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**Variation of lipid
biomarker fluxes at
6 h time scale**

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Short scale (6 h) temporal variation of sinking fluxes of planktonic and terrigeneous lipids at 200 m in the NW Mediterranean Sea

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Abstract

Drifting sediment trap experiments were carried out at high temporal frequency in the northwestern Mediterranean in the course of the DYNAPROC2 campaign, every 6 h at 200 m depth. Molecular biomarkers were analyzed in selected subsets of consecutive
5 samples. Fluxes of *n*-alkanes, long-chain alkenones, sterols and steroid ketones show high variability between consecutive 6-h' samples, comparable in range to seasonnal variability. *n*-Alkane export ranges from 1.4 to 29.7 μg m^{-2} d^{-1}, fluxes of C$_{37}$ alkenones varies from 0 to 14.2 μg m^{-2} d^{-1}. Fluxes of sterols, steroid ketones and C$_{30}$ alkane diol, respectively range from 31 to 377, 2.2 to 46 and 0.3 to 9.3 μg m^{-2} d^{-1}. The Biomarker
10 composition is consistent with reworked algal and zooplanktonic organic matter with a remarkable refractory character. After a rain event ensuing the intrusion of coastal water at the study site, the relative signature of higher plant increases and corresponds to higher export fluxes of long-chain odd *n*-alkanes. Most phytoplanktonic biomarkers show concurrent variability in fluxes. Linear correlations between fluxes of distinct
15 biomarkers and between fluxes of biomarkers and flux of total carbon suggest that the short term temporal variability of export fluxes depends primarily on physical constrains exerted by carrier particle dynamics. Linear correlation of their carbon-normalized concentrations explained a lower part of the variance, indicating that short-term variability in particle composition is a secondary driver of flux timing. At the end of summer strat-
20 ification, export fluxes account for ca. 1% of the primary productivity. In this studied situation, biomarkers have a long residence time in the water column before they are exported at 200 m. Biomarkers exported at 200 m may thus record processes averaged over a larger period than the sampling frequency. For instance, phytoplanktonic biomarker composition of sinking particles fails to reflect the community changes occur-
25 ring over the 4 weeks of study. At higher time resolution, the diel variability in primary productivity is not recorded by biomarker fluxes either. The coupling between primary productivity and biomarker export shows significant changes on time scales of days and even of 6 h.

1   Introduction

The fate of organic carbon produced by primary production is a central issue of the carbon cycle. Physical and biological forcing controls the carbon flow through ecosystem compartments and in the water column. The PECHE-DYNAPROC program aims at better understand these forcing in the Northwestern open Mediterranean Sea at the summer stratification-fall transition. An interdisciplinary approach was set up to relate physical forcing, phytoplanktonic, zooplanktonic and bacterial communities as well as related changes in inorganic and organic characteristics of dissolved and particulate phases (Andersen et al., 2008). In this frame, the response of vertical export to short-term processes, such as variations of planktonic productivity and wind stress, was tackled by deploying drifting sediment traps at 200 m depth under a temporal sampling frequency of 6 h.

The understanding of short-term variability is important in order to understand the factors driving the vertical fluxes of organic matter in the ocean. Many biological processes show a clear short term variability with strong diel variability. However, to which degree this variability is transferred to the export processes of organic matter remains unknown. Simplifying, the export of organic matter results from the production of organic matter, its aggregation/incorporation into particles, transformations, mainly bacterial, of this organic matter, recycling in the surface ocean and then vertical sinking. The final flux of organic compounds will be a mirror of the interplay of these processes, and the processes with the slower dynamics will control the variability of the export fluxes.

The present contribution reports a molecular-level study of the exported organic material, focusing on phytoplanktonic biomarkers. Several compound classes, such as aliphatic and steroidal alcohols, long-chain alkenones and hydrocarbons, were studied to determine the variations in delivery of primary-produced material. In addition, the comparison of the different markers with organic matter and other bulk indications allow to elucidate the drivers of these fluxes and their variability.

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2 Material and methods

2.1 Site description and sample collection

The DYNAPROC2 cruise took place between the 13 September and the 17 October, in the Northwestern Mediteranean Sea, 28 miles offshore from Nice, (France) (Andersen et al., 2008). Sinking particles were collected using PPS5 sediment traps (1 m^2 collecting area) drifting at 200 m depth. Carousels of 24 collecting cups were programmed with a 6 h-time resolution. Four series of samples were collected: the A series from the 17 to the 22 September, series B from 23 to 29 September, series C from 3 to 8 October and series D from 10 to 15 October. Before mooring, collecting cups were poisoned by a 2% buffered formalin solution made with filtered seawater. Upon trap recovery, swimmers were removed and the collected material was split using a wet suspension divider. One tenth of the samples was dedicated to this study and kept frozen until analysis. The formalin solution was analyzed using the same procedure as the samples to estimate whether it contributed targetted compounds to crude extracts of samples.

2.2 Lipid extraction, separation, and analysis

The supernatant of sediment trap samples were shown to contain lipidic compounds accounting for 15 to 75% of the total trap material when the collection time was in the order of weeks to one month (Körtzinger et al., 1994). In colder waters, the dissolution of fatty acids into the dissolved supernatant of the trap collecting cups still accounted for half of the flux (Budge and Parrish, 1998). Beside organics, about 30% of inorganic phosphorus was also reported to occur in sediment trap supernatant (O'Neill et al., 2005). A challenge of the present study was the small sample size: one tenth of 6 h-collection of sinking particles in a low productivity area. To maximize the recovery of lipids from the trap material, the extraction procedure was set to recover the lipids from the particles and from the supernatant of the trap, as well as lipids that may

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leach during freezing and thawing. After thawing, the samples were centrifuged and the water phase was extracted by liquid liquid extraction using CH_2Cl_2. The obtained solution was used to extract the particles according to a modified Bligh and Dyer (1959) method where CH_2Cl_2 replaced CH_3Cl_3. Known amounts of surrogates were added
to the samples prior extraction: $C_{24}D_{50}$, C_{21}-OH and androstanol were used as surrogates for hydrocarbons, alkanols and sterols, respectively. Particles were extracted by 15 min of contact in a CH_2Cl_2-H_2O-CH_3OH solution (1/0.8/2; v/v/v) and the liquid phase was pipetted out after 5 min of centrifugation. Two other extractions were carried out by sonication for 15 min in the solvent mixture and all the liquid phases were
combined into a decantation flask. After adding H_2O and CH_2Cl_2 to reach the proportions where two phases appear, the phases were shaken and allowed to decant for 30 min. The organic phase was collected, and the aqueous phase was rinsed twice with 20 ml of CH_2Cl_2. All combined organic extracts were dried overnight over $MgSO_4$, filtered and reduced by rota-evaporation. Total lipids were separated into various lipid
classes using SEP-PACK Si-NH$_2$ glass cartridges purchaged from Macherey Nagel. The method was adapted from Hinrichs et al. (2000) and the recovery of the selected lipid classes was validated using standards ($C_{24}D_{50}C_{36}H_{74}$ and squalene for hydrocarbons; a previously analyzed fraction of long chain alkenones for ketones; C_{21}-OH, androstanol, coprostanol, cholesterol and lanosterol for alcohols). The cartridge was
conditioned by 10 ml of hexane and the sample was spotted on its top in 150 µl of heptane. The first fraction was eluted by another 3.850 ml of hexane and contained the hydrocarbons. The second fraction, comprising long-chain alkenones was eluted by 6 ml of hexane/CH_2Cl_2 (3:1, v/v). The third fraction was eluted by 5 ml CH_2Cl_2/aceton (9:1, v/v) and contained n-alkanols, sterols, n-alkyl diols and hydroxy-ketones. The
fractions were reduced by rota-evaporation and transferred to vials for gas chromatography analysis.

The hydrocarbons were analyzed using a Hewlett-Packard HP5890 gas chromatograph (GC) and a JW DB5 (Chrompack) column (50 m, 0.32 mm internal diameter, 0.25 µm film thickness). The oven temperature was programmed to rise from 60°C to

100°C at 25°C min^{-1}, then to 310°C at 2°C min^{-1} (80 min hold time). The injector was an on-column injector programmed on the oven track mode, the detector temperature was 330°C and the carrier gas was Helium set at a pressure of 1.1 bar.

Long-chain ketones were analyzed using a non-polar column (CP Sil 5 CP, 50 m, 0.32 mm internal diameter, 0.25 μm film thickness) and a Hewlett-Packard HP5890 chromatograph, with the oven temperature rising from 80°C to 140°C at 30°C min^{-1}, then to 280°C at 15°C min^{-1}/and to 310°C at 0.5°C min^{-1}, followed by a temperature hold of 60 min. The GC was equipped with an on-column injector programmed to track the oven temperature and a FID detector at 320°C and helium was used as carrier gas at a pressure of 0.98 bar. Prior to analyses, a known amount of $C_{36}H_{74}$ was added as injection standard to the fractions.

Alcohols were transformed into the corresponding trimethylsilyl ether derivatives (TMS) using a mixture of bis(trimethylsilyl)-trifluoroacetamide and trimethylchlorosilane (99:1, Silyl-99) purchased from Macherey-Nagel (Germany) and pyridine during 60 min at 80°C. TMS of alcohols were analysed on a non-polar column (JW DB5, 30 m, 0.32 mm internal diameter, 0.25 μm film thickness) and an Agilent 6890N chromatograph, using the following oven temperature program: 60° (1 min)/25° min^{-1}/100°/15° min^{-1}/150°/3° min^{-1}/300° (>60 min). The GC was equipped with an on-column injector programmed to track the oven temperature and a FID detector at 320°C and helium was used as carrier gas at a pressure of 0.8 bar.

GC coupled to mass spectrometry (MS) and co-injection with authentic compounds of known structures confirmed the identities of the major components. GC/MS analysis of lipids was performed on an Agilent 6890 GC coupled to an Agilent 5973 quadrupole mass spectrometer. The GC was equipped with an on-column injector programmed on the oven track mode, a JW DB5-MS column (0.25 mm internal diameter, 0.25 μm film thickness) and the carrier gas was helium with a flow of 1.2 ml min^{-1}. The interface temperature was 280°C. MS operating conditions were: ion source temperature of 230°C, quadrupole temperature 150°C, electron impact energy of 70 eV, the scanned mass range was 40–600 atomic mass units at 0.6 scan s^{-1}. The chromatographic columns

used were DB5 with oven programs as previously described.

The quantification of hydrocarbons and sterols was carried out using the surrogates used as internal standards. Long-chain ketones were quantified using the injection standard.

2.3 Hydrocarbon and sterol nomenclature

The nomenclature used to design hydrocarbons is C_x for saturated aliphatic homologues, where x is the number of carbon of the aliphatic chain, and $C_{x:y}$ for unsaturated hydrocarbons, y being the number of double bonds. n-Alkanols are designed C_{x-OH}, x is the number of carbon of the aliphatic chain. The nomenclature used to design sterols is used for the graphics only and is detailed in the first figure's legend where they appear.

3 Results

Five groups of consecutive samples were selected for the present study on the basis of a sight examination of the samples. The first part of the A series (17 and 18 September) and the samples from the D series (12 and 13 October) showed few visible particles whereas particles could easily be observed in the other groups of consecutive samples from the A, B and C series.

3.1 Hydrocarbons

The formalin solution used to preserve the samples contributed some dissolved hydrocarbons in negligible quantities except for C_{19} and C_{23} n-alkanes; therefore both alkanes are not reported here. The hydrocarbon fluxes are reported in Table 2. They encompass n-alkanes in the C_{12}-C_{37} range with an even predominance from C_{12} to C_{26} and an odd predominance for the C_{27}-C_{36} homologues. The even predominance

of low molecular weight *n*-alkanes is an unusual profile, reported in other few situations. For instance, C_{16}, C_{18} and C_{20} also dominated hydrocarbons in sinking particles from the Western Mediterranean Sea and from the Laurentian Great Lakes (Dachs et al., 1998; Parrish et al., 1992). Odd alkanes also characterized sediment trap material

5 collected in the Mediteranean Sea, together with a high abundance of methylalkanes and diploptene, and were associated to the contribution of cyanobacteria (Dachs et al., 1998). The occurrence of alkanes with even carbon number has also been related to bacterial reworking of organic matter (Grimalt and Albaigés, 1987). In the present report, diplotene is a minor compound and methylalkanes could not be detected. Other

10 hydrocarbons detected in the samples have an algal origin: C_{15}, C_{17} (Clark and Blumer, 1967), pristane, lycopane (Damsté, 1993) as well as $C_{37:2}$ and $C_{37:3}$ synthesized by coccolithophorids (Volkman et al., 1980). These phytoplanktonic biomarkers occur in low percentages. At the same study site, a high flux event was recorded at 200 m in April 1987 and C_{17} was the dominant *n*-alkanes (20%, Marty et al., 1994). In compar-

15 ison, C_{17} abundances measured in the present time series samples are lower (0.8 to 5.2% of hydrocarbons) which indicates that fresh phytoplanktonic inputs did not dominate the sinking material or that there was an efficient degradation of low MW alkanes during sinking. The relative contribution of C_{17} to *n*-alkanes peaks at the beginning of the D series, on the night of the 12 to 13 October, while the D series corresponds to

20 weak fluxes. Odd-chain alkenes in the C_{15}-C_{19} range and $C_{21:6}$ are phytoplanktonic biomarkers commonly found in sinking particles rich in fresh phytoplanktonic residues (Burns et al., 2003) and they are rapidly degraded during particle degradation (Matsueda and Handa, 1986). None of these indicators for fresh algal residue could be detected in sinking particles collected during DYNAPROC2 cruise.

25 No unresolved hydrocarbon mixture, sourced by petroleum contamination, could be evidenced; however the detection of the corresponding humps on the chromatograms may have been impeded by the low quantities of material analyzed.

A moderate odd-to-even carbon number predominance or an even preference characterizes C_{24} to C_{34} *n*-alkanes in samples where long-chain *n*-alkanes fluxes showed

lowest contribution (Fig. 1). In contrast, the samples with a clear odd predominance of long-chain n-alkanes correspond to maxima in C_{25}-C_{37} odd n-alkanes fluxes ($>2\,\mu g\,m^{-2}\,d^{-1}$). This signature is characteristic of terrestrial higher plants (Eglinton and Hamilton, 1967) whereas lower CPI values point to petroleum or marine organism inputs (Davis, 1968; Han and Calvin, 1969; Cripps, 1990).

The hydrocarbons which relative abundances show greater variations are squalene, squalane and long-chain n-alkanes. Squalene is likely contributed by zooplankton (Wakeham and Canuel, 1986, 1988). Its observed variation trend is quite erratic with increases and decreases up to 5 folds in consecutives 6 h-samples. Moreover, maxima occurred during the day as well as at night. Total hydrocarbon fluxes describe ample variations between 1.4 and $29.7\,\mu g\,m^{-2}\,d^{-1}$ without clear day-night periodicity.

3.2 Long-chain alkenones

C_{37} and C_{38} unsaturated methyl and ethyl alkenones are synthesized by a few Haptophytes, in particular the worldwide distributed coccolithophorids *Emiliania huxleyi* and *Gephyrocapsa oceanica* (Conte et al., 1992). They are unequivocal biomarkers for coccolithophorids. They could be detected in most of the samples except for the D series where alkenone quantification could be carried out only in the two last samples. The alkenone unsaturation index UK'_{37} is related to the growth temperature of the algae and is used to reconstruct sea surface temperatures (SST) from UK'_{37} measured in old sediments (Prahl et al., 1988). Alkenone fluxes describe up to ten fold increase or decrease between consecutive 6 h-samples (Table 3 and Fig. 2). Their variation pattern follows the trend described by hydrocarbon flux for the A, B and C times series (17 September to 5 October) whereas particles of D series were impoverished in alkenones relatively to hydrocarbons (12–14 October). SST estimates reconstructed using the Prahl et al. (1988)'s calibration varied between 15 and 25°C. Highest SST estimates correspond to lowest flux values, when the analytical signal was closest to detection limits. In such chromatographic conditions and when the capillary column has been used for a while, temperature estimates may be overestimated (Villanueva

and Grimalt, 1996; Grimalt et al., 2001). The temperature maxima of two first samples of the A series and the two last samples of the D series are therefore dubious. For the other samples, reconstructed temperature estimates are in the range of the CTD hydrocast temperatures from 10 to 30 m for the A series-samples, from 20 to 50 m for the B series samples and from surface to 30 m for the C series samples.

Fluxes of alkenone and alkenoates, when detected, range from to 1.0 to 33.8 μg m^{-2} d^{-1}, and C$_{37}$ alkenone fluxes 0.4 to 14.28 μg m^{-2} d^{-1}. Flux maxima occurred during the A series on the night of the 21 September, during the B series on the night of 28 September and during the C series during the day of the 5 October. The beguinning of the A series, the 3 and 4 October and the D series were characterized by minima in fluxes. Pulses of high flux last for one or two samples, that is for 6 to 12 h and flux increases up to 6 folds during these events.

3.3 Alkanols, sterols and steroidal ketones

Alcohols constitute the most abundant of the targetted lipid classes with fluxes one order of magnitude above those of hydrocarbons and of long-chain alkenones. The alcohol fraction is dominated by 24-methylcholesta-5,22-dien-3β-ol (brassicasterol) and cholest-5-en-3β-ol (cholesterol). Four other sterols have abundances above 5%: 27-nor-24 methylcholesta-5,22-dien-3β-ol, cholesta-5,22-dien-3β-ol, 24-ethylcholesta-5,22-dien-3β-ol and 24-ethylcholestan-5-en-3β-ol (Fig. 3 and Table 4).

24-Methylcholesta-5,22-dien-3β-ol is almost the exclusive sterol of Haptophytes, it often accounts for more than 90% of sterols in some diatoms species and represents 53% of total sterols in the dinoflagellates *Gymnodinium simplex* (Conte et al., 1994; Volkman, 1986). It is not primarily attributed to diatoms here because it fingerprints species from productive area (*Chaetoceros simplex*, *Skeletonema costatum*, *Thalassiosira pseudonana*, *Nitzschia alba*) which are not detected in the plankton of the water column (Lasternas et al., 2008). Rather, 24-methylcholesta-5,22-dien-3β-ol indicates the occurrence of remains of Haptophytes and of some dinoflagellates (for instance *Gymnodinium simplex* species) to the sinking organic matter.

Cholest-5-en-3β-ol occurs in zooplanktonic material together with cholesta-5,22-dien-3β-ol, which represents from 4 to 11% of total sterols in the DYNAPROC2 sinking particles. High proportions of cholest-5-en-3β-ol are have also been reported in some dinoflagellates such as *Gonyaulax* genus, which is not an important phytoplanktonic component at the time of this study (Lasternas et al., 2008), in cyanobacteria and in some diatoms (Volkman, 1986). Interestingly, sterols in cyanobacteria are often dominated by a mixture of cholest-5-en-3β-ol and 24-ethylcholest-5-en-3β-ol (Volkman, 1986), and the high abundance of both compounds may denote the significance of cyanobacterial inputs to the exported matter. Beside cyanobacteria, 24-ethylcholestan-5-en-3β-ol is a dominant component of dinoflagellates and eustigmatophytes, of a Prymnesiophytes (*Pavlova*) and of some Raphidophytes (Volkman, 1986; Nichols et al., 1987; Volkman et al., 1993). Its occurrence in diatoms is not relevant here, as it concerns genera insignificant in the water column (*Asterionella* and *Navicula*, Lasternas et al., 2008). 24-Ethylsterols are also synthesized by higher plants but the low abundance of higher plant long-chain *n*-alkanols relatively to sterols argues for a dominant algal contribution to C_{24} ethyl substituted sterols. The significant contribution of 24-ethylcholesta-5,22-dien-3β-ol to total sterols fingerprints algal remains from the classes of Cryptophycea, Rhodophycea, Chlorophyceae and/or Chrysophyceae in the exported material (Volkman, 1986; Dunstan et al., 2005). 24-Ethylcholesterol proportion to alkyl diols denies that Eustigmatophytes are a formost source for this sterol (Volkman et al., 1992; Méjanelle et al., 2003).

4-Methylsterols having additional methyl groups substituted at C_{23} or both at C_{23} and C_{24} were identified in the sinking particles, with 4α,23,24-trimethylcholest-22-en-3β-ol (dinosterol) as the major homologue (2.5±0.5% of total sterols). Dinosterol and dinostanol are abundant components in dinoflagellates, in particular the genus *Gymnodinium* abundant during the DYNAPROC study (Volkman, 1986; Piretti et al., 1997; Mansour et al., 2003). Dinosterol also represents lqess than 4% of sterols in some pennate diatoms where 4α,24-dimethylcholest-22-en-3β-ol accounts for more than 9% of sterols (Volkman et al., 1993). In the present sinking particles, this latter

sterol is not detected. Other sterols stemming from dinoflagellates are identified in the sinking particles. 23,24-Dimethylcholesta-5,22-dien-3β-ol and its stanol counterpart contribute from 2.1 to 3.8% of total sterols, and 4α,24-dimethylcholestan-3β-ol occurs at trace levels. Sterols with methyl groups substituted at C_{23} and C_{24} represents up
5   to half of the sterols in some dinoflagellates (*Gonyaulax, Pyrocystis* and Prorocentrum genera) whilst 4α,24-dimethyl substitued sterols are identified in variable amounts in *Scripssiella* and *Gymnodinium* (Harvey et al., 1987; Mansour et al., 2003).

   C_{26} Sterols having 27-*nor* or 24-*nor* structures accounted for a non negligible part (6.5 to 12.5%) of total sterols, with 27-*nor*-24-methylcholesta-5,22-dien-3β-ol ranking
10 in the five more abundant sterols (4.7 to 8.7% of total sterols). C_{26} sterols have been identified in phytoplankton but the assignment of their biological precursors is confused because they are not systematically reported in studies dealing with sterols. However they occur in marine dinoflagellates, in particular in the genus *Gymnodinium* (Goad and Whithers, 1982; Volkman, 1986), that dominates the dinoflagellates during the present
15 study (Lasternas et al., 2008).

   24-Methylcholesta-5,24(28)-dien-3β-ol is the major sterol in some diatoms and is often used to fingerprint diatom occurrence. This sterol is also a constituent of dinoflagellates of the genus *Prorocentrum*, a minor constituent of the phytoplankton in the water column (Lasternas et al., 2008), and of some Prasinophytes, which compose
20 between an important fraction of the phytoplankton according to pigmemnt chemometry (Marty et al., 2008; Volkman, 1986). 24-Methylcholesta-5,24(28)-dien-3β-ol accounted for less than 5% of total sterols in most sedimenting particles collected during DYNAPROC2. C_{27} and C_{29} sterols with $\Delta 5, 24(28)$ double bond system are also identified in all samples in small amounts and synthesized by Prasinophyceae, dinoflag-
25 ellates and diatoms. 24-Propylcholesta-5,24(28)-dien-3β-ol is identified in the sinking particles and has been previously reported in Mediterranean samples (Tolosa et al., 2003). Its biological precursor is yet unknown.

   A series of steroid ketones was identified in the samples. They occurr in minor abundances in marine organisms and are produced by microbial oxidation of sterol

(Wakeham and Canuel, 1986, 1988; Burns et al., 2003). 24-norcholesta-4,22-dienone, cholestanone and cholest-4-en-3-one were chromatographically resolved from sterols whereas another isomer of cholestanone coeluted with $5\alpha(H)$-cholestan-3β-ol, and cholestadienone occurred in a composite peak with 4-methylcholesta-24(25)-en-3β-ol in some samples. Other homologues with mass peak of 412 and 414 eluted at the end of the elution time span of sterols. However, their poor peak shape and the mismatch between their retention time under GC and GC-MS conditions (constant gas pressure fit versus constant gas flow) made their quantification and their attribution tricky; therefore they were not further considered. Cholest-4-en-3-one was the dominant steroidal ketone and accounted for up to 19.5% of the compounds in the alcohol fraction, alike in sinking particles from various location (Wakeham and Canuel, 1986). The timing of its flux shares some similarities with that of sterols, with no obvious maxima at night. The timing of sterols and cholestenone fluxes also show some discrepancies: cholestenone increase on 21 September (end of the A series) is weaker than that of sterols and an additional spike occurs during the C series, on the night of 4 October.

C_{30} mid-chain alkane diols and C_{30} hydroxy mid-chain alkanone were detected in comparable amounts. Eustigmatophytes are generally considered as the source of mid-chain hydroxy alkanols in marine sediments (Volkman et al., 1992, 1999; Gelin et al., 1997; Versteegh et al., 2000). The same alkyl diol homologues and ketoaldehydes have also been reported in a fern of temperate zone, suggesting a possible terrigeneous source of C_{30} alkyl diols provided the occurrence of ketoaldehydes (Jetter and Riederer, 1999). Hydroxy alkenones with similar structures as alkyl diols occur in minute amounts in living Eustigmatophytes (Méjanelle et al., 2003). In sediments their concentrations at least equal those of alkyl diols and they are attributed to the oxidation of n-alkyl diols or to hydrolysis of complex mid-chain functionalized polymers (Gelin et al., 1997; Xu et al., 2007). The comparable amounts of alkyl diols and their hydroxyl alkanone counterparts in sinking particles signals that the Eustigmatophytes remains have suffered degradation. Flux variation of Eustigmatophtes biomarkers follows the temporal trend described by other phytoplanktonic indicators. Alkane diol flux

magnitude compares to that of fluxes recorded at a deeper depth (500 m) in the North Pacific, suggesting that the Eustigmatophyte source is lower here or that degradation has more intensely reduced the fluxes (Table 4).

High-molecular weight *n*-alkanols are indicative of terrigeneous higher plants and are little abundant in the present series of samples. Their flux pattern shows synchronous characteristics with that of long-chain *n*-alkanes, and linear correlation between both biomarker groups explains 67% of their variability (Fig. 1). Long-chain *n*-alkanes' abundance accounted for two to four folds those of long-chain *n*-alkanols except for the last series of samples where they reached 12 times long-chain *n*-alkanols' abundance.

Total sterol fluxes ranged from 31 to 377 μg m^{-2} d^{-1} and their timing is similar to that of long chain alkenones (Table 4).

4   Discussion

4.1   Occurrence and fluxes of lipids

The analysis of molecular biomarkers in one tenth of sediment trap material collected during 6 h in an oligotrophic area represented a challenge because of the low amounts of material. Hydrocarbons and sterols could be quantified in all studied samples, while alkenones could not be detected or unappropriately quantified in a few samples.

The suite of identified biomarkers fingerprints mostly phytoplanktonic and zooplanktonic remains in the exported material, whilst the higher plant molecular signature is tenuous. Molecular patterns of the lipid classes under study pinpoints reworked algal matter sourced by dinoflagellates, cyanobacteria, prasinophytes and prymnesiophytes. The relative proportion of alkane diols to 24-ethylcholest-5-en-3β-ol differs from that in live eustigmatophytes (Volkman et al., 1992; Méjanelle et al., 2003) and indicates a weak abundance of remains from eustigmatophytes in the exported particles. The characteristics of the exported algal remains are in good agreement with the microscopic determination of the phytoplankton and the pigment chemometry carried out

in the water column (Marty et al., 2008; Lasternas et al., 2008). The sterol composition shares some characteristics with sinking particles sampled at other locations in the Mediterranean Sea (Dachs et al., 1998; Tolosa et al., 2003). Diatom fingerprint is equally low as in exported particles of the winter Alboran Sea situation (Dachs et al., 1998) whereas it is lower than in sinking particles from the Alboran gyre (24-methylcholesta-5,24(28)dien-3β-ol accounts for non detected to to 4.7% in this work versus 7.4 to 18.9% in the report of Tolosa et al., 2003).

Another peculiarity of the sinking particles collected during DYNAPROC2 is the marked contribution of 24-ethylcholesterol, interpreted as a conspicuous cyanobacterial signature, and of cholesterol, stemming from both cyanobacteria and zooplankton. Both compounds are abundant in other Mediterranean particles, with higher cholesterol percentages and lower contribution of 24-ethylcholesterol. In winter sediment trap from the Alboran Sea, abundant methylalkanes were attributed to cyanobacterial matter (Dachs et al., 1998). This pattern was not observed in DYNAPROC2 sinking particles. Distinct cyanobacterial species may display different lipid composition, as illustrated in sterols (Volkman, 1986). Thus the discrepancies in exported particle compositions possibly indicate that distinct cyanobacterial species occur in the Alboran Sea in winter and in the Ligurian Sea at the fall transition. However, the predominance of even short chain alkanes and lack of methyl alkanes could be an indicator of effective bacterial degradative processes in the organic matter pool.

Steroid ketones are produced by marine organisms and microbial degradation and their relative abundance in sediment trap tend to increase with depth (Wakeham and Lee, 1989; Burns et al., 2003). Their abundance relatively to sterols corresponds to the values observed in oligotrophic conditions (Wakeham and Lee, 1989) and suggests that phytoplantonic remains at 200 m have been reworked.

4.2 Timing and drivers of biomarker flux variation

Little is known about particle export at high resolution time scale. One previous assessment studied the export of proteins and lipid classes with a 4-h time resolution at the

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same site during the spring transition and showed important variability of export fluxes (Goutx et al., 2000). Lipid biomarker composition was also investigated in drifting sediment traps from day and night in the Alboran Sea while fluxes were not given (Tolosa et al., 2003). The present study confirms a high variability of biomarker sedimentation at

5 6 h time resolution, characterized by pulses in fluxes up to 6-fold. For non aromatic hydrocarbons and alkenones, the range of the 6-h' variability compares well to seasonal variability magnitude at the same site (Ternois et al., 1997; Marty et al., 1994). Sterols decay during particle sinking complicate the comparison with other worldwide situations because the literature on sterol fluxes concern sediment traps mostly moored at

10 deeper depths (Table 5). Sterol fluxes measured during DYNAPROC2 compare well to those measured in High Nutrient Low Chlorophyll Antarctic site at the same depth (Table 5), which characterizes a weak export. This is in good agreement with bulk parameter export fluxes measured during DYNAPROC2 and with the relatively low primary productivity (Andersen et al., 2008; Marty et al., 2009).

15 The temporal variation of biomarker fluxes is likely driven by two factors. The first control is exerted by carrier particle flux: when the particle mass flux is higher, all biomarker fluxes are higher. The second driver of biomarker fluxes is the composition of sinking particle: at equal mass flux values, change of particles' biomarker concentration will follow in similar changes in the flux of this biomarker. These changes in the

20 concentration of a given biomarker can be due to variable source intensity or different degradation strength before it reaches the 200 sampling depth. Understanding flux variability therefore relies on these aspects of flux variability.

All biomarker fluxes depict concurrent maxima and minima in their temporal pattern. R^2 values show significant linear correlation between biomarker fluxes suggest that

25 the main flux driver affects equally the precursors targeted by the lipids biomarkers: dinoflagellates, coccolithophorids, eustigmatophytes, cyanobacteria, higher plants, zooplankton and detritus reworked by bacteria. The overall synchronous variation of all biomarkers and of total C suggests that the flux variability at 6 h time scale is mainly driven by physical or biological control on carrier particle formation.

Linear correlations between fluxes of biomarkers stemming from dinoflagellates, diatoms, coccolithophorids, eustigmatophytes explain 74 to 97% of their variance.

Linear correlations between phytoplanktonic biomarker fluxes and oxidation, zooplanktonic or higher plant biomarker fluxes are significant but they explain a lower fraction of the variance, 40 to 65%. This indicates some divergence in the high frequency dynamics of fluxes of higher plant, zooplanktonic and phytoplankton constituents during DYNAPROC2, which was previously observed for zooplanktonic and phytoplanktonic lipid classes' fluxes after late spring bloom conditions (Goutx et al., 2000). In addition, cholestenone, indicating oxidation of phytoplankton (cholestenone), cholesta-5,22-dien-3β-ol and cholest-5-en-3β-ol, biomarkers of zooplankton are poorly correlated in the present flux dataset, suggesting that they characterize pools of organic matter with different high frequency dynamics. (The dual origin of cholest-5-en-3β-ol, zooplankton and cyanobacteria, may explain its flux variability.)

Thus, compositional changes in sinking particles exert some control on biomarker flux dynamics.

In the following discussion, total carbon (TC) will be considered as the indicator for carrier particles. Linear correlations between TC-normalized abundances of phytoplantonic biomarkers are weaker than those relating their fluxes in the present dataset (Table 6). This would support that compositional changes are secondary drivers of the export fluxes of organic matter, while processes controlling aggregation and sinking of particles have the most driving influence, as discussed above.

During the peak of biomarker fluxes of 18 September, sinking particles are indeed enriched in all types of phytoplanktonic remains, as shown by biomarker abundances normalized to total carbon (Fig. 5b). In contrast, high flux events of 21 and the 28 September correspond to particles not enriched in phytoplanktonic sterols. Other compositional changes occur on 21, 28 September, 4 and 5 October, when alkenone enrichment partly drive the increases in alkenone fluxes. Normalized alkenone concentration increases up to 4 folds when their flux increases 10 times (28 September): a change in particles' nature and an increase in mass flux both combine to yield the

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pulse in alkenone flux.

The present study aim at tackling the reponse of exported fluxes to processes associated to distinct time scales from weeks to days. On a time scale of a few days, phytoplanktonic community evolved from the A, B, C to the D series (Lasternas et al., 2008). Phytosterol composition of the exported matter failed to reflect this evolution. Multiple sources of sterols coupled to degradation processes may account for the consistency of sterol composition. Interestingly, biomarker export pattern do neither reflect the integrated chlorophyll variation. While integrated chlorophyll-*a* moderately increased from ca. 30–40 to 33–45 mg m^{-2} between 17–18 and 21–22 September (Julian Days 265–266 and 261–262) (Marty et al., 2008, Fig. 7), biomarkers fluxes were considerably higher during 21–22 September (Figs. 2 and 4a). Moreover the integrated chlorophyll-*a* decreased during the B series of samples whereas corresponding fluxes showed the most intense spikes in fluxes. During C and D series (3, 4, 5, and 12, 13, 14 October; Julian days 277–280 and 287–288) series, the low integrated chlorophyll-*a* (18 to 22, and 15 to 22 mg m^{-2}, respectively) is traduced by distinct reponses in fluxes, with notably higher export of biomarkers during the C series. Clearly the coupling between primary production and export production is susceptible to significant change on time scales of days and even of 6 h.

Chlorophyll-*a* integrated on the water column showed a diel variation during DYNAPROC2 cruise (Marty et al., 2008), and the exported particulate organic matter (POC) flux echoed this variation (Marty et al., 2009). Fluxes of some lipids also showed maxima at night at the same site at the end of the spring (Goutx et al., 2000). However, for the subset of 31 samples under consideration here POC fluxes failed to show an obvious day-night periodicity. (POC equivals TC in DYNAPROC2). In the samples selected for our study, temporal variation of fluxes of hydrocarbons, alkenones and sterols, mirrors the timing of TC fluxes and show no consistent diel periodicity. Cholesterol and dehydrocholesterol, markers of zooplankton, do neither show this diel variability. This indicates that diel migration of grazers and the associated emission of fecal pellets alone do not drive the biomarker flux timing in the studied situation. Since

all biomarkers follow the short-term variability of TC, it is possible that if all the dataset (74 samples) had been analyzed for biomarkers, the diel variability would have been as significant as it is for the complete POC dataset.

The inventory of organic matter, and of the lipid biomarkers studied here, in the photic zone is 100 fold higher than the settling fluxes (Marty et al., 2009). Therefore, lipids have a long residence time before they are exported. This results in a temporal and spatial integration of all sources and transformation processes of lipids before they are exported to 200 m. This integration, in addition to differences in sinking rates of particles and aggregation-dissagregation processes may have blurred the chlorophyll periodicity existing in the water column. Therefore, the signal recorded in sediment trap during late summer to autumn transition can hardly catch the diel variability of biological processes in terms of sources and degradation under the conditions of coupling experienced during DYNAPROC2. When the export ratio is so low, short term sediment traps will rather record short term variability in the magnitude of carrier particle fluxes than in changes of sources. The observed short term variabilility in fluxes is due to the fast dynamics of aggregation and production of settling particles.

Under this general scenario, various sources of organic matter are reworked in the water column until the physical controls of aggregation and settling of particles drive their export ot the deep waters. If the export ratio is high, the composition of exported lipids will better reflect high frequence variation in their source than when the export ratio is low. During DYNAPROC2, some internal dynamic events may have enhanced the coupling between production and sinking, such as the destratification occurring before our samples of the D series, or such as the entrance of fast sinking atmospheric particles during rain events of 21–22 September and the beginning of October.

Another factor modifying the record of high frequency events is the reduced efficiency of degradative processes when water column residence times get shorter. Interestingly, this may have happened during our field study of the short term variability. Indeed, during the C and D sampling series, successive strong wind events occurred, resulting in destratification of the water column and a strong cooling of the mixed-layer water.

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This process may have resulted in shorter residence times of lipids in the surface layer. Marked compositional changes oppose sinking particles of the A, B and C series, when biomarkers fluxes reach higher values, from the exported particles of the D series, when all fluxes are lower. During the D series period exported particles are notably richer in hydrocarbons, and show spikes in cholesterol and cholestanone normalized concentrations, possibly reflecting high frequency increase in fecal pellet production and associated oxidation of sterols (Fig. 5b). The intrusion of coastal water during the rain and wind event of 21 September also corresponds to an enhanced higher plant fingerprint (Fig. 1).

5 Conclusions

Exported particles derive mostly from reworked phytoplankton and display degradation characteristics. Sinking particle composition is independent to phytoplanktonic community changes and is correlated to sinking fluxes of other lipids. High frequency sampling of biomarkers exported at 200 m shows a variation range of the same magnitude as seasonal variation. The coupling between productivity (integrated chlorophyll-*a*) and biomarker exported fluxes is variable. The results stongly suggest that the short term temporal variability of export fluxes depends primarily on physical constrains exerted by carrier particle dynamics, and to lower extend, by particle composition. Little compositional changes seem to affect significantly biomarker fluxes.

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Table 1. Positions and dates of mooring and recovering of drifting sediment traps.

Series of samples	A	B	C	D
Mooring location	N 43°24.80 E 8°00.61	N 43°23.06 E 8°01.52	N 43°23.59 E 8°02.78	N 43°23.79 E 8°00.36
Recovering location	N 43°22.72 E 7°51.75	N 43°18.68 E 8°04.93	N 43°19.31 E 7°46.09	N 43°25.36 E 8°00.18
Date	17 to 22 September 2004	24 to 29 September 2004	3 to 8 October 2004	10 to 15 October 2004
Mass Flux in $mg\,m^{-2}\,d^{-1}$	3.17±0.01	1.73±0.01	2.41±0.01	0.95±0.01

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Table 2. Hydrocarbon composition of sinking particles collected by drifting sediment traps, in percent of identified hydrocarbons, and total hydrocarbon flux.

Date →	17 Sep			18 Sep		21 Sep			28 Sep				29 Sep		3 Oct		4 Oct				5 Oct		12 Oct		13 Oct			14 Oct
Starting time (h)	8	14	20	2	8	8	14	20	2	8	14	20	2	8	14	20	2	8	14	20	2	8	20	2	8	14	20	2
C_{12}	n.d.	n.d.	n.d.	6.7	15.3	n.d.	n.d.	9.8	n.d.	3.0	1.4	1.0	3.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
C_{13}	n.d.	n.d.	n.d.	n.d.	0.2	n.d.	10.5	0.2	n.d.	n.d.	n.d.	0.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
C_{14}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.1	n.d.	0.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
C_{15}	0.8	0.7	1.9	2.9	1.2	1.9	1.3	0.4	n.d.	3.4	0.9	0.9	n.d.	2.7	3.3	1.7	2.4	0.6	1.9	0.7	0.6	0.8	4.9	4.3	1.7	1.1	1.3	1.8
C_{16}	2.2	1.6	3.5	4.0	1.3	1.9	2.0	0.8	2.9	2.9	1.6	0.8	1.9	3.2	6.8	3.4	4.3	1.2	2.3	1.9	2.3	0.8	7.5	29.0	4.0	4.2	2.5	2.5
C_{17}	0.8	0.8	3.2	4.0	1.5	3.0	2.8	2.1	1.6	3.0	2.1	1.1	2.0	2.9	1.5	3.0	3.1	1.8	2.1	2.0	2.9	1.5	5.2	4.5	2.3	1.8	1.3	1.7
pristane	n.d.	1.0	2.7	n.d.	1.2	2.2	3.4	1.3	2.5	2.6	2.1	2.0	1.7	1.3	n.d.	1.6	1.8	n.d.	1.3	1.0	2.2	1.0	2.1	1.4	3.5	3.3	0.7	n.d.
C_{18}	2.5	2.9	5.4	4.7	1.9	5.4	5.3	7.0	4.6	4.3	2.6	2.0	2.3	3.4	6.0	5.2	5.5	3.3	4.8	3.0	3.6	2.3	6.3	4.3	6.2	7.1	2.8	3.8
Phytane	1.0	0.4	1.0	n.d.	0.9	1.4	1.5	1.2	2.2	n.d.	1.2	1.2	1.6	1.1	n.d.	0.8	0.9	0.7	n.d.	0.6	1.6	0.4	1.0	n.d.	0.4	1.4	0.3	1.5
C_{20}	9.1	7.9	7.6	11.4	7.8	16.8	11.1	15.0	12.6	8.7	3.4	4.0	4.8	5.3	4.6	8.5	10.0	9.3	11.4	7.8	6.2	6.5	9.6	6.2	7.0	9.4	13.6	15.3
C_{21}	5.1	3.5	6.2	8.5	3.9	10.6	8.4	9.2	5.9	6.8	2.9	3.5	6.8	4.0	8.5	5.4	6.7	7.4	7.8	6.3	5.3	6.2	6.9	4.6	2.9	3.8	12.3	14.2
C_{22}	7.0	5.9	6.1	5.2	3.0	5.0	6.5	4.3	5.3	5.0	2.9	2.9	5.9	3.3	2.7	7.0	9.0	6.3	8.2	7.1	7.0	6.9	5.5	4.6	6.0	8.7	8.1	9.7
C_{24}	4.9	5.2	3.3	5.2	15.7	1.8	3.0	1.1	6.4	4.8	2.1	2.6	3.3	1.5	33.6	5.6	6.6	3.0	5.0	5.3	5.2	5.0	5.0	4.4	5.0	7.5	3.1	3.1
C_{25}	4.0	2.3	2.7	4.5	12.8	5.5	2.7	1.5	3.8	2.3	4.0	3.0	2.8	3.4	9.2	2.5	2.8	2.9	2.9	2.9	1.8	4.1	3.4	3.8	1.8	2.1	1.9	6.8
C_{26}	3.9	4.5	2.5	0.9	0.7	0.9	0.8	0.6	1.9	2.1	1.3	1.1	n.d.	0.8	0.6	2.1	2.5	1.7	2.3	1.9	1.9	1.9	2.1	2.9	3.4	4.3	2.4	1.7
Squalane	14.9	9.8	11.0	2.5	2.4	3.0	3.4	5.1	11.1	11.6	4.4	1.7	4.8	4.0	n.d.	4.3	5.4	10.4	12.0	6.1	3.9	12.4	4.7	0.9	13.4	16.5	7.5	8.5
C_{27}	4.5	6.4	4.5	6.3	2.3	9.2	4.6	4.4	5.4	5.1	8.9	10.2	6.9	9.2	3.2	5.9	4.7	4.8	4.8	6.9	8.9	8.1	3.7	3.9	2.4	3.0	3.7	2.2
C_{28}	3.7	4.8	2.9	1.5	1.1	1.2	0.9	1.1	2.0	2.1	1.7	1.6	1.6	1.3	1.7	1.9	2.0	1.9	1.7	1.9	1.8	1.9	1.4	2.4	6.9	3.9	2.7	1.9
Squalene	13.5	11.7	12.9	7.3	4.5	2.1	2.6	4.1	7.0	7.6	13.5	5.8	16.9	13.4	5.2	22.5	11.8	23.9	6.2	11.3	11.8	9.4	14.7	5.6	17.2	4.0	12.2	14.3
C_{29}	2.8	3.6	5.4	5.3	4.1	8.8	12.2	7.5	6.7	6.9	15.0	18.0	12.3	13.1	1.9	8.1	6.7	7.2	9.3	11.3	12.7	12.2	4.1	5.0	2.4	2.8	6.0	3.3
C_{30}	3.9	4.6	3.0	1.2	0.7	0.9	1.1	1.1	2.0	2.0	1.2	1.4	n.d.	1.1	3.8	1.4	1.9	1.7	2.2	2.9	2.9	0.7	1.3	2.8	2.8	3.5	2.5	2.5
C_{31}	2.8	3.2	3.6	3.4	2.6	4.0	5.2	4.0	3.4	3.4	6.5	8.1	5.0	6.5	0.8	2.8	3.9	3.6	4.9	5.2	4.0	3.1	3.9	4.4	3.0	4.6	4.2	1.6
C_{32}	2.0	2.7	1.7	0.9	1.8	0.4	n.d.	0.8	1.7	n.d.	n.d.	n.d.	0.9	2.7	0.9	1.3	1.2	1.3	1.1	0.8	0.9	0.9	0.7	1.5	2.2	n.d.	2.2	0.8
Diploptene	n.d.	n.d.	n.d.	n.d.	1.0	tr	n.d.	0.3	n.d.	n.d.	0.4	0.6	n.d.	n.d.	n.d.	0.3	n.d.	n.d.	n.d.	0.7	n.d.	0.9	n.d.	n.d.	n.d.	2.4	n.d.	n.d.
C_{33}	1.6	1.8	2.1	1.4	1.1	0.8	1.6	1.5	1.4	2.0	2.5	2.6	1.9	2.1	3.8	1.1	1.6	1.7	1.7	3.5	1.5	2.1	1.4	1.7	2.0	1.8	2.7	0.9
C_{34}	1.1	1.4	0.8	n.d.	n.d.	0.4	n.d.	0.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.6	0.6	0.9	n.d.	0.7	n.d.	0.6	n.d.	0.5	1.3	1.5	1.4	n.d.
Lycopane	0.8	0.8	0.9	1.1	0.6	2.2	2.2	1.4	n.d.	n.d.	2.3	2.9	1.7	2.1	n.d.	1.1	1.5	1.6	3.4	2.1	0.4	2.6	0.3	n.d.	0.3	0.5	0.7	1.5
C_{35}	0.4	0.8	0.9	n.d.	1.3	0.4	n.d.	0.5	n.d.	n.d.	n.d.	n.d.	n.d.	0.9	n.d.	0.6	0.5	0.5	n.d.	0.6	0.3	0.7	1.6	0.9	0.4	0.8	0.9	0.2
C_{36}	n.d.	n.d.	0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.4	n.d.	n.d.	0.4	n.d.	n.d.	1.0	n.d.	0.6	n.d.	n.d.	n.d.	n.d.	1.4	n.d.
$C_{37:3}$	2.3	4.2	2.6	6.9	5.0	7.4	6.7	8.8	5.9	6.6	9.0	12.1	6.9	9.0	n.d.	1.2	2.4	1.9	2.6	3.2	7.9	5.1	1.5	0.4	n.d.	n.d.	0.8	n.d.
C_{37}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.5	n.d.
$C_{38:3}$	4.6	7.7	1.0	4.4	4.1	2.7	n.d.	3.1	3.5	2.9	6.0	8.6	5.4	3.3	n.d.	0.2	n.d.	0.6	n.d.	1.1	2.6	1.7	1.3	n.d.	1.6	n.d.	n.d.	n.d.
Total hydrocarbon flux ($\mu g\,m^{-2}\,d^{-1}$)	5.6	4.9	5.5	5.9	15.8	14.9	8.9	29.7	12.4	9.5	16.3	14.0	9.3	14.3	1.4	7.6	6.7	7.0	4.7	8.5	7.8	9.3	10.2	21.1	9.9	7.0	8.4	8.1

n.d.: non detected

[a] Hydrocarbon fractions of three samples were lost.

Variation of lipid biomarker fluxes at 6 h time scale

L. Méjanelle and J. Dachs

Table 3. Fluxes of long chain alkenones and alkenoates recorded by drifting sediment traps during the DYNAPROC2 cruise, in $\mu g\,m^{-2}\,d^{-1}$ and values of the alkenone unsaturation index, UK'37. Methyl alkenones and ethyl alkanones are designated by the the corresponding prefixes. The OMethyl prefix stands for methyl alkanoate.

Date	17 Sep			18 Sep		21 Sep				28 Sep				29 Sep		3 Oct		4 Oct				5 Oct				12 Oct		13 Oct			14 Oct
Starting time (h)	8	14	20	2	8	2	8	14	20	2	8	14	20	2	8	14	20	2	8	14	20	2	8	14	20	20	2	8	14	20	2
Compounds:																															
Methyl $C_{37:3}$	0.1	0.1	0.2	0.4	1.1	1.7	2.5	2.3	4.1	1.9	1.0	0.4	3.7	5.9	0.6	0.3	0.3	0.3	0.2	0.4	0.4	1.1	1.2	1.7	2.6	n.d.	n.d.	n.d.	n.d.	0.1	0.1
Methyl $C_{37:2}$	0.4	0.7	0.5	0.5	1.6	3.1	4.5	3.7	7.4	3.3	1.2	0.6	4.9	7.4	0.6	0.4	0.8	0.7	0.4	0.7	0.8	2.0	1.6	3.5	4.6	n.d.	n.d.	n.d.	n.d.	0.3	0.3
OMethyl $C_{36:2}$	n.d.	0.0	0.1	0.1	0.2	0.4	0.6	0.3	1.0	0.2	0.1	0.2	0.4	0.8	0.2	n.d.	n.d.	0.2	n.d.	0.04	0.1	0.1	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ethyl $C_{38:3}$	0.05	0.0	0.2	0.3	0.5	0.8	1.1	1.3	2.7	1.2	0.7	0.02	1.8	3.2	0.1	0.1	0.2	0.2	0.2	0.2	0.3	1.6	0.6	2.1	4.4	n.d.	n.d.	n.d.	n.d.	0.5	0.1
Methyl $C_{38:3}$	0.03	0.1	0.1	0.0	0.1	1.0	1.3	1.2	2.2	1.0	0.6	0.1	2.2	3.5	0.3	0.2	0.1	n.d.	n.d.	0.2	0.2	0.6	0.7	n.d.	1.7	n.d.	n.d.	n.d.	n.d.	n.d.	0.1
Ethyl $C_{38:2}$	0.3	0.4	0.5	0.2	0.7	2.4	3.3	3.2	6.1	2.7	1.1	0.1	3.9	6.4	0.3	0.1	0.7	0.7	0.5	1.0	1.1	2.7	2.0	4.2	6.1	n.d.	n.d.	n.d.	n.d.	n.d.	0.2
Methyl $C_{38:2}$	n.d.	n.d.	n.d.	n.d.	n.d.	1.7	2.7	1.7	3.6	1.6	0.6	0.2	3.1	3.8	0.4	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methyl $C_{39:3}$	n.d.	0.03	0.03	0.1	0.2	0.2	0.3	0.3	0.6	0.2	0.1	n.d.	0.4	0.9	n.d.	n.d.	0.03	0.05	0.09	0.1	0.1	0.2	0.2	0.3	0.6	n.d.	n.d.	n.d.	n.d.	n.d.	0.0
Methyl $C_{39:2}$	0.2	0.1	0.3	0.4	0.3	0.7	1.0	0.9	1.7	0.7	0.3	0.3	1.2	1.8	n.d.	n.d.	0.1	0.3	0.1	0.2	0.3	0.6	0.4	0.9	1.0	n.d.	n.d.	n.d.	n.d.	0.3	0.2
UK'$_{37}$ (RU)	0.80	0.85	0.68	0.60	0.59	0.64	0.64	0.62	0.64	0.64	0.55	0.61	0.57	0.56	0.50	0.57	0.75	0.70	0.70	0.66	0.66	0.64	0.57	0.67	0.64					0.69	0.67

n.d.: non detected

Table 4. Fluxes of sterols, n-alkanols, alkane diol and steroidal ketones in sinking particles collected by drifting sediment traps during the DYNAPROC2 cruise, in $\mu g\,m^{-2}\,d^{-1}$. n.d.: non detected. Sterols are designed by $x\,\Delta y,z$, where x indicates substituents and their location on the side chain or on the A ring; x can also indicate the 24-nor or 27-nor configuration. In this nomenclature, y and z indicate double bond locations. $\Delta0$ is used to design 5α-(H)stanols.

| Date | 17 Sep | | | 18 Sep | | | 21 Sep | | | | 28 Sep | | | 29 Sep | | 3 Oct | | | 4 Oct | | | | 5 Oct | | 12 Oct | 13 Oct | | | | 14 Oct |
Starting time (h)	8	14	20	8	14	2	8	14	20	2	8	14	20	2	8	14	20	2	8	14	20	2	8	14	20	8	14	20	2	2
C_{22}-OH	0.7	0.3	0.1	0.4	0.4	0.4	0.6	0.4	0.9	0.5	0.6	0.5	1.0	1.1	0.4	0.6	n.d.	0.1	0.5	0.4	0.5	0.8	n.d.	0.7	0.6	0.2	0.7	0.3	0.2	0.6
C_{24}-OH	n.d.	n.d.	0.1	0.6	0.3	0.3	0.5	0.3	0.3	0.3	0.3	0.2	0.6	0.5	0.2	0.4	0.1	0.1	0.1	n.d.	n.d.	0.1	n.d.	0.1	0.1	n.d.	0.1	0.1	0.0	0.1
C_{26}-OH	0.4	0.1	0.2	0.9	1.5	0.6	0.9	0.5	0.6	0.5	0.3	0.3	1.0	1.3	0.3	0.7	0.1	0.2	0.2	0.1	n.d.	0.1	n.d.	0.2	n.d.	n.d.	0.3	n.d.	0.1	0.3
24-nor $\Delta5,22$	0.7	0.8	0.6	1.0	2.1	2.9	4.5	2.8	5.4	2.6	2.4	1.9	4.8	6.4	2.1	3.6	0.9	1.4	1.4	1.5	2.7	1.8	2.4	3.3	0.7	0.8	0.7	0.3	0.8	0.5
24-nor $\Delta5$	0.2	0.3	0.3	0.4	1.0	0.8	1.5	0.8	1.5	0.6	0.3	0.3	0.8	1.0	0.3	0.7	0.1	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.6	0.1	0.2	0.2	0.1	0.2
24-nor-cholesta-4,22-dienone	0.3	0.1	0.2	0.3	0.7	0.6	1.5	1.2	1.6	1.1	0.7	0.8	2.1	2.4	0.6	1.7	0.2	0.3	0.3	0.6	0.3	1.0	0.2	0.5	0.5	n.d.	0.2	n.d.	n.d.	0.3
Cholestan-3β-one	0.4	0.3	0.3	0.1	0.3	0.3	0.8	0.6	0.8	0.5	0.4	0.4	1.2	1.3	0.3	1.1	0.5	0.3	0.2	0.3	0.1	1.1	0.4	n.d.	1.1	0.1	0.1			
27-nor $\Delta5,22$	3.6	3.7	3.8	5.5	13.2	16.9	25.8	16.0	29.4	17.1	14.3	11.8	27.6	35.2	11.8	20.3	5.3	4.7	8.5	7.7	8.3	14.5	10.5	13.7	18.2	4.3	6.5	4.0	2.5	4.3
27-nor $\Delta5$	0.6	1.0	0.9	1.7	4.2	3.6	5.5	3.5	5.8	2.5	1.6	1.5	3.7	5.7	1.6	3.1	0.4	0.4	0.6	0.6	0.7	1.5	1.5	2.9	2.0	0.7	0.8	0.7	0.3	0.6
$\Delta5,22$	3.3	3.3	5.2	3.6	9.0	12.0	16.8	10.5	18.1	23.5	11.4	7.6	18.8	21.2	8.4	12.6	5.6	5.3	11.1	8.0	8.6	13.2	7.9	11.7	13.1	3.3	5.8	2.6	1.5	3.6
$\Delta22$	0.8	1.7	1.5	1.7	3.5	3.6	5.2	2.9	5.7	2.4	1.9	1.7	4.4	5.6	1.8	3.3	1.4	1.4	1.5	1.5	1.3	3.1	3.2	5.0	3.5	1.3	1.3	0.9	0.5	1.3
C_{28}-OH	0.1	0.1	0.1	2.9	2.1	1.5	2.5	1.8	0.7	1.0	n.d.	0.4	2.5	7.7	16.7	2.1	n.d.	n.d.	n.d.	n.d.	n.d.	0.4	n.d.	0.2	0.7	0.1	0.1	n.d.	n.d.	
$\Delta5$	11.5	11.1	9.9	7.2	17.9	18.9	23.7	18.3	47.6	16.5	22.0	13.0	34.6	25.0	3.0	20.3	13.8	12.8	23.3	20.2	21.1	36.6	12.9	22.1	44.4	6.0	10.1	16.4	6.9	21.9
$\Delta\emptyset$ [a]	1.3	1.3	2.2	2.1	3.8	4.9	7.0	4.2	8.6	3.8	3.2	2.7	8.4	8.7	0.6	5.2	1.6	1.6	2.2	2.3	2.5	3.6	2.7	4.2	4.2	1.4	1.6	1.3	1.0	1.7
$\Delta 5,24(28)$ [b]	0.3	0.2	0.3	1.2	1.4	1.3	1.9	1.2	1.9	0.9	0.8	0.9	1.2	1.8	1.9	1.1	1.6	1.3	1.4	1.7	1.2	1.3	3.2	1.1	3.8	0.3	0.2	0.6	0.3	0.9
$4\alpha Me\Delta24(25)$ [b]	n.d.	n.d.	n.d.	1.1	1.4	0.9	1.8	2.9	3.5	2.9	1.8	2.5	4.0	5.4	0.7	4.5	0.3	0.3	0.5	0.4	0.6	0.5	0.9	0.8	0.3	0.9	0.8	0.3	0.5	0.4
Cholesta-4,22-dien-3β-one	0.3	n.d.	0.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.6	n.d.	n.d.	n.d.	n.d.	0.6	0.5	0.3	1.5	n.d.	2.5	4.2	2.2	0.8	0.2	n.d.	n.d.	n.d.	0.7	0.2
24-Methyl $\Delta5,22$	6.5	7.6	7.8	12.4	29.5	36.1	52.9	35.4	62.2	38.7	34.1	28.1	65.1	83.0	26.6	51.2	9.8	9.0	17.3	14.5	16.1	27.7	22.7	29.7	39.5	10.6	17.7	10.2	5.1	9.4
24-Methyl$\Delta22$	1.9	2.3	2.4	2.8	6.9	7.2	10.1	5.4	10.5	4.7	3.4	3.1	13.2	9.9	3.0	8.8	2.7	2.4	2.1	4.8	2.6	7.7	11.3	8.3	6.3	2.2	2.8	1.6	0.9	3.2
Cholestediol	0.1	0.1	0.1	1.4	0.4	0.1	n.d.	0.2	0.2	0.2	0.1	n.d.	0.3	n.d.	0.1	n.d.	0.4	0.4	0.2	0.2	0.2	0.6	0.8	0.8	1.0	n.d.	0.0	0.1	0.1	0.4
Cholest-4-en-3-one	3.8	4.2	4.4	3.4	9.3	6.0	12.3	14.5	17.1	12.6	12.6	14.4	33.8	35.2	11.8	28.8	9.1	8.7	5.6	15.0	7.5	24.1	37.0	20.0	15.0	3.6	4.5	2.3	1.2	11.3
24-Methyl $\Delta5,24(28)$	n.d.	n.d.	n.d.	2.4	6.2	8.8	11.5	6.8	13.1	6.3	5.1	4.4	15.1	14.5	4.3	10.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.8	3.5	1.5	0.7	n.d.	n.d.		
24-Methyl $\Delta5$	0.5	0.9	0.9	1.7	4.0	3.5	5.6	3.9	6.3	3.1	2.1	1.9	4.9	5.3	1.0	3.3	0.8	0.5	0.8	0.7	0.7	0.8	2.3	2.7	0.9	1.0	0.4	0.4	0.2	0.4
24-Methyl$\Delta5,7,22$	n.d.	n.d.	n.d.	0.3	0.5	0.6	0.8	0.4	0.9	0.4	0.5	0.6	1.2	1.4	0.4	0.8	0.3	0.4	0.5	0.6	n.d.	1.6	n.d.	1.3	2.2	0.4	0.3	0.2	0.1	0.6
23,24-Dimethyl $\Delta5,22$	0.6	0.7	0.7	1.3	3.3	2.2	4.3	3.5	6.1	2.5	3.0	3.1	5.8	7.9	2.3	6.3	1.8	1.5	3.1	3.0	n.d.	n.d.	1.4	1.6	1.4	1.2	1.2	0.7		
23,24-Dimethyl $\Delta22$	0.3	0.2	0.2	0.3	1.1	0.8	1.7	2.4	1.3	2.5	1.5	2.1	2.7	2.4	1.3	2.7	0.3	0.3	0.3	0.4	0.2	0.5	0.6	0.7	0.6	0.3	0.2	0.2	0.1	0.3
24-Ethyl $\Delta5,22$	1.7	2.1	2.5	3.5	8.6	10.1	15.7	9.3	17.7	11.6	7.9	7.5	20.3	24.7	7.7	5.1	2.5	2.5	5.5	4.6	5.0	11.3	8.8	12.8	15.9	3.8	5.4	4.1	1.9	3.3
24-Ethyl $\Delta22$ [c]	0.8	1.0	1.0	1.5	3.8	4.1	5.5	3.5	5.5	3.4	2.7	2.8	6.8	8.6	2.3	1.0	2.9	2.7	1.0	3.3	2.9	4.1	8.3	3.1	2.8	1.1	1.1	0.9	0.5	1.4
24-Methyl $\Delta7,24(28)$	0.1	0.3	0.3	1.2	0.6	0.6	1.2	0.8	2.6	0.9	0.3	0.8	1.3	9.8	1.4	0.6	0.2	0.1	0.2	0.2	0.4	0.9	1.1	0.7	0.9	0.9	0.1	0.2	0.2	0.1
23,24-dimethyl $\Delta5$	n.d.	n.d.	n.d.	2.4	3.6	2.8	4.1	2.8	3.2	2.6	1.1	1.5	3.9	9.4	1.8	3.5	1.3	1.4	1.5	1.8	1.0	3.0	1.8	3.6	5.2	n.d.	0.9	n.d.	0.2	1.4
24-Ethyl $\Delta5$	4.5	4.7	5.2	6.8	17.2	17.8	26.4	17.3	31.0	17.6	14.3	13.5	30.2	38.1	12.7	24.1	4.9	4.8	8.5	7.4	7.6	14.4	11.9	17.1	20.5	5.4	7.2	5.3	3.4	6.0
24-Ethyl $\Delta\emptyset$	0.5	0.4	0.3	1.8	5.5	4.3	7.4	4.6	7.6	4.0	3.1	3.0	7.0	9.0	2.4	6.3	0.6	0.5	0.3	1.3	0.1	1.1	2.2	0.8	1.5	1.4	1.3	1.3	0.8	0.9
24 -Ethyl $\Delta5,24(28)$	1.7	1.8	2.1	1.7	2.2	3.2	3.3	2.1	4.3	2.6	2.4	2.6	5.0	6.8	2.3	3.3	1.8	1.9	3.0	2.3	1.9	4.8	5.2	7.0	7.5	1.1	2.0	1.1	0.7	n.d.
$4\alpha,23,24$-Trimethyl $\Delta22,24(28)$	n.d.	n.d.	n.d.	1.0	1.6	1.7	2.5	1.9	3.6	1.4	1.2	1.6	1.3	3.1	0.8	1.6	n.d.	n.d.	0.1	0.7	0.3	n.d.	n.d.	0.3	0.3	0.6	0.3	0.2	3.4	1.8
$4\alpha,23,24$-Trimethyl $\Delta28$	1.1	1.8	1.6	2.0	5.3	5.8	8.4	5.6	10.4	5.5	4.0	4.8	9.9	13.4	4.0	8.0	1.5	1.3	2.1	2.1	1.8	4.1	5.2	6.2	7.2	1.3	1.7	1.4	0.7	1.7
24-Propyl $\Delta5,24(28)$ isomer	n.d.	n.d.	n.d.	0.2	0.2	0.2	0.4	n.d.	0.4	0.1	0.1	n.d.	0.3	0.2	0.1	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
$4\alpha,23,24$-Trimethyl $\Delta7$	0.1	0.2	0.2	n.d.	n.d.	0.2	n.d.	0.1	0.9	n.d.	0.3	0.2	0.1	0.2	n.d.	0.2	0.5	0.4	0.5	0.9	2.9	1.2	0.2	n.d.	n.d.	0.0	0.5	0.2		
24-Propyl $\Delta5,24(28)$	0.4	0.7	0.7	0.7	2.2	1.8	2.8	1.3	2.4	2.3	2.4	2.9	2.5	4.1	1.5	2.8	0.9	1.0	1.7	1.0	1.8	2.1	5.1	3.7	2.9	0.4	1.3	1.0	0.4	1.1
$4\alpha,23,24$-Trimethyl $\Delta7$	0.4	0.1	0.1	0.4	1.2	1.1	0.7	0.4	0.6	0.2	1.2	1.0	0.5	0.5	0.8	0.8	0.4	0.6	0.3	1.3	0.1	1.1	0.6	0.5	0.7	0.1	0.6	0.5	0.3	0.2
$4\alpha,23,24$-Trimethyl $\Delta5$ [d]	0.4	0.4	0.4	0.4	1.2	1.0	1.0	0.7	1.5	0.5	0.5	0.8	0.8	1.4	0.5	0.9	0.4	0.3	0.5	0.7	0.9	0.5	1.3	1.3	0.3	0.3	0.5	0.3	0.5	0.2
$4\alpha,23,24$-Trimethyl $\Delta\emptyset$	0.6	0.4	0.7	0.4	1.9	1.0	1.7	2.2	3.1	2.3	1.4	2.2	3.0	3.5	1.3	2.6	1.1	0.9	1.2	1.7	0.8	3.5	0.6	4.5	3.4	0.3	0.6	0.4	0.2	1.1
$4\alpha,24$-Dimethyl $\Delta\emptyset$	n.d.	0.2	n.d.	0.4	1.5	0.9	1.7	0.5	1.6	0.5	0.6	1.0	2.4	2.7	0.8	1.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.5	n.d.	n.d.	0.3	0.5	0.3	0.1
C_{30} alkane 1,15 diol (+1,14 + 1,13)	0.4	0.8	0.6	1.3	3.3	3.8	7.9	4.5	7.7	4.1	2.0	2.6	4.4	7.5	2.0	4.1	0.8	0.6	1.2	1.4	1.5	3.6	5.2	5.1	7.1	0.6	0.5	0.6	0.5	0.7
C_{30} kétol	1.3	0.7	1.0	1.2	3.3	4.4	6.7	4.0	5.8	3.5	1.9	2.4	3.2	9.3	1.7	3.5	0.8	1.0	1.4	1.2	1.4	4.2	4.5	4.7	5.9	0.3	0.3	0.7	0.4	1.1
Mid-chain alkanol	0.2	0.1	0.1	0.3	1.0	0.8	1.1	0.4	0.6	0.5	0.3	0.6	0.5	2.1	0.3	0.9	0.1	0.2	0.3	0.2	0.1	0.4	0.2	n.d.	0.7	n.d.	n.d.	0.3	0.2	0.1

[a] coeluting with an isomer of cholestan-3β-one in minor amounts.
[b] coeluting with minor amounts of acholesta-4,22-dien-3β-one isomer in some samples.
[c] coeluting with 4α-24dimethyl $\Delta22$ in minor amounts.
[d] coeluting with $4\alpha,4\beta,24$-trimethyl $\Delta0$.

Table 5. Comparison of the biomarker fluxes measured in DYNAPROC2 high frequency sediment trap experiment and selected literature.

Location	Depth	Resolved hydrocarbons	C_{37} alkenones	C_{30} alkane diol	Sum sterols	Reference
New Guinea Coast	300–1460 m	2.6–46.5			13–602	Burns et al. (2004)
Australian Shelf	300–1430 m	29.7–36.8			6.0–16.5	Burns et al. (2001)
NW Autralian Shelf	200–600 m	30–37			6–16.5	Burns et al. (2003)
Eastern North Pacific						
High productivity site	740–4750 m	2.7–5.6				Matsueda and Handa (1986)
Low productivity site	741–4750 m	0.37–0.82				Matsueda and Handa (1986)
Arabian Sea	2220 m	0.22–2.64	0.87–40.8 [a]		nd–7.92[b]	Prahl et al. (2000)
Antarctic HLNC zone	200 m	0.1–8.3	0–77.2[c]		68–661	Ternois et al. (1998)
SW Pacific Ocean	300–1000 m		0.05–95		Oct-98	Sikes et al. (2005)
N Pacific	140 m				ca. 50–220	Wakeham and Lee (1989)
N Pacific	100 m				ca. 1200	
N Pacific	505–3380 m		0.11–1.97[d]	2.6–9.29	3.7–16.4[e]	Wakeham et al. (2002)
N Pacific	1235–3815				15–110	Grimalt et al. (1990)
N Atlantic	2865–4730				19–78	Grimalt et al. (1990)
NE Atlantic	3700 m		nd–5			Rosell-Melé et al. (2000)
Mediterranan, DYFAMED site	200 m	2.1–34.7				Marty et al. (1994)
Mediterranan, DYFAMED site	200 m		0–9			Ternois et al. (1997)
Mediterranan, DYFAMED site	200 m	1.4–29.7	0–14.2	0.3–9.3	31–377	This work

[a] Flux of thes sum of C_{37}, C_{38} and C_{39} alkenones.
[b] Flux of 4α,23,23-trimethylcholest-22-en-3β-ol (dinosterol).
[c] Flux of the summed C_{37} and C_{38} alkenones.
[d] Flux of $C_{37:2}$ methyl alkenone.
[e] Flux of 24-methylcholesta-5,24(28)-dien-3β-ol.

Table 6. R^2 values of the correlation between selected fluxes and C-normalized abundances of biomarkers. $n=31$, significant correlations are indicated by numbers in bold.

Correlation with fluxes of:	4α,23,24 triMe Δ22	24MeD5,22	Correlation with C-normalized abundances of:	4α,23,24 triMe Δ22	24MeD5,22
Sum C_{37} alkenones	**0.827**	**0.793**	Sum C_{37} alkenones	0.289	0.139
Δ5, 22	**0.729**	**0.788**	Δ5, 22	**0.356**	**0.465**
Δ5	**0.403**	**0.392**	Δ5	0.095	0.085
24-Methyl Δ5,22	**0.961**	–	24-Methyl Δ5,22	**0.783**	
Cholest-4-en-3-one	**0.557**	**0.498**	Cholest-4-en-3-one	0.169	0.092
24-Methyl Δ5,24(28)	**0.933**	**0.939**	24-Methyl Δ5,24(28)	**0.676**	**0.827**
24-Ethyl Δ5	**0.984**	**0.986**	24-Ethyl Δ5	**0.866**	**0.893**
4α,23,24-Trimethyl Δ22	–	**0.961**	4α,23,24-Trimethyl Δ22		
C_{30} alka-1,15-diol	**0.838**	**0.744**	C_{30} alka-1,15-diol	**0.650**	**0.399**
Sum C_{22}-C_{26-OH}	**0.587**	**0.647**	Sum C_{22}-C_{26-OH}	**0.348**	**0.329**
$C_{37:3}$ Methyl alkanone	**0.815**	**0.797**	$C_{37:3}$ Methyl alkanone	**0.637**	**0.466**
Sum odd HNA $C\geq25$	**0.787**	**0.829**	Sum odd HNA $C\geq25$	**0.323**	**0.543**
Total C	**0.708**	**0.679**			
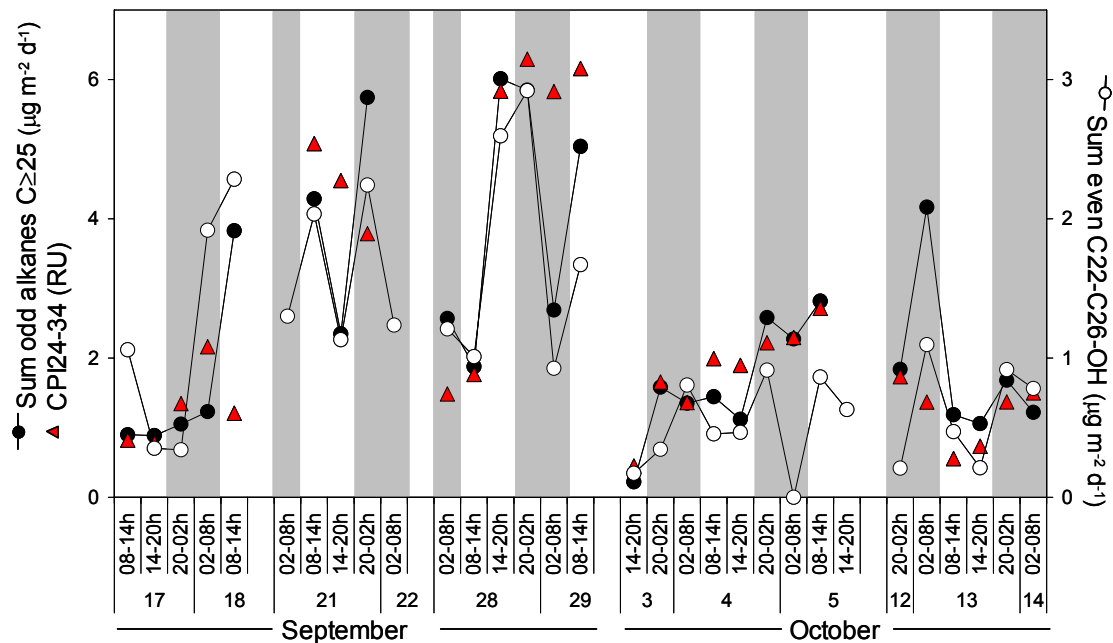
Fig. 1. Fluxes of higher plant biomarkers: odd n-alkanes having 25 C atoms and more and even n-alkanols having 22, 24 and 26 C atoms. Red triangles indicate the Carbon Preference Index of n-alkanes in the C range C_{24} to C_{34}. Grey filling indicate night-time collection of particles.
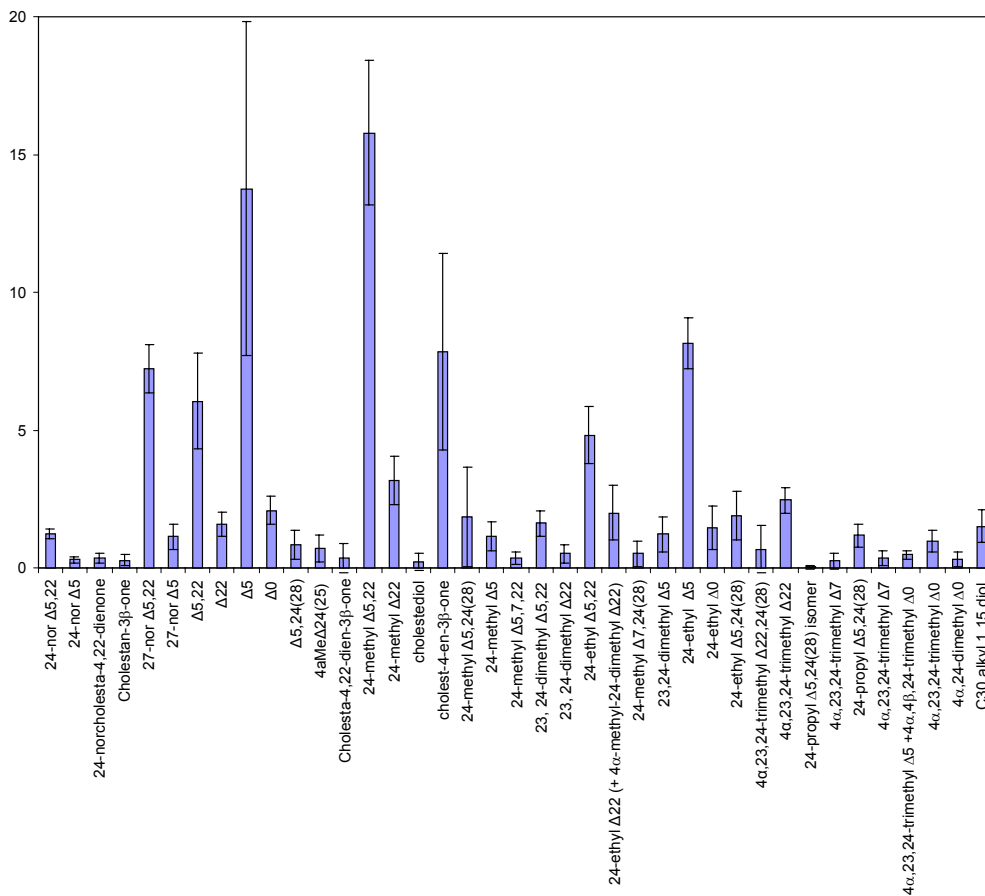
Fig. 2. Average composition of sterols. Sterol abundance are given in percent of all identified compounds in the alcohol fractions: sterols, *n*-alkanols, alkane diols, hydroxy alkenones and steroidal ketones.
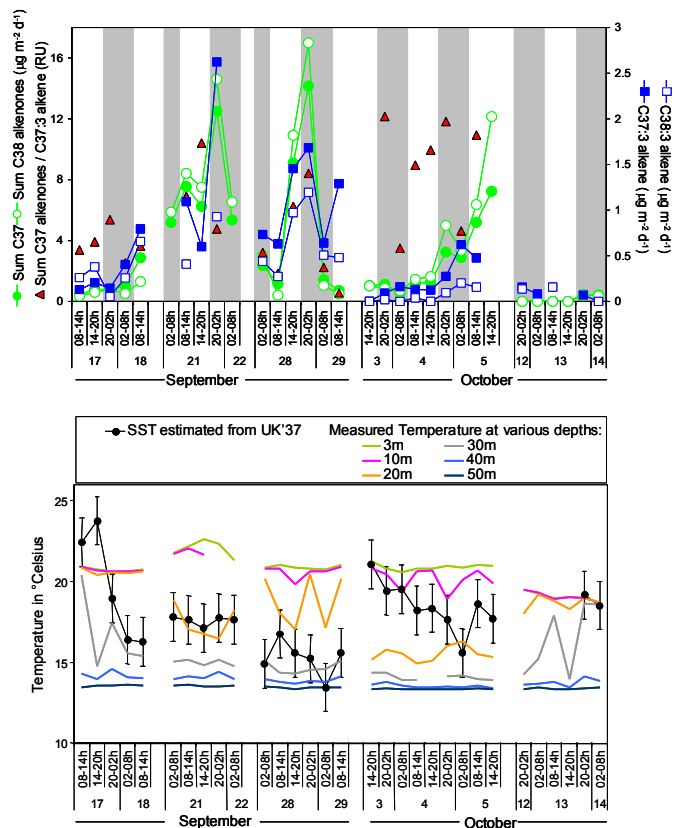
Fig. 3. (a) Fluxes of biomarkers for alkenone-producing Haptophytes, mainly of the genera *Emiliana* and *Gephyrocapsa*. Sum C_{37}: sum of C_{37} alkenones and alkenoates; Sum C_{38}: sum of C_{38} alkenones and alkenoates. $C_{37:3}$ alkene and $C_{38:3}$ alkene are the fluxes of the corresponding long-chain alkenes. Red triangles indicate the ratio of C_{37} alkenones and alkenoates to the alkene $C_{37:3}$. Grey filling indicate night-time collection of particles. **(b)** Comparison of reconstructed SST to hydrocast temperatures at various depths.
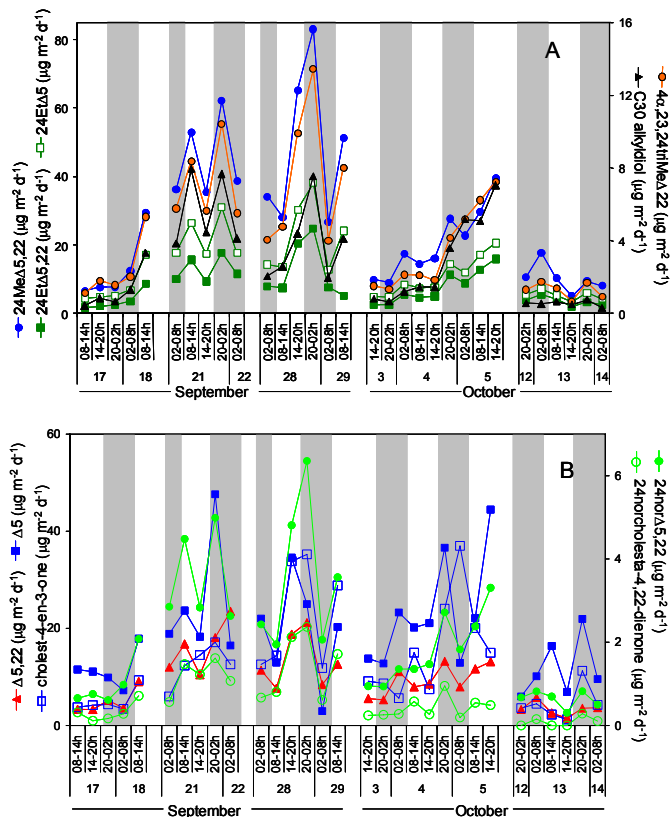
Fig. 4. **(A)** Fluxes of selected phytoplanktonic biomarkers: sterols and C30 alkane diol. **(B)** Fluxes of sterols in part contributed by zooplankton: Δ5: cholest-5-en-3β-ol: Δ5,22:cholesta-5,22-dien-3β-ol. 24-norΔ5,22: flux of 24-nor-cholesta-5,22-dien-3β-ol. Fluxes of steroid ketones: cholest-4-en-3-one, oxidation product of cholest-5-en-3β-ol, and 24norcholesta-4,22-dienone, oxidation product of 24-nor-cholesta-5,22-dien-3β-ol. Grey filling indicate night-time collection of particles.
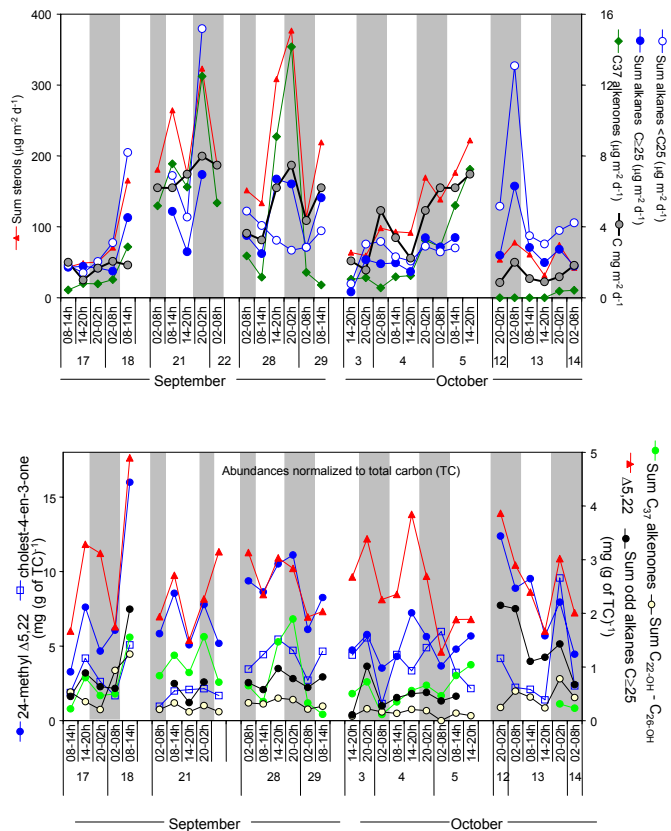
Fig. 5. (A) Comparison of fluxes of some lipid classes under study (sterols, short and long-chain *n*-alkanes and C_{37} alkenones) to the flux of total C. Grey filling indicate night-time collection of particles. **(B)** Fluxes of selected biomarkers normalized to total C.