2016
New Zealand coast		158 000 - 516 000		nd-830 000										Sikes et al., 2009
<i>Lacustrine environments</i>														
Equatorial Africa, Lake Challa										des-A triterpenoids			20 - 700	van Bree et al., 2016
Caspian Sea	C14-C32	249 200 - 3 899 500						897 000-25 541 000		Hopanes	429 - 21691			Shirneshan et al., 2016
<i>Cretaceous Black Shales</i>														
										Neohopenes		nd-87		Sinninghe Damsté et al., 2014

The three sediments from the Congo River show an identical hydrocarbon composition, maximizing at $n\text{-C}_{29}$, and with the $n\text{-C}_{23}$ to $n\text{-C}_{35}$ mode accounting from 91% to 95% of total non cyclic hydrocarbons. These patterns are consistent with the molecular composition described for suspended particles in the Congo River (Hemingway et al., 2016). This strong higher plant signature is mirrored in alkane molecular patterns from many of the studied sediments: the levee of site A, the channel at site C, and in the deeper part of the site E (>10 cm horizons), confirming that the Congo River is the primary supply of the organic matter accumulated in the lobe complex (Fig. 3). In the sinking particles collected by sediment traps, the higher plant fingerprint is faint at the Regab site, located away from the active channel, marked at the canyon site, and variable at site A (Fig. 3).

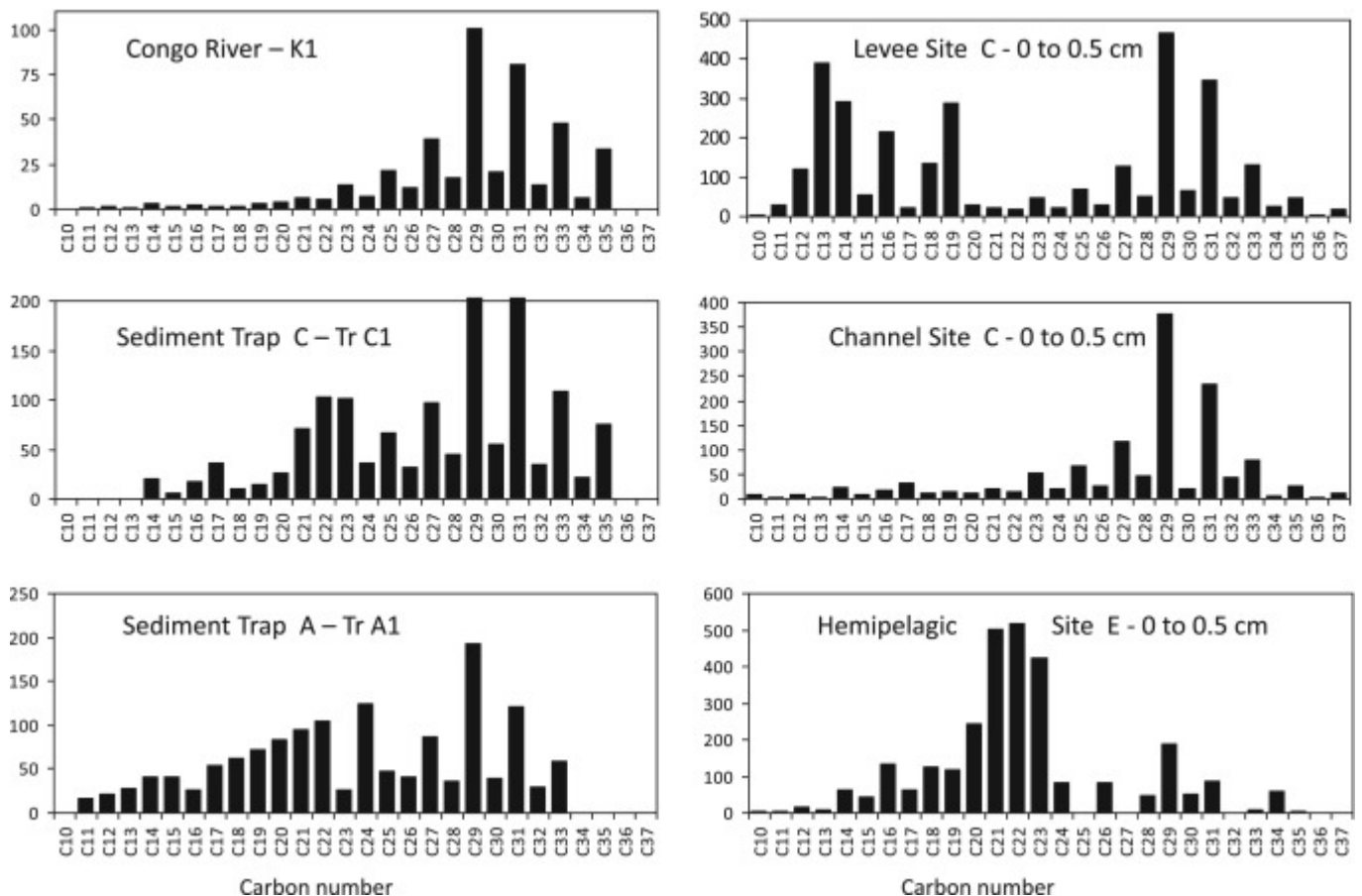


Fig. 2. Molecular profiles of n -alkanes in River sediments (K1), in sediment traps collected during WACS at 3420 m (TrC1) and at the site A (TrA1), and in surficial (0–0.5 cm) sediments collected in the terminal lobe complex, in the levee of site C (CL 0–0.5), in the channel of site C (CC 0–0.5) and at site E (E 0–0.5). n -Alkane homologues are assigned by their carbon number, and their abundance is expressed as concentrations, in ng per gram of dry weight (ng g_{DW}⁻¹).

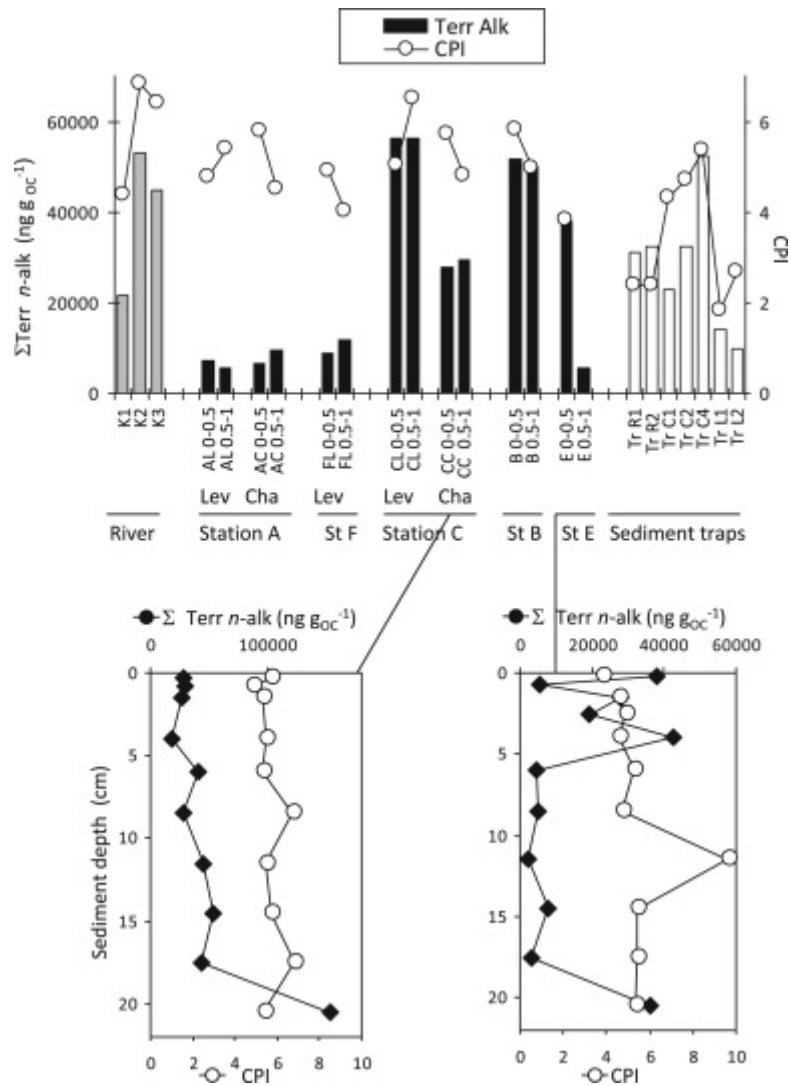


Fig. 3. Top panel shows the spatial distribution of terrestrial *n*-alkane concentrations normalized to organic carbon, in sediments from the Congo River (grey bars), in surficial sediments collected from the Congo deep-sea fan (black bars, Lev: levee, Cha: channel, sediment layers from 0 to 0.5 cm and from 0.5 to 1 cm), and in sediment trap samples (white bars). Terrestrial *n*-alkanes are defined here as odd *n*-alkanes from C₂₅ to C₃₇. *n*-Alkanes levels are expressed in ng per gram of organic carbon (ng g_{OC}⁻¹). Carbon Preference Index (CPI) calculated from C₂₅ to C₃₅ is plotted on the right axis. Bottom panels show the vertical profiles of terrestrial *n*-alkane concentrations and CPI in two cores, from the channel at site C, and from site E.

In sediments from the channel of site A, the levee of site F, the levee and upper horizons of the channel at site C and of site E, the terrestrial imprint co-occurs with a low molecular weight mode of *n*-alkanes, with even predominance maximizing at *n*-C₁₄ and *n*-C₁₆ (Fig. 2, right middle and bottom panels; Fig. 4). The phytoplanktonic biomarker *n*-C₁₇ indicates recent input of phytoplanktonic biomass (Table 2; Marty et al., 1994). Its higher contribution in sediment trap particles than in sediments and soils underlines the predominantly marine origin of the sinking particles, in line with Rock-Eval assessment (Baudin et al., 2017a).

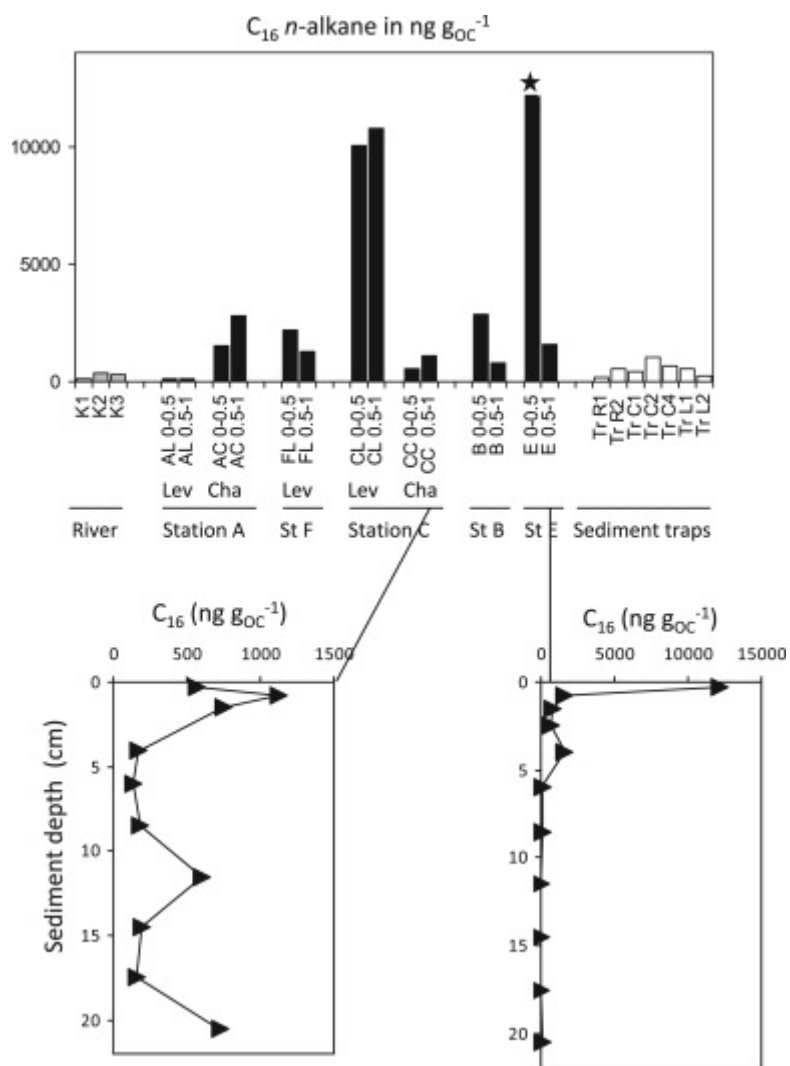


Fig. 4. Top panel shows the spatial distribution of C₁₆n-alkane concentrations normalized to organic carbon, in sediments from the Congo River (grey bars), in surficial sediments collected from the Congo deep-sea fan (black bars, Lev: levee, Cha: channel, sediment layers from 0 to 0.5 cm and from 0.5 to 1 cm), and in sediment trap samples (white bars). C₁₆ levels are expressed in ng g_{OC}⁻¹. Bottom panels show the vertical profiles of C₁₆ concentration in two cores, from the channel at site C, and from site E. The star indicates petroleum contamination, in this sample the low molecular mode of alkane showed no even predominance.

Chromatographically unresolved hydrocarbons were detected in 12 samples. The unresolved complex mixture (UCM), potentially composed of over 250 000 cyclic and branched hydrocarbons (Sutton et al., 2005) brings evidence for the occurrence of petrogenic hydrocarbons (Table 2). UCM concentration was the highest in the surface sediments of site E (10 500 ng g_{DW}⁻¹), and took lower values in some sediments of the sites A and B (up to 8 000 ng g_{DW}⁻¹ and up to 1 500 ng g_{DW}⁻¹, respectively).

Three phytadiene isomers were the dominant isoprenoids in the vast majority of sediment samples, but they were absent in river sediments and nearly absent in sinking particles (Fig. 5). The concentrations of the three isomers were similar and that of the third one took a maximum value 202 ng g_{DW}⁻¹ in the surface sediment of the levee at site C, and of 1 ng g_{DW}⁻¹ in the sole trap sample where phytadienes could be identified.

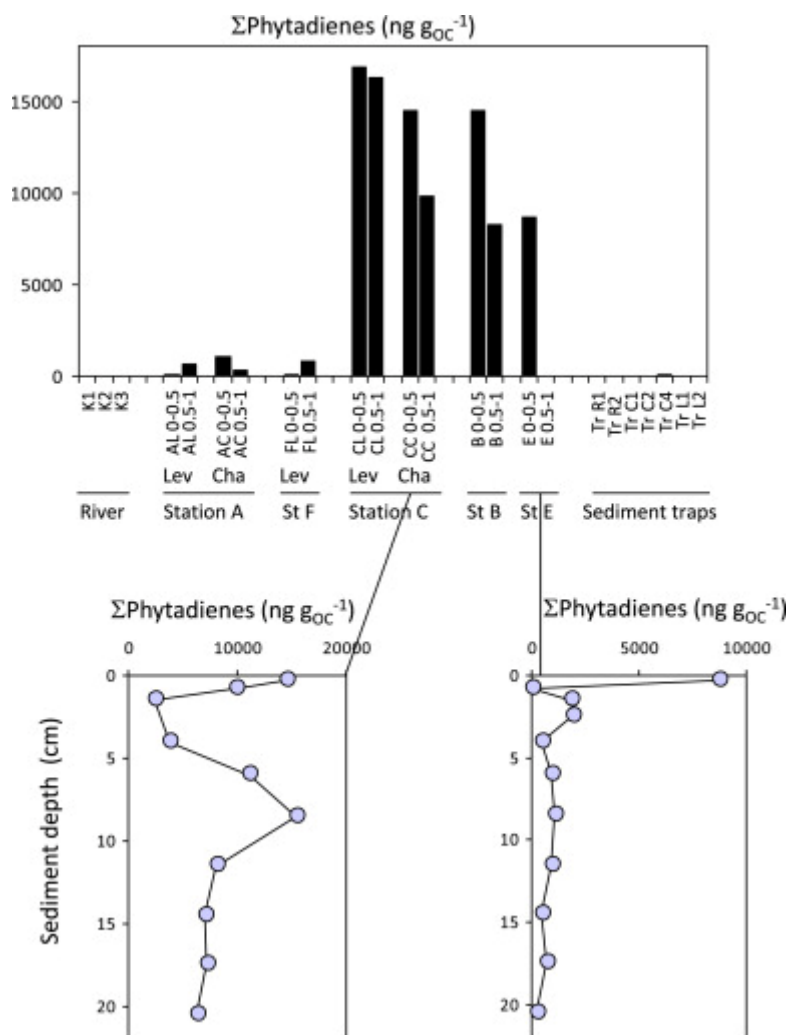


Fig. 5. Top panel shows the spatial distribution of phytadiene concentrations normalized to organic carbon, in sediments from the Congo River (grey bars), in surficial sediments collected from the Congo deep-sea fan (black bars, Lev: levee, Cha: channel, sediment layers from 0 to 0.5 cm and from 0.5 to 1 cm), and in sediment trap samples (white bars). The sum of three phytadiene levels are expressed in $\text{ng g}_{\text{OC}}^{-1}$. Bottom panels show the vertical profiles of concentration of phytadienes, in two cores, from the channel at site C, and from site E.

3.2. Triterpene molecular profiles

Substantial amounts of triterpenes were present in the sediment extracts from the terminal lobe, in particular at site C. The hopane and hopene mass spectra interpretation was inferred from retention times and published spectra. Representative $m/z=191$ hopanograms and mass spectra of the major hopanoids are presented in the Supplementary material (Figs. S2, S3, S4 and S5, p. 59-62).

Triterpene distribution patterns within the lobe complex sediments shared common features such as the predominance of C_{30} and C_{31} hopanes in the $17\beta(\text{H}),21\beta(\text{H})$ ($\beta\beta$) and $17\beta(\text{H}),21\alpha(\text{H})$ ($\beta\alpha$) configurations, and of unsaturated hopanoids (Figs. 6–8). Both characteristics are a clear signature of recent immature organic matter, as opposed to oil contamination. Hopane and C_{31} homohopane having retained their precursor $\beta\beta$ configuration are abundant in terrestrial clays and sediments (Kvenvolden et al., 1990; Marynowski et al., 2007a). In the lobe complex sediments, they likely traced soil inputs (Fig. 7). A few samples showed contrasting composition: in surficial sediments (0–0.5 cm and 0.5–1 cm) of the disconnected E site, tricyclic diterpanes with 20, 21, 23, 24 and 25 carbon

atoms were the dominant homologues, and hopenes were less abundant or non detected (Fig. 6, Fig. S2 in Supplementary material, p. 59). Tricyclic diterpanes have been described as the major homologues in saline lacustrine and marine crude oils (Tao et al., 2015), and their occurrence points to oil contamination of site E surficial sediment, in agreement with the UCM concentrations and CPI values. However the hopane profile in the lobe complex sediments did not show the characteristics of a mature oil ($\alpha\beta$ and moretane dominance over $\beta\beta$ -hopanes), as the hopene profile was the same as in the other non-contaminated sites, and as in the non-contaminated deeper horizons at site E (hop-17(21)-ene, $\beta\beta$ -C₃₀ hopane and $\beta\beta$ -C₃₁-homohopane (Fig. 6) (Fig. 8).

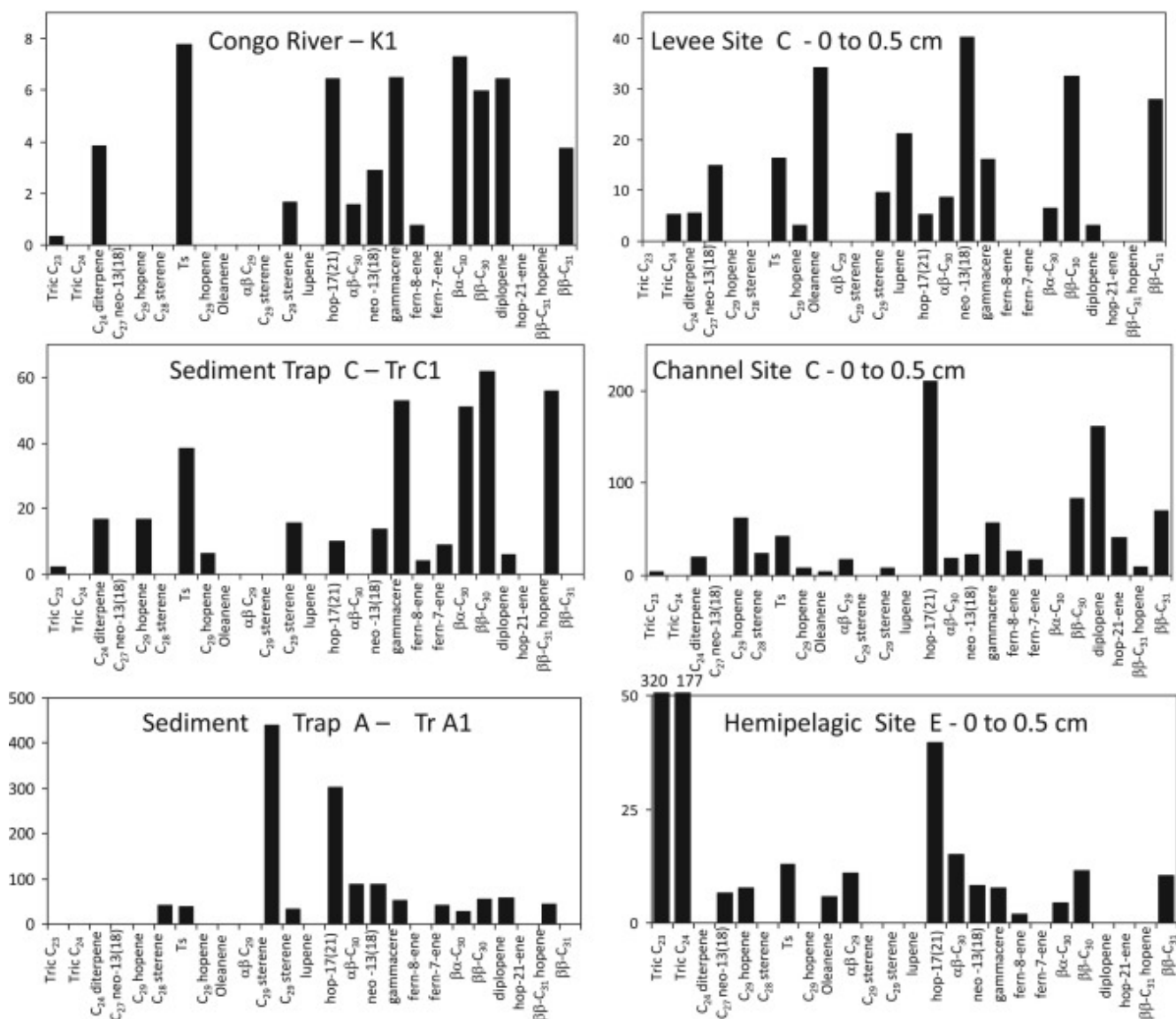


Fig. 6. Molecular profiles of dominant triterpenes in River sediments (K1), in sediment traps collected during WACS at 3420 m (TrC1) and at the site A (TrA1), and in surficial (0–0.5 cm) sediments collected in the terminal lobe complex, in the levee of site A (AL 0–0.5), in the channel of site C (CC 0–0.5) and at site E (E 0–0.5). Hopanes, hopenes and other triterpenes are quantified as peak area in the fragmentogram $m/z=191$, and by relating their area to the area of hop-17(21)-ene, quantified by GC-FID. Triterpene levels are expressed in $\text{ng g}_{\text{Dw}}^{-1}$.

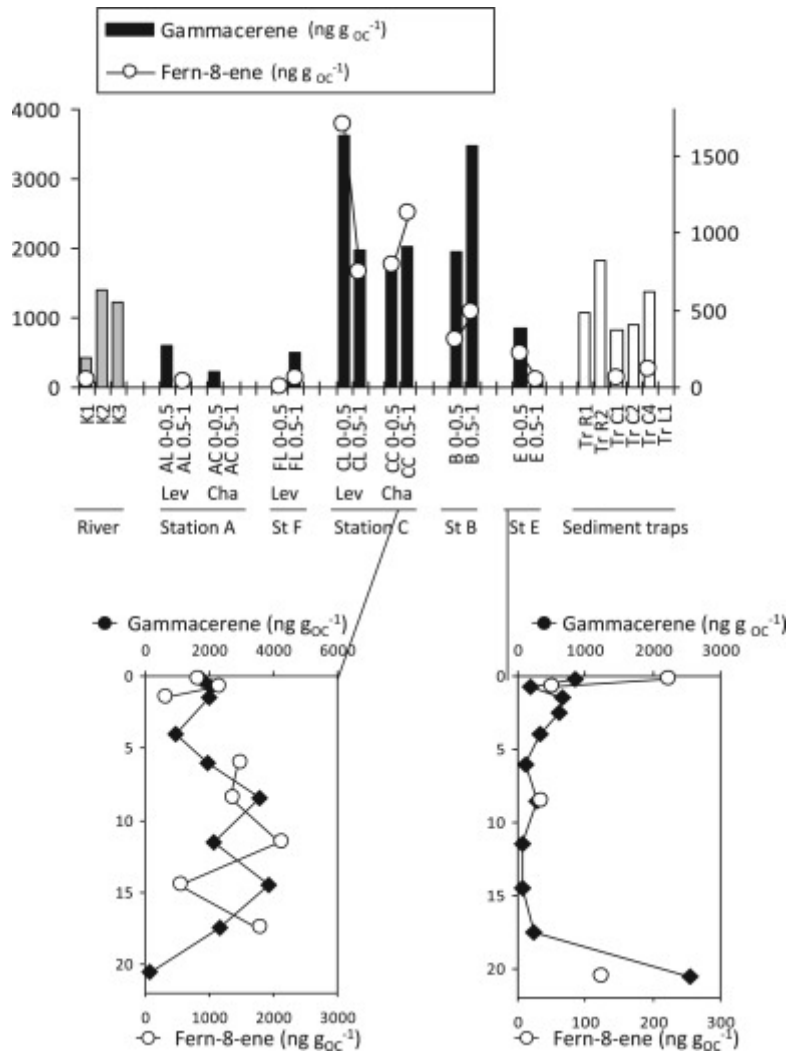


Fig. 7. Top panel shows the spatial distribution of gammacerene concentrations normalized to organic carbon, in sediments from the Congo River (grey bars), in surficial sediments collected from the Congo deep-sea fan (black bars, Lev: levee, Cha: channel, sediment layers from 0 to 0.5 cm and from 0.5 to 1 cm), and in sediment trap samples (white bars). Fernene level is represented by white circles, plotted on the right axis. Gammacerene and fernene are terrestrial biomarkers, while fernene can also be sourced by microorganisms. Their levels are expressed in $\text{ng g}_{\text{OC}}^{-1}$. Bottom panels show the vertical profiles of concentrations of gammacerene and fernene, in two cores: from the channel at site C, and from site E.

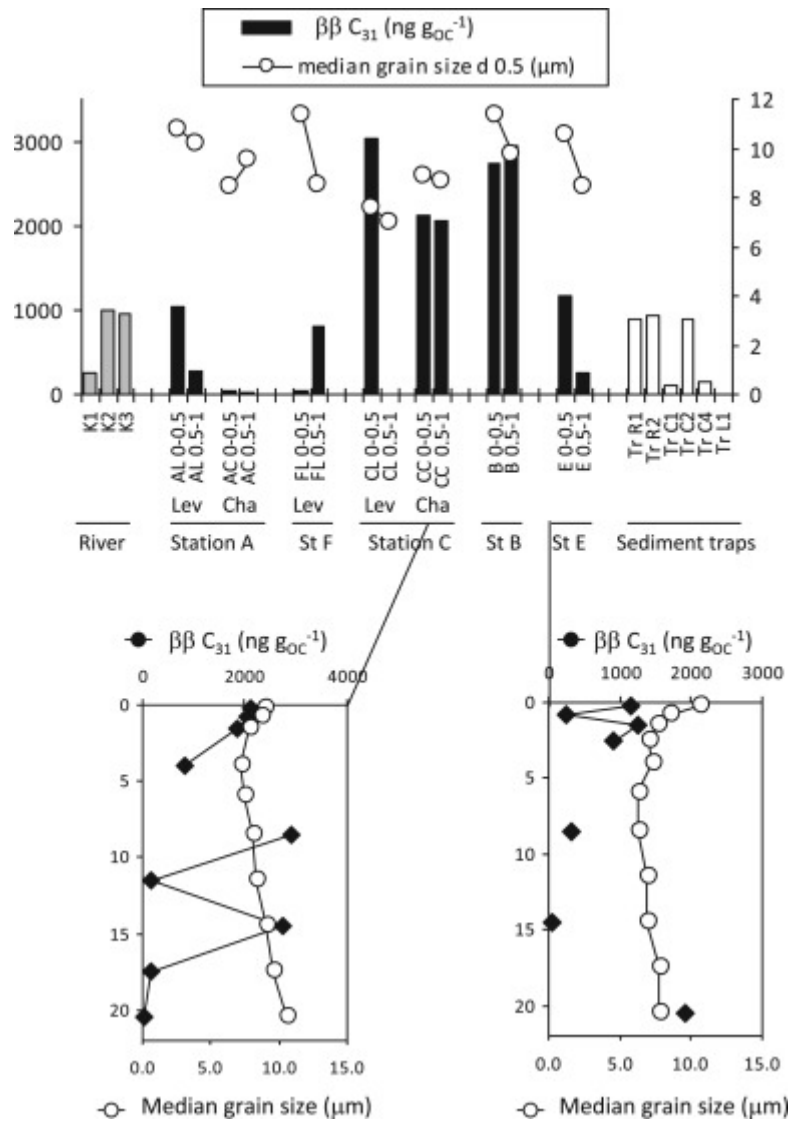


Fig. 8. The top panel shows the spatial distribution of the concentrations of C_{31} $\beta\beta$ -homohopane normalized to organic carbon, in sediments from the Congo River (grey bars), in surficial sediments collected from the Congo deep-sea fan (black bars, Lev: levee, Cha: channel, sediment layers from 0 to 0.5 cm and from 0.5 to 1 cm), and in sediment trap samples (white bars). C_{31} $\beta\beta$ -homohopane levels are expressed in $\text{ng } g_{OC}^{-1}$. White circles represent the mean grain size of the lobe complex sediment, in μm and is plotted on the right axis. Bottom panels show the vertical profiles of concentration of C_{31} $\beta\beta$ -homohopane and of mean grain size, in two cores: from the channel at site C, and from site E.

In most lobe sediments, hop-17(21)-ene, $\beta\beta$ -hopane and diploptene (hop-22(29)-ene) were the dominant homologues (Figs. 9 and 10). Diploptene is present in various types of bacteria and is related to the membrane constituent bacterihopanetetraol (Table 2). In contemporary sediments, its diagenesis starts with double bond migration into hop-21-ene, then into hop-17(21)-ene, and further proceeds by rearrangement and migration of the methyl at C-18 to the position C-17 forming norneohop-13(18)-ene (Simoneit, 2005). In the present sample set, the four isomers were detected in variable proportions. Hop-17(21)-ene prevailed in most sediments, in particular at the site C, and also in the sinking particles collected by sediment traps. Hop-17(21)-ene concentrations were from non detected to $9 \text{ ng } g_{DW}^{-1}$ in the Congo River sediments, maximized at $335 \text{ ng } g_{DW}^{-1}$ in some sediments of the site C and varied from non detected to $303 \text{ ng } g_{DW}^{-1}$ in the sediment trap samples.

In river samples and in a few samples (site A levee, site C surficial layers), diploptene was equally prominent in the m/z 191 fragmentograms. Diploptene concentrations reached $25 \text{ ng g}_{\text{DW}}^{-1}$ in the Congo River sediments, $294 \text{ ng g}_{\text{DW}}^{-1}$ in some sediments of the site C and $215 \text{ ng g}_{\text{DW}}^{-1}$ in the sediment trap samples. Neohop-13(18)-ene seldomly prevailed, for instance in surficial sediment of the levee of the site A (Fig. 6). A C_{27} 22,29,30trisinorhop-13(18)-ene was also detected in most samples (Figs. S3 and S4, Supplementary material, p. 60).

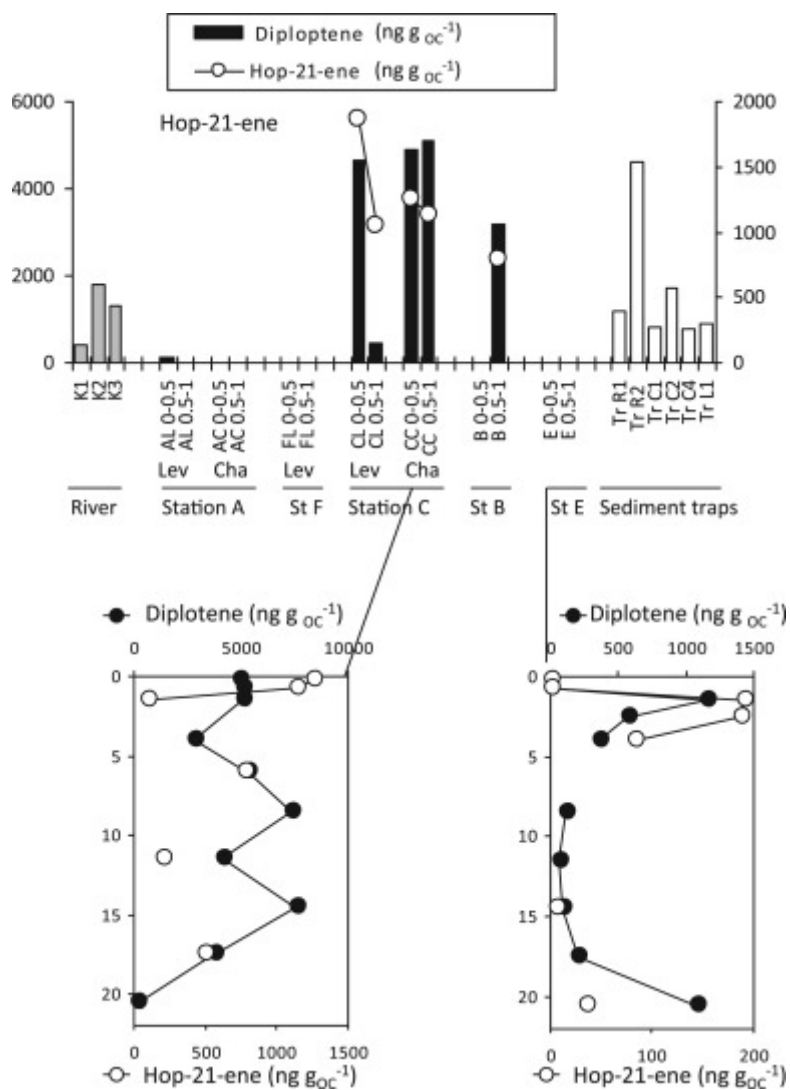


Fig. 9. Top panel shows the spatial distribution of diploptene concentrations normalized to organic carbon, in sediments from the Congo River (grey bars), in surficial sediments collected from the Congo deep-sea fan (black bars, sediment layers from 0 to 0.5 cm and from 0.5 to 1 cm), and in sediment trap samples (white bars). Hop-21-ene concentration is represented by white circles, plotted on the right axis. Diploptene is a terrestrial biomarker (soil microorganisms), and marine bacteria can also be its biological precursor. Diploptene and hop-21-ene levels are expressed in $\text{ng g}_{\text{OC}}^{-1}$. Bottom panels show the vertical profiles of concentration of diploptene and hop-21-ene, in two cores: from the channel at site C, and from site E.

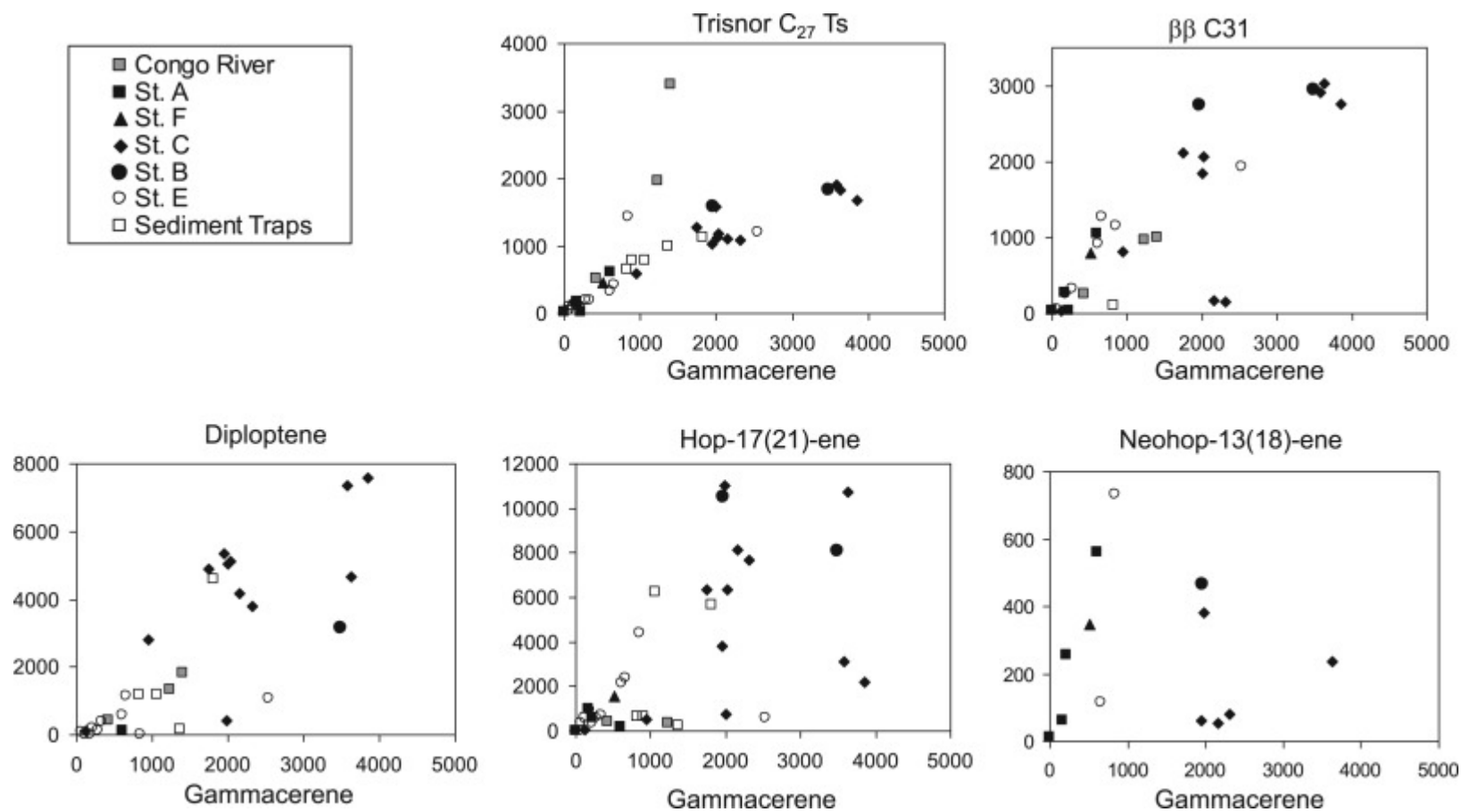


Fig. 10. Scatter plots of OC-normalized concentrations of selected terpenoids versus gammacerene concentration. Gammacerene is synthesized by ferns and bacteria. In the Congo terminal lobe system, it covariates with $\delta^{13}\text{C}$, therefore has a terrestrial origin.

Gammacerene was the most abundant non-hopanoid triterpene in the lobe sediments. It differs from hopanoid by a six-, instead of 5-, membered E ring. Other non-hopanoid triterpenes produced by higher plants were detected in the lobe sediments: oleanene, lupene, ursene and ferenes (Fig. 6). The ursane and oleanane skeletons derive from α - and β -amyrins and are the most frequently encountered in recent sediments (Simoneit, 2005). Oleanene accounted for a higher portion of triterpenes at the levee of site A, and was less abundant at the other sites (Fig. 6). Even though bulk indices showed a rather homogeneous, mostly terrestrial, organic matter at the sites A, F and C of the lobe, the contribution of vascular plants and soil bacterial biomarkers may differ by as much as one order of magnitude in the terminal lobe sediments (Figs. 2, 7 and 8). Oleanene, ursenes, and hop-17(21)-ene are reported in shelf sediments at other locations worldwide and in terrestrial clays (Brassell, 1984; Ten Havens and Rullkötter, 1989; van Dongen et al., 2006; Marynowski et al., 2007a). $\beta\beta$ -homohopane is also one of the dominant terpenoids in immature terrestrial organic matter (Kvenvolden et al., 1990). The saturated homologues of higher plant triterpenes were not detected, nor gammacerane, bringing another evidence of the immaturity of the soil and plant organic matter present in the sediments. Pearson correlations show that gammacerene is related to the bulk terrestrial indicator $\delta^{13}\text{C}$, suggesting that it quantitatively contributed to the bulk terrestrial matter, while oleanene and ferenes did not, and may represent a less abundant higher plant contribution (Table S2, Supplementary material, p. 48-58). Des-A-triterpenoids are formed by A-ring degradation under anoxic conditions (Van Bree et al., 2016). They are detected in low levels in the terminal lobe system and indicate the occurrence of degraded C3/C4 plants (Table S1, Supplementary material, p. 40-47).

Steranes, sterenes and diasterenes showed a minor contribution to the Congo River and lobe sediments. Higher C_{29} sterene concentrations characterized the sediment trap samples. They more probably stem from the degradation of higher plant and phytoplankton sterols.

4. Discussion

4.1. Organic matter sources and degradation by microorganisms, spatial heterogeneity

Sedimentary hydrocarbons in the terminal lobe complex show a conspicuous dominance of terrestrial *n*-alkanes, and of terrestrial and microbial triterpenes. Their dominance evidences the primary terrigenous source of the organic matter, which is already established by $\delta^{13}\text{C}$ and C/N values of the same sediments (Stetten et al., 2015), and by their Rock-Eval characterization (Baudin et al., 2017a, 2007b). Rock-Eval results typified the organic matter as non mature Type III kerogen, sourced by terrestrial biomass and soils. The CPI values confirm that the lobe complex is a site of large accumulation of terrestrial organic carbon exported from the Congo catchment area to the deep ocean. The concentrations of terrestrial *n*-alkanes were in the same range as other marine coastal and marginal locations such as the Mediterranean Rhône and Ebro prodelta (Table 3), showing that the massive export of terrestrial organic matter through the Congo canyon results in similar terrestrial fingerprint as coastal shallow deposition sites, but at an abyssal location.

On top of this general homogeneous trend, terrestrial biomarker concentrations show some degree of variability (Figs. 3 and 8), which will be discussed in the present section.

Site B is located in the lobe 3 where a branch of the northern channel is only a few meter deep and is supposed to convey much less turbiditic inputs than the active southern channel ending at site C.

Terrestrial *n*-alkane signatures at site B and site C are however comparable, revealing that B receives the same organic matter as C, either from the northern channel or from overspilling of the turbidites going through the southern active channel.

At disconnected site E, $\delta^{13}\text{C}$ values show a dominance of marine organic matter (-22.8 to -24.2% , Stetten et al., 2015). Phytadienes reflect the decay of recent algal remains in anaerobic conditions. Other phytoplanktonic fingerprints (*n*- C_{17} dominance) were not present. The lower accumulation rate (0.1 cm yr^{-1}) and the larger oxic layer (6.6 cm, Pozzato et al., 2017) than at the other studied sites involve a more extensive degradation at this site. The first centimetre of sediment has been accumulated during at least 20 years and the reported degradation rates of marine short-chain *n*-alkanes are coherent with their decay during this time period (Cheng et al., 2014; Grossi et al., 2002; Miralles et al., 2007). The sediment core collected at site E has been deposited in less than a thousand years, while the corresponding channel ceased to fuel river particles to the lobe ca 4 kyr ago (Rabouille et al., 2017). A striking characteristic of the upper 13 cm of the sediments at site E is that its higher plant biomarker content compares well to that of sites A, F, or B, presently connected to the active canyon, despite the large difference in $\delta^{13}\text{C}$ opposing the site to the others (Fig. S1, Supplementary material, p. 59). Given the hemipelagic source of the organic matter at E, a marked contribution of *n*- C_{17} , a planktonic alkane, would be expected, but is not found (Fig. 2). A plausible explanation to this mismatch is the faster degradation of short-chain marine alkanes, relatively to more refractory terrestrial hydrocarbons. The molecular fingerprint (proportions in *n*- C_{29} , gammacerene and hop-17(21)-ene) of the terrestrial organic matter at site E reflects the same origin as at sites connected to the Congo canyon, and can be ascribed to Congo River inputs rather than from atmospheric aerosol deposition, the dominant source of terrestrial hydrocarbons at other open sea locations (Gogou et al., 2000). This is a striking evidence that significant river matter is admixed to the pelagic particles at site E, 45 km away from the active channel. The deeper sedimentary horizons of site E showed an increase in several higher plant indicators, a feature also observed in the deeper horizon of the channel at site C. These signals seem to reveal an input of higher plant detritus in these horizons, in line with the slightly higher grain size and terrestrial phytoclasts (Stetten et al., 2015; Schnyder et al., 2017).

Pearson correlations of hydrocarbons concentrations normalized to organic carbon are shown in Table S2 (Supplementary material, p. 48-58). They indicated that hydrocarbons with similar structures covaried, for instance, long-chain homologues on one hand, and short-chain homologues on the other, pointing to common source and comparable sensitivity to degradation (Table S2, Supplementary material, p. 48-58). The Spearman correlations show that vascular plant *n*-alkanes covaried with some hopanes with $\alpha\beta$ (C_{20}) and $\beta\alpha$ (C_{30}) configurations, but vascular plant alkane concentrations showed no covariation neither with those of gammacerene nor fernene, biomarkers of ferns, nor with concentrations of oleanene and ursene, biomarkers of angiosperms. This suggests the occurrence of terrestrial remains from distinct types of vegetation and from soils. Palynofacies also showed variable relative abundances of amorphous organic matter (AmOM) and terrestrial phytoclasts (T-Phyt), however they did not allow to distinguish fern and angiosperm remains (Schnyder et al., 2017). The denser T-Phyt were enriched in the channel of station A relatively to the less dense AmOM, whereas AmOM was enriched in the levee sediments at station A and C, suggesting hydraulic sorting of the turbiditic particles. In the sediments enriched in AmOM, hydrocarbon concentrations are higher. It could be hypothesized that the lighter particles may be enriched in hydrocarbons. The enrichment in terrestrial alkanes in the deepest (19–22 cm) horizons

of the channel of station C and of station E corresponds to the highest T-Phyt palynomorphs and a more terrestrial organic matter as seen by $\delta^{13}\text{C}$ values (Fig. S1, Supplementary material, p. 59). It suggests either a physical sorting of particles within the same turbidite, or the occurrence of a second turbidite in the deepest layers, enriched in coarser terrestrial particles.

Interestingly, $\delta^{13}\text{C}$ and CPI, both classical indicators of higher plant contribution, showed no significant covariation in the present data set (Table S2, Supplementary material, p. 48-58). $\delta^{13}\text{C}$ did not covary significantly with any of the concentrations of aliphatic nor terpenoid terrestrial indicators. In the channel of site C, $\delta^{13}\text{C}$ of the organic matter is shifted towards more negative values, and the proportion of terrestrial phytoclasts in the palynofacies is higher. Both signals agree to indicate a higher fraction of non degraded terrestrial matter at this site.

Hydrocarbons are effectively degraded under oxic conditions. Experiments in coastal sediments have showed that alkanes having less than 25 C atoms were degraded within one year. For example, between 29% and 84% of *n*-C₁₇ alkane was degraded in 500 days (Grossi et al., 2002; Miralles et al., 2007). The degradation of longer chain hydrocarbons is slower but also effective (80% in one year, Grossi et al., 2002; 20–88% in 500 days, Miralles et al., 2007). The efficient mineralization of long-chain alkanols, another class of terrestrial lipids, was previously evidenced at a site located closer to the canyon head (Treignier et al., 2006). Diffusive oxygen uptake values showed that organic carbon was actively remineralized in the first centimeters of the Congo lobe sediments (Pozzato et al., 2017). The average sediment accumulation at site C was exceptionally high, with a turbidite layer (of 10–20 cm) being deposited every 2–3 years, while the sediment accumulation at A and F is one order of magnitude lower (Rabouille et al., 2017). Therefore the organic matter at station C remains in the oxic layer ca 10 times less than at A and F. This shorter exposure to oxic degradation may result in less degraded terrestrial material at the distal site C than at site A.

Phytadienes are produced by degradation of the phytol side chain of chlorophylls during early diagenesis, while they are not produced during water column degradation processes (Grossi, 1996; Grossi et al., 1998). They have been shown to be readily degraded in aerobic sediments while low oxygen exposure favoured their preservation in cyanobacterial mats (Grossi, 1996; Pagès et al., 2014; Slowakiewicz et al., 2014). The spatial distribution pattern of phytadienes in the Congo lobe system contrasts with that of terrestrial *n*-alkanes and terpenoids (gammacerene, fernene, diploptene) by their absence in the river sediments and sediment traps and their marked enrichment at the site C where they almost reach the concentrations of terrestrial *n*-alkanes. Phytadienes' occurrence confirms a greater input of labile chlorophylls, present in fresh plants or algae, to the sites C and B, followed by their hydrolysis into phytadienes and the preservation of phytadienes under anaerobic conditions. The longer residence of turbidite particles in the oxic layer at sites A and F may have resulted in chlorophyll hydrolysis before they reached the anaerobic layer and explain the low abundance of phytadienes in these cores. Whereas covariation was observed for hydrocarbons with similar structures (short-chain and long-chain alkanes, short-chain even hydrocarbons, hopenes, phytadienes), phytadienes and terpenoids, of markedly difference structures, show significant covariation (Table S2, Supplementary material, p. 48-58). It evidences that phytadienes and terpenoids share a common source and shows that terpenoids are associated with recent inputs of terrestrial matter.

The bulk terrestrial signature at all sites is equivalent, but all aliphatic and terpenoid terrestrial hydrocarbons have higher concentrations at sites C and B, normalized to organic carbon or to dry weight. The higher concentrations at site C could indicate that terrestrial hydrocarbons have been exposed to degradation for a shorter time within the sediments of site C relatively to sites A and F, and that terrestrial hydrocarbons decay faster than bulk terrestrial organic matter. According to its location at the end of an inactive channel, site B has a low sediment accumulation rate (0.3 cm yr⁻¹, Rabouille et al., 2017), comparable to that of site A. Therefore its hydrocarbon content was expected to be in the same range as that of site A. Surprisingly, concentrations of terrestrial *n*-alkanes, of terrestrial terpenes, and of phytadienes at site B are similar to those of site C and in turn, much higher than those of sites A and F (Figs. 3, 5, 7, 8 and 9). Amongst the studies carried out by the Congolobe consortium, only palynofacies characterization evidenced differences in the contribution of terrestrial organic matter pools between stations A and C, but station B was not considered (Schnyder et al., 2017). Bulk characteristics, like $\delta^{13}\text{C}$ and C/N did not differentiate sediments from sites A, F, B and C. The enrichment in phytadienes and terrestrial hydrocarbons indicates a larger fraction of recent terrestrial organic matter at sites C and B, within an organic matter that is equally predominantly terrestrial at all sites A, F, C and B. Site B is located 10 km away from the active channel. In march 2001 sediment overspilling over the channel levees caused a significant flux of particles at site ZD, located 13 km off the channel (Khrpounoff et al., 2003; Vangriesheim et al., 2009). The sedimentation rate recorded at site B (Rabouille et al., 2017) is consistent with aggradation due to spillover from the feeding channel, and the less dense upper part of the turbidity currents may reach site B (Dennielou et al., 2017). Therefore the larger proportion of terrestrial hydrocarbons at site B may reflect deposition of labile terrestrial organic matter having recently overflowed the levee. The morphology of the sediments at sites A and F showed blocks and headscars (Dennielou et al., 2017) and indicates that sediments are eroded by sliding and levee dismantling. The lower proportion of phytadienes at sites A and F may be linked to the erosion of recent turbiditic deposits at these sites.

4.2. Processes driving the hopene and triterpene spatial and temporal variabilities

The prevalence of hopanes and hopenes over steranes and sterenes indicates some contribution of microbiota as source of organic matter (Peters et al., 2005; Simoneit, 2005; Volkman et al., 1986; Volkman, 2005). The biological sources of the dominant triterpenes in the lobe sediments, hop-17(21)-ene, $\beta\beta$ -hopane and diploptene (hop-22(29)-ene) are microorganisms and ferns (Douka et al., 2001; Innes et al., 1997, 1998; Patitucci et al., 1995; Rohmer et al., 1984; Rohmer, 1993; Rontani and Volkman, 2005; Sinninghe-Damsté et al., 2014; Welander et al., 2010). They are dominant triterpenes in terrestrial environments with low maturity of the organic matter (Garel et al., 2014). Their predominance in the Congo River sediments suggests that the export of land particles to the lobe complex is a significant source of these triterpenes (Fig. 6). The three river samples showed a larger abundance of the C₃₀ moretane ($\alpha\beta$ -hopane) than lobe sediments, suggesting that other inputs than river sediment contribute to hopenes in the lobe sediments.

Diploptene is a well-recognized terrestrial biomarker (Prahl et al., 1992) and gammacerene is a constituent of ciliates, ferns, purple non-sulfur bacteria and N-fixing symbionts of plant roots (Bravo et al., 2001; Hamed al, 2014; Kleemann et al., 1990). Both are the only hydrocarbons covarying with the bulk terrestrial indicator $\delta^{13}\text{C}$ (Table S2, Supplementary material, p. 48-58), which shows that their spatial variability is related to the dominant fraction of terrestrial organic carbon. Both marine

and terrestrial lineages of aerobic methane-oxidizing bacteria were characterized in the studied sediments (Bessette et al., 2017) and diploptene and gammacerene variations may reflect alive bacteria associated to soil and river organic matter.

Spearman correlations discriminate fern-8-ene, β,α -hopane and hop-21-ene from the other terpenoids because in addition to covarying with other terpenoids, they also show significant covariance with terrestrial *n*-alkanes. Most terpenoids of Congo River sediments were transferred to the lobe sediments in similar relative proportions (Ts, hop-17(21)-ene, gammacerene, $\alpha\beta$ - and $\beta\beta$ -hopane, $\beta\beta$ -C₃₁homohopane). In contrast, hop-17(21)-ene and diploptene showed a variable contribution to total terpenoids (some sediments are devoid of diploptene), and both dominate at site C (Fig. 6). Diploptene and hop-21-ene are constituents of anaerobic *Geobacter* and *Zygomonas* bacteria (Douka et al., 2001; Hartner et al., 2005), and the similarity in their vertical profiles favors the interpretation of a common anaerobic bacterial source for these isomers (Fig. 9). Clay-catalyzed isomerisation of diploptene into hop-21-ene, further isomerisation into hop-17(21)-ene, and further degradation into neohop-13(18)-ene occur in immature sediments and may alter the precursor signature (Simoneit, 2005; Sinninghe-Damsté et al., 2014). The interplay between the soil contribution and the prediagenetic production of diploptene is illustrated by plotting the selected terpenoids concentrations versus that of gammacerene, synthesized by ciliates and bacteria, and generally considered as a terrestrial biomarker. In the present set of samples gammacerene covaries with $\delta^{13}\text{C}$ and is therefore considered to stem from terrestrial bacteria or ciliates (Table S2, Supplementary material, p. 48-58). The covariation of gammacerene with C₂₇ 18(H)-22,29,30-trisnorhopane (Ts) shown in the cross plot of their concentrations is consistent with a same continental source of both compounds (Fig. 10). In contrast, the scatter in the plots of neohop-13(18)-ene and hop-17(21)-ene versus gammacerene suggests additional contributions of organic matter than those from terrestrial origin (Fig. 10). The plot of diploptene versus gammacerene concentrations shows some degree of scatter but still with a clear covariance, suggesting the existence of a mixture of terrestrial organic matter inputs with other inputs of organic matter, more likely a contribution from marine bacteria added to terrestrial soil microorganisms.

Diploptene and its $\Delta 21$ isomer show identical subsurface peaks at site E (Fig. 9). In the upper sediment layers of site E, palynofacies and $\delta^{13}\text{C}$ values indicate low proportion of higher plant remains and bacteria may be major contributors to these hopenes. Almost identical vertical profiles of hop-17(21)-ene and neohop-13(18)-ene at sites C and E suggest either common precursor organisms or sequential isomerisation of hop-21-ene into hop-17(21)-ene and further transformation into neohop-13(18)-ene (Fig. 11). Similar correlations were observed in a more mature terrestrial set of samples (Garel et al., 2014). In a large set of immature marine and lacustrine samples, matching $\delta^{13}\text{C}$ values of both compounds evidenced a diagenetic relationship or a common source (Sinninghe-Damsté et al., 2014). The series of neohop-13(18)-enes identified in a range of recent and ancient sediments included C₂₇ to C₃₀ homologues. In the Congo lobe sediments, the series was limited to the C₃₀ and C₂₇ neohop-13(18)-enes, and corresponds to the composition of recent sediments from other locations (Sinninghe-Damsté et al., 2014).

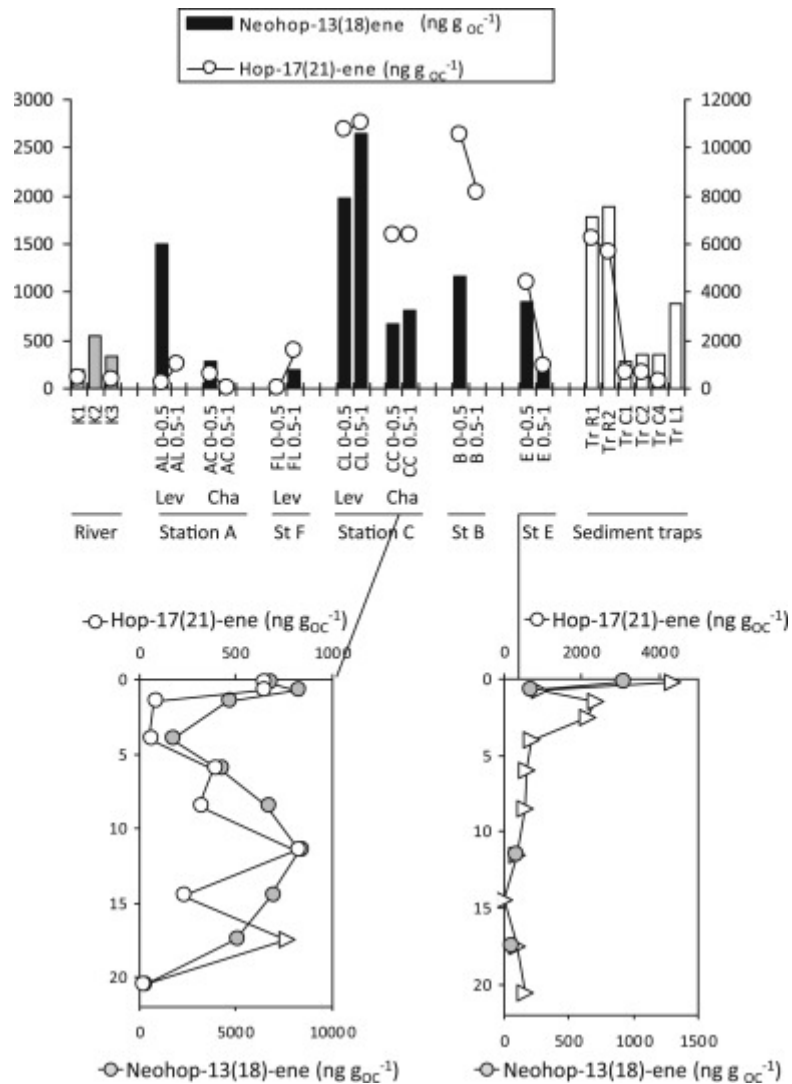


Fig. 11. The top panel shows the spatial distribution of neohop-13(18)-ene concentrations normalized to organic carbon, in sediments from the Congo River (grey bars), in surficial sediments collected from the Congo deep-sea fan (black bars, Lev: levee, Cha: channel. sediment layers from 0 to 0.5 cm and from 0.5 to 1 cm), and in sediment trap samples (white bars). Concentrations of hop-17(21)-ene are represented by white circles plotted on the right axis. Diploptene and hop-17(21)-ene levels are expressed in $\text{ng g}_{\text{OC}}^{-1}$. Bottom panels show the vertical profiles of concentration of neohop-13(18)-ene and hop-17(21)-ene, in two cores: from the channel at site C, and from site E.

4.3. Petroleum contamination

The occurrence of oil hydrocarbons (UCM, C_{23} and C_{24} tricyclic triterpanes) indicate a notable petroleum contamination of the first surface centimetre of the sediment at site E, but absent underneath (Table S1, Supplementary material, p.40-47). Below the contaminated layers, the CPI is consistent with a higher plant source of the high molecular weight alkanes, alike at the other studied sites. Oil hydrocarbons are also evidenced in lower concentrations at site A and C. A strong petroleum odour was noted when slicing the top of contaminated cores (site E, site C). UCM and alkanes concentrations remained on the same order of magnitude as moderately contaminated coastal sites (Bouloubassi et al., 2001; Tolosa et al., 1996) and are at least one order of magnitude less abundant than in heavily contaminated coastal areas such as Alexandria harbor, the Rhine

estuary and hydrocarbon seepage area (Aboul-Kassim and Simoneit, 1995; Burns et al., 2010; Stronkhorst and van Hattum, 2003). UCM covariates with short-chain alkanes in the range C₁₅-C₁₈, with pristane, phytane, and C₂₃ and C₂₄ tricyclic diterpanes, suggesting a fossil source for these compounds (Table S2, Supplementary material, p. 48-58). Another molecular evidence for petroleum occurrence is the series of tricyclic diterpanes from C₂₁ to C₂₆ dominating over other terpanes and terpenes on the *m/z*=191 fragmentogram of the surficial sediment of site E and absent in non-contaminated location nearby (Fig. S3, Supplementary material, p. 60).

The origin of this crude oil contamination is difficult to assert with certainty. The background oil occurrence characterized in sediments along the end of the canyon may come from soil particles from Kinshasa, from hydrocarbon accidental release from Matadi and Boma harbours and from the Banana oil terminal. Crude oil is extracted from the offshore blocks located close to the coast on the Northern side of the canyon (Congo-brazzaville-hydrocarbons-blocks: ©Copyright, 2017) and the possibility that accidental oil spills may have reached the lobe area cannot be ruled out.

The striking enrichment in short chain alkanes with an even predominance at the levee of site C is difficult to explain. These compounds are unusual in marine systems, and are consistent with several sources of organic matter. They were first characterized in evaporitic environments in which the highly reducing conditions favor reduction of fatty acids rather than their β -decarboxylation (Moldowan et al., 1985; Zhang and Paul, 2012). They were also observed in oxygenated environments and were interpreted as a direct microbiota inputs generated by β -decarboxylation of bacterial odd fatty acids (Grimalt and Albaigés, 1987; Nishimura and Baker, 1986). The predominance of C₁₈ in lacustrine sediments was considered to be inherited from planktonic and/or bacterial cells (Affouri and Sahraoui, 2017). A short chain mode of even alkanes was observed in C3 trees and C4 grasses, woodland and grassland soils (Table 2). It was also identified in charred biomass and in soils with a coal fraction, however maximizing at C₁₆ and C₁₈ (Eckmeier and Wiesenberg, 2009). Finally, $\Delta^{14}\text{C}$ values of hydrocarbons from sediments from the China East margin Sea showed that C₁₆ and C₁₈ had a fossil origin (Tao et al., 2015). In the sedimentary context of Congo lobe complex, this signature is consistent with a higher plant, a bacterial and a fossil contribution. It is present in most of the samples from the lobe system, in the river sediments and even in some sediment trap samples. However the fainter C₁₆ and C₁₈ fingerprint in the river sediment samples argues for another origin than higher plants (Fig. 4). C₁₄, C₁₆ and C₁₈*n*-alkanes were correlated to the chromatographically unresolved hydrocarbons (UCM) (Table S2, Supplementary material, p. 48-58). However, these alkanes were more abundant than their odd counterparts in many samples where UCM cannot be quantified. The last likely sources expected to yield a broad repartition of short-chain alkanes are soil bacteria, shown to contribute to alive microbial communities of aerobic methane-oxidizing bacteria (Bessette et al., 2017). The degradation products of diploptene, hop-21-ene and neoho-13(18)-ene also displayed their highest concentrations at the levee of site C (Figs. 4 and 11). The occurrence of this group of hopenes in bacteria (Table 3) evokes a possible bacterial source for both groups of hydrocarbons.¹⁴C isotopic ratios of alkanes would unequivocally ascribe the source of even short-chain alkanes but they were not available in the present study.

4.4. Dynamics of terrestrial organic matter inputs

Fluxes of alkanes are seldom reported, and the highest values of terrestrial alkanes are measured in subtropical shelf (Sikes et al., 2009). The accumulation fluxes of terrestrial

alkanes measured in the Congo terminal lobe are in the upper range of previous measurements in deep marine environments (Table 3). Terrestrial *n*-alkanes and triterpenes fingerprint two different sources of terrestrial organic matter, as shown by the Pearson correlation of $\delta^{13}\text{C}$ to gammacerene and diploptene, and not to odd *n*-alkanes in the range $\text{C}_{25}\text{-C}_{37}$ (Table S2, Supplementary material, p. 48-58). However the dynamics of both terrestrial components in the terminal lobe sediments is equally driven by the accumulation of particles fuelled by the canyon. This overwhelming lateral input of particles masks the contribution of atmospheric deposition, which generally dominates abyssal fluxes of terrestrial *n*-alkanes in the open ocean. The concentration gradient of terrestrial *n*- C_{29} and gammacerene at the different sites (Sites C and B > Site B > Site E) combines with the mass accumulation rates (Site C > Site A and B > Site E) to yield a decreasing magnitude of accumulation fluxes from site C, sites A and B, and the disconnected site E (Fig. 12).

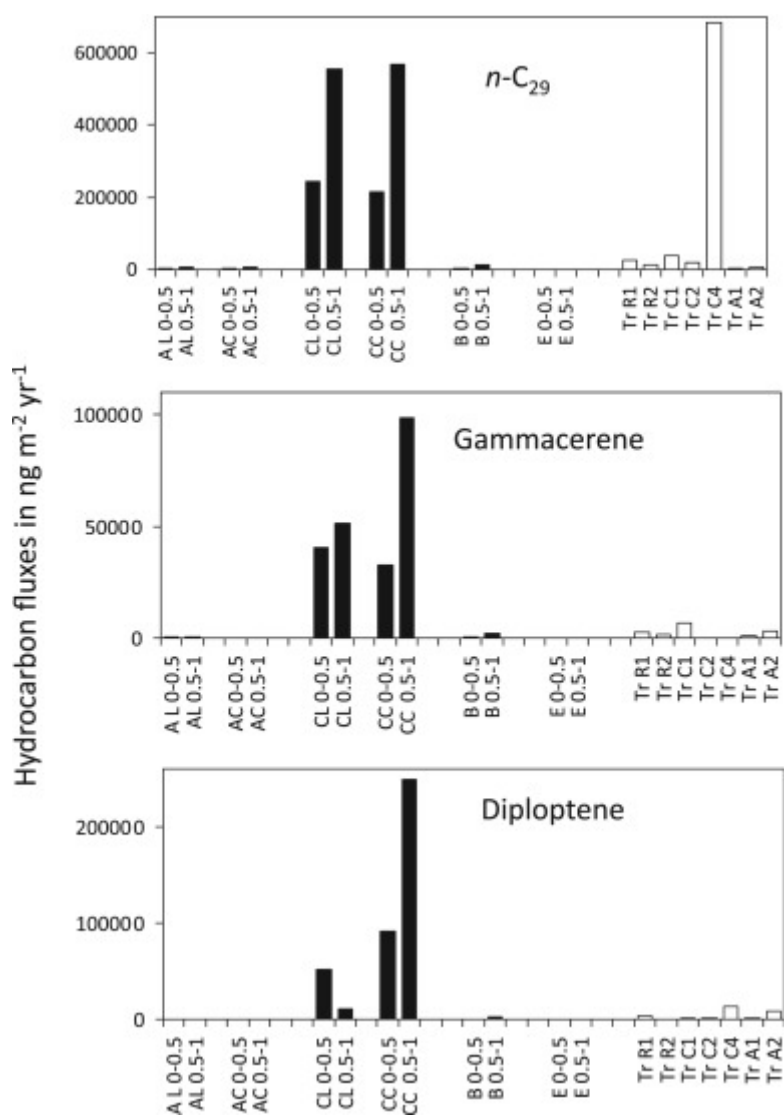


Fig. 12. Hydrocarbon accumulation rates in sediments from sites A, F and C are represented by back bars. Hydrocarbon sedimentation fluxes, measured by sediment traps 40 m above the sediment are showed by white bars. Selected hydrocarbons are the dominant terrestrial alkane, *n*-C₂₉, an terrestrial indicator,

gammacerene, and diploptene. Diploptene has a dual source, from terrestrial and marine bacteria. Fluxes are given in $\text{ng m}^{-2} \text{yr}^{-1}$.

One-year time series of sediment trap sampling in the lobe complex and at sites located upstream showed a typical pelagic flux for most of the year (Khripounoff, personal communication) with 2 peaks of particles at the site located upstream in the channel (Regab Z', Tr C1 February 2011, Tr C4 from the 29th of March to the 13th of April 2011). Mass flux peak at Tr C1 and Tr C4 showed likely erosion of the flanks or of the levees of the channel (124 and $877 \text{ g m}^{-2} \text{yr}^{-1}$). Except for these events, mass flux was within a range consistent with pelagic sinking fluxes of particles ($25\text{--}49 \text{ g m}^{-2} \text{yr}^{-1}$). The sinking particles were enriched in the planktonic $n\text{-C}_{17}$ in relation to others alkanes (Fig. S2, Supplementary Material, p. 59). The sedimentation of particles 40 m above the sediment fuels about one tenth of the terrestrial n -alkanes flux accumulated in the sediments at site C (Fig. 12). It clearly shows that the vertical rain of particles contributes a minor fraction of the organic matter preserved in the sediments at site C, and that the sediment is controlled by lateral transport of particles through the canyon (Fig. 12). When the canyon flanks and levees are destabilized, a massive input of particle is captured by the sediment trap (Tr C4), yielding unusually high sedimentation of terrestrial alkanes, reaching the high alkane sedimentary accumulation rates at C. At sites A, B and E the similar order of magnitude of sediment accumulation rates in one hand, and of vertical flux supported by sinking particles on the other, evidences that river inputs are not preserved into these sediments, either they are degraded by the microorganisms or they are further transported towards site C. Eventhough site B, receiving overspilling particles from the active channel, shows a similar proportion of labile hydrocarbons sourced by higher plant debris as site C sediments, their sedimentary accumulation rates at B show that these inputs are little significant in terms of fluxes.

5. Conclusions

Hydrocarbons of the Congo lobe complex have a marked higher plant fingerprint, in agreement with the bulk geochemical characteristics showing the dominance of terrestrial matter. Terrestrial biomarkers from higher plants, ferns, bacteria and angiosperms show ample variations in their contributions, indicating heterogeneous sources of the soil and vegetation detritus delivered to the sediments of the terminal lobe system at the end of the Congo submarine canyon. Hydrocarbon composition variations may reflect both different sources of the organic matter and different exposure to degradation, implied by the two-fold difference in mass accumulation rates of sediments of the terminal lobe complex.

At the more distal site C, the sediment accumulation is higher and the sediments spend less time in the oxic layer than at other sites. These sediments displayed higher organic carbon-normalized concentrations of terrestrial hydrocarbons than those where the exposure to oxic degradation is longer, suggesting that bulk organic carbon degrades faster than terrestrial hydrocarbons in the first steps of the pre-diagenesis. Despite their much smaller concentrations, terrestrial hydrocarbons and terrestrial terpenes are still present at the site disconnected from the active channel (site E) bringing evidences for the admixture of some river particles to the planktonic organic matter, dominant at this site.

The occurrence of a minor terrestrial signal in the sediment traps shows that some sediment from the levees may be destabilized, and form nepheloid layers that are admixed to the vertical flux of pelagic sinking particles. Corresponding vertical flux may produce pulses of terrestrial hydrocarbons

but the general vertical fluxes of terrestrial hydrocarbons are one order of magnitude lower than hydrocarbon accumulation fluxes in the sediment at site C. It evidences the magnitude of the inputs delivered by turbidites through the active channel and clearly demonstrates that lateral transport controls the supply of organic matter to the terminal lobe complex.

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Aliphatic hydrocarbons and triterpenes of the Congo deep sea fan - Supplementary material -

Laurence Méjanelle^{(1)*}, Béatrice Rivière⁽¹⁾, Laurence Pinturier⁽²⁾, Alexis Khripounoff⁽³⁾, François Baudin⁽⁴⁾ and Jordi Dachs⁽⁵⁾

List of supplementary materials:

Table S1, pages 40 to 47: Concentrations of aliphatic hydrocarbons in ng.(g of dry weight)⁻¹ in the Congo lobe sediments.

Table S2, pages 48 to 58: Non parametric Spearman correlation of biomarker concentrations expressed in ng g_{OC}⁻¹.

Figure S1, page 59: Variation of organic carbon percent, plotted on the left axis and of $\delta^{13}\text{C}$, plotted on the right axis, in the surficial sediments of the studied sample set

Figure S2, page 59: Distribution of terpenoids (Selected Ion Current $m/z = 191$) in the most contaminated sediment of the studied area, on the bottom panel. This sediment layer, collected at site E (0-0.5cm layer) showed the highest UCM concentrations. The m/z fragmentogram of a non-contaminated sample, the 0-0.5cm sediment layer at the channel of site C, is presented on the top panel. A series of tricyclic terpanes from C_{20} to C_{26} is indicated on the bottom $m/z=191$ current by shorthand notation TC_{20} , TC_{21} , ... etc. These compounds are present in petroleum but not in recent organic matter.

Figure S3, page 60: Distribution of terpenoids (Selected Ion Current $m/z = 191$) in the 0-0.5 cm layer at the channel of site C. Peaks are labeled by their structural identification. Ts is the shorthand denomination for 18α -22,29,30-trisnorhopane and G stands for gammacerene.

Figure S4, page 60: Distribution of terpenoids (Selected Ion Current $m/z = 191$) in the 0-0.5 cm layer at the levee of site A. Peaks are labeled by their structural identification.

Figure S5, page 61 to 62: Mass spectra of dominant hopanoids and non-hopanoid triterpenes.

Table S1. Concentrations of aliphatic hydrocarbons in ng.(g of dry weight) ⁻¹ in River and lobe sediments. To be continued.

Sample	K1	K2	K3	A L 0-0.5	AL 0.5-1	AC 0-0.5	AC 0.5-1	FL 0-0.5	FL 0.5-1	CL 0-0.5	CL 0.5-1
Alkanes	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
C10					0	1	1	2	1	5	19
C11	0.6	1.8	10.1	0.3	0.3	2	1	4	4	30	53
C12	1.6	1.4	16.6	0.9	1.0	10	11	18	12	120	18
C13	0.7	3.1	7.6		0.3	4	4	15	16	389	145
C14	3.2	1.0	11.4	2.3	2.3	44	61	53	34	291	510
C15	1.6	2.0	4.8	0.7	1.2	10	12	6	7	54	72
C16	2.0	4.3	8.0	3.8	3.3	41	75	55	31	216	283
C17	2.0	3.2	17.3	3.4	2.6	4	20	8	9	22	116
Pristane	1.4	2.1	7.5		0.2	1	8	2	2	19	35
C18	1.8	2.4	5.4	3.8	2.9	15	32	31	20	134	150
Phytane			5.0	1.2	1.0	2	6	3	1	14	21
Phytadiene1					6	6	5	1	3	111	139
Phytadiene2				1.4	6.7	17	4	0	13	99	145
Phytadiene3				1.1	6.8	5	0	0	3	153	145
C19	4	2	10	2	2	3	9	2	3	290	33
C20	4	5	7	3	2	4	18	9	8	29	43
C21	7	7	18	4	1	3	15	4	5	22	27
C22	6	6	10	3	2	2	0	4	5	17	21
C23	14	17	29	7	5	7	12	8	13	49	60
C24	7	8	14	3	2	3	5	4	6	21	27
C25	21	32	56	10	8	10	16	12	19	69	86
C26	12	15	23	4	3	4	7	5	8	28	35
Squalane	2	3	66	2	2	2	3	2	4	12	16
C27	39	77	131	19	16	19	31	22	37	126	157
C28	18	24	39	10	5	1	14	10	16	52	66
Squalene				2	1	1	1		2	15	18
C29	101	225	349	72	61	67	113	84	64	469	562
C30	21	28	54	12	9	11	12	12	19	65	14
C31	81	164	298	61	46	53	46	64	103	345	434
C32	14	15	35	10	7	9	15	12	17	49	70
C33	48	77	168	21	17	19	31	24	35	133	158
C34	6	8	14	1	2	4	2	0	3	27	14
Lycopane				2				2	1		3
C35	33	68	126	7	6	7	12	9	12	48	55
C36			6	1.2	0.8		1.6	1.2	1.5	5	8
C37		bql	20	2.7	2.3	2.5	4.4	3.4	4.9	18	22
C38				1.2	0.9	1.1	2.0	1.5	2.4	6	9
C39		bql		1.4	1.0		2.3	1.6	2.7	9	10
C40											
UCM				883	586		7995		7	1185	
CPI	4.4	6.8487	6.4	4.8	5.4	5.8	4.5	4.9	4.0	5.0	6.5

Table S1. Concentrations of aliphatic hydrocarbons in ng.(g of dry weight)⁻¹ in the Congo lobe sediments. To be continued.

Sample	CC 0-0.5	CC 0.5-1	CC 1-2cm	CC 3-5cm	CC 5-7cm	CC 7-10cm	CC 10-13cm	CC 13-16cm	CC 16-19cm	CC 19-22cm	B 0-0.5	B 0.5-1
Alkanes	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
C10	10	1.1	1.8	3.2	1.8	2.2	1.0	2.0	0.6	1.2	1.4	1.9
C11	3	2.5	5.3	6.1		2.5		3.4	1.1	3.0	4.4	6.1
C12	9	6	7	6	4	4	5	4	2	8	14	14
C13	2	3	7	6		4	7	4	3	5		
C14	22	22	19	6	6	7	13	6	5	23	52	28
C15	8	8	6	6		5	9	7	5	15	10	
C16	19	41	30	6	5	7	25	8	6	29	62	19
C17	32	36	25	21	42	44	64	45	42	169	24	2
Pristane	5		3	1			4	2		12		
C18	13	30	19	6	9	0	25	12	12	42	31	11
Phytane	2	17	9		3		4	4	3	14	5	
Phytadiene1	145	127	37	55	136	229	124	110	99	101	79	59
Phytadiene2	130	95	22	28	110	165	80	59	67	55	105	52
Phytadiene3	202	138	33	45	169	240	130	102	112	92	129	89
C19	14	18	9	6	15	29	20	17	16	46	26	13
C20	11	19	12		13	13	21	15	17	48	14	11
C21	21	6	15	9	23	1	29	25	2	86	19	5
C22	15	17	10	6	15	13	20	18	20	58	13	16
C23	51	58	35	23	56	44	69	62	70	207	44	53
C24	20	24	14	9	22	18	27	24	28	84	18	22
C25	68	76	52	34	82	60	100	93	96	298	62	72
C26	25	30	21	13	33	24	39	36	38	124	25	29
Squalane	12	14	9	5	14	11	17	14	17	57	10	14
C27	116	126	106	67	166	119	198	198	183	604	116	135
C28	48	52	43	21	51	3	77	77	2	250	3	59
Squalene	23	28	15	11	23	49	28	25	27	64		16
C29	377	427	406	252	582	459	740	825	652	2424	448	517
C30	20	57	57	33	85	61	96	104	86	316	69	70
C31	232	292	301	179	418	349	526	579	456	1701	308	351
C32	44	54	49	29	73	59	84	85	75	264	48	52
C33	78	101	121	74	171	132	197	221	174	669	118	65
C34	6	8	10	10	14	11	16	17	13	65	26	10
Lycopane	7	2				3		4		13		
C35	26	35	44	29	63	46	74	82	62	239	40	48
C36	3	5	6	4	9	5	9	12	7	32	5	7
C37	11	13	17	11	26	17	29	33	24	89	16	18
C38	4	6	7	4	10	7	12	15	11	37	6	8
C39	5	7	9	6	12	8	16	19	13	48	7	9
C40										10		
UCM		1540	248				201	150				
CPI	5.7	4.8	5.3	5.5	5.4	6.7	5.5	5.7	6.8	5.4	5.8	5.0

Table S1. Concentrations of the compounds in ng.(g of dry weight)⁻¹ in Congo terminal lobe sediments. To be continued.

Sample	E 0-0.5	E 0.5-1	E 1-2	E 2-3	E 3-5	E 5-7	E 7-10	E 10-13	E 13-16	E 16-19	E 19-22
Alkanes	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
C10	4	5	4	6	16	4	1	4	4	0.9	0.3
C11	4	3.2	1.0	1.4	5.8	0.4	0.7	0.2	0.4		0.6
C12	16	4.9	2.8	3.4	10.0	0.8	1.3	0.4	0.6	0.5	1.7
C13	7		1.2	0.9	3.4	0.5	0.8		0.5		1.1
C14	62	11	8	7	14	1	2	0.6	1.0	0.6	3.4
C15	42				3	1	1				1.6
C16	132	14	6	5	11	1	2		0.9		2.8
C17	61		2	2	5		1		1.2	0.5	5.2
Pristane	17										
C18	124		3.4	2.3	6.6	0.7	1.0				3.1
Phytane	53										
Phytadiene1	24		5.4	4.4		2.2	4.3	4.4	3.5	6.9	2.6
Phytadiene2	36		3.3	3.1		1.8	3.7	3.5	1.9	3.8	1.0
Phytadiene3	18		5.5	5.4		3.1	5.5	5.3	2.8	6.2	1.8
C19	117		2.4	1.5	4.2	0.6	1.0		1.1	0.5	4.8
C20	241		3	2	5	1	1	1	1		5
C21	502		5	3	8	1	2	1	3	1	15
C22	518		4	3	7	1	1		2	1	10
C23	424		10	7	15	2	3	1	6	4	39
C24	83		6	4	9	1	1		2	1	15
C25			14	9	20	2	4	2	8	5	54
C26	84		7	5	10	1	2	1	3	2	21
Squalane						0	1	0	2	0	2
C27			24	16	32	4	7	3	15	9	100
C28	46		11	7	16	2	2	1	6	3	42
Squalene			5	4	5	1	1		0	1	4
C29	188	27	79	49	105	12	25	12	55	34	410
C30	50		11	6	15	2	3	0	6	4	53
C31	87	21	61	37	79	9	17	8	36	22	283
C32			10	6	13	2	3	1	6	3	44
C33	7		25	15	35	4	7	3	14	8	108
C34	59		2	2	4		2		1	2	11
Lycopane	7										2
C35	4		8.3	4.6	12.9	1.3	2.4	1.1	4.5	2.5	33
C36			1.5						0.8		5
C37			2.7	1.1	3.1	0.3	0.7	0.2	1.7	1.0	15
C38			1.0						0.7		5.7
C39			0.6						0.7		7.9
C40											1.6
UCM	10471	276	86								
CPI	3.8		4.6	4.8	4.6	5.3	4.8	9.6	5.4	5.4	5.3

Table S1. Concentrations of aliphatic hydrocarbons in ng.(g of dry weight)⁻¹ in sediment traps moored 40m above the sediments in the Congo terminal lobe system. To be continued.

Sample	Tr1	Tr 2	Tr C1	Tr C2	Tr C4	Tr L1	Tr L2
Alkanes	-----	-----	-----	-----	-----	-----	-----
C10							
C11	3			4		16	7
C12	34	172		10		21	10
C13	5	15		2		28	13
C14	38	19	20	44	50	42	15
C15	33	7	5	20		41	14
C16	9	32	17	40	26	25	10
C17	126	48	36	30	27	54	106
Pristane	10		6	7	4		8
C18	12	27	10	31	14	62	12
Phytane		15	4	6	4		
Phytadiene1					1		
Phytadiene2					1		
Phytadiene3					1		
C19	14	27	14	15	13	72	34
C20	73	72	26	15	23	83	39
C21	134	148	71	23	46	94	45
C22	108	127	102	24	60	104	49
C23	165	188	102	59	92	26	54
C24	144	161	37	23	43	124	11
C25	181	266	67	77	110	47	27
C26	150	207	32	40	52	41	16
Squalane							
C27	286	402	97	170	218	87	59
C28	140	188	45	61	81	35	25
Squalene							
C29	512	496	310	400	780	193	145
C30	162	185	55	74	96	40	27
C31	355	433	229	358	543	121	103
C32	88	118	34	46	64	29	19
C33	181	235	108	158	220	58	48
C34	46	39	22	18	29		
Lycopane							
C35	170	153	76	93	97		
C36	30	26		9	17		
C37	33			19	52		
C38	31			12	17		
C39	21			10	21		
C40	18				7		
UCM							
CPI	2.4	2.4	4.3	4.7	5.4	1.8	2.7

Table S1. Concentrations of terpenoid hydrocarbons in ng.(g of dry weight)⁻¹ in sediments from the Congo River and from the Congo canyon terminal lobe system. To be continued.

Sample	K1	K2	K3	A L 0-0.5	AL 0.5-1	AC 0-0.5	AC 0.5-1	FL 0-0.5	FL 0.5-1	CL 0-0.5	CL 0.5-1
C20H36 Tricyclic				3.5			0.6				
C21H38 Tricyclic	1.2			6.9	2.0	1.7	1.1				
C21H36 Triterpene							0.1				
C23H42 Tricyclic 1					2.9		0.2				
C24H44 Tricyclic 1										9.6	
C23H42 Tricyclic 2	0.3					2.2	1.2				
C23H42 Tricyclic 3	0.3										
C23H40 Tri-terpene	0.5										
C24H44 Tricyclic 2				5.2	1.1		32.8				5.5
des-A-Olean-13(18)-ene											
des-A-Oleanediene											
des-A-lupane	3.8	8.8	19.7	5.4	1.8	2.3	12.6		4.8	15.8	18.8
des-A-terpene											
C25H44 Tri-terpene											
C25H46 Tricyclic 1											
C25H46 Tricyclic 2							0.19				
C24H42 Tri-terpene 2	0.7						0.13				
C24H42 Tri-terpene 3	0.9	2.5					0.08				
C24H42 Tri-terpene 4	0.4										
C27sterane				3.9		0.5	0.02		1.2		
C28sterene 1											
C26sterene				4.2							
C28sterene 2											
C29sterene			3.2	4.0		0.6	0.03		1.6		
C27 Trisnorhopene							0.16				
C27 Trisnorhopene							0.06				
C28sterane							0.03				
22,29,30-trisnorneohop-13(18)-ene				15.0	1.7	6.9	0.28	0.4	8.2	5.1	10.0
C27sterane 2											
C27 Trisnorhopene 1											
C27 Trisnorhopene 2											
22,29,30-trisnorneohop-17(21)-ene					3.7					44.2	43.1
Cholestene	0.7								1.8		
C30hop-di-ene							0.04				
C28sterene 3										17.6	
C29diasterene	0.6				0.9		0.02				
18 α (H)-22,29,30-trisnorhop	7.8	41.1	50.2	16.3	4.6	0.7	0.44	0.7	10.7	39.3	41.6
C29 Tri-terpene				3.1	1.2		0.06	0.1	2.5	7.6	7.9
17 α (H)-22,29,30-trisnorhop	8.6					5.9					
Adiantene 1											
Oleanene				34.2	1.2	4.1	1.34	1.6	13.4		
C29 α,β -norhopane S	9.0										16.9
C29 α,β -norhopane R					1.4	1.6		0.2	4.1	12.5	
C29 sterene											
C29 sterene	1.7	19.0	5.1	9.7		1.8	0.13	0.2	12.0	7.0	8.1
Lupene				21.3	1.2	7.0	0.31	0.6			2.0
C30 hop-7(21)-ene	6.4		9.2	5.3	26.4	15.6	0.11	0.1	37.3	231	290
Adiantene 2							0.13	0.2			
C30 α,β -hopane R	1.5			8.6	2.1	2.6	0.27			18.0	20.6
C30 α,β -hopane S											
neohop-13(18)-ene	2.9	6.7	8.7	40.3		7.8	0.69	0.9	4.6	43	69
Adiantane or β,β -C29 hopar	2.8				4.8		0.35	0.6	19.4		
Gammacerene	6.5	17.0	31.5	16.2	4.8	5.9	0.05		12.2	78	52
Fern-8-ene	0.7				1.0			0.1	1.3	37	20
Fern-7-ene										12.8	15.7
C31 α,β -homohopane	1.5	6.2	7.4								
C30 β,α -hopane	7.3	27.1	38.3	6.5	1.7	2.0	0.12	0.2	3.6	56	
C31 β,α -homohopane				25.8	7.2	9.8	0.63	0.9	16.8		69.9
C30 β,β -hopane											
C30 β,α -hopane	6.0	14.1	32.1	32.6	9.1	11.6			21.7	79.6	
C31Hopene					0.7	9.6	0.02	0.1	2.2		
Diploptene	6.4	22.0	33.8	3.2						101	11
Hop-21-ene										40	28
C31 methyl-hopene											
C32 α,β -homohopane				2.8							
C31 β,β -homohopane										7.4	
ab/baC32	1.9	6.0	6.9								7.8
C31 β,β -homohopane	3.7	12.0	24.7	27.9	7.4	1.0	0.7	1.1	19.0	65	
C32 β,β -homohopane				2.2	0.7	6.3	0.1	0.2	1.8	4.7	6.6

Table S1. Concentrations of terpenoid hydrocarbons in ng.(g of dry weight)⁻¹ in sediments from the Congo River and from the Congo canyon terminal lobe system. To be continued.

Sample	CC 0-0.5	CC 0.5-1	CC 1-2cm	CC 3-5cm	CC 5-7cm	CC 7-10cm	CC 10-13cm	CC 13-16cm	CC 16-19cm	CC 19-22cm	B 0-0.5	B 0.5-1
C20H36 Tricyclic			22.8	2.5		5.6	7.4	3.0			10.2	
C21H38 Tricyclic	4.9	21.5					11.9	4.6		0.2	16.5	
C21H36 Triterpene	5.8	4.8	7.7	4.1	5.7	10.6	7.9	6.9	5.2			
C23H42 Tricyclic 1		5.7									14.6	
C24H44 Tricyclic 1			15.2									
C23H42 Tricyclic 2	4.0	15.8		1.9	2.6	3.7	10.5	5.5				
C23H42 Tricyclic 3												
C23H40 Tri-terpene												
C24H44 Tricyclic 2		6.3	3.9				3.9	2.7			6.8	
des-A-Olean-13(18)-ene								1.2				
des-A-Oleanediene								2.2				
des-A-lupane	20.0	21.9	22.0	11.4	18.5	40.7	22.4		17.7		22.5	15.8
des-A-terpene						5.4		5.1				
C25H44 Tri-terpene						2.8						
C25H46 Tricyclic 1												
C25H46 Tricyclic 2												
C24H42 Tri-terpene 2												
C24H42 Tri-terpene 3						6.1						3.1
C24H42 Tri-terpene 4												
C27sterane												
C28sterene 1								1.8				
C26sterene												
C28sterene 2								1.7				
C29sterene												
C27 Trisnorhopene												
C27 Trisnorhopene												
C28sterane												
22,29,30-trisnorhop-13(18)-ene					2.3		2.2		3.1		10.0	
C27sterane 2							1.2		1.4			
C27 Trisnorhopene 1							1.6		1.4			
C27 Trisnorhopene 2							3.2		2.5			
22,29,30-trisnorhop-17(21)-ene	62.7	68.4	63.6	36.3	72.9	117.8	69.5	69.5	69.3	2.4	27.7	47.0
Cholestene												
C30hop-di-ene												
C28sterene 3	24.4	17.0			12.2	13.5	8.6	21.6	14.5		4.3	17.8
C29diasterene												
18 α (H)-22,29,30-trisnorhopane (Ts)	42.2	43.2	44.6	20.7	38.8	78.3	45.9	65.1	41.8	6.9	34.1	44.5
C29 Tri-terpene	7.7	6.2	7.3	2.4	6.1	18.8	7.3	12.2	9.5	0.3	10.3	8.1
17 α (H)-22,29,30-trisnorhopane (Tm)												
Adiantene 1												
Oleanene	4.3	5.5									15.0	
C29 α,β -norhopane S			19.6									1.9
C29 α,β -norhopane R	17.2	19.1									14.6	14.7
C29 sterene												
C29 sterene	7.6	6.4	5.3	9.7	19.3		24.4	33.0	22.7	1.9	13.4	5.3
Lupene											23.4	
C30 hop-7(21)-ene	210	233	29	19	144	129	335	86	296	2.1	228	197
Adiantene 2												
C 30 α,β -hopane R	18.7	21.2	18.6	7.7	11.8	34.4	21.8	24.6		1.7	19.4	22.1
C 30 α,β -hopane S												
neohop-13(18)-ene	22	30	18	6	16	27	34	26	19	0.6	25.4	
Adiantane or β,β -C29 hopane									36			29.1
Gammacerene	57	74	80	33	73	148	89	149	90	4.8	42.5	84.5
Fern-8-ene	26	41	11		54	55	86	21	68		6.7	11.8
Fern-7-ene	16.9	20.2	13.0	6.4	11.4	31.5	16.4	20.1	12.9	1.4	12.4	15.7
C31 α,β -homohopane												
C30 β,α -hopane		69	67	31	52	118	69	95	60		54	67
C31 β,α -homohopane	66.2											
C30 β,β -hopane												
C30 β,α -hopane	83.7	87.9	85.0	37.1	60.1	135.1	80.6	120.3	73.6	5.7	73	85
C31Hopene												
Diploptene	161	187	202	99	201	303	172	294	146	4.7		76.8
Hop-21-ene	41	42	4		29		8		19			19.1
C31 methyl-hopene									4.9			
C32 α,β -homohopane					4.7		10.4	3.9	8.0			
C31 β,β -homohopene	9.4	10.5	10.8	6.0	52.5	17.6	71.3	16.1	62.9	2.9	4.9	3.3
ab/baC32												8.7
C31 β,β -homohopane	70	75	73	29		120	7	107	6.2	1.2	59.4	71.6
C32 β,β -homohopane	7.0	6.1				13.4		10.1		3.5	5.5	10.1

Table S1. Concentrations of terpenoid hydrocarbons in ng.(g of dry weight)⁻¹ in sediment traps particles sinking 40m above the sediment bed, in the Congo River terminal lobe system.

Sample	Tr1	Tr 2	Tr C1	Tr C2	Tr C4	Tr L1	Tr L2
C20H36 Tricyclic							
C21H38 Tricyclic						57.6	54.2
C21H36 Triterpene			2.4				
C23H42 Tricyclic 1							
C24H44 Tricyclic 1							
C23H42 Tricyclic 2			2.2				
C23H42 Tricyclic 3							
C23H40 Tri-terpene							
C24H44 Tricyclic 2							
des-A-Olean-13(18)-ene							
des-A-Oleanediene							
des-A-lupane		15.3	17.0				
des-A-terpene		1.3					
C25H44 Tri-terpene							
C25H46 Tricyclic 1							
C25H46 Tricyclic 2							
C24H42 Tri-terpene 2						91.6	98.3
C24H42 Tri-terpene 3			2.6			22.8	38.6
C24H42 Tri-terpene 4						36.0	38.5
C27sterane			2.1				
C28sterene 1							
C26sterene							
C28sterene 2							
C29sterene							
C27 Trisnorhopene							
C27 Trisnorhopene							
C28sterane							
22,29,30-trisnorneohop-13(18)-ene							
C27sterane 2							
C27 Trisnorhopene 1			2.9				
C27 Trisnorhopene 2							
22,29,30-trisnorneohop-17(21)-ene		27.7	16.7				
Cholestene	1.8					16.2	
C30hop-di-ene							
C28sterene 3				31.4	37.0	41.3	43.2
C29diasterene						30.0	19.7
18 α (H)-22,29,30-trisnorhopane (Ts)	36.3	47.6	38.5			37.9	52.4
C29 Tri-terpene	6.5	7.5	6.3				
17 α (H)-22,29,30-trisnorhopane (Tm)							
Adiantene 1						97.8	
Oleanene							
C29 α,β -norhopane S						48.4	33.7
C29 α,β -norhopane R							
C29 sterene						440	433
C29 sterene	22.0	14.0	15.5			33.5	11.9
Lupene							
C30 hop-7(21)-ene	35	38	10			303	263
Adiantene 2							
C 30 α,β -hopane R						87	116
C 30 α,β -hopane S						61	88
neohop-13(18)-ene	16	22	14	35	13	87	88
Adiantane or β,β -C29 hopane	11	17	8				
Gammacerene	47	55	53			52	85
Fern-8-ene	3		4				
Fern-7-ene		13	9			40	41
C31 α,β -homohopane							40
C30 β,α -hopane		65	51	12	8	28	47
C31 β,α -homohopane	9					50	
C30 β,β -hopane						29	
C30 β,α -hopane	59	77	62			54	47
C31Hopene							
Diploptene	66		6	35	15	58	215
Hop-21-ene	46						
C31 methyl-hopane							
C32 α,β -homohopane	4			7	42	15	17
C31 β,β -homohopane	60	8	56		10	43	44
ab/baC32		55	6				
C31 β,β -homohopane	6						
C32 β,β -homohopane							

Table S2. Non parametric Spearman correlation of biomarker concentrations expressed in ng g_{OC}⁻¹. For each pair of compound, the correlation is given on the first line, and N, the number of samples used for the calculation, is given on the second line. The compounds that were detected in most samples have been selected for this analysis, and the compound occasionally detected were not considered. *: the correlation is significant at the 0.05 level (2-tailed). **: the correlation is significant at the 0.01 level (2-tailed).

	median grain size d 0.5µm	OC	δ ¹⁵ N ‰	δ ¹³ C ‰	C/N molar	C10	C11	C12	C13	C14	C15	C16	C17	Pristane	C18	
median grain size d 0.5 µm	Pearson correlation N	1 31	.360 31	-.363 31	-.241 31	.383 31	-.322 30	-.235 28	-.040 31	-.171 24	-.111 31	.016 23	.075 29	.237 28	-.063 14	.134 27
OC	Pearson correlation N	.360 31	1 41	-.842 31	-.945 31	.902 31	-.562 30	-.157 35	-.009 39	-1.04 32	-.153 41	-.267 32	-.265 39	.100 38	-.445 22	-.262 37
δ ¹⁵ N ‰	Pearson correlation N	-.363 31	-.842 31	1 31	.876 31	-.844 31	.571 30	-.126 28	-.052 31	-.261 24	-.197 31	.085 23	-.038 29	-.078 28	.424 14	.047 27
δ ¹³ C ‰	Pearson correlation N	-.241 31	-.945 31	.876 31	1 31	-.947 31	.592 30	.067 28	.148 31	-.069 24	.027 31	.381 23	.203 29	.085 28	.669 14	.280 27
C/N molar	Pearson correlation N	.383 31	.902 31	-.844 31	-.947 31	1 31	-.603 30	-.170 28	-.230 31	-.065 24	-.119 31	-.425 23	-.263 29	-.135 28	-.783 14	-.317 27
C10	Pearson correlation N	-.322 30	-.562 30	.571 30	.592 30	-.603 30	1 30	.444 27	.230 30	.044 24	.220 30	.213 22	.169 28	.119 27	.819 14	.145 26
C11	Pearson correlation N	-.235 28	-.157 35	-.126 28	.067 28	-.170 27	.444 35	1 35	.630 30	.709 35	.934 29	.656 34	.722 34	.416 32	.694 19	.554 32
C12	Pearson correlation N	-.040 31	-.009 39	-.052 31	.148 31	-.230 31	.230 30	.630 35	1 39	.836 32	.562 39	.521 31	.581 37	.173 36	.509 20	.511 35
C13	Pearson correlation N	-.171 24	-.104 32	-.261 24	-.069 24	-.065 24	.044 24	.709 30	.836 32	1 32	.736 32	.502 29	.594 32	.122 31	.434 20	.445 31
C14	Pearson correlation N	-.111 31	-.153 41	-.197 31	.027 31	-.119 31	.220 30	.934 35	.562 39	.736 32	1 41	.763 32	.848 39	.506 38	.769 22	.681 37
C15	Pearson correlation N	.016 23	-.267 32	.085 23	.381 23	-.425 23	.213 22	.656 29	.521 31	.502 29	.763 32	1 32	.968 32	.780 31	.980 21	.981 32
C16	Pearson correlation N	.075 29	-.265 39	-.038 29	.203 29	-.263 29	.169 28	.722 34	.581 37	.594 32	.848 39	.968 32	1 39	.701 37	.962 22	.959 37
C17	Pearson correlation N	.237 28	.100 38	-.078 28	.085 28	-.135 28	.119 27	.416 32	.173 36	.122 32	.506 36	.780 31	.701 37	1 38	.820 22	.765 36
Pristane	Pearson correlation N	-.063 14	-.445 22	.424 14	.669 14	-.783 14	.819 14	.694 19	.509 20	.434 20	.769 22	.980 21	.962 22	.820 22	1 22	.958 22
C18	Pearson correlation N	.134 27	-.262 37	.047 27	.280 27	-.317 27	.145 26	.554 32	.511 35	.445 31	.681 37	.981 32	.959 37	.765 36	.958 22	1 37
Phytane	Pearson correlation N	.148 18	-.501 23	.661 18	.782 18	-.755 18	.518 17	.218 18	.257 21	.065 18	.336 23	.858 21	.779 23	.796 23	.840 17	.919 23
Phytadiene1	Pearson correlation N	.190 29	.398 30	-.492 29	-.405 29	.231 29	-.117 29	.486 26	.335 29	.476 24	.484 30	.385 22	.395 28	.451 28	.551 15	.322 27
Phytadiene2	Pearson correlation N	.177 30	.194 31	-.369 30	-.225 30	.075 30	-.049 30	.580 27	.415 30	.528 24	.619 31	.594 23	.602 29	.557 29	.764 15	.527 28
Phytadiene3	Pearson correlation N	.142 30	.326 31	-.448 30	-.359 30	.189 30	-.115 29	.470 27	.400 30	.565 24	.460 31	.322 23	.346 29	.319 29	.441 15	.251 28
C19	Pearson correlation N	.097 29	-.196 39	-.011 29	.199 29	-.277 29	.065 28	.482 33	.759 37	.707 32	.579 39	.845 32	.831 38	.539 38	.776 22	.867 37
C20	Pearson correlation N	.248 28	-.186 38	.192 28	.333 28	-.312 28	.093 27	.165 33	.241 36	.032 31	.280 38	.814 31	.722 37	.741 36	.791 21	.879 36
C21	Pearson correlation N	.253 30	-.193 40	.213 30	.348 30	-.324 30	.095 29	.122 34	.222 38	-.002 32	.238 40	.785 32	.690 38	.719 38	.761 22	.855 37
C22	Pearson correlation N	.250 29	-.203 39	.220 29	.365 29	-.342 29	.092 28	.114 33	.214 37	-.005 32	.231 39	.781 32	.685 38	.711 38	.757 22	.852 37

Table S2 continued.

		Phytadiene1	Phytadiene2	Phytadiene3	C19	C20	C21	C22	C23	C24	C25	C26	Squalane	C27	C28
median grain size d 0.5 µm	Pearson correlation N	.190 29	.177 30	.142 30	.097 29	.248 28	.253 30	.250 29	.278 30	.278 29	.270 29	.315 30	.330 26	.298 29	.216 30
OC	Pearson correlation N	.398 30	.194 31	.326 31	-.196 39	-.186 38	-.193 40	-.203 39	-.175 40	.009 39	.319 39	.017 40	.213 29	.282 39	.118 40
δ ¹⁵ N ‰	Pearson correlation N	-.492 29	-.369 30	-.448 30	-.011 29	.192 28	.213 30	.220 29	.187 30	.194 29	-.262 29	.141 30	-.499 26	-.310 29	-.058 30
δ ¹³ C ‰	Pearson correlation N	-.405 29	-.225 30	-.359 30	.199 29	.333 28	.348 30	.365 29	.323 30	.349 29	-.221 29	.281 30	-.356 26	-.267 29	.054 30
C/N molar	Pearson correlation N	.231 29	.075 30	.189 30	-.277 29	-.312 28	-.324 30	-.342 29	-.301 30	-.332 29	.197 29	-.261 30	.294 26	.251 29	-.050 30
C10	Pearson correlation N	-.117 29	-.049 29	-.115 29	.065 28	.093 27	.095 29	.092 28	.098 29	.172 28	.136 28	.161 29	.055 25	.069 28	.208 29
C11	Pearson correlation N	.486 26	.580 27	.470 27	.482 33	.165 33	.122 34	.114 33	.142 34	.187 33	.315 33	.203 34	.245 26	.275 33	.330 34
C12	Pearson correlation N	.335 29	.415 30	.400 30	.759 37	.241 36	.222 38	.214 37	.239 38	.328 37	.335 37	.358 38	.171 29	.260 37	.364 38
C13	Pearson correlation N	.476 24	.528 24	.565 24	.707 32	.032 31	-.002 32	-.005 32	.016 32	.031 32	.207 31	.042 32	.099 23	.185 31	.174 32
C14	Pearson correlation N	.484 30	.619 31	.460 31	.579 39	.280 38	.238 40	.231 39	.256 40	.251 39	.236 39	.266 40	.121 29	.210 39	.306 40
C15	Pearson correlation N	.385 22	.594 23	.322 23	.845 32	.814 31	.785 32	.781 32	.790 32	.764 32	.274 31	.740 32	.140 24	.248 31	.525 32
C16	Pearson correlation N	.395 28	.602 29	.346 29	.831 38	.722 37	.690 38	.685 38	.698 38	.638 38	.218 37	.637 38	.091 27	.192 37	.445 38
C17	Pearson correlation N	.451 28	.557 29	.319 29	.539 38	.741 36	.719 38	.711 38	.752 38	.772 38	.641 37	.794 38	.413 27	.639 37	.708 38
Pristane	Pearson correlation N	.551 15	.764 15	.441 15	.776 22	.791 21	.761 22	.757 22	.774 22	.771 22	.381 21	.769 22	.245 16	.338 21	.587 22
C18	Pearson correlation N	.322 27	.527 28	.251 28	.867 37	.879 36	.855 37	.852 37	.860 37	.800 37	.269 36	.785 37	.122 26	.245 36	.515 37
Phytane	Pearson correlation N	.156 18	.366 19	.043 19	.732 23	.994 23	.988 23	.986 23	.987 23	.952 23	.463 22	.918 23	.234 18	.425 22	.552 23
Phytadiene1	Pearson correlation N	1 30	.937 30	.968 30	.387 29	.131 28	.107 30	.101 29	.154 30	.193 29	.492 29	.245 30	.579 25	.475 29	.302 30
Phytadiene2	Pearson correlation N	.937 30	1 31	.935 31	.506 30	.312 29	.285 31	.280 30	.324 31	.358 30	.446 30	.392 31	.519 26	.420 30	.319 31
Phytadiene3	Pearson correlation N	.968 30	.935 31	1 31	.371 30	.035 29	.014 31	.007 30	.061 31	.105 30	.478 30	.157 31	.552 26	.454 30	.223 31
C19	Pearson correlation N	.387 29	.506 30	.371 30	1 39	.703 37	.682 39	.680 39	.691 39	.655 39	.241 38	.644 39	.137 28	.223 38	.453 39
C20	Pearson correlation N	.131 28	.312 29	.035 29	.703 37	1 38	.998 38	.998 37	.994 38	.927 37	.564 37	.900 38	.343 27	.500 37	.507 38
C21	Pearson correlation N	.107 30	.285 31	.014 31	.682 39	.998 38	1 40	.999 39	.995 40	.921 39	.664 39	.897 40	.566 29	.589 39	.503 40
C22	Pearson correlation N	.101 29	.280 30	.007 30	.680 39	.998 37	.999 39	1 39	.994 39	.918 39	.515 38	.893 39	.532 28	.429 38	.490 39

Table S2 continued.

		C29	C30	C31	C32	C33	C34	Lycopane	C35	C36	C37	C38	C39	UCM	CPI
median grain size d 0.5 µm	Pearson correlation N	.337 31	.439 [*] 30	.293 31	.309 29	.219 30	.285 28	.371 11	.255 30	.130 22	.329 29	.196 23	.165 22	.357 26	-.229 30
OC	Pearson correlation N	.146 41	.179 40	.168 41	.259 39	.196 40	-.030 38	-.527 11	.302 40	.493 ^{**} 27	.429 ^{**} 33	.498 ^{**} 26	.395 25	-.238 26	-.233 39
δ ¹⁵ N ‰	Pearson correlation N	-.317 31	-.142 30	-.341 31	-.331 29	-.309 30	.192 28	.567 11	-.333 30	-.255 22	-.402 [*] 29	-.341 23	-.402 22	.183 26	-.265 30
δ ¹³ C ‰	Pearson correlation N	-.254 31	-.057 30	-.280 31	-.295 29	-.290 30	.355 28	.704 [*] 11	-.286 30	-.184 22	-.354 29	-.278 23	-.346 22	.285 26	-.305 30
C/N molar	Pearson correlation N	.248 31	.088 30	.271 31	.278 29	.267 30	-.361 28	-.685 [*] 11	.281 30	.181 22	.345 29	.273 23	.335 22	-.246 26	.232 30
C10	Pearson correlation N	.010 30	.008 29	.024 30	.047 28	.067 29	.122 27	.411 10	.060 29	.037 21	-.047 28	.001 22	-.084 21	.030 25	-.146 29
C11	Pearson correlation N	.257 35	.089 34	.282 35	.281 33	.253 34	.189 32	.114 11	.170 34	.133 23	.260 29	.150 23	.174 22	.072 23	.005 33
C12	Pearson correlation N	.177 39	.303 38	.181 39	.204 37	.162 38	.278 36	.778 ^{**} 11	.125 38	.177 26	.185 32	.071 25	.124 24	.240 26	-.271 37
C13	Pearson correlation N	.203 32	.110 32	.222 32	.189 31	.191 32	.095 31	-.024 10	.075 32	.054 22	.199 26	.077 21	.146 20	-.009 21	.067 31
C14	Pearson correlation N	.248 41	.093 40	.250 41	.246 39	.173 40	.247 38	.215 11	.037 40	.073 27	.201 33	.105 26	.127 25	.226 26	.000 39
C15	Pearson correlation N	.266 32	.360 [*] 32	.189 32	.269 31	.020 32	.749 ^{**} 31	.802 ^{**} 11	-.027 32	.176 22	.273 25	.209 21	.210 20	.764 ^{**} 19	-.354 31
C16	Pearson correlation N	.245 39	.290 38	.185 39	.233 37	.038 38	.612 ^{**} 37	.717 ^{**} 11	-.078 38	.038 27	.167 31	.069 26	.111 25	.696 ^{**} 24	-.225 37
C17	Pearson correlation N	.547 ^{**} 38	.611 ^{**} 38	.476 ^{**} 38	.704 ^{**} 37	.347 ^{**} 38	.740 ^{**} 38	.861 ^{**} 11	.243 38	.666 ^{**} 27	.705 ^{**} 31	.744 ^{**} 26	.709 ^{**} 25	.778 ^{**} 23	-.338 [*] 37
Pristane	Pearson correlation N	.307 22	.381 22	.230 22	.360 21	.057 22	.775 ^{**} 22	.743 7	-.028 22	.175 16	.269 17	.219 16	.213 15	.735 ^{**} 12	-.351 21
C18	Pearson correlation N	.250 37	.389 [*] 37	.165 37	.286 36	-.006 37	.774 ^{**} 36	.855 ^{**} 11	-.077 37	.080 26	.229 30	.123 25	.170 24	.843 ^{**} 22	-.368 [*] 36
Phytane	Pearson correlation N	.178 23	.453 [*] 23	.056 23	.439 [*] 22	-.138 23	.962 ^{**} 23	.913 ^{**} 9	-.131 23	.302 20	.340 20	.327 19	.310 18	.960 ^{**} 15	-.666 ^{**} 23
Phytadiene1	Pearson correlation N	.466 ^{**} 30	.347 30	.463 ^{**} 30	.492 ^{**} 29	.399 30	.206 28	.127 10	.397 30	.213 22	.400 [*] 29	.312 23	.270 22	.094 24	.107 30
Phytadiene2	Pearson correlation N	.413 31	.348 31	.393 [*] 31	.428 [*] 30	.301 31	.386 [*] 29	.388 11	.303 31	.180 23	.343 30	.255 24	.209 23	.307 25	-.009 31
Phytadiene3	Pearson correlation N	.431 31	.308 31	.433 [*] 31	.455 [*] 30	.376 31	.135 29	.077 11	.380 [*] 31	.204 23	.373 [*] 30	.290 24	.247 23	.006 25	.155 31
C19	Pearson correlation N	.267 39	.429 ^{**} 39	.200 39	.224 38	.069 39	.684 ^{**} 38	.933 ^{**} 11	.011 39	.093 27	.224 32	.115 26	.190 25	.673 ^{**} 24	-.337 [*] 38
C20	Pearson correlation N	.173 38	.443 ^{**} 38	.062 38	.475 ^{**} 37	-.108 38	.868 ^{**} 36	.920 ^{**} 11	-.085 38	.656 ^{**} 26	.604 ^{**} 31	.649 ^{**} 25	.568 ^{**} 24	.969 ^{**} 23	-.476 ^{**} 37
C21	Pearson correlation N	.169 40	.445 ^{**} 40	.060 40	.504 ^{**} 39	-.104 40	.854 ^{**} 38	.921 ^{**} 11	-.080 40	.853 ^{**} 27	.719 ^{**} 33	.837 ^{**} 26	.711 ^{**} 25	.968 ^{**} 25	-.475 ^{**} 39
C22	Pearson correlation N	.155 39	.436 ^{**} 39	.044 39	.337 [*] 38	-.125 39	.853 ^{**} 38	.916 ^{**} 11	-.097 39	.853 ^{**} 27	.726 ^{**} 32	.851 ^{**} 26	.703 ^{**} 25	.966 ^{**} 24	-.529 ^{**} 38

Table S2 continued.

		C ₂₄ Tricyclic 2	C ₂₄ Triterpen e 1	Trisnoeoh op-13(18)- ene	Trisnorhop- 17(21)-ene	C ₂₈ sterene 3	Trisnor C ₂₇ Ts	C ₂₉ Triterpen e	Oleanene	αβ C ₂₉ R	C ₂₉ sterene A	Lupene	Hop-17(21)- ene	αβ C ₃₀ S
median grain size d 0.5 μm	Pearson correlation N	.287 12	.387 23	.165 14	.170 26	.406 16	.204 31	.031 24	.476 12	.408 16	-.200 19	.502 8	.183 31	.358 27
OC	Pearson correlation N	-.519 12	.342 28	-.499 14	.265 28	.611** 20	-.156 39	.069 27	-.142 12	-.001 16	-.369 27	-.586 8	.124 38	.356 30
δ ¹⁵ N ‰	Pearson correlation N	.431 12	-.574** 23	.200 14	-.390 26	-.565 16	-.458** 31	-.275 24	-.088 12	-.034 16	.698** 19	.135 8	-.343 31	-.102 27
δ ¹³ C ‰	Pearson correlation N	.595 12	-.456 23	.432 14	-.347 26	-.432 16	-.396 31	-.225 24	.176 12	.056 16	.657** 19	.556 8	-.211 31	.086 27
C/N molar	Pearson correlation N	-.576 12	.316 23	-.478 14	.267 26	.397 16	.312 31	.111 24	-.148 12	-.133 16	-.555 19	-.542 8	.121 31	-.138 27
C10	Pearson correlation N	.022 11	-.099 22	.473 13	-.123 26	-.138 16	-.165 30	.001 23	.009 11	-.077 16	.428 18	-.120 7	-.049 30	.013 26
C11	Pearson correlation N	.041 11	.382 23	.225 12	.209 23	.410 16	.270 34	.324 22	.191 12	.324 16	-.059 23	-.219 7	.561** 33	.219 27
C12	Pearson correlation N	.681 12	.265 27	.181 14	.128 27	.357 19	.190 38	.228 26	.152 12	.364 16	-.109 26	.050 8	.327 37	.220 30
C13	Pearson correlation N	-.019 9	.328 21	.150 11	.277 21	.336 14	.270 31	.389 21	.778** 10	.271 14	-.067 22	-.064 5	.569** 30	.140 23
C14	Pearson correlation N	.202 12	.319 28	.323 14	.232 28	.320 20	.238 39	.308 27	.170 12	.499 16	-.095 27	-.186 8	.562** 38	.225 30
C15	Pearson correlation N	.854** 11	.337 21	.594 12	.100 20	.454 12	.221 31	.303 21	.211 11	.789** 12	-.045 24	-.233 7	.445 30	.418 22
C16	Pearson correlation N	.763** 12	.349 26	.579 14	.111 26	.243 18	.216 37	.304 26	.219 12	.735** 16	-.121 27	-.230 7	.456** 36	.330 28
C17	Pearson correlation N	.819** 11	.513** 27	.589 14	-.005 25	.459 19	.174 36	.127 27	.235 12	.794** 16	-.167 27	-.076 8	.309 35	.459 28
Pristane	Pearson correlation N	.788 7	.569 13	.817** 9	.089 11	.268 7	.291 20	.525 14	.664 7	.938** 7	-.065 18	-.114 5	.542 19	.438 14
C18	Pearson correlation N	.925** 11	.338 25	.634 14	.008 24	.284 17	.193 35	.275 25	.237 12	.757** 15	-.112 27	-.224 7	.363 34	.389 26
Phytane	Pearson correlation N	.991** 10	.537 16	.642 13	-.152 15	.215 10	.236 21	.335 18	.195 10	.791 9	-.225 19	-.171 7	.131 21	.773** 15
Phytadiene1	Pearson correlation N	.078 10	.888** 22	.343 13	.747** 25	.422 17	.825** 29	.709** 23	.402 11	.734** 16	-.052 18	.452 7	.787 29	.656** 25
Phytadiene2	Pearson correlation N	.327 11	.885** 23	.434 14	.613** 25	.387 17	.795** 30	.743** 24	.208 12	.830** 16	-.054 19	.371 8	.846** 30	.761** 26
Phytadiene3	Pearson correlation N	-.042 11	.895** 23	.145 14	.729** 25	.449 17	.809** 30	.751** 24	.075 12	.632** 16	-.033 19	.452 8	.847** 30	.614** 26
C19	Pearson correlation N	.993** 11	.297 27	.465 14	.133 26	.315 19	.266 37	.331 27	.256 12	.683** 16	-.052 27	.387 8	.393 36	.386 28
C20	Pearson correlation N	.997** 11	.500** 26	.631 14	-.080 25	.642** 19	.133 36	.118 25	.239 12	.720** 16	-.103 26	-.169 7	.107 35	.405 27
C21	Pearson correlation N	.998** 11	.288 28	.627 14	-.086 27	.627** 20	.128 38	-.044 27	.242 12	.708** 16	-.017 27	.294 8	.073 37	.382 29
C22	Pearson correlation N	.998** 11	.244 27	.626 14	-.097 26	.724** 19	.126 37	.059 27	.241 12	.709** 16	.019 27	.331 8	.073 36	.388 28

Table S2 continued.

		Gammaac erene	Fern-8- ene	Fern-7- ene	$\beta\alpha$ C ₃₀	$\beta\beta$ C ₃₀	Diplopte ne	Hop-21- ene	$\beta\beta$ C ₃₁ hopene	$\beta\beta$ C ₃₁
median grain size d 0.5 μm	Pearson correlation N	.189 30	-.099 19	.345 20	.170 28	.341 28	.242 25	.192 20	.299 17	-.028 25
OC	Pearson correlation N	.350 [*] 38	.375 22	.357 24	.261 37	.287 36	.486 ^{**} 34	.434 [*] 21	.445 [*] 23	.081 29
$\delta^{15}\text{N}$ ‰	Pearson correlation N	-.545 ^{**} 30	-.484 [*] 19	-.442 20	-.426 [*] 28	-.483 ^{**} 28	-.612 ^{**} 25	-.608 ^{**} 20	-.362 17	-.210 25
$\delta^{13}\text{C}$ ‰	Pearson correlation N	-.498 ^{**} 30	-.558 [*] 19	-.374 20	-.423 [*] 28	-.431 [*] 28	-.642 ^{**} 25	-.464 [*] 20	-.469 17	-.198 25
C/N molar	Pearson correlation N	.434 [*] 30	.350 19	.310 20	.349 28	.380 [*] 28	.604 ^{**} 25	.346 20	.458 17	.096 25
C10	Pearson correlation N	-.235 29	-.129 19	-.247 20	-.201 27	-.257 27	-.374 24	-.144 20	-.373 17	-.021 24
C11	Pearson correlation N	.249 33	.310 19	.204 20	.244 31	.266 31	-.073 29	.479 [*] 18	-.028 18	.372 28
C12	Pearson correlation N	.247 37	.242 21	.088 23	.233 35	.314 35	.073 32	.555 ^{**} 21	-.143 21	.343 29
C13	Pearson correlation N	.414 [*] 30	.375 17	.249 20	.353 28	.453 [*] 28	.138 26	.698 ^{**} 16	-.076 17	.424 [*] 25
C14	Pearson correlation N	.239 38	.168 22	.255 24	.183 37	.351 [*] 36	-.059 34	.519 [*] 21	-.111 23	.311 29
C15	Pearson correlation N	.107 30	.072 19	.318 19	.009 28	.137 28	-.188 25	.200 13	-.080 17	.168 24
C16	Pearson correlation N	.133 36	.073 22	.266 24	.045 35	.212 34	-.119 32	.290 19	-.149 22	.198 29
C17	Pearson correlation N	.044 35	.066 21	.194 24	.067 34	-.007 33	-.092 31	.093 18	.230 22	-.036 28
Pristane	Pearson correlation N	.138 19	.151 13	.318 10	.084 18	.185 17	-.307 17	-.012 7	-.174 11	.256 17
C18	Pearson correlation N	.070 34	.024 21	.266 23	-.011 33	.122 32	-.157 30	.120 17	-.131 21	.130 27
Phytane	Pearson correlation N	-.083 20	-.167 15	.387 13	-.081 20	-.057 18	-.299 16	-.380 9	-.490 13	.064 17
Phytadiene1	Pearson correlation N	.714 ^{**} 28	.658 ^{**} 18	.805 ^{**} 20	.836 ^{**} 27	.760 ^{**} 26	.640 ^{**} 24	.875 ^{**} 19	.316 18	.662 ^{**} 23
Phytadiene2	Pearson correlation N	.595 ^{**} 29	.423 18	.789 ^{**} 20	.730 ^{**} 28	.720 ^{**} 27	.463 25	.788 ^{**} 19	.205 18	.649 ^{**} 24
Phytadiene3	Pearson correlation N	.716 ^{**} 29	.611 ^{**} 18	.811 ^{**} 20	.853 ^{**} 28	.787 ^{**} 27	.655 ^{**} 25	.937 ^{**} 19	.249 18	.700 ^{**} 24
C19	Pearson correlation N	.241 36	.197 21	.247 24	.188 35	.286 34	.035 32	.338 19	-.075 22	.295 28
C20	Pearson correlation N	-.059 35	-.125 21	.361 23	-.088 34	-.018 33	-.172 31	-.159 19	.176 22	.010 27
C21	Pearson correlation N	-.070 37	-.146 21	-.042 24	-.092 36	-.025 35	-.178 33	-.177 20	.169 23	.000 28
C22	Pearson correlation N	-.071 36	-.146 21	.099 24	-.097 35	-.029 34	-.184 32	-.194 19	.262 22	.007 28

1 Table S2 continued.

		Phytadie ne1	Phytadie ne2	Phytadie ne3	C19	C20	C21	C22	C23	C24	C25	C26	Squalane	C27	C28
C23	Pearson correlation N	.154 30	.324 31	.061 31	.691** 39	.994** 38	.995** 40	.994** 39	1 40	.930** 39	.958** 39	.923** 40	.535** 29	.915** 39	.565** 40
C24	Pearson correlation N	.193 29	.358 30	.105 30	.655** 39	.927** 37	.921** 39	.918** 39	.930** 39	1 39	.700** 38	.971** 39	.555** 28	.615** 38	.673** 39
C25	Pearson correlation N	.492** 29	.446** 30	.478** 30	.241 38	.564** 37	.664** 39	.515** 38	.958** 39	.700** 38	1 39	.907** 39	.585** 29	.982** 39	.915** 39
C26	Pearson correlation N	.245 30	.392** 31	.157 31	.644** 39	.900** 38	.897** 40	.893** 39	.923** 40	.971** 39	.907** 39	1 40	.582** 29	.841** 39	.770** 40
squalane	Pearson correlation N	.579** 25	.519** 26	.552** 26	.137 28	.343 27	.566** 29	.532** 28	.535** 29	.555** 28	.585** 29	.582** 29	1 29	.618** 29	.534** 29
C27	Pearson correlation N	.475** 29	.420** 30	.454** 30	.223 38	.500** 37	.589** 39	.429** 38	.915** 39	.615** 38	.982** 39	.841** 39	.618** 29	1 39	.905** 39
C28	Pearson correlation N	.302 30	.319 31	.223 31	.453** 39	.507** 38	.503** 40	.490** 39	.565** 40	.673** 39	.915** 39	.770** 40	.534** 29	.905** 39	1 40
squalane	Pearson correlation N	.681** 25	.575** 26	.639** 26	.215 26	.565** 24	.654** 26	.845** 26	.866** 26	.853** 26	.860** 26	.855** 26	.870** 23	.847** 26	.732** 26
C29	Pearson correlation N	.466** 30	.413** 31	.431** 31	.267 39	.173 38	.169 40	.155 39	.254 40	.312 39	.901** 39	.441** 40	.554** 29	.947** 39	.793** 40
C30	Pearson correlation N	.347 30	.348 31	.308 31	.429** 39	.443** 38	.445** 40	.436** 39	.517** 40	.610** 39	.926** 39	.718** 40	.555** 29	.942** 39	.866** 40
C31	Pearson correlation N	.463** 30	.393** 31	.433** 31	.200 39	.062 38	.060 40	.044 39	.147 40	.215 39	.910** 39	.355** 40	.588** 29	.957** 39	.760** 40
C32	Pearson correlation N	.492** 29	.428** 30	.455** 30	.224 38	.475** 37	.504** 39	.337** 38	.881** 39	.532** 38	.944** 39	.750** 39	.546** 29	.958** 39	.865** 39
C33	Pearson correlation N	.399** 30	.301** 31	.376** 31	.069 39	-.108 38	-.104 40	-.125 39	-.023 40	.076 39	.909** 39	.224 40	.653** 29	.958** 39	.675** 40
C34	Pearson correlation N	.206 28	.386** 29	.135 29	.684** 38	.868** 36	.854** 38	.853** 38	.848** 38	.903** 38	.311 37	.821** 38	.506** 27	.318 37	.526** 38
Lycopane	Pearson correlation N	.127 10	.388 11	.077 11	.933** 11	.920** 11	.921** 11	.916** 11	.940** 11	.965** 11	.879** 10	.977** 11	.896** 10	.874** 10	.780** 11
C35	Pearson correlation N	.397** 30	.303 31	.380** 31	.011 39	-.085 38	-.080 40	-.097 39	-.032 40	.157 39	.732** 39	.225 40	.722** 29	.790** 39	.565** 40
C36	Pearson correlation N	.213 22	.180 23	.204 23	.093 27	.656** 26	.853** 27	.853** 27	.946** 27	.862** 27	.925** 27	.902** 27	.546** 22	.914** 27	.878** 27
C37	Pearson correlation N	.400** 29	.343** 30	.373** 30	.224 32	.604** 31	.719** 33	.726** 32	.911** 33	.712** 32	.934** 33	.832** 33	.643** 27	.962** 33	.856** 33
C38	Pearson correlation N	.312 23	.255 24	.290 24	.115 26	.649** 25	.837** 26	.851** 26	.958** 26	.878** 26	.945** 26	.949** 26	.950** 22	.948** 26	.873** 26
C39	Pearson correlation N	.270 22	.209 23	.247 23	.190 25	.568** 24	.711** 25	.703** 25	.925** 25	.727** 25	.947** 25	.845** 25	.938** 21	.971** 25	.881** 25
UCM	Pearson correlation N	.094 24	.307 25	.006 25	.673** 24	.969** 23	.968** 25	.966** 24	.963** 25	.944** 24	-.087 24	.932** 25	-.056 21	-.092 24	.692** 25
CPI	Pearson correlation N	.107 30	-.009 31	.155 31	-.337** 38	-.476** 37	-.475** 39	-.529** 38	-.456** 39	-.651** 38	-.094 38	-.533** 39	.140 28	-.021 38	-.357** 39
C ₂₃ Tricyclic_2	Pearson correlation N	.069 12	.424 12	-.064 12	.999** 14	1.000** 13	.999** 14	.999** 14	.999** 14	.991** 14	.318 13	.990** 14	.655** 11	.297 13	.837** 14

3 Table S2 continued.

		C29	C30	C31	C32	C33	C34	Lycopane	C35	C36	C37	C38	C39	UCM	CPI
C23	Pearson correlation N	.254 40	.517** 40	.147 40	.881** 39	-.023 40	.848** 38	.940** 11	-.032 40	.946** 27	.911** 33	.958** 26	.925** 25	.963** 25	-.456** 39
C24	Pearson correlation N	.312 39	.610** 39	.215 39	.532** 38	.076 39	.903** 38	.965** 11	.157 39	.862** 27	.712** 32	.878** 26	.727** 25	.944** 24	-.651** 38
C25	Pearson correlation N	.901** 39	.926** 39	.910** 39	.944** 39	.909** 39	.311 37	.879** 10	.732** 39	.925** 27	.934** 33	.945** 26	.947** 25	-.087 24	-.094 38
C26	Pearson correlation N	.441** 40	.718** 40	.355 40	.750** 39	.224 40	.821** 38	.977** 11	.225 40	.902** 27	.832** 33	.949** 26	.845** 25	.932** 25	-.533** 39
squalane	Pearson correlation N	.554** 29	.555** 29	.588** 29	.546** 29	.653** 29	.506** 27	.896** 10	.722** 29	.546** 22	.643** 27	.950** 22	.938** 21	-.056 21	.140 28
C27	Pearson correlation N	.947** 39	.942** 39	.957** 39	.958** 39	.958** 39	.318 37	.874** 10	.790** 39	.914** 27	.962** 33	.948** 26	.971** 25	-.092 24	-.021 38
C28	Pearson correlation N	.793** 40	.866** 40	.760** 40	.865** 39	.675** 40	.526** 38	.780** 11	.565** 40	.878** 27	.856** 33	.873** 26	.881** 25	.692** 25	-.357** 39
squalene	Pearson correlation N	.829** 26	.783** 26	.831** 26	.845** 26	.816** 26	.723** 25	.779** 9	.826** 26	.773** 20	.801** 26	.797** 21	.759** 20	-.206 22	.316 26
C29	Pearson correlation N	1 41	.878** 40	.989** 41	.972** 39	.920** 40	.265 38	.437 11	.651** 40	.790** 27	.958** 33	.886** 26	.962** 25	.286 26	.065 39
C30	Pearson correlation N	.878** 40	1 40	.842** 40	.922** 39	.765** 40	.511** 38	.705** 11	.610** 40	.884** 27	.914** 33	.909** 26	.929** 25	.670** 25	-.249 39
C31	Pearson correlation N	.989** 41	.842** 40	1 41	.974** 39	.958** 40	.167 38	.303 11	.692** 40	.798** 27	.959** 33	.888** 26	.961** 25	.082 26	.110 39
C32	Pearson correlation N	.972** 39	.922** 39	.974** 39	1 39	.943** 39	.281 37	.860** 10	.646** 39	.837** 27	.934** 33	.898** 26	.951** 25	-.087 24	.053 38
C33	Pearson correlation N	.920** 40	.765** 40	.958** 40	.943** 39	1 40	.034 38	.124 11	.786** 40	.826** 27	.953** 33	.898** 26	.960** 25	-.203 25	.147 39
C34	Pearson correlation N	.265 38	.511** 38	.167 38	.281 37	.034 38	1 38	.965** 11	.200 38	.827** 27	.839** 31	.835** 26	.829** 25	.945** 23	-.660** 37
Lycopane	Pearson correlation N	.437 11	.705** 11	.303 11	.860** 10	.124 11	.965** 11	1 11	.169 11	.824** 10	.839** 10	.828** 10	.826** 10	.990** 8	-.718** 11
C35	Pearson correlation N	.651** 40	.610** 40	.692** 40	.646** 39	.786** 40	.200 38	.169 11	1 40	.853** 27	.883** 33	.986** 26	.958** 25	-.140 25	-.151 39
C36	Pearson correlation N	.790** 27	.884** 27	.798** 27	.837** 27	.826** 27	.827** 27	.824** 10	.853** 27	1 27	.912** 26	.986** 25	.921** 25	-.237 17	-.242 27
C37	Pearson correlation N	.958** 33	.914** 33	.959** 33	.934** 33	.953** 33	.839** 31	.839** 10	.883** 33	.912** 26	1 33	.935** 26	.982** 25	-.080 24	-.005 33
C38	Pearson correlation N	.886** 26	.909** 26	.888** 26	.898** 26	.898** 26	.835** 26	.828** 10	.986** 26	.986** 25	.935** 26	1 26	.954** 25	-.200 18	-.087 26
C39	Pearson correlation N	.962** 25	.929** 25	.961** 25	.951** 25	.960** 25	.829** 25	.826** 10	.958** 25	.921** 25	.982** 25	.954** 25	1 25	-.206 17	.114 25
UCM	Pearson correlation N	.286 26	.670** 25	.082 26	-.087 24	-.203 25	.945** 23	.990** 8	-.140 25	-.237 17	-.080 24	-.200 18	-.206 17	1 26	-.656** 25
CPI	Pearson correlation N	.065 39	-.249 39	.110 39	.053 38	.147 39	-.660** 37	-.718** 11	-.151 39	-.242 27	-.005 33	-.087 26	.114 25	-.656** 25	1 39
C ₂₃ Tricyclic_2	Pearson correlation N	.414 15	.833** 14	.124 15	.311 13	-.423 14	.995** 14	.979** 6	-.338 14	.113 9	.152 11	.219 10	.136 9	.967** 11	-.858** 14

5 Table S2 continued.

		C ₂₄ Tricyclic 2	C ₂₄ Triterpene 1	Trisnorheoh op-13(18)- ene	Trisnorhop- 17(21)-ene	C ₂₈ sterene 3	Trisnor C ₂₇ Ts	C ₂₉ Triterpene	Oleanene	αβ C ₂₉ R	C ₂₉ sterene A	Lupene	Hop-17(21)- ene	αβ C ₃₀ S
C23	Pearson correlation N	.996** 11	.602** 28	.628* 14	-.063 27	.563** 20	.161 38	.209 27	.239 12	.738** 16	-.037 27	.367 8	.106 37	.374* 29
C24	Pearson correlation N	.985** 11	.360 27	.632* 14	-.103 26	.507** 19	.155 37	.072 27	.235 12	.768** 16	.046 27	.339 8	.128 36	.446* 28
C25	Pearson correlation N	-.321 10	.667** 28	.122 13	.132 26	.445** 20	.340* 37	.222 27	-.026 11	.833** 15	.004 27	.363 8	.289 36	.025 28
C26	Pearson correlation N	.979** 11	.434* 28	.630* 14	-.062 27	.573** 20	.215 38	.087 27	.235 12	.792** 16	.008 27	.362 8	.127 37	.366 29
squalane	Pearson correlation N	-.272 9	.502* 24	.147 12	.231 21	.797** 14	.353 29	.195 22	.105 10	.917** 12	-.128 21	.327 8	.138 28	.356 23
C27	Pearson correlation N	-.324 10	.737** 28	.105 13	.142 26	.469* 20	.398* 37	.221 27	.010 11	.856** 15	.032 27	.375 8	.284 36	.024 28
C28	Pearson correlation N	.788** 11	.361 28	.488 14	-.049 27	.564** 20	.244 38	-.033 27	.099 12	.776** 16	-.033 27	-.255 8	.118 37	.156 29
squalene	Pearson correlation N	-.463 9	.831** 21	-.234 11	.473* 22	.571** 14	.473* 26	.393 22	-.271 9	.736** 13	.051 17	-.153 6	.416* 26	.477* 23
C29	Pearson correlation N	.226 12	.772** 28	.269 14	.176 28	.365 20	.374* 39	.250 27	.136 12	.820** 16	.015 27	.407 8	.326* 38	.048 30
C30	Pearson correlation N	.761** 11	.648** 28	.463 14	.030 27	.347 20	.304 38	.172 27	.285 12	.892** 16	.001 27	.776* 8	.168 37	.150 29
C31	Pearson correlation N	-.034 12	.780** 28	.168 14	.189 28	.367 20	.377* 39	.254 27	.150 12	.674** 16	.027 27	.381 8	.314 38	.008 30
C32	Pearson correlation N	-.313 10	.741** 28	.110 13	.160 26	.315 20	.264 37	.224 27	.036 11	.849** 15	-.055 27	.348 8	.294 36	-.007 28
C33	Pearson correlation N	-.404 11	.745** 28	-.099 14	.104 27	.336 20	.333* 38	.179 27	-.008 12	.295 16	.051 27	.382 8	.187 37	-.097 29
C34	Pearson correlation N	.981** 11	.633** 27	.663** 14	-.107 25	.530* 19	.186 36	.314 27	.273 12	.792** 16	.073 27	.664 8	.236 35	.657** 28
Lycopane	Pearson correlation N	.996** 5	.506 7	.667 5	-.435 8	.857 4	.111 11	-.249 10	.131 7	.907** 6	-.374 8	-.661 3	.112 11	.658 9
C35	Pearson correlation N	-.330 11	.603** 28	-.073 14	.077 27	.756** 20	.523** 38	.155 27	.052 12	.410 16	.167 27	.367 8	.156 37	.254 29
C36	Pearson correlation N	-.302 9	.423 20	.133 12	-.249 19	.561* 14	.097 25	.038 24	.027 9	.850** 11	-.050 21	.316 6	.037 25	.061 19
C37	Pearson correlation N	-.293 10	.782** 24	.094 13	.147 24	.712** 18	.407* 31	.230 25	.093 11	.863** 15	-.062 21	.373 8	.313 31	.285 25
C38	Pearson correlation N	-.300 9	.698** 19	.100 13	-.143 18	.573* 14	.216 24	.121 23	.069 10	.907** 12	-.068 20	.302 7	.171 24	.151 20
C39	Pearson correlation N	-.333 9	.622** 18	.082 12	-.178 18	.549* 14	.185 23	.126 23	-.035 9	.833** 11	-.175 19	.266 6	.165 23	.049 19
UCM	Pearson correlation N	.959** 11	.256 19	.608* 13	-.081 21	.735** 13	.203 26	-.232 19	.210 9	.862** 12	-.236 15	-.170 7	.081 26	.662** 22
CPI	Pearson correlation N	-.911** 11	.106 27	-.503 14	.107 27	-.487* 20	.022 37	.406* 27	-.280 12	-.567* 16	-.042 26	.082 8	.027 37	-.592** 29
C ₂₃ Tricyclic_2	Pearson correlation N	.982** 7	.353 10	.948* 5	-.194 12	-.076 6	.244 15	-.007 10	.978** 6	.885** 6	.152 10	1.000** 2	.192 15	.825** 14

7 Table S2 continued.

		Gammac erene	Fern-8- ene	Fern-7- ene	$\beta\alpha$ C ₃₀	$\beta\beta$ C ₃₀	Diplopte ne	Hop-21- ene	$\beta\beta$ C ₃₁ hopene	$\beta\beta$ C ₃₁
C23	Pearson correlation N	-.029 37	-.118 21	-.154 24	-.039 36	.013 35	-.159 33	-.141 20	.077 23	.025 28
C24	Pearson correlation N	-.047 36	-.120 21	.041 24	-.013 35	-.005 34	-.215 32	-.086 19	.063 22	.017 28
C25	Pearson correlation N	.279 36	.461 20	-.170 24	.643** 35	.272 34	.067 32	.678** 19	-.045 23	.179 27
C26	Pearson correlation N	.003 37	-.091 21	-.186 24	.069 36	.042 35	-.170 33	-.030 20	-.018 23	.026 28
squalane	Pearson correlation N	.154 28	.616** 18	.042 17	.365 26	.125 26	-.005 23	.811** 15	.033 16	.062 24
C27	Pearson correlation N	.294 36	.520** 20	-.147 24	.685** 35	.262 34	.082 32	.669** 19	-.047 23	.159 27
C28	Pearson correlation N	.093 37	.018 21	-.233 24	.253 36	.067 35	-.125 33	.280 20	-.139 23	.055 28
squalene	Pearson correlation N	.442 26	.728** 15	.307 19	.810** 23	.393 24	.374 22	.636** 17	.106 15	.339 21
C29	Pearson correlation N	.336** 38	.530** 22	-.125 24	.727** 37	.307 36	.121 34	.548** 21	-.071 23	.219 29
C30	Pearson correlation N	.213 37	.180 21	-.200 24	.535** 36	.227 35	.025 33	.194 20	-.027 23	.137 28
C31	Pearson correlation N	.343** 38	.579** 22	-.134 24	.755** 37	.301 36	.126 34	.594** 21	-.071 23	.218 29
C32	Pearson correlation N	.305 36	.578** 20	-.145 24	.758** 35	.278 34	.139 32	.626** 19	-.045 23	.169 27
C33	Pearson correlation N	.242 37	.568** 21	-.212 24	.651** 36	.183 35	.073 33	.568** 20	-.035 23	.091 28
C34	Pearson correlation N	-.020 35	-.093 21	.449** 24	-.014 34	-.017 33	-.188 31	-.107 18	.124 22	.075 28
Lycopane	Pearson correlation N	-.357 10	-.164 9	-.602 7	-.191 8	-.359 9	-.403 9	-.508 5	-.857 5	-.211 10
C35	Pearson correlation N	.178 37	.251 21	.094 24	.464** 36	.081 35	-.021 33	.578** 20	.148 23	.016 28
C36	Pearson correlation N	.009 24	.050 17	-.258 18	.377 23	-.106 22	-.277 21	.260 13	-.038 18	-.036 22
C37	Pearson correlation N	.344 30	.483** 18	.022 20	.596** 29	.275 28	.089 27	.630** 19	.060 19	.148 25
C38	Pearson correlation N	.155 23	.141 17	-.145 17	.548** 22	.037 21	-.210 20	.305 13	.059 17	.029 22
C39	Pearson correlation N	.157 22	.414 17	-.185 17	.554** 21	.007 20	-.132 20	.409 13	.008 17	.024 21
UCM	Pearson correlation N	-.089 25	-.192 15	.418 15	-.111 25	.025 23	-.193 21	-.130 17	-.161 13	.006 20
CPI	Pearson correlation N	.136 36	.457** 21	-.142 24	.149 35	.087 34	.147 32	-.006 20	-.167 23	.189 27
C ₂₃ Tricyclic_2	Pearson correlation N	-.146 15	-.237 11	.459 10	-.201 14	-.103 14	-.320 13	-.333 8	-.093 8	-.017 12

9 Table S2 continued.

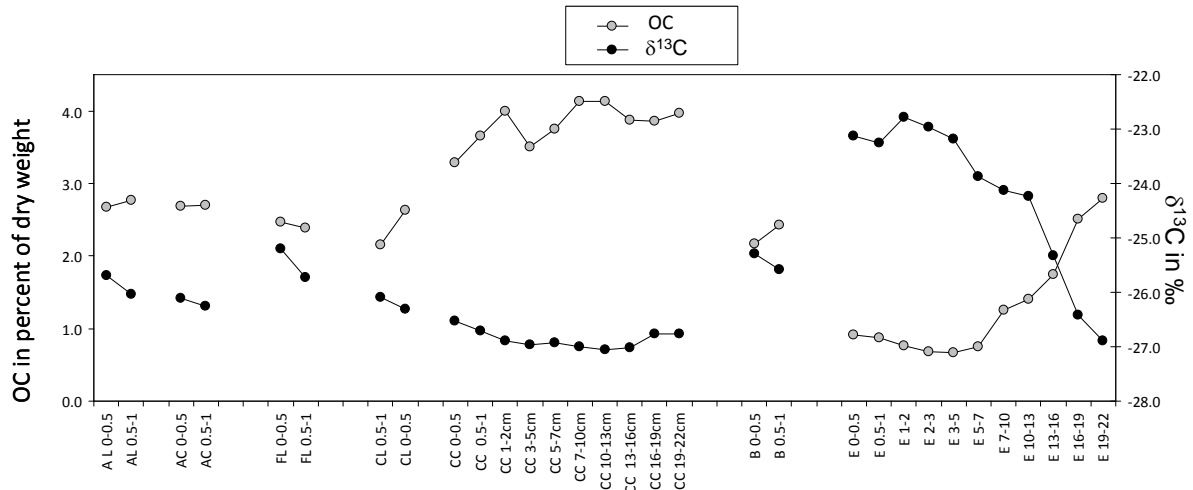
		C ₂₄ Tricyclic 2	C ₂₄ Triterpene 1	Trisnorhop- op-13(18)- ene	Trisnorhop- 17(21)-ene	C ₂₈ sterene 3	Trisnor C ₂₇ Ts	C ₂₉ Triterpene	Oleanene	αβ C ₂₉ R	C ₂₉ sterene A	Lupene	Hop-17(21)- ene	αβ C ₃₀ S
C ₂₄ Tricyclic 2	Pearson correlation N	1 12	.742 7	.619 7	-.280 10	-.529 4	.162 12	-.354 9	.130 6	.831 5	-.536 8	-.282 5	-.014 12	.749** 12
C ₂₄ Triterpene 1	Pearson correlation N	.742 7	1 28	.252 11	.720** 22	.605** 15	.832** 28	.845** 22	.243 9	.917** 13	-.144 20	.582 6	.674** 27	.887** 22
22,29,30- trisnorhop- 13(18)-ene	Pearson correlation N	.619 7	.252 11	1 14	-.260 9	.064 6	.446 14	.518 12	.810* 8	.869** 8	-.061 12	.804* 7	.182 14	.732* 11
Trisnorhopene 368	Pearson correlation N	-.280 10	.720** 22	-.260 9	1 28	.683** 16	.770** 28	.650** 22	.040 7	.471 13	.242 16	.444 4	.648** 28	.578** 24
C ₂₈ sterene 3	Pearson correlation N	-.529 4	.605* 15	.064 6	.683** 16	1 20	.637** 18	.531 14	-.319 4	.742** 9	-.498 12	1.000** 2	.588** 18	.790** 17
Trisnor C ₂₇ Ts	Pearson correlation N	.162 12	.832** 28	.446 14	.770** 28	.637** 18	1 39	.940** 27	.308 12	.843** 16	.324 27	.569 8	.651** 38	.574** 30
C ₂₉ Triterpene	Pearson correlation N	-.354 9	.845** 22	.518 12	.650** 22	.531 14	.940** 27	1 27	.246 10	.892** 12	.081 21	.708 7	.689** 27	.903** 21
Oleanene	Pearson correlation N	.130 6	.243 9	.810* 8	.040 7	-.319 4	.308 12	.246 10	1 12	.636** 10	.694 8	.834* 6	.166 12	.385 10
αβ C ₂₉ R	Pearson correlation N	.831 5	.917** 13	.869** 8	.471 13	.742** 9	.843** 16	.892** 12	.636** 10	1 16	.021 9	.985** 4	.708** 16	.985** 14
C ₂₉ sterene A	Pearson correlation N	-.536 8	-.144 20	-.061 12	.242 16	-.498 12	.324 27	.081 21	.694 8	.021 9	1 27	.870* 6	.133 26	.098 19
Lupene	Pearson correlation N	-.282 5	.582 6	.804* 7	.444 4	1.000** 2	.569 8	.708 7	.834* 6	.985** 4	.870* 6	1 8	.406 8	.604 7
Hop-17(21)-ene	Pearson correlation N	-.014 12	.674** 27	.182 14	.648** 28	.588** 18	.651** 38	.689** 27	.166 12	.708** 16	.133 26	.406 8	1 38	.577** 30
αβ C ₃₀ S	Pearson correlation N	.749** 12	.887** 22	.732* 11	.578** 24	.790** 17	.574** 30	.903** 21	.385 10	.985** 14	.098 19	.604 7	.577** 30	1 30
Neohop-13(18)-ene	Pearson correlation N	-.043 11	.587** 26	.486 13	.516** 26	.707** 19	.485** 37	.577** 25	.818** 11	.688** 14	-.042 26	.336 7	.767** 36	.696** 28
Gammacerene	Pearson correlation N	-.218 12	.751** 28	-.056 13	.797** 28	.587** 18	.737** 38	.871** 26	-.050 11	.539** 15	.055 26	.501 7	.627** 37	.421* 30
Fern-8-ene	Pearson correlation N	-.283 9	.467 17	-.388 10	.728** 18	.076 11	.509 22	.298 18	-.135 8	.367 11	.319 16	.108 4	.642** 22	.190 17
Fern-7ene	Pearson correlation N	.705 7	.877** 19	.826* 7	.839** 22	.800** 16	.753** 24	.855** 20	.634 5	.978** 11	-.077 18	-1.000** 2	.685** 24	.867** 21
βα C ₃₀	Pearson correlation N	-.269 11	.879** 26	.018 13	.836** 25	.202 19	.845** 35	.912** 23	.067 11	.577** 15	.251 23	.811* 7	.661** 34	.334 27
ββ C ₃₀	Pearson correlation N	-.202 10	.789** 27	.065 11	.801** 27	.510 18	.699** 36	.938** 24	.068 10	.633** 15	.018 24	.913* 5	.702** 35	.350 28
Diploptene	Pearson correlation N	-.396 9	.687** 23	-.778* 8	.826** 25	.293 19	.505** 32	.624** 21	-.481 6	.305 11	-.067 21	-.652 3	.433* 31	.288 26
Hop-21-ene	Pearson correlation N	-.389 7	.798** 16	-.127 7	.736** 20	.920** 13	.690** 21	.590* 15	-.295 5	.312 11	-.428 11	1.000** 2	.754** 21	.373 18
ββ C ₃₁ hopene	Pearson correlation N	-.381 5	.187 17	-.675 6	.266 19	.082 17	.183 22	.020 18	-.999* 3	.817** 8	-.007 18	^b 1	.252 22	.380 18
ββ C ₃₁	Pearson correlation N	-.109 10	.666** 22	.470 12	.682** 20	.692** 13	.645** 29	.849** 22	.237 12	.670** 15	.139 21	.922** 6	.573** 28	.660** 23

11 Table S2 continued.

		Gammacerene	Fern-8-ene	Fern-7-ene	$\beta\alpha$ C ₃₀	$\beta\beta$ C ₃₀	Diploptene	Hop-21-ene	$\beta\beta$ C ₃₁ hopene	$\beta\beta$ C ₃₁
C ₂₄ Tricyclic 2	Pearson correlation	-.218	-.283	.705	-.269	-.202	-.396	-.389	-.381	-.109
	N	12	9	7	11	10	9	7	5	10
C ₂₄ Triterpene 1	Pearson correlation	.751**	.467	.877**	.879**	.789**	.687**	.798**	.187	.666*
	N	28	17	19	26	27	23	16	17	22
22,29,30-trisnorneohop-13(18)-ene	Pearson correlation	-.056	-.388	.826*	.018	.065	-.778*	-.127	-.675	.470
	N	13	10	7	13	11	8	7	6	12
Trisnorhopene 368	Pearson correlation	.797**	.728**	.839**	.836**	.801**	.826**	.736**	.266	.682**
	N	28	18	22	25	27	25	20	19	20
C ₂₈ sterene 3	Pearson correlation	.587*	.076	.800**	.202	.510*	.293	.920**	.082	.692**
	N	18	11	16	19	18	19	13	17	13
Trisnor C ₂₇ Ts	Pearson correlation	.737**	.509*	.753**	.845**	.699**	.505**	.690**	.183	.645**
	N	38	22	24	35	36	32	21	22	29
C ₂₉ Triterpene	Pearson correlation	.871**	.298	.855**	.912**	.938**	.624**	.590*	.020	.849**
	N	26	18	20	23	24	21	15	18	22
Oleanene	Pearson correlation	-.050	-.135	.634	.067	.068	-.481	-.295	-.999*	.237
	N	11	8	5	11	10	6	5	3	12
$\alpha\beta$ C ₂₉ R	Pearson correlation	.539*	.367	.978**	.577*	.633*	.305	.312	.817*	.670**
	N	15	11	11	15	15	11	11	8	15
C ₂₉ sterene A	Pearson correlation	.055	.319	-.077	.251	.018	-.067	-.428	-.007	.139
	N	26	16	18	23	24	21	11	18	21
Lupene	Pearson correlation	.501	.108	-1.000**	.811*	.913*	-.652	1.000**	. ^b	.922**
	N	7	4	2	7	5	3	2	1	6
Hop-17(21)-ene	Pearson correlation	.627**	.642**	.685**	.661**	.702**	.433	.754**	.252	.573**
	N	37	22	24	34	35	31	21	22	28
$\alpha\beta$ C ₃₀ S	Pearson correlation	.421*	.190	.867**	.334	.350	.288	.373	.380	.660**
	N	30	17	21	27	28	26	18	18	23
Neohop-13(18)-ene	Pearson correlation	.491**	.427	.805**	.398*	.515**	.259	.710**	.251	.596**
	N	36	20	23	35	34	33	20	22	27
Gammacerene	Pearson correlation	1	.577**	.651**	.919**	.934**	.816**	.684**	.199	.831**
	N	38	21	24	34	36	32	21	22	28
Fern-8-ene	Pearson correlation	.577**	1	.315	.556*	.482*	.613**	.448	.449	.244
	N	21	22	15	19	20	18	14	14	19
Fern-7ene	Pearson correlation	.651**	.315	1	.583**	.623**	.565**	.817**	.180	.845**
	N	24	15	24	21	23	22	15	20	17
$\beta\alpha$ C ₃₀	Pearson correlation	.919**	.556*	.583**	1	.925**	.792**	.770**	.107	.840**
	N	34	19	21	37	33	30	18	20	26
$\beta\beta$ C ₃₀	Pearson correlation	.934**	.482*	.623**	.925**	1	.778**	.747**	.047	.913**
	N	36	20	23	33	36	31	20	22	27
Diploptene	Pearson correlation	.816**	.613**	.565**	.792**	.778**	1	.632**	.179	.695**
	N	32	18	22	30	31	34	21	21	23
Hop-21-ene	Pearson correlation	.684**	.448	.817**	.770**	.747**	.632**	1	.062	.613*
	N	21	14	15	18	20	21	21	13	15
$\beta\beta$ C ₃₁ hopene	Pearson correlation	.199	.449	.180	.107	.047	.179	.062	1	-.347
	N	22	14	20	20	22	21	13	23	16
$\beta\beta$ C ₃₁	Pearson correlation	.831**	.244	.845**	.840**	.913**	.695**	.613*	-.347	1
	N	28	19	17	26	27	23	15	16	29

13 **Supplementary figures**

14 **Figure S1.** Variation of organic carbon percent, plotted on the left axis and of $\delta^{13}\text{C}$, plotted on the right axis, in the surficial sediments of the studied sample set (Data previously published in Stetten et al., 2015).



17 **Figure S2.** Distribution of terpenoids (Selected Ion Current $m/z = 191$) in the most contaminated sediment of the studied area, on the bottom panel. This sediment layer, collected at site E (0-0.5cm layer) showed the highest UCM concentrations. The m/z fragmentogram of a non-contaminated sample, the 0-0.5cm sediment layer at the channel of site C, is presented on the top panel. A series of tricyclic terpanes from C_{20} to C_{26} is indicated on the bottom $m/z=191$ current by shorthand notation TC_{20} , TC_{21} , ... etc. These compounds are present in petroleum but not in recent organic matter.

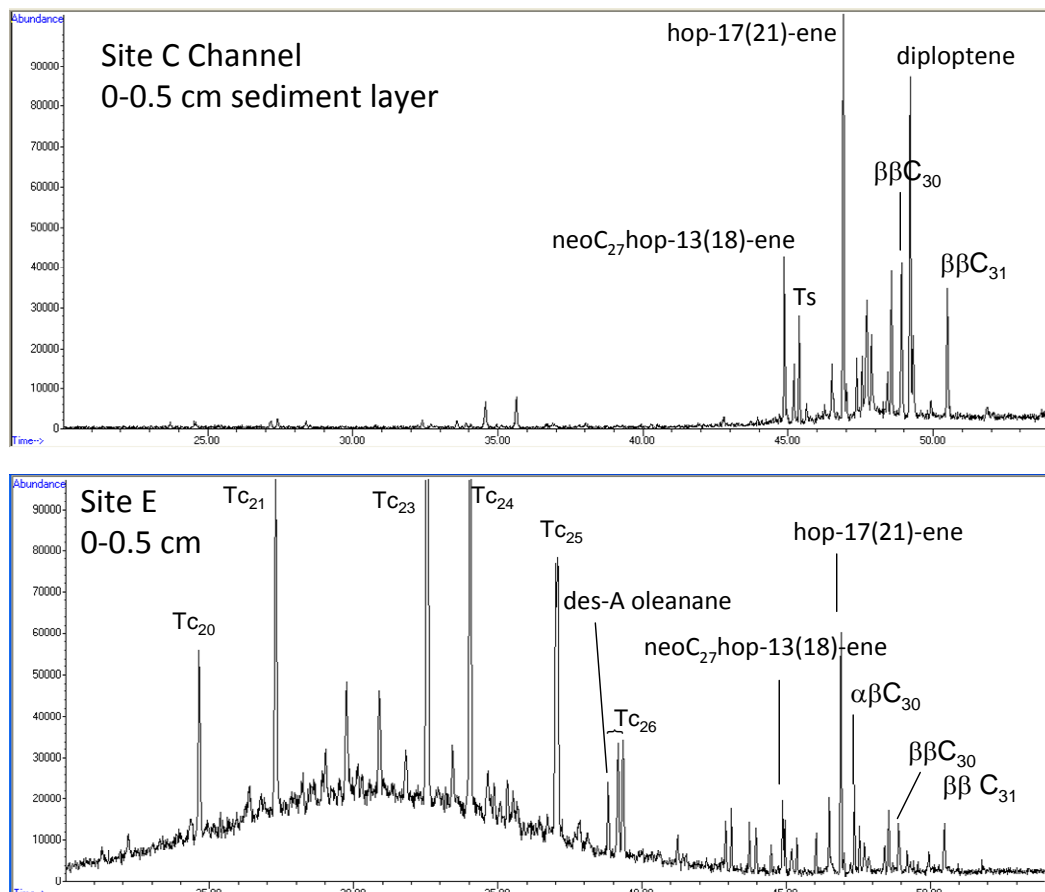


Figure S3. Distribution of terpenoids (Selected Ion Current $m/z = 191$) in the 0-0.5 cm layer at the channel of site C. Peaks are labeled by their structural identification. Ts is the shorthand denomination for 18α -22,29,30-trisnorhopane and G stands for gammacerene.

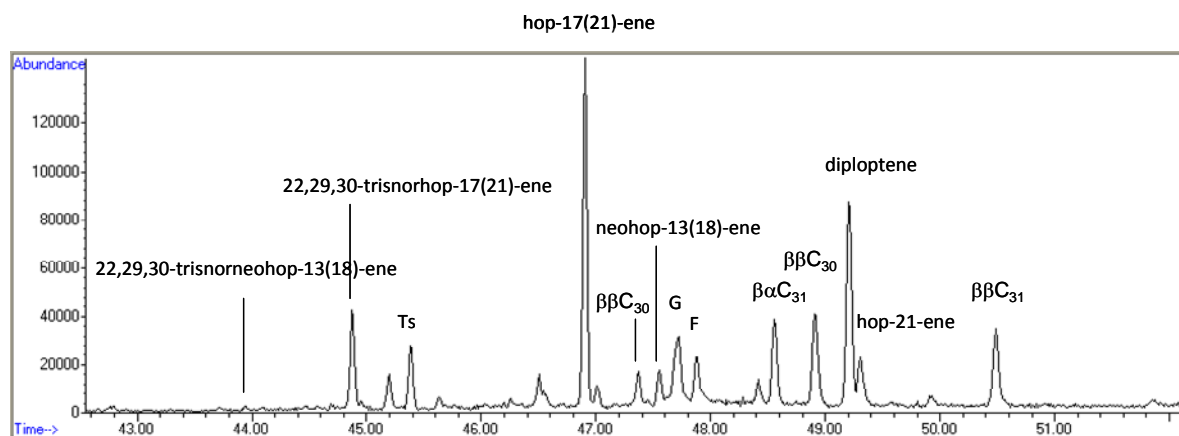


Figure S4. Distribution of terpenoids (Selected Ion Current $m/z = 191$) in the 0-0.5 cm layer at the levee of site A. Peaks are labeled by their structural identification. Ts stands for 18α -22,29,30-trisnorhopane. O, L and G are shorthand denominations for oleanene, lupene and gammacerene, respectively.

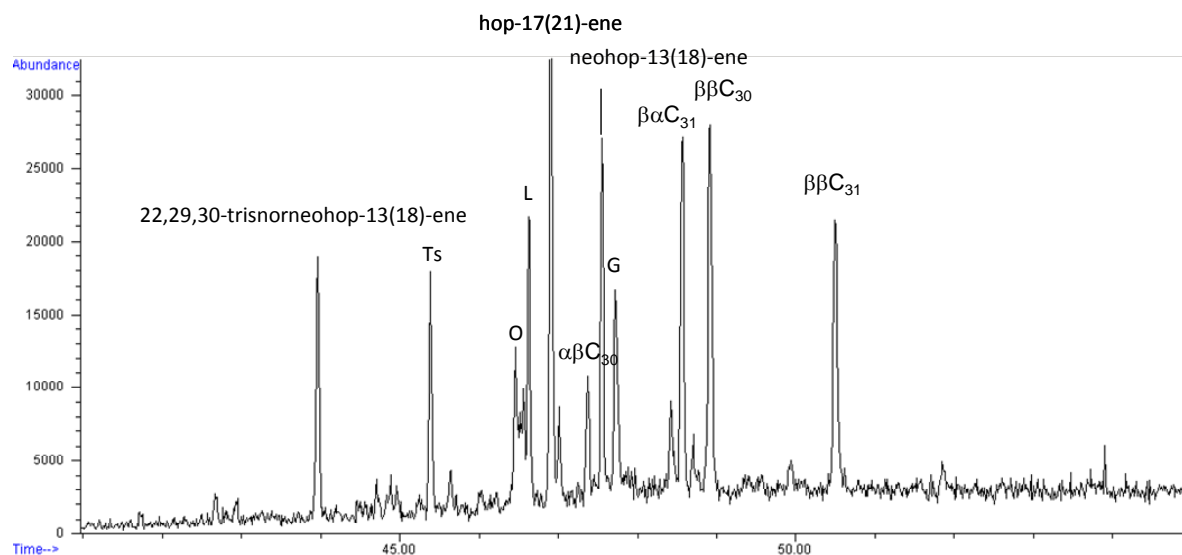


Figure S5. Mass spectra of dominant hopanoids and non-hopanoid triterpenes.

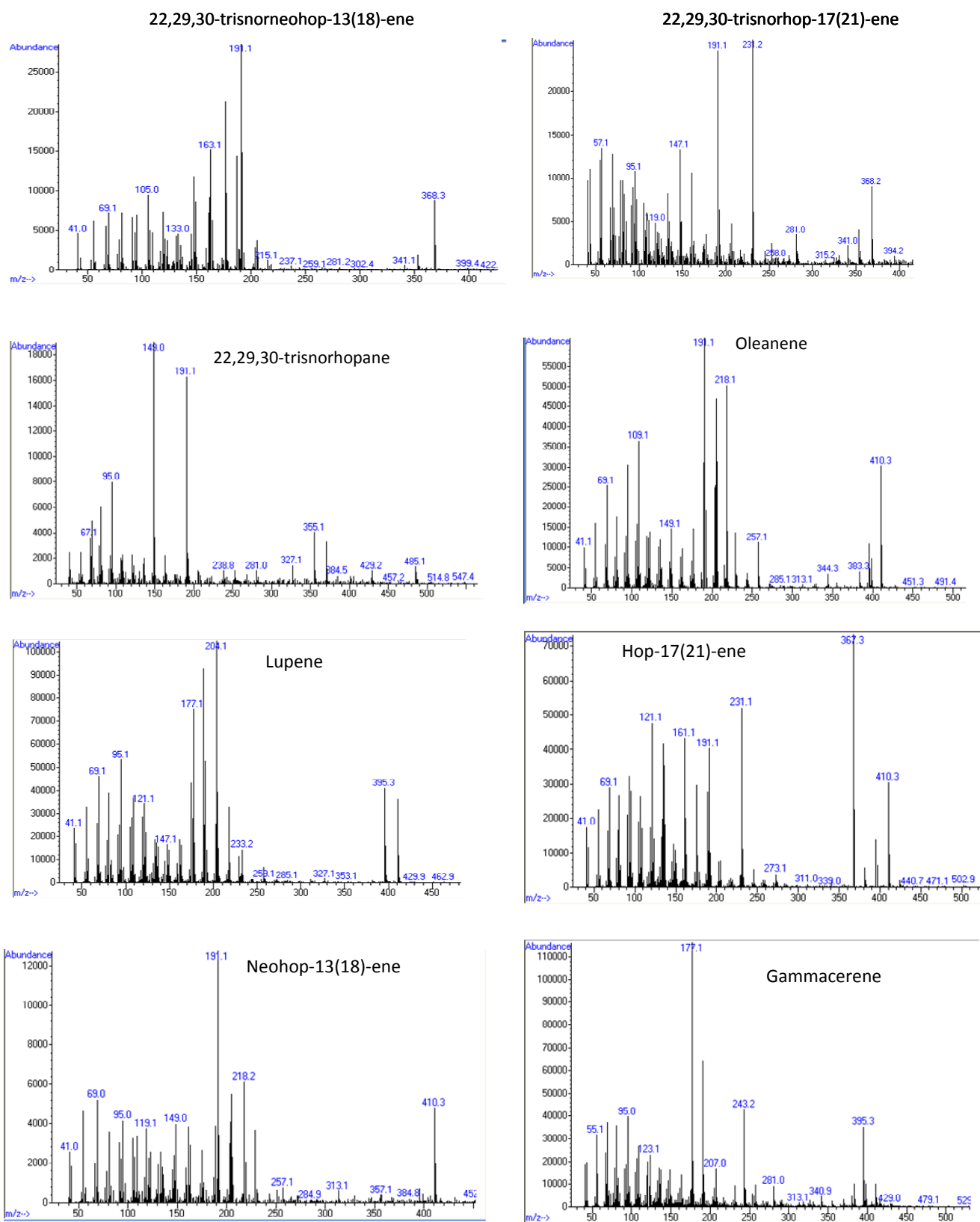
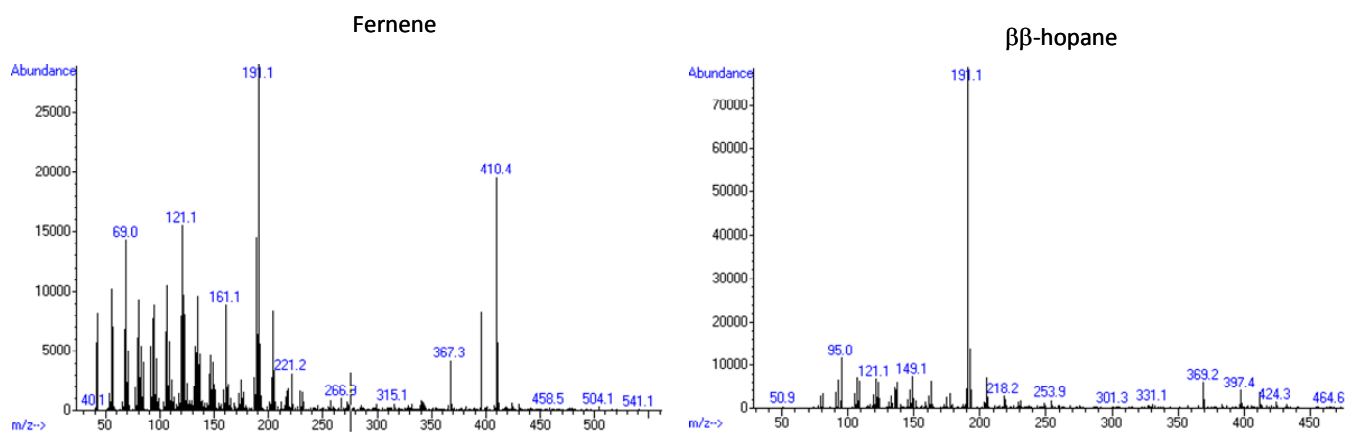
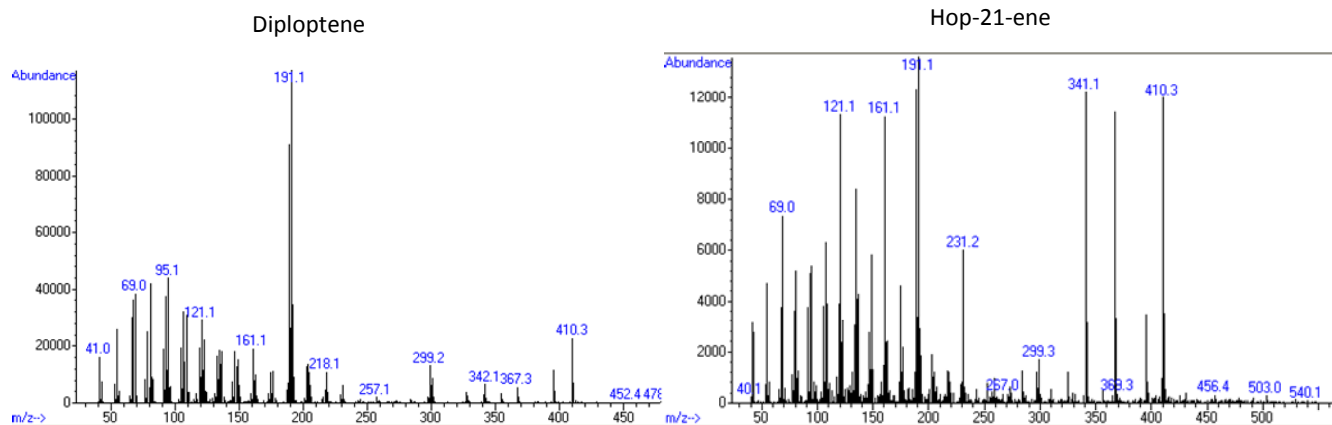


Figure S5 continued. Mass spectra of dominant hopanoids and non-hopanoid triterpenes.



412



24

