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Short term variability of dissolved lipid classes during summer to autumn transition in the Ligurian sea (NW Mediterranean)

M. Goutx[1], C. Guigue[1], D. Aritio[1], J. Ghiglione[2,3], M. Pujo-Pay[2,3], and V. Andersen[4]

[1]CNRS-INSU UMR 6117, Laboratoire de Microbiologie, Géochimie et Ecologie Marines, Observatoire du Centre d'Océanologie de Marseille, Campus de Luminy, 13288 Marseille Cedex 09, France
[2]CNRS, UMR 7621, Laboratoire d'Océanographie Biologique de Banyuls, Avenue Fontaulé, BP44, 66650 Banyuls sur mer, France
[3]UPMC, Univ. Paris 06, UMR 7621, Laboratoire ARAGO, Avenue Fontaulé, BP 44, 66650 Banyuls sur mer, France

[4] Observatoire Océanologique de Villefranche-sur-mer; Université Pierre et Marie Curie-Paris 6; Institut National des Sciences de l'Univers (INSU), CNRS(UMR 7093), BP28, 06234 Villefranche sur mer, France

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Correspondence to: M. Goutx (madeleine.goutx@univmed.fr)

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Abstract

Changes in concentration and composition of dissolved lipid classes (Iatroscan TLC/FID) were examined at daily to month scale, in relation to the hydrological and biological situation at a central site of the Ligurian sea, NW Mediterranean during the PECHE-DYNAPROC 2 experiment (14 September to 17 October). Dissolved lipid concentrations (TLd) and lipid to DOC ratios varied in the range 5.3–48.5 $\mu g\, l^{-1}$ and 0.01 to 0.08 respectively, along the 0–1000 m water column. The highest TLd concentration values were found in the 0–150 m surface layer coinciding with phytoplankton biomass. Lipid class composition provided valuable information on the origin of DOM, and the changes that occurred during the period investigated. The significant correlations ($p<0.01$, $n=87$) between glycolipids from chloroplast membrane (MGDG) (38.7±8.5% of TLd, $n=166$), and various phytoplankton pigments (chlorophyll cs-170, violaxanthin, diadinoxanthin, zeaxanthin, and lutein), suggested that picoeucaryotes were the major source of dissolved lipids. Lipid metabolites (37.6±11.1%, $n=166$), the second most important compounds in TLd, showed a greater degree of degradation of lipids in this transition period than previously observed earlier in the year. A contribution of lipids to DOM in the mesopelagic zone was observed before the winter mixing: At mid time of the cruise (4–6 October), zooplankton wax esters biomarkers (WE, 5.5–13.6 $\mu g\, L^{-1}$) appeared in the 0–150 m surface layer. WE were observed later and deeper in the mesopelagic layer (6 to 11 October), accompanied by re-increases of hydrocarbons (6–8 October) and phospholipids concentrations (12 October) in the 400–1000 m depth layer. Zooplankton migration and/or fecal pellets egestion, followed by DOM release from POM, were likely responsible for the appearance of these lipid signatures in the mesopelagic layer, which occurred during the period of low wind (<15 knots) (28 September–12 October). The low salinity water lenses that appeared twice during the cruise in the 40–80 m surface layer had little effect on total biogenic lipid concentrations. Lower concentrations in phosphoglycerides and hydrocarbons than the nearby sea water suggested different microbial assemblages and different

level of HC contamination in this less-salted water.

1 Introduction

Marine dissolved organic matter (DOM) is an essential reservoir for the carbon cycle on the Earth (Hansell and Carlson, 2002). In the ocean upper layer, primary production by photosynthetic microorganisms is a major sources of DOM, primarily composed of proteins, carbohydrates and lipids. Understanding the dynamics of these biomolecules, their resistance to remineralization and their transformation to more complex and refractory substances is essential to predict the response of biogeochemical cycles to climatic changes. Only a small proportion (<11%) of DOM is identifiable using current analytical technics (Benner, 2002). Athough DOM complex molecular assemblages are the major candidate for further characterisation (Mopper et al., 2007), the distribution of identifiable peptides, carbohydrates and lipids in DOM has not yet been clearly documented in the marine environment mainly due to limitations in methodologies

Lipids represent from a few percent to 40% of the easily identifiable carbon fraction of DOM. They are membrane compounds, reserve products or metabolites from anabolism or catabolism in plankton cells (Parrish, 1988). Qualitative changes in their composition can be studied through the variability of selected lipid classes (Parrish, 1988), namely the cell membranes phospholipids and sterols from living organisms, the chloroplast membrane lipids (pigments and glycolipids) from autotrophic cells and phytodetritus, the reserve lipids from zooplankton (wax esters and triglycerides) and phytoplankton (triglycerides) and the degradation metabolites of these source lipids, indicating the degradation status of the organic material (Goutx et al., 2000, 2003, 2005). They are released from living organisms through exudation, cell lysis or grazing, fueling the dissolved pool, and further used by heterotrophic bacteria and/or exported to depth. The constitutive fatty acids of various lipids have been extensively used as biogeochemical markers of sources and diagenetic process of organic matter in suspended, sinking particles, and sediments (Saliot et al., 1991; Wakeham et al., 1995).

Comparatively, dissolved lipid classes concentrations in the marine environment are poorly documented.

Dissolved lipids are operationnally defined by the GF/F 0.7 µm membranes that separate suspended particles from truly dissolved lipids, colloids, and bacteria (Liu et al., 1998). Intact dissolved lipid classes have been studied in the extracellular medium of microalgae culture to evaluate their capacity as food web substrates (Kattner et al., 1983; Parrish and Wangersky, 1987; Lombardi and Wangersky, 1991), to characterize extracellular substances that may be responsible for the toxicity of phytoplankton blooms (Parrish et al., 1994) and to identify tensio active substances in bacterial culture growing on hydrophobic substrates (Goutx et al., 1987, 1990). Recently, the need to find new biomarkers in the polar lipid fatty acids (glycolipids, phospholipids), and to understand the potential role of phospholipids in phosphorus cycling, have revived research on intact polar lipids and revealed the lack of data, on phospholipids in particular, and other intact dissolved lipids, in the marine environment (Suzumura, 2005). Comprehensive studies of the distribution and dynamics of dissolved lipid classes have mainly focussed on the transport of lipid DOM by rivers, estuaries and urban discharge at land/ocean interfaces (Parrish, 1987; Leveau et al., 1990; Jaffé et al., 1995; Derieux et al., 1998; Mannino and Harvey, 1999; Rütters et al., 2002). Only few studies have reported on the distribution of dissolved lipid classes in the open sea (Parrish et al., 1988; Goutx et al., 1990; Gérin and Goutx, 1994; Parrish et al., 1995).

Analytical limitations due to low lipid class concentrations in the open ocean are a major obstacle to the study of dissolved lipids in marine systems. The traditional methods of thin-layer or column chromatography, require a significant amount of material, which can be problematic in field studies. The analytical TLC/FID technic on an "Iatroscan" apparatus allows detection of low concentrations of lipids without prior splitting of the extract, and opens very interesting prospects by removing a major obstacle to the study of neutral and polar lipid classes in the marine environment. This technique involves a qualitative separation of the lipid extract by thin-layer chromatography on chromarods coupled to a quantification of separated compounds by flame ionization

detection. Developments in the Iatroscan lipid analytical protocole have been proposed by Delmas et al. (1984), Gérin and Goutx (1993), Parrish et al. (1996) and Striby et al. (1999). As this methodology requires a little extract for lipid class separation compared to current methodologies, it requires a less important drawdown of seawater and therefore seemed to be a priori a technic of choice enabling the exhaustive sampling required for describing short temporal or spatial scale variability of chemical organic species in marine ecosystems.

In the present study, using this last technique, we examined the short term changes in abundance and composition of neutral and polar dissolved lipid classes in the 0–1000 m water column. By processing a large set of ∼90 samples at daily and monthly time scale at a fixed station in the open Ligurian sea, in the NW Mediterranean Sea, our overall objective was to better understand relationships between physical and biological forcings, and the short time variability of the organic chemical content in the water column, during the summer oligotrophy to autumn transition period, in Northwestern Mediterranean.

2 Material and methods

2.1 Study area and sample collection

The sampling was made at a central point (PC, 43°25′ N, 8° E; circa 30 miles offshore) in the Ligurian sea (North-Western Mediterranean) during the 2004 DYNAPROC 2 cruise (14 September to 17 October) on board the O/V Thalassa (Fig. 1). The dynamics of the biological system was studied in the 0–1000 m water column during four cycles of 5 days each (Andersen et al., 2008), two cycles during Leg 1 (C1 and C2; 17 to 29 September) and two cycles during Leg 2 (C3 and C4; 3 to 16 October). Sampling frequency was 3 h or 12 h depending on parameter and process. For dissolved lipids, a minimum of two 0–1000 m CTD profiles were sampled at the beginning of each cycle (two profiles at C1, C2 and C4, and five profiles at C3) at 12 h interval (one around

midnight and one around midday). Additionnal 0–150 m surface profiles at C1, and sub-surface (0–10 m) and chlorophyll maximum samples during the whole cruise, were collected in order to obtain a continuous pattern of dissolved lipids in the surface layer.

2.2 Dissolved lipid analysis

Water was transferred from the Niskin bottles with a Teflon tube into 5 litre glass bottles previously washed with chloride acid 2N and rinsed with MilliQ water. Four liters were gently filtered (pressure <15 mm Hg) onto pre-combusted (6 h at 450°C) glass fiber filters (GF/F) using all-glass cylinders and filtration kits to separate suspended particles from dissolved organic material. All glassware was previously washed with RBS detergent, HCl 2 N, then rinsed with MilliQ water and combusted for 6 h at 450°C or rinsed with acetone.

After addition of 100 µl internal standard (hexadecanone solution), dissolved fractions (2 l) were liquid-liquid extracted on board using 4 times 100 ml dichloromethane (Rathburn Chemical Ltd, HPLC grade) (2 times at pH<2). After decantation, the organic phases were combined, the volume reduced with a rotary evaporator and stored at −18°C under nitrogen atmosphere until analysis. The recovery of dissolved lipids was 70%±13 (n=167) based on Ketone internal standard.

Dissolved lipid classes were separated on chromarods and quantified on a thin layer chromatography/flame ionisation detection (TLC/FID) Iatroscan TH10 apparatus model MK-IV (hydrogen flow, 160 ml/min; air flow, 2000 ml/min) coupled to a compatible PC equipped with a Boreal integration system (Flotec company, 1989). Samples (4–6 µl of a 30 µl solution of the lipid extract in dichloromethane) were spotted using a 2 µl Hamilton syringe onto chomarods SIII previously calibrated with standard compounds (Sigma Chemical Ltd, GC grade). Analyses were run in triplicate.

The separation scheme involved five elution steps in solvent systems of increasing polarity: hexane+diethylether+formic acid, acetone, chloroform+methanol and chloroform+methanol+ammonium hydroxide according to a modified procedure of Goutx et al. (1990) described in Striby et al. (1999). The use of these elution systems separated

neutral lipid classes (hydrocarbons, sterol esters co-eluting with wax esters, ketone as internal standard, triacylglycerols, free fatty acids, alcohols, sterols and diglycerides), chloroplast lipids (pigments, glycolipids) and monoglycerides, and non-nitrogen containing phospholipids (diphosphatidylglycerides co-eluting with phosphatidylglycerides) from nitrogen containing phospholipids (phosphatidylethanolamine and phosphatidylcholine). The relative standard deviation of replicate samples (n=3) for Iatroscan TLC-FID analysis was below 12%. Total dissolved lipids concentration (TLd) was calculated by the sum of all lipid compound classes except hydrocarbons. As the biogenic origin of hydrocarbons cannot be ascertained, this lipid class is not included in Tld that thus referred to biogenic lipids. Hydrocarbon dynamic was then treated separately.

2.3 Dissolved organic carbon

Samples were filtered through 2 precombusted (24 h, 450°C) glass fiber filters (Whatman GF/F, 25 mm), collected into precombusted glass tubes (closed with a screw cap and a Teflon liner), poisoned with Orthophosphoric acid (H3PO4) and stored at room temperature until analysis. Dissolved organic carbon (DOC) was analyzed on a Shimadzu TOC-V using the high- temperature catalytic oxidation (HTCO) technique (Sugimura and Suzuki, 1988; Cauwet, 1994). Analytical precision of measurements was close to 2 µM. Deep Sargasso Sea reference water (47 mol L^{-1} C, ±0.5 SE, http://www.rsmas.miami.edu/groups/biogeochem/CRM.html) was injected every 10–12 samples to insure stable operating conditions.

2.4 Ancillary parameters

Meteorological (wind, rain), hydrological (temperature, salinity, density, nutrients, oxygen), biogeochemical (CDOM, pigments) and biological (bacteria, flagellates & ciliates, microphytoplancton, pico & nanophytoplankton, meso- and macrozooplankton) parameters were measured during this multidisciplinary cruise. Data are available on the web site, in previously published papers (Marty et al., 2008) and in companion papers

in the present BGS volume (Raybaud et al., 2008; Ghiglione et al., 2008; Lasternas et al., 2008; Mevel et al., 2008; Raybaud et al., 2008).

2.5 Statistics

Correlation analyses between lipid classes and ancillary parameters were conducted using the statistics package of Microsoft Excel (Microsoft Office Professional Edition 2003). Pearson's correlation coefficients were determined for pair-wise comparisons of total lipids, individual lipid classes and other environmental parameters (depth, salinity, temperature, oxygen, nutrients, DOC, particulate carbon, CDOM, Chl-*a*, phytoplankton pigments) with a significance level of $P<0.05$ assessed by Student's two-tailed t-test were considered significant. Values of $P<0.001$ were considered highly significant. The significance of mean comparison was assessed by ANOVA test using StatView 5 software.

3 Results

3.1 General hydrological conditions

The main hydro-biological characteristics during the cruise are presented in Andersen et al. (this issue#1). Briefly, the DYNAPROC 2 cruise was conducted during the seasonal transition period between summer and fall, a period marked by a decline in air temperature and the collapse of the summer water column stratification due to successive meteorologically forced mixing events. The cruise extended during two legs 14–29 September (Leg 1) and 2–17 October (Leg 2). We observed a strong water column stratification partially disrupted at the end of the cruise, low nutrients stocks and successive meteorological events. During Leg 1, two wind events from NE occurred (17 and 25 September). At the end of the cruise, a succession of gusts of wind from opposite directions: SW, NE and SW occurred. Temperature profiles showed

a highly stratified water column from the beginning of the cruise to 10 October. The thermocline was strongly marked, with a mixed-layer temperature higher than 20°C (22°C during weak wind periods). This thermocline was located at approximately 25 m depth throughout the cruise. At the end of the cruise, the thermocline deepened to 40 m depth after two successive strong wind events (11–16 October) accompanied by a decrease of air temperature and a cooling of the mixed water layer, which suggested the beginning of autumnal de-stratification.

Two intrusions of low salinity water masses (<38.2 psu) occurred below the thermocline (between 40 and 80 m). The first intrusion (LSW-1) lasted 5 days from 21 to 30 September (from JD265) and the second intrusion (LSW-2) for 4 days from 9 to 12 October (from JD283). At the early beginning of the cruise, two deep-chlorophyll maxima (DCM, 50–60 m and 90 m depth) were detected, resulting in a phytoplankton biomass exceptionally high for this time of the year (Chl-*a* concentration of 35–40 mg m^{-2}). After two days at the fixed station (19 Sep, JD263), only one DCM was observed at 40–50 m depth with a 0–150 m integrated value Chl-*a* concentration of 20–25 mg m^{-2} (Marty et al., 2008). The integrated primary production was 200 mg C m^{-2} d^{-1} on average, varying from 400 mg C m^{-2} d^{-1} at the early beginning of the cruise (thus 50 % higher than usually observed), down to 100 mg C m^{-2} d^{-1} at the end of the cruise. The overall characteristics of the site show that the DYNAPROC2 cruise covered a period of transient regime between late summer and autumn, but with hydrological and nutrient resources (N/P) similar to summer oligotrophic conditions (Andersen et al., this issue#(1).

3.2 Total dissolved lipids (TLd), TLd/DOC

TLd concentrations varied from 5.3 to 48.5 µg C L^{-1} (0.4 to 4 µM) (Supplement Table 1 http://www.biogeosciences-discuss.net/6/27/2009/bgd-6-27-2009-supplement.pdf). The highest values were found in the 0–150 m surface layer (Fig. 2). The concentration gradient with depth was more pronounced during Leg 1, with values ≤18 µg C L^{-1} below 100 m, than during Leg 2 when concentrations below the surface layer were up to 40 µg L^{-1} (Fig. 2). An increase of concentrations in the mesopelagic layer occurred twice dur-

ing the cruise, shortly at the beginning of Leg 1, 19 September (27.4 µg L^{-1}) at 600 m depth, and several times during Leg 2 (up to 43.9 µg L^{-1} between 6 and 12 October) in the 400–800 m layer. The day/night pattern of TLd profiles was not significant throughout the period investigated although lower concentrations at night than during the day were observed during Leg 2 (Fig. 3). DOC varied by a factor of 2 from surface to depth in the range 38–70 µM. Concentrations (70±2.9 µM) were maximal in the 0–10 m subsurface waters, then decreased following a moderate gradient down to 51.4±1.7 µM in the 60–70 m water layer and almost homogeneous values down to a minimum concentration at 1000 m depth (39.8±0.7 µM) and no apparent difference between days and night (Fig. 4). The contribution of TLd to DOC varied in the range 0.9–9.1% (Fig. 5). The highest values (≥7%) were observed within the 400–800 m depth layer, during the Leg 2 on 6 October during day and night, and 8 October during the day, a pattern due to the increase of lipid concentrations while DOC concentrations remained quite stable. The only significant re-increase of DOC (+20 µg L^{-1}) at depth (700 m) was noticeable later at the end of Leg 2 (12 October). An increase of the percentage of TLd in DOC (>5%) was occasionally observed on a day profile, during Leg 1 (19 Sep at 700 m). In order to emphasize the lipid pattern in DOC at seasonal scale, the average concentrations of DOC and total lipids were computed in the 0–150 m surface and the 150–1000 m mesopelagic layers during Leg 1 and 2 (Table 1). Overall, there was an increase in the contribution of dissolved lipids to DOC in the mesopelagic layer from an average 3.3±1.1% in September (Leg 1) to 4.3±1.8% in October (Leg 2) (ANOVA, $p<0.05$, $n=31$), whereas the TLd/DOC ratio in the 0–150 m surface layer were similar (2.9±1.1% and 3.1±1.1%, respectively). Daily variations of TLd contribution to DOC were not significant.

3.3 Lipid classes

Lipid class concentrations are presented in the Supplement Table http://www.biogeosciences-discuss.net/6/27/2009/bgd-6-27-2009-supplement.pdf. The

relative contribution of phospholipids, chloroplast lipids (glycolipids and pigments), triglycerides, wax esters and metabolites to the lipid pool showed a quite stable pattern during the sampling period (Fig. 6). Table 2 provides the average concentration of lipid classes during the whole cruise (all depths). Except hydrocarbons, the glycolipids (monogalactosyldiglycerides) were the major lipid class, followed by pigments, monoglycerides and non nitrogen containing phosholipids (phosphoglycerides). Thus the so-called chloroplast lipids that includes glycolipids and pigments, varied between 2.1 µgC L^{-1} and 21.9 µg C L^{-1} (Supplement Table http://www.biogeosciences-discuss.net/6/27/2009/bgd-6-27-2009-supplement.pdf) and dominated the lipid pool (38.7±8.5% on average, $n=166$) (Table 2), which suggested a phytoplankton source for DOM. The highest values were measured in the 0–80 m upper layer, at the beginning of Leg 2. High values (circa 10–14 µg C L^{-1} were also found at depth in the 400–800 m layer (6 and 8 October) (cf. Supplement Table http://www.biogeosciences-discuss.net/6/27/2009/bgd-6-27-2009-supplement.pdf). The second most important class of compounds were the lipid metabolites (FFA, ALC, MG and DG) (37.6±11.1% on average, $n=166$) (Table 2 and the Supplement Table http://www.biogeosciences-discuss.net/6/27/2009/bgd-6-27-2009-supplement.pdf), indicating hydrolysis of lipid DOM. Other intact lipids (PL, TG, WE) were present in lower proportions (on average 9.5±6.0%). Phospholipids were the less abundant lipid class in the concentration range 0–3.7 µg C L^{-1} (mean 1.0±0.6 µg C L^{-1}, $n=166$). A marked re-increase of PL concentrations was noticeable during Leg 2 at 150–200 m and 700 m depth (mean 3.1±0.3 µg C L^{-1}, $n=4$) (Fig. 7, 12 October, upper panel). The storage lipids, triglycerides (TG) and wax esters (WE), varied in the range 0–6.0 and 0–13.6 µg C L^{-1}, respectively. They were minor compounds not always present in the total lipids. The pattern of variation of TG and WE over time and depth is well described by comparing the 0–150 m and 150–1000 m integrated concentration values (normalized to a 150 m depth water column for the 150–1000 m values) (Fig. 8). During Leg 1, TG integrated values were higher in the 0–150 m surface waters than in the 150–1000 m mesopelagic layer, whereas an opposite pattern prevailed during Leg 2 that is TG integrated values in the mesopelagic layer were much

higher than TG integrated values in surface layer (Fig. 8, upper panel). During Leg 2, night concentrations were higher than day concentrations in the mesopelagic layer. WE occasionally appeared in the lipid pool during the Leg 1. WE contribution was much higher during Leg 2 than during Leg 1 both in the surface (4–6 October) (JD278-280) and in the 400–1000 m mesopelagic layer (6 to 11 October) (Fig. 8, lower panel).

Finally, the hydrocarbon pool varied in the range 0.9–21.9 µg C L^{-1} amounting 6.3±1.8%, on average, of the total lipids (Table 2). An increase of concentrations at 400–800 m depth occurred in 6–8 October (Fig. 7, lower panel).

3.4 Relationships between total lipids, individual lipid classes and environmental parameters (Salinity, Temperature, nutrients, chlorophyll-*a* , phytoplankton pigments)

Cross-correlations between bulk organic compounds (DOC, particulate carbon, CDOM), individual lipid classes, and environmental parameters (salinity, temperature, nutrients, Chl-*a*, phytoplankton pigments) were carried out using Pearson's product–moment correlation coefficient. In the 0–1000 m water column, significant correlations were found between total dissolved lipids, and concentrations of hydrocarbons, triglycerides, chloroplast lipids and metabolites (free fatty acids and alcohols) ($p<0.01$, $n=167$) (Table 3). These results which reflected the major contribution of these individual lipid classes to the dissolved lipid pool, whereas the minor lipid classes (wax esters and phospholipids) were not correlated with total lipids. This distribution reflected the background phytodetrital character of the lipid pool in the 0–1000 m water column and the episodic contribution of lipids from heterotrophs, zooplankton and bacteria.

Particulate carbon (PC) and DOC distribution in the 0–150 m upper water column were correlated (0.72, $p<0.01$), suggesting that DOC was formed through either exudation of living seston and/or particle dissolution (Table 3). In contrast, total dissolved lipid concentrations were not correlated with neither DOC nor PC, probably because other components like proteins and carbohydrates were the major contributors to these two pools. The only class of dissolved lipids, that was correlated with DOC and PC (0.57 and 0.45, $p<0.01$, respectively) was the glycolipids constitutive of the chloro-

plast membrane (the monogalactosylglycerides, MGDG). They were also significantly correlated with several individual pigments such as chlorophyll cs-170 (0.54, $p<0.01$), violaxanthin (0.43, $p<0.01$), diadinoxanthin (0.47, $p<0.01$), zeaxanthin (0.52, $p<0.01$), and lutein (0.49, $p<0.01$), which all together indicated a picoplanktonic sources of material, and suggests a direct transfer of MGDG from the intracellular picoplankton lipid pool to the dissolved lipids. In contrast, MGDG and coloured dissolved organic matter (CDOM) were not related to each other. CDOM unlike MGDG was not related to DOC, but was correlated with particulate carbon ($p<0.05$, $n=81$), total fluorescence and almost all individual pigments including the five pigments cited above (cf. Table 3). Particulate carbon, DOC, MGDG and CDOM were tighly related to most bacterial parameters.

4 Discussion

Our study provides the first data set on total lipid concentrations and lipid class composition in DOM from the surface to the mesopelagic layer in the open Ligurian sea. The potential of such data as a reference for the late summer to autumn period in North Western Mediterranean is extremely strong. The amount of lipids that we measured in 2004 were in the lower range of values previously reported for marine coastal inlets and open sea areas (11–580 µg L^{-1}) (Table 4).

4.1 Seasonal variations of the total lipid pool

Measurements of lipid class concentrations in the 0–150 m euphotic layer at the Dyfamed site have been previously obtained at different times of the year 1999 (unpublished data) in the framework of the Dyfamed time series observations (Marty et al., 2002). Lipid class concentrations were also measured at this site in March and June 2003 (Ghiglione et al., 2007; Bourguet et al., 2008) in the framework of the PECHE project (Production and Exportation of carbon: Control by HEterotrophs at short time

scale). It is thus possible to extend the temporal scale of the average lipid class concentrations measured in the 0–150 m euphotic layer during the Dynaproc2 cruise to an annual time series (Fig. 9): Dissolved lipid concentrations were generally low in winter, maxima in summer oligotrophy (June–August 1999 and June 2003) and returned to low values in autumn. Interestingly, this pattern suggests that lipid accumulations that occurred during summer oligotrophy (Van Wambeke et al., 2001; Bourguet et al., 2008) did not persit at the surface until the winter mixing. During late summer and autum, lipids may be either remineralized, transformed through biotic and abiotic process into another type of material which is not captured by our analytical methodology or exported to depth by other means than the mixing of water masses.

4.2 Source of dissolved lipids in the surface 0–150 m layer

Lipids are an important component of photosynthetically-produced organic matter and a close relationship between chlorophyll-*a* and lipids was expected. However computations of literature data (cf. Table 4) did not show any significant relationship between TLd and Chl-*a* despite a couple of high lipid concentrations acompanying the highest Chl-*a* values in the Bedford Basin (Parrish, 1987) or in the Rhone river plume (Leveau et al., 1990). Similarly, at a smaller spatial scale, time series observation of dissolved lipid class concentrations during phytoplankton blooms did not show significant correlation between Chl-*a* and TLd (Morris et al., 1983; Parrish, 1987). In these studies, only intracellular TG concentrations were related to Chl-*a*, which supported the conclusion by the authors that nitrogen availability was the major factor driving lipid content in particles at the time of phytoplankton blooms; TLd rather accumulated before and after the blooms. This suggests that either the dissolution of the detritic phytoplankton biomass into the dissolved pool was not the major factor of distribution of dissolved lipid classes, or that partially fractionnated polar lipid classes would not be the best proxies for evidencing such relation. Indeed in the studies cited above (cf. Table 4), there was no separation of the acetone mobile polar lipid (AMPL) peak, the so-called chloroplast lipids, into its various components, i.e. monoglycerides (MG), pigments, and glycolipids

(MGDG). These compounds have different origin and different susceptibility to bacterial attack. Degradation rates have been reported by several authors (Harvey et al., 1995, 1997; Goutx et al., 2003; Caradec et al., 2004; Goutx et al., 2007; Moriceau et al. 2008). Goutx et al., and Moriceau et al., both reported that as soon as mineral dissolution started, MGDG turned over more rapidly than the other AMPL lipids, i.e. the monoglycerides and pigments. Hence, due to difference in residence time, lipid classes resulting from diagenetic processes may have hidden the origin of dissolved lipids. In our study, the AMPL peak was fractionnated into its various components (Striby et al., 1999), which may be the cause of the significant relation observed between glycolipids (i.e. MGDG) and specific picoplankton pigments.

A striking feature of the relationship between phytoplankton lipid biomarkers and organic matter descriptors was the significant correlations between particulate carbon (PC), DOC, glycolipids (MGDG) and picoplankton pigments on the one hand, and PC, CDOM, Chl-*a*, and most pigments on the other hand. This pattern suggested differences in formation process of CDOM and DOC during the summer to autumn transition period. CDOM would rather be formed through intramolecular reactions of organic biomolecules from the decaying pico- and microphytoplankton under a combinaison of biotic and abiotic factors including light radiation (Yentsch and Reichert, 1961; Sieburth and Jensen, 1969); DOC dynamics would mostly be controlled by the release of material from picoplankton, probably through lysis and/or grazing, as suggested by the double correlation with glycolipids and picoplankton pigments.

Below 60 m depth, the decrease of lipid concentrations suggested that stratification limited the transfert of phytoplankton lipids (and by extrapolation, of other phytoplankton material) from the productive layer to the mesopelagic layer. These conditions would set up conditions of carbon limitation for the microbial population below this depth, which is consistent with observations made by Van Wambeke et al. (2008) during the Dyanproc2 cruise.

4.3 Degradation statuts of the dissolved lipid pool

The second major dissolved lipid pool was the lipid metabolites (FFA, ALC, MG and DG). Release of metabolites occurs through the enzymatic clivage of esters bounds of source glyceride lipids (Goutx et al., 2003). When the readily available molecules derived from phytoplankton start to be depleted, bacteria activate their enzymatic systems that cleave biopolymers into monomers (Hoppe, 1993). In our study, bacterial production was significantly correlated with the various organic matter descriptors (particulate carbon, DOC, MGDG and CDOM). This observation supports the view that labile carbon material available for bacteria metabolism was becoming increasingly scarce and that bacteria were hydrolyzing biopolymers from a wide range of organic material as the system was ageing. Enzyme activity and bacterial production are not always tightly coupled, and accumulation of monomers (i.e. metabolites) is a function of this coupling/decoupling (Van Wambeke et al., 2001; Mullholand et al., 2007; Bourguet et al.; 2008). Small lipid metabolites may be less reactive to bacteria than more complex and fresh biopolymers (Loh et al., 2004). In addition, lipid metabolites accumulation may be inferred to the presence of zooplankton digestive enzymes (Weeks et al., 1993). Finally, the accumulation of acyl lipid metabolites in the system may result from the maturation and shift of communities from autotrophic to heterotrophic as already reported in the Ligurian sea (Van Wambeke et al., 2001). This view is supported by the high contribution of metabolites to total dissolved lipids during late summer to autumn 2004 (on average 37.6±11.1%, n=166), compared to spring and summer 2003 period (23.9±16.9% (n=12) and 28.1±6.0% (n=16), respectively) (Bourguet et al., 2008). At the end of the stratification period, MG constituted the largest pool of metabolites. This dominance suggests that MG was poorly digested by bacteria compared to free fatty acids and alcohols according to Gurr and James (1980).

4.4 Inputs of dissolved lipids to depth

Few studies have considered the dynamics of dissolved lipids beyond the euphotic layer. In our study, lipid concentrations exhibited a remarkable stability with a maximum of 40% variability in concentrations from surface to 1000 m depth throughout the period investigated. Such stability characterized several other biological and chemical parameters (Ghiglione et al., 2008; Lasternas et al., 2008; Marty et al., 2008; Mevel et al., 2008; Raybaud et al., 2008) that were studied during the Dynaproc cruise, probably due to the exceptional hydrological calm encountered during this late summer to autumn transition period.

In such hydrological conditions with limited physical and hydrological forcings, the impact of biology on dissolved lipid distribution prevailed. The larger variations of lipid concentrations in the 0–150 m surface layer compared to the 150–1000 m layer (cf. Table 1), were due to microbiological production in the euphotic layer reported by Marty et al. (2008) and Mevel et al. (2008). Below 150 m depth during Leg 2, peaks of lipid concentrations (cf. Fig. 2) reflected an export of lipids from surface to depth that was not related to the DOC export through the deepening of the mixed layer that we observed the last days of the cruise. It suggests that carriers responsible for lipid transport to the mesopelagic layer were different from those transporting the other DOC components. Because of the presence of zooplankton biomarkers in the 0–150 m layer in the early Leg 2 and later in the 400–700 m deep lipid peaks, one potential carrier may be the zooplankton through its daily migration (i.e., Raybaud et al., 2008), in addition to the transfert to depth and dissolution of their fecal pellets. The double signature of TG and WE in sinking particles has already been inferred to fecal pellets of carnivorous euphausiids during Dynaproc 1 experiment (Goutx et al., 2000). Moreover, carnivorous zooplankton was identified as a major trophic element during the Leg 2 (Mousseau et al., 2008).

The export of hydrophobic contaminants like hydrocarbons has been previously related to the vertical transport of lipid material in sedimenting particle (Andersson et al.,

1993). As inferred during periods of increasing productivity, the nature of sinking particles may also impact the hydrocarbon flux. Bouloubassi et al. (2006) showed that the flux of fecal pellets was able to carry a significant fraction of hydrocarbon oil to depth. During the Dynaproc 2 cruise, the high HC concentrations observed at 700 m during Leg 2 may be related to egestion of fecal pellets from zooplankton, followed by disagregation/dissolution of the pellets within the mesopelagic layer, a scenario supported by the presence of zooplankton biomarkers at depth during Leg 2. At the surface, the origin of hydrocarbons may probably result from a background contamination of the lipid pool by anthropogenic HC, as revealed by the high HC percentage (24.7%±3.2) in TLd (Goutx, 1988).

The phospholipid signatures that were noticeable later on during Leg 2 (12 October) in the mesopelagic zone, were accompanied by the significant re-increase of DOC at depth. This change in PL concentration at 700 m depth between 6–8 October and 12 October amounted 1.5–2 µg L^{-1}. Marine bacteria contain a range of ∼2–7% lipids in total carbon, most lipids being under the form of membrane phospholipids (88±5% TL) (Goutx et al., 1990; Goutx, unpublished). Because most bacteria may pass through the 0.7 µm membrane, operationally defined for isolation of suspended particles from dissolved matter, bacteria may account for a substantial fraction of this deep "phospholipid" pool, as suggested by Wakeham et al. (2003). However, between 6–8 October and 12 October, the total bacterial biomass did not increase at this depth (Mevel et al., 2008). Increases were observed in free or non-particle associated bacterial production (x5) and abundance (higher of 9×10^5 cells L^{-1}) (Mevel et al., 2008) and ecto-enzyme activities (Van Wambeke, personal communication). Using the conversion factor of Findlay et al. (1989) for naturally occurring mixed population (3.4×10^9 cells or 192 mg of C per 100 nmol of phospholipid), we evaluated the PL increase as equivalent to 10^7–10^8 cells L^{-1} bacteria, which is far above estimated bacterial concentrations, and do not support the idea that these PL would represent the only BB increase. Phospholipid signature most probably derived from the flux of sinking particles described above, and reflected an input of fresh biopolymers at these depth through particle dis-

solution and bacterial enzyme attack. It is most probable that this input of fresh biopolymers stimulated the production of free living bacteria and may promote a mesopelagic microbial food web, which limited the bacterial abundance according to Tanaka and Rassoulzadegan (2004). This interpretation is consistent with previous observations that slowly sinking particles derived from trophic chains based on small particles would rather dissolve within the mesopelagic layer at Dyfamed (Goutx et al., 2007). It also supports the conclusion of Bendtsen et al. (2002) about the Greenland Sea, that deep-sea labile DOC may only be explained by a DOC released from the sinking flux of POC. Dissolution of POM would led to formation of colloids known to preferentially shelter phospholipids (Liu et al., 1998).

4.5 Relationship between lipid classes and low salinity index

An index in the range 0–1 of the presence of de-salted or diluted waters in the upper water column was calculated, based on average salinity S in the 40–70 m water layer, following the formula: Index(sta)=(Smax-S(sta))/(Smax-Smin); S(sta) is the average salinity in the 40–70 m layer, Smin is that of the water taken as reference for dessalted water (coastal waters in our case), Smax is that of the salinity waters without anomaly.

Average lipid class concentrations were calculated similarly in the 40–80 m (we had no sample at 70 m depth). Regression between the de-salted index and lipid classes resulted in significant correlations (Fig. 10) showing that the low salinity water (LSW) had lower concentrations in phosphoglycerides and hydrocarbons than the nearby sea water (HSW), Phosphoglycerides are among the major phospholipids in cell membranes of procaryotes and eucaryotes. Recent studies have attempted to determine their relative distribution among bacteria, pico- and microphytoplankton (Van Mooy et al. 2006). The decrease of PG concentration in the LSW reflected the change in microbial assemblages in LSW compared to HSW, reported by Mevel et al. (2008) and Lasternas et al. (2008). Dissolution properties of hydrophobic compounds may account for the difference in HC concentrations. It has been long established that organic compounds are generally less soluble in aqueous salt solutions, such as seawater, than

in pure water (reduced by 1.36), a phenomenon termed "the salting-out effect" (Xie et al., 1997). Studies examining the influence of salinity on hydrocarbons and PAH solubility in seawater have yielded similar conclusions. For 12 aromatic hydrocarbons, Sutton and Calder (1975) and McAuliffe (1987) found that the mean reduction in solubility at 25°C in seawater was about 68%, relative to fresh water. In our study, solubility was certainly not involved in the distribution of HC since there was an opposite relationship between HC dissolution and salinity. Interactions between PAH and particles can be affected by salinity. Unfortunately particle size distribution was not investigated during the Dynaproc2 cruise. In our study, the higher concentrations of HC in the HSW was surprising. Indeed, a higher contamination would be expected in waters coming from the coast, rather than from offshore sea water, due to ship concentration and/or resuspension of HC rich sediments in coastal zones. Finally, the time series of total dissolved hydrocarbon concentrations constitutes a unique data set for these compounds in offshore Mediterranean waters that may be of further used in environmental studies.

5 Conclusions

This study contributes to advances in DOM characterization and to the understanding of processes involved in short temporal and spatial scale variability of dissolved lipids at the oligotrophic Dynaproc2 station in the central ligurian sea, NW Mediterranean. Different processes were controlling the concentrations of lipid classes in the dissolved fractions throughout the water column. Changes in concentration and composition of dissolved lipid classes varied along the water column but significant variations also occurred during the summer to autumn transition. Values were high in the surface layer in relation with the phytoplankton biomass where picoeucaryotes appeared to be the major source of dissolved lipids. It is mostly that the supply of high-energy compounds far exceeded the demand by heterotrophs at that time. In parallel, the variations of the system over time during the seasonal transition marked by nutrient limitations, led to lipid degradation and metabolite accumulation that were higher than

previously observed earlier in the year. During the transition period, the stratification of the system was a factor limiting the distribution of fresh dissolved matter to depth. In these conditions, the lipid biomarker pattern in the mesopelagic layer highly suggested that the mesopelagic community was taking benefit from DOM release from sinking POM before the wintertime convection.

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Table 1. Average concentrations (±standard deviation) of dissolved organic carbon (DOC) and dissolved total lipids (TLd-HC) (hydrocarbons not included) and percentage of TLd-HC in DOC, in the water column (0–1000 m), the surface (0–150 m) and the mesopelagic layers (150–1000 m) during the two legs of the cruise, September (Leg 1) and October (Leg 2).

Dissolved Matter			DOC µM	TLd-HC µg C l^{-1}	TLd-HC/DOC %
Water column	0–1000 m	September	53.6 ±11.1 (*n*=62)	18.4 ±7.24 (*n*=72)	3.0 ±1.2 (*n*=62)
		October	52.4 ±11.3 (*n*=91)	21.2 ±8.42 (*n*=95)	3.5 ±1.5 (*n*=90)
Surface	0–150 m	September	57.9 ±9.75 (*n*=46)	19.6 ±7.3 (*n*=46)	2.9 ±1.1 (*n*=46)
		October	58.0 ±10.1 (*n*=63)	21.0 ±7.9 (*n*=64)	3.1 ±1.1 (*n*=63)
Mesopelagic	150–1000 m	September	41.3 ±1.9 (*n*=16)	16.3 ±6.5 (*n*=16)	3.3 ±1.3 (*n*=16)
		October	41.8 ±1.8 (*n*=32)	21.5 ±8.9 (*n*=31)	4.3 ±1.8 (*n*=31)

Table 2. Mean dissolved lipid class concentrations (n=167) in the water column at the Dynaproc 2 central station during the summer to autumn transition period (14 September–17 October). Abbreviations used for lipid classes. Contribution of each lipid class to total dissolved lipids including HC (TLd) and contribution to total dissolved lipids (not including HC).

Lipid class	Abbreviation	Concentration		Contribution to TLd		Contribution to TLd-HC	
		µg L^{-1}	±SD	%	±SD	%	±SD
Hydrocarbons	HC	6.33	1.81	24.69	3.25		
Wax and steryl esters	WE	0.53	1.08	2.10	1.51	2.32	1.61
Triglycerides	TG	0.68	0.31	2.60	0.84	2.94	1.14
Free fatty acids	FFA	2.62	2.00	10.10	3.65	11.38	4.62
Free aliphatic alcohols	ALC	2.84	0.89	11.10	2.42	12.34	2.57
1.3 Diglycerides	1.3DG	0.08	0.34	0.32	0.39	0.37	0.49
Free sterols	ST	0.01	0.08	0.04	0.10	0.05	0.11
1.2 Diglycerides	1.2DG	0.01	0.06	0.04	0.06	0.05	0.08
Chlorophyll pigments	PIG	3.13	1.08	12.17	2.09	13.58	2.45
Monoglycerides	MG	2.73	1.36	10.64	2.85	11.84	3.37
Monogalactosyldiglycerides	MGDG	5.78	0.94	22.38	4.60	25.09	6.11
Phosphoglycerides	PG	0.86	0.23	3.31	0.80	3.71	1.00
Phosphatidylethanolamines	PE	0.11	0.05	0.41	0.11	0.46	0.12
Phosphatidylcholines	PC	0.01	0.02	0.04	0.03	0.04	0.03

Table 3. Results from pairwise moment correlation coefficients matrix.
Significance of the correlation H0: R+0; *d.f.*=n−2=40. Dark grey =p<0.01; light grey =p<0.05; NS=Non significantly different from zero –> non correlated.

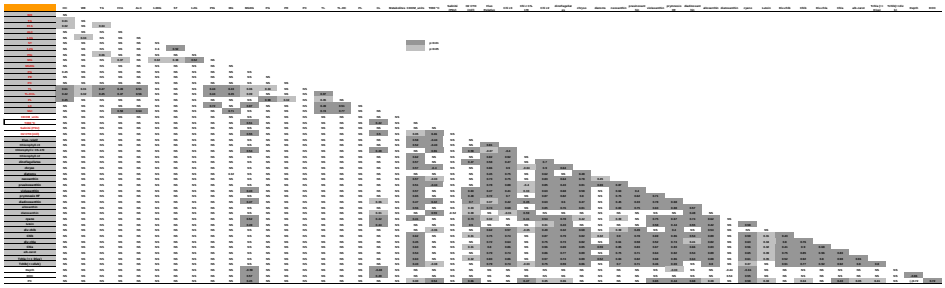

Table 4. Literature data of water column total dissolved lipid concentrations (TLd, µg L^{-1}) and total dissolved lipids not including hydrocarbons (TLd-HC, µg L^{-1}). All data were obtained by using TLC/FID except in Andersson et al. (1993) in which lipid extracts were weighted.

References	Location	Latitude	Longitude	Depth	TLd µg L^{-1}	TL-HCLd µg L^{-1}
Parrish 1987	Bedford basin, May-June 1982	44°41N	63°39W	bottom of surface mixed layer	75-498	71–468
Parrish et al., 1988	Scotian slope, April 1982	44°39–44°41N	63°34W–63°39W	under the picnoclyne	25–54	13–48
Parrish et al., 1992	Nova Scotia inlet (Urban & Rural), August 1989	44°39N	63°34W–63°39W	euphotic layer	96–156	86–144
Liu et al., 1998	Conception Bay, time series 1991–1993	47°32N	53°06W	euphotic layer (10–28 m)	18-56	nd
Striby & Goutx 1997	Gibraltar straight West, June 1997	35°55–36-06°N	5°19W	10–230 m	nd	17-135
Striby & Goutx 1997	Gibraltar straight East, June 1997	35°53–36-04°N	5°51W	10–300 m	nd	94–229
Grin & Goutx 1994	Almeria-Oran front, April 1991	35°43–36°51N	0°31–1°55E	0–1600m	11-273	9-113
Striby 2000	Almeria Oran front, December 1997	35°43–36°51N	1°55–0°31E	0–200 m	nd	2-134
Goutx et al., 1993	NW Mediterranean, Avril 1989	43°35–43°31N	7°29–7°38E	0–1000 m	45-126	33-112
Van Wambeke 2001	NW Mediterranean, May 1995	43°25N	7°52E	0–50 m	nd	21–234
Bourguet et al., 2008	NW Mediterranean, March 2003	43°25'N	7°52E	3–500 m	nd	12.4–40
Bourguet et al., 2008	NW Mediterranean, June 2003	43°25'N	7°52E	3–500 m	nd	11.8–78
Leveau et al., 1990	Rhone plume, May 1988	43°19N	4°5E	plume, interface plume–sea water	50–300	35-152
Derieux et al., 1998	Gulf of Trieste, June 1995	45°39N	13°29E	euphotic layer	49–88	49-77
Andersson et al., 1993	Baltic sea, time series 1982	63°31N	19°50E	euphotic layer (0–14 m)	25–270	nd
Nichols & Espey 1991	Malabar sewage (Sydney)	34°N	151°5E	air-sea interface	190–580	190–580

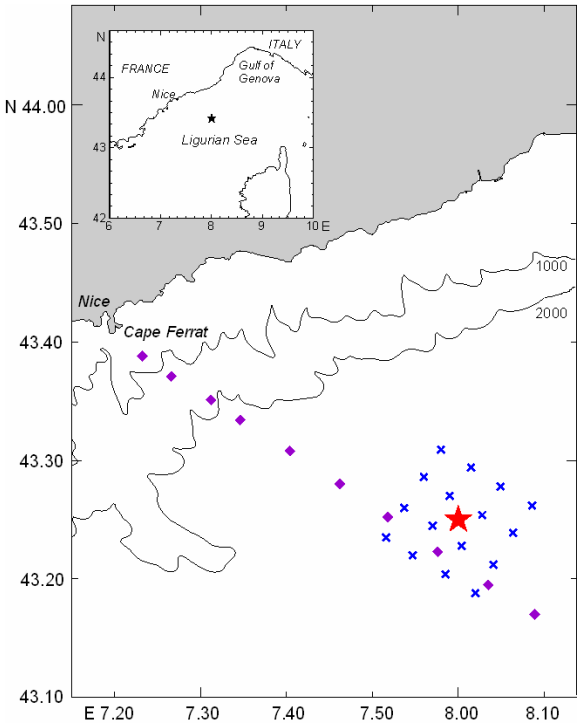

Fig. 1. Location of the time series station (*) sampled during the Dynaproc2 cruise, and grid of stations that enabled to characterize the physics and hydrology of the area.

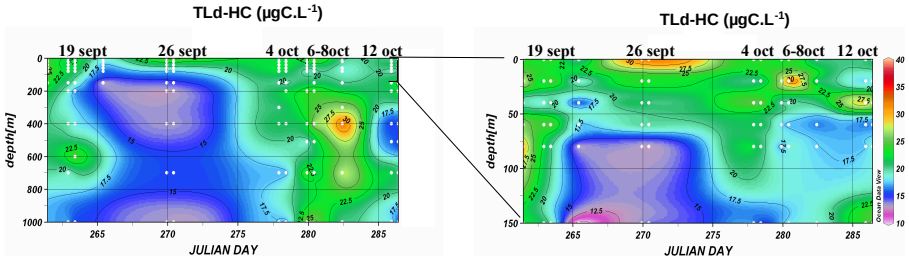

Fig. 2. Concentrations of total biogenic lipids (µg C L^{-1}) in the 1000 m (left) and in the surface 0–150 m (right) water column. Extrapolation ODV X and Y scale length 150.

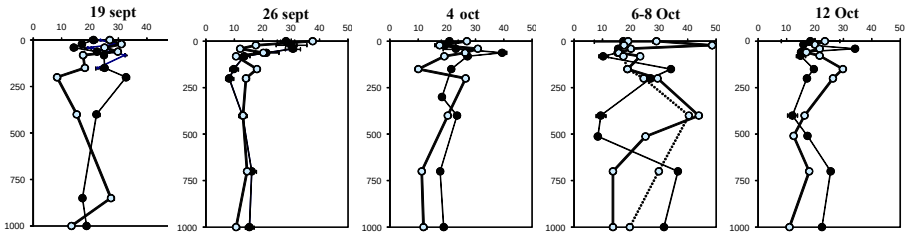

Fig. 3. Total dissolved lipids (HC not included) (µg C L^{-1}) in the 0–1000 m of the water column. days (open symbols) and nights (filled symbols) profiles.

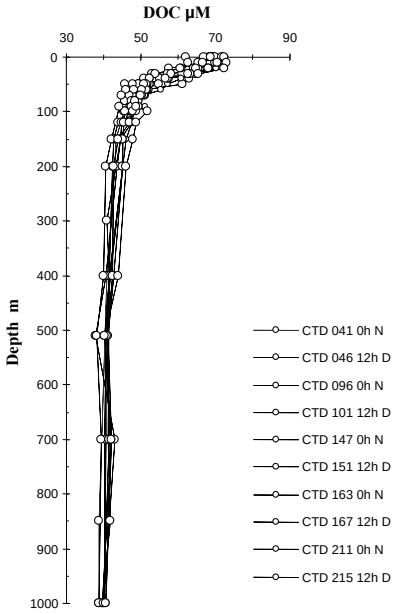

Fig. 4. Dissolved organic carbon concentrations.

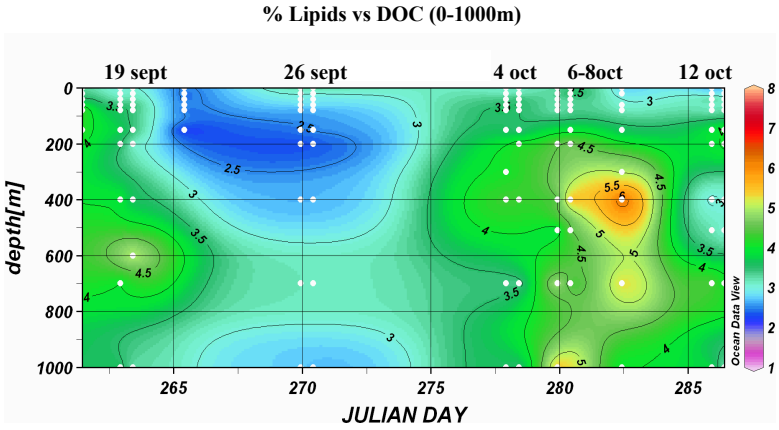

Fig. 5. Relative percentage of total lipids in DOC. Extrapolation ODV X et Y scale length 150.

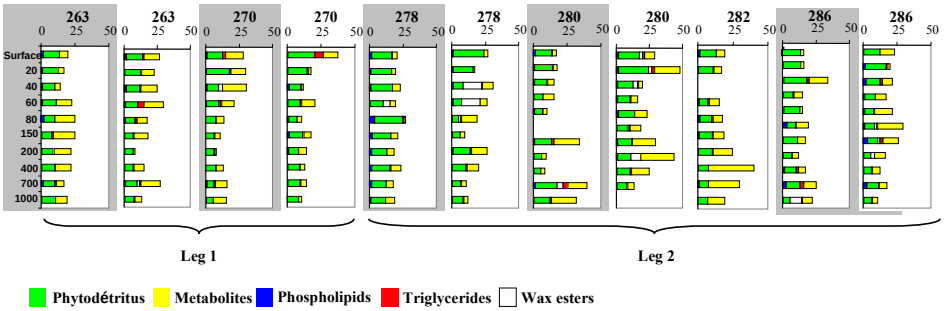

Fig. 6. Time series of dissolved lipid class distribution (μg C L^{-1}) during night and days sampling.

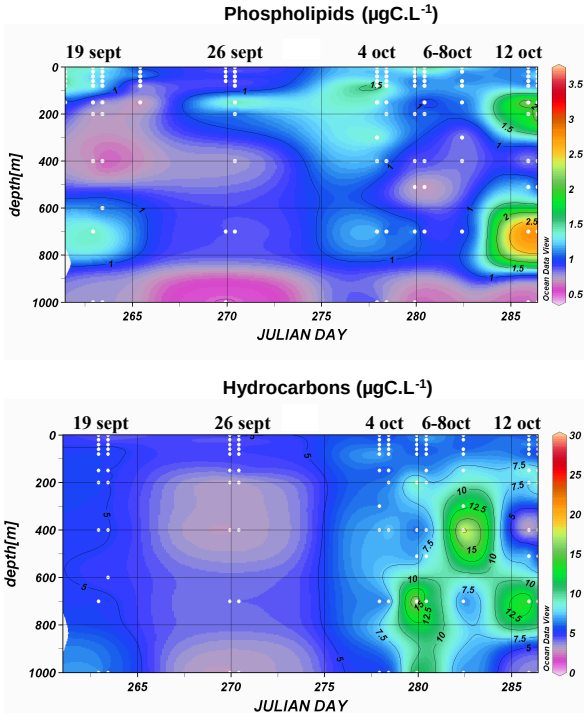

Fig. 7. Distribution of specific lipid markers (µ g C L^{-1}). Dissolved phospholipids (upper panel), and hydrocarbons (lower panel). Extrapolation ODV X et Y scale length 150.

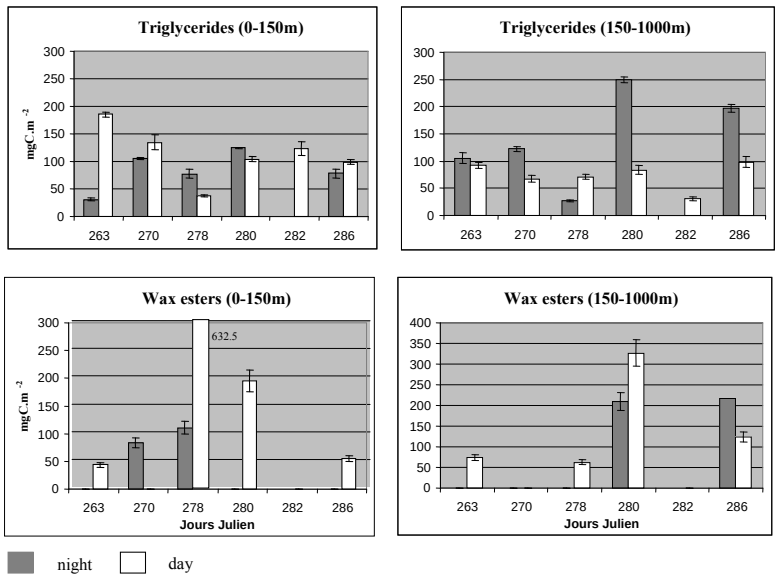

Fig. 8. Triglycerides (upper panel) and wax esters (lower panel) integrated concentrations in the 0–150 m surface and mesopelagic 150–1000 m layers.

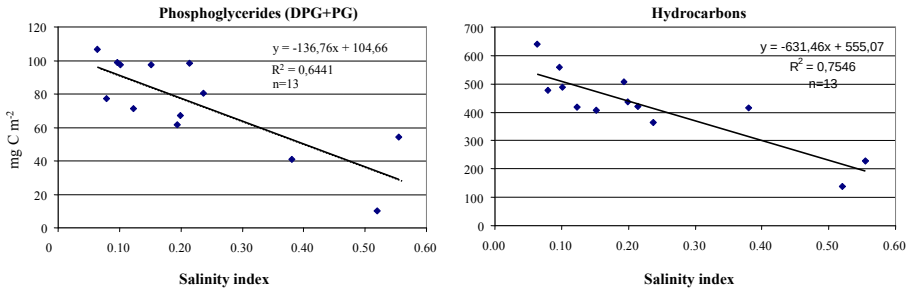

Fig. 9. Relationships between lipid biomarkers and salinity index. Lipid concentrations and Salinity index are integrated value between surface and 70 m depth.

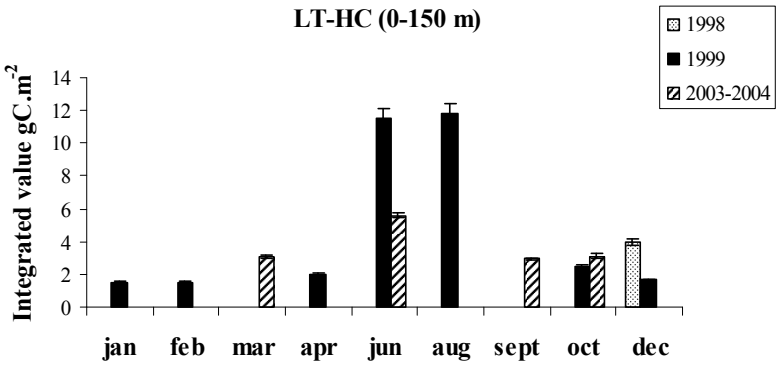

Fig. 10. Composite of total lipid concentrations measured in the framework of the Dyfamed time series observations (1998–1999) and in the framework of the PECHE project (March and June 2003, and September and October 2004).