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

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Abstract. Changes in concentration and composition of latroscan-measured dissolved lipids were examined at a daily to month scale, in relation to the hydrological and biological context at a central site of the Ligurian sea, NW Mediterranean during the PECHE-DYNAPROC 2 experiment (14 September to 17 October 2004). Lipid concentrations (excluding hydrocarbons) (TLd-HC) and TLd-HC to DOC ratios in the 0–1000 m water column, varied from 5.3 to 48.5 $\mu\text{g l}^{-1}$ and 0.01 to 0.09, respectively. The highest TLd-HC concentration values were found in the 0–50 m surface layer, coinciding with phytoplankton biomass. Significant correlations ($p < 0.01$, $n = 87$) between glycolipids from chloroplast membranes, namely the monogalactosyldiacylglycerols, a major component of dissolved lipids ($25.1 \pm 10.8\%$ of TLd-HC, $n = 166$), and various phytoplankton pigments (chlorophyll *cs*-170, violaxanthin, diadinoxanthin, zeaxanthin, and lutein), suggested that picoeucaryote phytoplankton were a major source of dissolved lipids. Lipid metabolites (free fatty acids, alcohols, diacylglycerols and monoacylglycerols), an other important component of TLd-HC ($37.6 \pm 11.1\%$, $n = 166$), showed a greater degree of degradation of lipids in this transitional period than previously observed earlier in the year. Zooplankton wax and steryl ester biomarkers (WSE) and triacylglycerols showed a distinct periodicity in the mesopelagic layer throughout the

period investigated. Concentrations of WSE (5.5–13.6 $\mu\text{g l}^{-1}$) increased in the 0–150 m surface layer, mid-way through the cruise (4–6 October), before the winter mixing. WSE were observed later and deeper in the mesopelagic layer (6–11 October), accompanied by rebounds in hydrocarbons (6–8 October) and phospholipid concentrations (12 October) in the 400–1000 m depth layer. Zooplankton migration and/or fecal pellet egestion, followed by DOM release from POM, were likely responsible for the appearance of these lipid signatures in the mesopelagic layer. Because we observed these signatures during low wind period only (< 15 knots: 28 September–12 October), it may indicate that this organic matter transfer to depth was related to undisturbed trophic web in the water column above. The low salinity water lenses that appeared twice during the cruise in the 40–80 m surface layer had little effect on dissolved lipid concentrations. Lower concentrations in phosphoglycerides and hydrocarbons (HC) than in nearby sea water suggested different microbial assemblages and different level of HC contamination in this low salinity water.

1 Introduction

Marine dissolved organic matter (DOM) is an essential reservoir for the carbon cycle on Earth (Hansell and Carlson, 2002). In the ocean upper layer, photosynthesis yields organic material from inorganic carbon. Upon cell death, the



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photosynthetically produced substances are released to the medium as dissolved compounds or particulate detritus that may be further transformed into DOM. Thus, primary production is one of the most important source of DOM even though DOM can be produced at each step of the food web. Proteins, carbohydrates and lipids are the major constituents of the fraction of DOM characterized at molecular level. Considerable attention has been given to this easily identifiable fraction because it is biologically labile, it contains bioavailable moieties of biogeochemical interest like phosphorus and nitrogen and is a major substrate for marine bacteria. In addition, they may be used as biogeochemical markers to track the source, fate and transport of freshly biosynthesized DOM from the euphotic layer through the mesopelagic domain, under environmental forcings. Hence, despite the low percentage of these compounds (less than 11%) in the DOM surface pool (Benner, 2002), understanding variations in concentrations, resistance to remineralization and transformation to more complex and refractory substances in the water column, is essential to better depict the process involved in the sequestration of photosynthetically-produced organic carbon. Although DOM complex molecular assemblages would be better candidate for further characterisation (Mopper et al. 2007), the distribution of peptides, carbohydrates and lipids 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 triacylglycerols) and phytoplankton (triacylglycerols) and the degradation metabolites (free fatty acids, alcohols, di- and monoacylglycerols) 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 are 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 operationally defined by filters that separate suspended particles from material including dissolved lipids, colloids, viruses and bacteria (Liu et al., 1998). Intact dissolved lipid classes have been studied in the extracellular medium of microalgae cultures to evaluate their pro-

duction of 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, has 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 a 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; Liu et al., 1998).

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 TLC/FID technique involving 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 analytical 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 protocol 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 small extract for lipid class separation compared to current methodologies, it requires less seawater and therefore seemed to be a priori a technique of choice enabling the exhaustive sampling required for describing short temporal or spatial scale variability of chemical organic species in marine ecosystems.

The project PECHE (Production and Export of Carbon: control by Heterotrophic organisms at short temporal scale) and its main operation, the oceanographic campaign DYNAPROC 2 (DYNAMics of rapid PROCesses), was designed by Valérie Andersen with the specific goal of assessing variability in the pelagic food web and its effect on biogeochemistry of the mesopelagic zone, targeting an oligotrophic system, the NW Mediterranean Sea at the end of the summer 2004. In the present study, using TLC/FID, 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 scales at a fixed station in the open Ligurian 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 transitional period, in Northwestern Mediterranean.

2 Material and methods

2.1 Study area and sample collection

Samples were collected at a Time Series Station (TSS, 43°25'N, 8°E; ca. 48 km 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, in particular the phyto-, microzoo- and macrozooplankton biomasses and bacterioplankton, were studied in the 0–1000 m water column during four cycles of 5 days each (Andersen et al., 2009), two cycles during Leg 1 (C1 and C2; 17–29 September) and two cycles during Leg 2 (C3 and C4; 3–16 October). Sampling frequency was 3 h or 12 h depending on the parameter. 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). Additional samples for lipid analysis were taken on two 0–150 m surface CTD/rosette profiles at C1, and at the sub-surface and chlorophyll maximum depths during the whole cruise, in order to obtain a continuous pattern of dissolved lipids in the surface layer (see the Supplement Table for the complete list of samples <http://www.biogeosciences.net/6/1229/2009/bg-6-1229-2009-supplement.pdf>).

2.2 Dissolved lipid analysis

Water was transferred from the Niskin bottles with a Teflon tube into 5 litre glass bottles previously washed with 2 M HCl and rinsed with MilliQ water. Four liters were gently filtered (pressure < 15 mm Hg) onto pre-combusted (6 h at 450°C) 47 mm 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, 2 M HCl, then rinsed with MilliQ water and combusted for 6 h at 450°C or rinsed with acetone.

After adding the internal standard (I.S.) (100 µl of an hexadecanone solution at 0.2 mg ml⁻¹ in dichloromethane), 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 phase separation, 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 the ketone internal standard. In order to examine the possibility of interference between

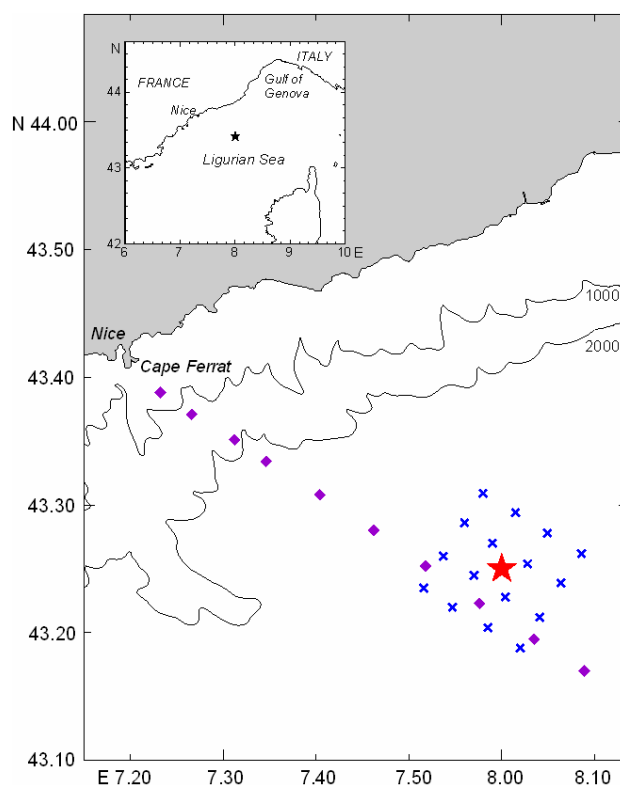


Fig. 1. Location of the time series station (★) sampled during the Dynaproc2 cruise, and grid of stations that enabled to characterize the physics and hydrology of the area.

I.S. and natural ketones that might affect our extraction rates, a few additional samples were extracted without addition of the I.S. during extraction. In the particular case of these dissolved lipid extracts, in our analytical conditions, material at retention time similar to that of the I.S. remained below the detection level.

Dissolved lipid classes were separated on Chromarods by thin layer chromatography and quantified with flame ionisation detection (TLC/FID) in an Iatroscan apparatus model MK-6 s (hydrogen flow, 160 ml min⁻¹; air flow, 2000 mL min⁻¹) coupled to a compatible PC equipped with an i-Chromstar 6.1 integration system (SCPA-Bremen, Germany). Samples (usually 4–6 µl of a 30 µl solution of the lipid extract in dichloromethane) were spotted using a 2 µl Hamilton syringe onto Chromarods-SIII previously calibrated with standard compounds (Sigma Chemical Ltd, GC grade). Analyses were run in triplicate.

The separation scheme involved five elution steps in solvents of increasing polarity: hexane+diethyl ether+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%. Detection limit was $0.02 \mu\text{g L}^{-1}$. Total dissolved lipids concentration (TLd-HC) was calculated by the summing of all lipid classes except hydrocarbons. As the biogenic origin of hydrocarbons could not be ascertained here, this lipid class is not included in TLd-HC that are thus referred to as biogenic lipids. Hydrocarbon dynamics were then treated separately. Molarity was calculated on the basis of the molecular weight of the reference standard for each lipid compound class.

2.3 Dissolved organic carbon

The samples were filtered through 2 precombusted (24 h, 450°) glass fiber filters (Whatman GF/F, 25 mm), collected into precombusted glass tubes (closed with a screw cap and a Teflon liner), acidified with Orthophosphoric acid (H_3PO_4) and immediately analysed on board on a Shimadzu TOC-V analyser. Dissolved organic carbon (DOC) was analyzed by high temperature catalytic oxidation (HTCO) (Cauwet, 1994, Cauwet 1999). Typical analytical precision is ± 0.1 – 0.5 (SD) or 0.2 – 1% (CV). Deep Sargasso Sea reference water ($47 \mu\text{M}$, ± 0.5 SE, <http://www.rsmas.miami.edu/groups/biogeochem/CRM.html>) was injected every 10 to 12 samples to insure stable operating conditions.

2.4 Ancillary parameters

Meteorological (wind, rain), hydrological (temperature, salinity, density), biogeochemical (nutrients, oxygen, colored dissolved organic matter and pigments) and biological (bacteria, flagellates and ciliates, microphytoplankton, pico and nanophytoplankton, meso- and macrozooplankton) parameters were measured during this multidisciplinary cruise. CTD profiles were performed by using a Seabird SBE 25 probe measuring temperature, salinity, pressure, fluorescence, O_2 and irradiance. Composition of phytoplankton was determined on the basis of a fine HPLC resolution of chlorophyll and carotenoid pigments, which for example included all chlorophylls, i.e. chl-*a* and divinyl chl-*a*, chl-*b* and divinyl chl-*b*, and chl-*c* including c1, c2 and cs-170 (Marty et al., 2008). Colored dissolved organic matter (CDOM) substances were extracted from 500 ml sea water samples by adsorption on C18 microcolumns. CDOM was eluted from the microcolumn with methanol and quantified by light-absorbance at 412 nm. Data are available on the web site, in previously published papers (Marty et al., 2008) and in companion papers in the present BGS volume (Ghiglione et al.,

2008; Lasternas et al., 2008; Mevel et al., 2008; Mousseau et al., 2009; Raybaud et al., 2008, 2009)

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 pairwise 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 being considered significant. Values of $P < 0.001$ were considered highly significant. The significance of mean comparison was assessed by ANOVA using the StatView 5 software.

3 Results

3.1 General hydrological conditions

The main hydro-biological characteristics during the cruise are presented in Fig. 2. Briefly, the DYNAPROC 2 cruise was conducted during the seasonal transitional 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 for two legs, 14–29 September (Leg1) and 2–17 October (Leg2). Concentrations of nutrients were low throughout the cruise (Marty et al., 2008). During Leg 1, two wind events from the NE occurred (17 and 25 September). At the end of the cruise, a succession of wind gusts (>20 Knots) from opposite directions: SW, NE and SW occurred over periods of 24 h, 60 h and longer until the end of the cruise from 10, 11 and 16 October, respectively. Temperature profiles showed a highly stratified water column from the beginning of the cruise to 10 October, being partially disrupted at the end of the cruise (Fig. 2a). 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 the last two successive strong wind events accompanied by a decrease of air temperature and a cooling of the mixed water layer, which suggested the beginning of fall mixing.

Two intrusions of low salinity water masses (LSW) (<38.3 psu) occurred below the thermocline (between 40 and 80 m) (Fig. 2b). The first intrusion (LSW-1) lasted 5 days from julian day (JD) 265 (21–30 September) and the second intrusion (LSW-2) lasted for 4 days from JD283 (9–12 October). The coastal LSW did not affect the depths exceeding 300 m. In 2004, the Levantine water was much more noticeable at the DYFAMED site than in previous years

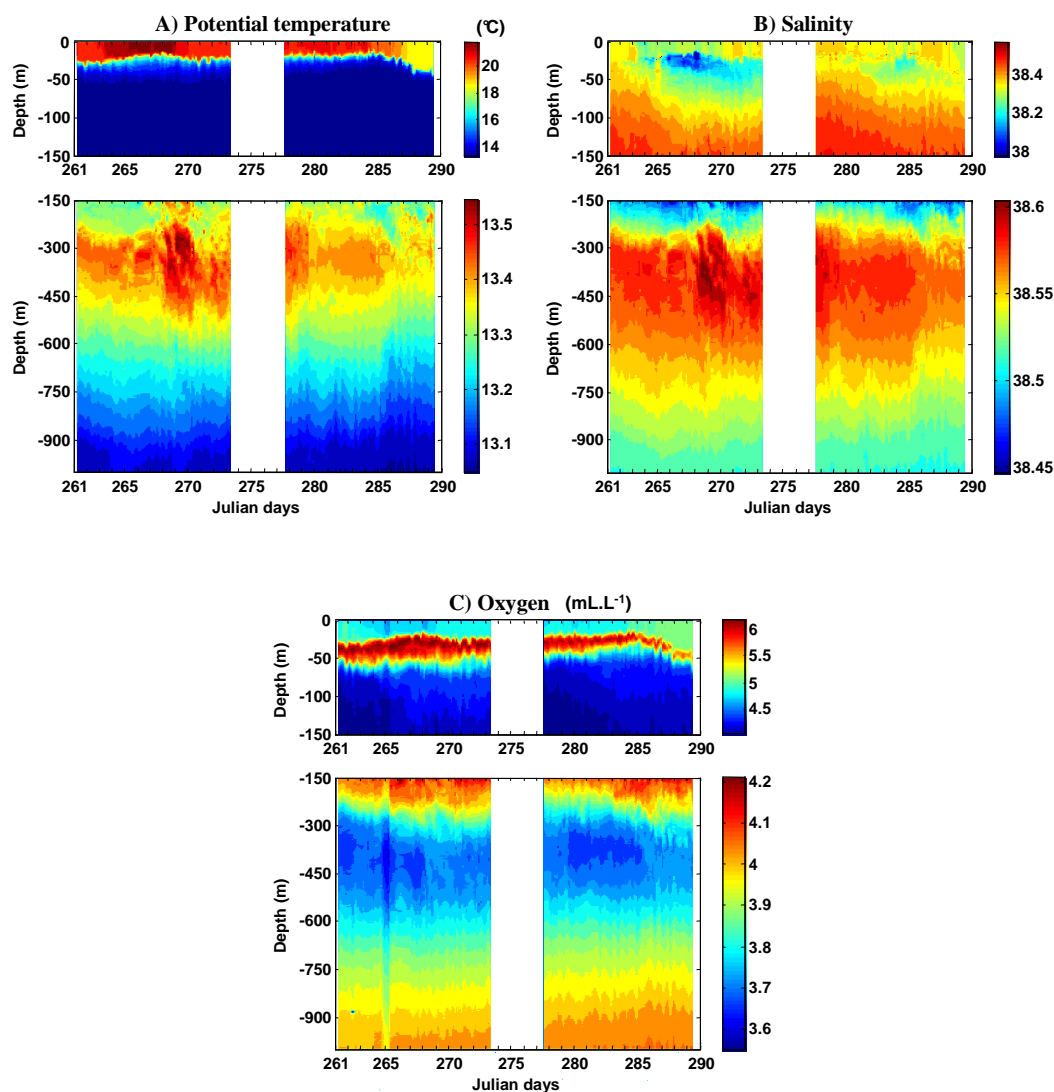


Fig. 2. Potential temperature (°C), salinity (p.s.u.) and oxygen (ml L⁻¹) at the Dynaproc 2 time series station (43°25 N, 8° E) during the late summer to autumn transitional period.

(1970–1995) and remained at levels between 250 to 400 m depth in contrast to the frontal zone where it is found between 350 and over 600 m depth, taking salinity > 38.54 and temperature $\theta > 13.4^{\circ}\text{C}$ as a criterion for Levantine water at depth (below the temperature minimum of the surface layer). In 2004, the minimum of oxygen that characterized the Levantine water was $\text{O}_2 < 3.8 \text{ mL L}^{-1}$ (Fig. 2c). Variations in the thickness of the Levantine water during the DYNAPROC2 cruise remained within the bounds of small-scale spatial variability in the center of the Ligurian Sea. At the beginning of the cruise, two deep-chlorophyll maxima (DCM, 50–60 m and 90 m depth) were detected, displaying a phytoplankton biomass exceptionally high for this time of the year (integrated Chl-*a* concentration of 35–40 mg m⁻²). After two days at the fixed station, only one

DCM (19 September, JD263), 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 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 the transitional regime between late summer and autumn (Andersen et al., 2009), but with hydrological and nutrient resources (N/P) similar to summer oligotrophic conditions (Marty et al., 2008).

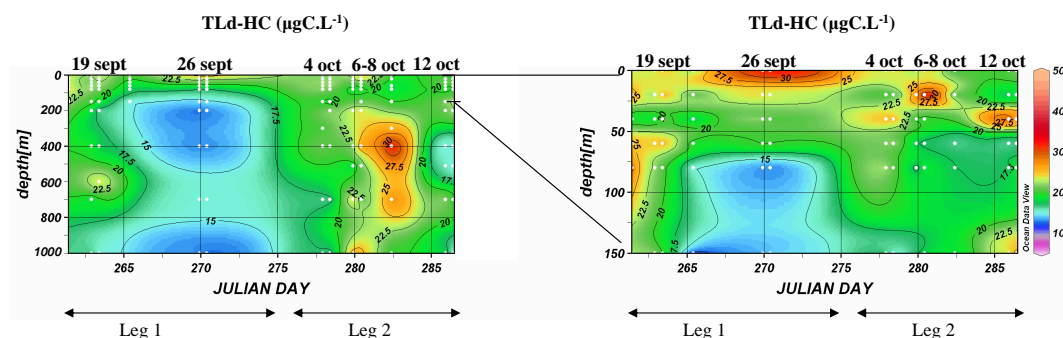


Fig. 3. Concentrations of total dissolved lipids (hydrocarbons not included) ($\mu\text{gC.L}^{-1}$) in the 1000 m (left) and in the surface 0–150 m (right) water column. Extrapolation ODV X and Y scale length 150.

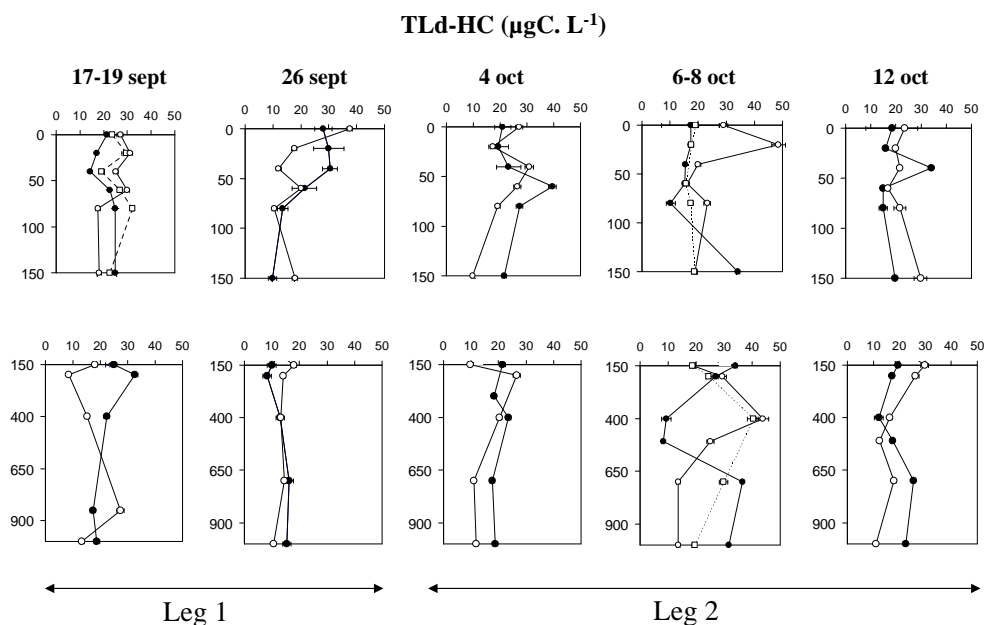


Fig. 4. Profiles of total dissolved lipids (hydrocarbons not included) ($\mu\text{gC.L}^{-1}$) in the 0–1000 m of the water column. Days (open symbols) and nights (filled symbols). Two additional day profiles (17 September and 8 October) are in dotted line.

3.2 TLd-HC, TLd-HC to DOC ratios

Lipid concentrations, hydrocarbons not included (TLd-HC), varied from 5.3 to $48.5 \mu\text{gC.L}^{-1}$ (0.4 to $4 \mu\text{M}$) (See the supplemental data table <http://www.biogeosciences.net/6/1229/2009/bg-6-1229-2009-supplement.pdf>). The highest values were found in the upper 50 m of the water column (with exception of the data collected 19 September and 4 October) (Fig. 3). The concentration gradient with depth was more pronounced during Leg1, with TLd-HC values $\leq 18 \mu\text{gC.L}^{-1}$ below 100 m, than during Leg 2 when TLd-HC concentrations below the surface layer were up to $40 \mu\text{gC.L}^{-1}$ (Fig. 3). An increase of concentrations in the mesopelagic layer occurred twice during the cruise, shortly at the beginning of Leg 1 ($27.4 \mu\text{gC.L}^{-1}$, 19 September) at 600 m depth, and sev-

eral times during Leg 2 (up to $43.9 \mu\text{gC.L}^{-1}$, between 6 and 12 October) in the 400–800 m layer. There was no clear day/night periodicity pattern in the TLd-HC profiles throughout the period investigated (Fig. 4): in the 0–150 m surface layer, peaks were observed at night in 3 over the 5 day/night profiles (26 September, 4 and 12 October). During leg 2 below 500 m, TLd-HC concentrations were higher during the night than during the day (Fig. 4). DOC varied by a factor of 2 from surface to depth in the range 38.6 – $73.8 \mu\text{M}$. Concentrations ($70 \pm 2.5 \mu\text{M}$) were maximal in the 0–10 m subsurface waters, then decreased following a moderate gradient down to $50.7 \pm 2.1 \mu\text{M}$ in the 60–70 m water layer and were almost homogeneous down to a minimum value at 1000 m depth ($39.3 \pm 0.6 \mu\text{M}$). There was no apparent difference between days and nights (Fig. 5). The contribution of TLd-HC

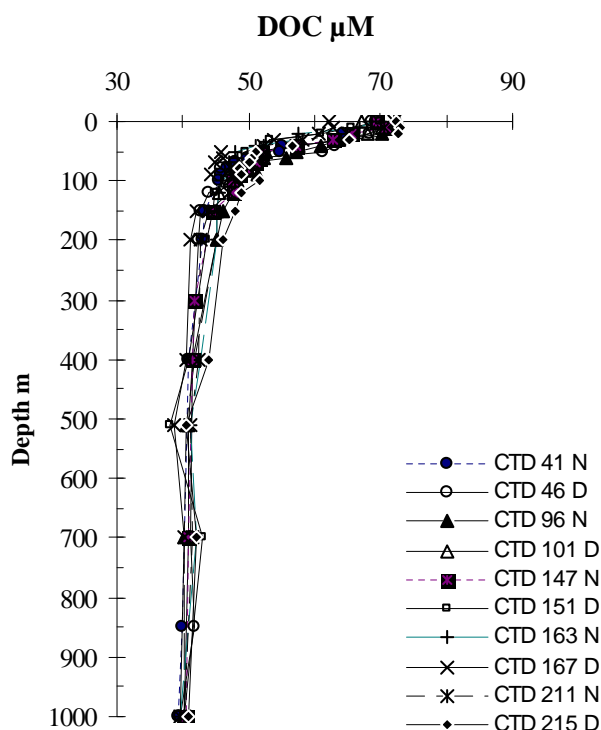


Fig. 5. Dissolved organic carbon concentrations (μM). N=night, D=day.

to DOC varied in the range 0.9–9.1% (Fig. 6). The highest values ($\geq 7\%$) 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 only, a pattern due to the increase of lipid concentrations while DOC concentrations remained quite stable. An increase in the percentage of TLd-HC in DOC ($>5\%$) was occasionally observed on a day profile, during Leg 1 (19 September at 700 m, Julian day 263). In order to examine the lipid pattern in DOC at a 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 $3.3 \pm 1.1\%$ in September (Leg 1) to $4.3 \pm 1.8\%$ in October (Leg 2) (ANOVA, $p < 0.05$, $n = 31$), whereas the TLd-HC/DOC ratio in the 0–150 m surface layer was similar ($2.9 \pm 1.1\%$ and $3.1 \pm 1.1\%$, during Leg 1 and Leg 2, respectively). There were no obvious differences in the daily variations of TLd-HC contribution to DOC (data not shown).

3.3 Lipid classes

Lipid class concentrations are presented in supplemental Table 1 <http://www.biogeosciences.net/6/1229/2009/bg-6-1229-2009-supplement.pdf>. The relative contribution of phospholipids, chloroplast lipids (glycolipids and

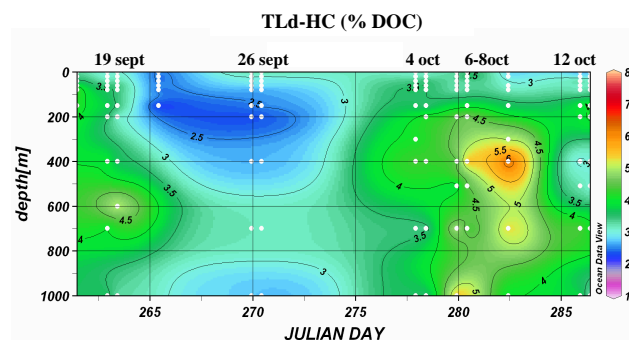


Fig. 6. Relative percentage of total dissolved lipids (hydrocarbons not included) in DOC. Extrapolation ODV X et Y scale length 150.

pigments), triacylglycerols (TG), wax and sterol esters (WSE) and metabolites (free fatty acids, alcohols, di- and monoacylglycerols) to the lipid pool showed a quite stable pattern during the sampling period (Fig. 7) with the exception of an increase of WSE and TG contribution to TLd-HC, from 5.1 ($n=1$) to $15.1 \pm 11.7\%$ ($n=8$) and from 4.1 ± 1.8 ($n=12$) to $4.0 \pm 3.0\%$ ($n=19$) (data computed from supplemental Table 1 <http://www.biogeosciences.net/6/1229/2009/bg-6-1229-2009-supplement.pdf>), respectively, beyond 200 m depth in the mesopelagic layer between Leg 1 and Leg 2. Table 2 provides the average concentration and percentage of lipid classes in TLd and TLd-HC during the whole cruise (all depths). Except for hydrocarbons, the glycolipids (monogalactosyl diacylglycerols) (25.09%) were the major lipid class, followed by pigments (13.58%), free aliphatic alcohols (12.34%), the monoacylglycerols (11.84%) and free fatty acids (11.38%), and finally the phospholipids (PL). Thus the so-called chloroplast lipids, which include glycolipids and pigments, varied between $2.1 \mu\text{gCL}^{-1}$ and $21.9 \mu\text{gCL}^{-1}$ (see supplemental Table 1 <http://www.biogeosciences.net/6/1229/2009/bg-6-1229-2009-supplement.pdf>) and dominated the lipid pool ($38.7 \pm 8.5\%$ 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 (ca. $10\text{--}14 \mu\text{gCL}^{-1}$) were also found at depth in the 400–800 m layer (6 and 8 October) (see supplemental Table 1 <http://www.biogeosciences.net/6/1229/2009/bg-6-1229-2009-supplement.pdf>). The other most important class of compounds were the lipid metabolites (FFA, ALC, MG and DG) ($37.6 \pm 11.1\%$ on average, $n=166$) (Table 2 and supplemental Table 1 <http://www.biogeosciences.net/6/1229/2009/bg-6-1229-2009-supplement.pdf>), indicating hydrolysis of lipid DOM. The average concentration of each lipid class per depth (data not shown) showed that free fatty acids had a maximal average concentration ($5.2 \pm 0.7 \mu\text{gCL}^{-1}$) at 400 m depth, at the bottom of the Levantine water body. However, we did not sample properly the Levantine waters (only one sample was taken at 400 m

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



Fig. 7. Time series of TLd-HC ($\mu\text{g L}^{-1}$) and dissolved lipid class distribution (% of TLd-HC) during night (■) and days (□) sampling. Julian days are above the graph.

depth in this water mass) and further characterisation of the lipid distribution in Levantine waters may not be performed straightforward. Other intact lipids (phospholipids, triacylglycerols, wax and sterol-esters) were present in lower proportions (on average $9.5\pm 6.0\%$). Phospholipids (PL) were the least abundant lipid class in the concentration range 0– $3.7\mu\text{gCL}^{-1}$ (mean $1.0\pm 0.6\mu\text{gCL}^{-1}$, $n=166$). A marked increase in PL concentrations was noticeable during leg2 at 150–200 m and 700 m depth (mean $3.1\pm 0.3\mu\text{gCL}^{-1}$, $n=4$) (Fig. 8, 12 October, upper panel). Finally, the hydrocarbon pool varied in the range $0.9\text{--}21.9\mu\text{gCL}^{-1}$ (on average $6.3\pm 1.8\mu\text{gCL}^{-1}$), which represented $24.7\pm 3.2\%$ of the TLd (Table 2). An increase of concentrations at 400–800 m depth occurred in 6 and 8 October (Fig. 8, lower panel).

The storage lipids, triacylglycerols (TG) and wax and sterol esters (WSE), varied in the range 0–6.0 and 0– $13.6\mu\text{gCL}^{-1}$, respectively. They were minor compounds not always present in the total lipids. Triacylglycerols are re-

serve lipids in microalgae and zooplankton (Parrish, 1988). Wax and sterol esters cannot be easily separated by Iatroscan TLC/FID and there is no reports on wax versus sterol esters in dissolved lipids by using this technic. Sterol esters usually represent a small contribution to particulate WSE (usually less than 8%) (Wakeham et al., 1980; Hudson et al., 2001). However, it is not always the case as shown by the high concentration measured in mesopelagic sediment trap in the Atlantic ocean (Wakeham et al., 1980). Ciliated protozoa also, are able to synthesize quantity of sterol esters (Kaneshiro, 1987). Whatever their relative proportions, wax and sterol esters are related to the presence of zooplankton (Sargent et al., 1976; Sargent et al., 1977; Sargent, 1978; Cavaletto et al., 1989; Kattner, 1989). In our study, the pattern of variation of TG and WSE over time and depth was well described by comparing the 0–150 m and 150–1000 m average concentrations (Fig. 9). During Leg 1, TG night average concentration values were always lower at surface (0–150 m) than in

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	
		$\mu\text{g L}^{-1}$	$\pm\text{SD}$	%	$\pm\text{SD}$	%	$\pm\text{SD}$
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

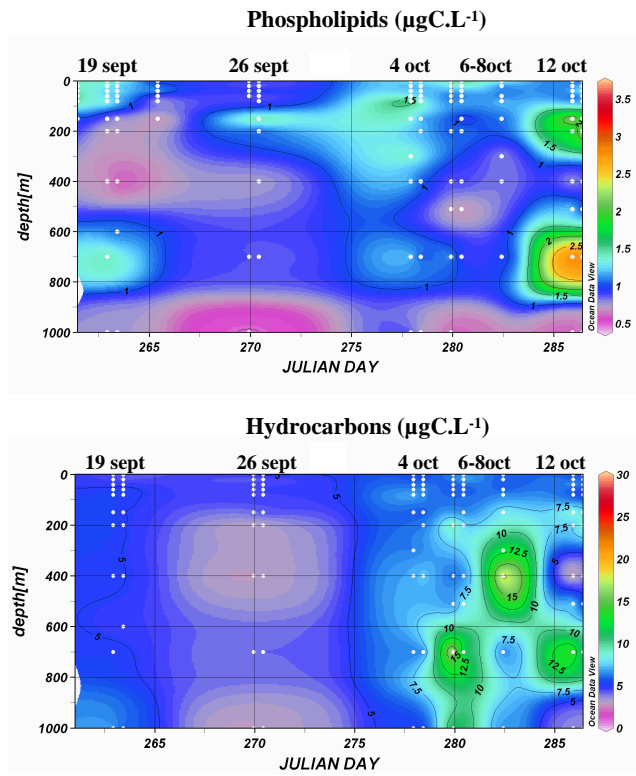


Fig. 8. Distribution of specific lipid markers ($\mu\text{gC L}^{-1}$). Dissolved phospholipids (upper panel), and hydrocarbons (lower panel). Extrapolation ODV X et Y scale length 150.

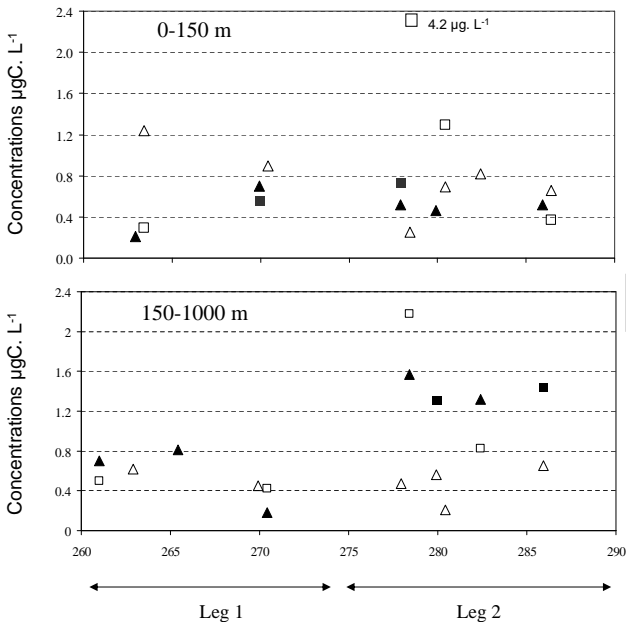


Fig. 9. Triacylglycerols (triangle) and wax esters (square) average concentrations ($\mu\text{gC L}^{-1}$) based on integrated concentrations in the 0–150 m surface (upper panel) and mesopelagic 150–1000 m (lower panel) layers. Day (open symbols) and night (filled symbols).

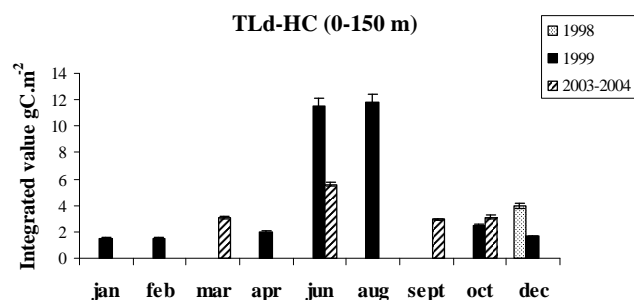


Fig. 10. Composite of total lipid concentrations measured in the framework of the Dyfamed time series observations (1998–1999) and in the framework of the PECHE project (March and June, 2003).

the mesopelagic layer, if we exclude night value observed at julian day 278. An opposite trend was observed for the TG day values, they were always higher at surface than in the mesopelagic layer. WSE occasionally appeared in the lipid pool during Leg 1 (Fig. 9). Like TG, WSE night values were lower at surface than in the mesopelagic layer but the day pattern was less obvious.

3.4 Relationships between total lipids, individual lipid classes, and hydrological and biogeochemical parameters

Correlations between bulk organic compounds (DOC, particulate carbon, CDOM), TLd and TLd-HC, individual lipid classes, and environmental parameters (salinity, temperature, nutrients, Chl-*a*, phytoplankton pigments) were examined using Pearson's product-moment correlation coefficient. Correlations were computed on two matrices, a 0–150 m matrix including all parameters cited above, and a 0–1000 m matrix not including pigments because they were analyzed in the surface water column only. In the 0–1000 m water column, significant correlations were found between total dissolved lipids (both TLd and TLd-HC) and concentrations of hydrocarbons, triacylglycerols, chloroplast lipids and metabolites (free fatty acids and alcohols) ($p < 0.01$, $n = 167$) whereas the minor lipid classes (wax esters and phospholipids) were not correlated with total lipids (data not shown).

As chloroplast lipids (CL) were the major components of the lipid pool, the correlation between TLd-HC and CL suggests that phytoplankton were one major source of lipids in the 0–1000 m water column. In the 0–150 m surface water column, the monogalactosylglycerides (MGDG), which are constituents of CL in microalgae, were the only class of lipids that was significantly correlated with several individual pigments (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 support the idea of a picoplanktonic sources of

MGDG in the dissolved lipid pool (Table 3). Such correlations between one component of the dissolved lipid fraction and pigments that are located inside the cells, suggest that a direct transfer of MGDG from the picoplankton intracellular lipid pool to dissolved lipids possibly occurred. MGDG was also correlated with DOC and particulate carbon (PC) (0.57 and 0.45, $p < 0.01$) (Table 3). This suggests that both PC and DOC contained a similar picoplankton material as TLd and/or that a PC to DOC transfer through picoplankton lysis and grazing is possible. 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 picoplankton pigments cited above (Table 3) indicating different CDOM sources from that of DOC.

4 Discussion

Our study provides the first high frequency time series measurements of total lipid concentrations and lipid class composition in DOM from the surface to the mesopelagic layer in the open Ligurian sea, which represents a reference for the late summer to autumn period in North Western Mediterranean. 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 ($11\text{--}580 \mu\text{g L}^{-1}$) (Table 4).

4.1 Seasonal variations of the total lipid pool

Previous measurements of dissolved lipid concentrations (unpublished data; Ghiglione et al., 2007; Bourguet et al., 2009) at the Dyfamed TSS (Marty et al., 2002) during the 1998–1999 years, and during two additional PECHE short-cruises conducted in March and June 2003 (Andersen et al., 2009), enable 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. 10): dissolved lipid concentrations were generally low in winter, maximal during summer oligotrophic period (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., 2009) did not persist at the surface until the winter mixing. During late summer and autumn, 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, namely through aggregation/dissolution and migration of zooplankton.

Table 3. Results from pairwise moment correlation coefficients matrix. Significance of the correlation $H_0 : R=0$; d.f.= $n-2=40$. Dark grey= $p<0.01$; light grey= $p<0.05$; ns=non significantly different from zero—>non correlated.

	HC	TC	TG	FFA	FFA2	ALC	LDL	LDL2	LDL3	LDL4	LDL5	LDL6	LDL7	LDL8	LDL9	LDL10	LDL11	LDL12	LDL13	LDL14	LDL15	LDL16	LDL17	LDL18	LDL19	LDL20	LDL21	LDL22	LDL23	LDL24	LDL25	LDL26	LDL27	LDL28	LDL29	LDL30	LDL31	LDL32	LDL33	LDL34	LDL35	LDL36	LDL37	LDL38	LDL39	LDL40	LDL41	LDL42	LDL43	LDL44	LDL45	LDL46	LDL47	LDL48	LDL49	LDL50	LDL51	LDL52	LDL53	LDL54	LDL55	LDL56	LDL57	LDL58	LDL59	LDL60	LDL61	LDL62	LDL63	LDL64	LDL65	LDL66	LDL67	LDL68	LDL69	LDL70	LDL71	LDL72	LDL73	LDL74	LDL75	LDL76	LDL77	LDL78	LDL79	LDL80	LDL81	LDL82	LDL83	LDL84	LDL85	LDL86	LDL87	LDL88	LDL89	LDL90	LDL91	LDL92	LDL93	LDL94	LDL95	LDL96	LDL97	LDL98	LDL99	LDL100	LDL101	LDL102	LDL103	LDL104	LDL105	LDL106	LDL107	LDL108	LDL109	LDL110	LDL111	LDL112	LDL113	LDL114	LDL115	LDL116	LDL117	LDL118	LDL119	LDL120	LDL121	LDL122	LDL123	LDL124	LDL125	LDL126	LDL127	LDL128	LDL129	LDL130	LDL131	LDL132	LDL133	LDL134	LDL135	LDL136	LDL137	LDL138	LDL139	LDL140	LDL141	LDL142	LDL143	LDL144	LDL145	LDL146	LDL147	LDL148	LDL149	LDL150	LDL151	LDL152	LDL153	LDL154	LDL155	LDL156	LDL157	LDL158	LDL159	LDL160	LDL161	LDL162	LDL163	LDL164	LDL165	LDL166	LDL167	LDL168	LDL169	LDL170	LDL171	LDL172	LDL173	LDL174	LDL175	LDL176	LDL177	LDL178	LDL179	LDL180	LDL181	LDL182	LDL183	LDL184	LDL185	LDL186	LDL187	LDL188	LDL189	LDL190	LDL191	LDL192	LDL193	LDL194	LDL195	LDL196	LDL197	LDL198	LDL199	LDL200	LDL201	LDL202	LDL203	LDL204	LDL205	LDL206	LDL207	LDL208	LDL209	LDL210	LDL211	LDL212	LDL213	LDL214	LDL215	LDL216	LDL217	LDL218	LDL219	LDL220	LDL221	LDL222	LDL223	LDL224	LDL225	LDL226	LDL227	LDL228	LDL229	LDL230	LDL231	LDL232	LDL233	LDL234	LDL235	LDL236	LDL237	LDL238	LDL239	LDL240	LDL241	LDL242	LDL243	LDL244	LDL245	LDL246	LDL247	LDL248	LDL249	LDL250	LDL251	LDL252	LDL253	LDL254	LDL255	LDL256	LDL257	LDL258	LDL259	LDL260	LDL261	LDL262	LDL263	LDL264	LDL265	LDL266	LDL267	LDL268	LDL269	LDL270	LDL271	LDL272	LDL273	LDL274	LDL275	LDL276	LDL277	LDL278	LDL279	LDL280	LDL281	LDL282	LDL283	LDL284	LDL285	LDL286	LDL287	LDL288	LDL289	LDL290	LDL291	LDL292	LDL293	LDL294	LDL295	LDL296	LDL297	LDL298	LDL299	LDL300	LDL301	LDL302	LDL303	LDL304	LDL305	LDL306	LDL307	LDL308	LDL309	LDL310	LDL311	LDL312	LDL313	LDL314	LDL315	LDL316	LDL317	LDL318	LDL319	LDL320	LDL321	LDL322	LDL323	LDL324	LDL325	LDL326	LDL327	LDL328	LDL329	LDL330	LDL331	LDL332	LDL333	LDL334	LDL335	LDL336	LDL337	LDL338	LDL339	LDL340	LDL341	LDL342	LDL343	LDL344	LDL345	LDL346	LDL347	LDL348	LDL349	LDL350	LDL351	LDL352	LDL353	LDL354	LDL355	LDL356	LDL357	LDL358	LDL359	LDL360	LDL361	LDL362	LDL363	LDL364	LDL365	LDL366	LDL367	LDL368	LDL369	LDL370	LDL371	LDL372	LDL373	LDL374	LDL375	LDL376	LDL377	LDL378	LDL379	LDL380	LDL381	LDL382	LDL383	LDL384	LDL385	LDL386	LDL387	LDL388	LDL389	LDL390	LDL391	LDL392	LDL393	LDL394	LDL395	LDL396	LDL397	LDL398	LDL399	LDL400	LDL401	LDL402	LDL403	LDL404	LDL405	LDL406	LDL407	LDL408	LDL409	LDL410	LDL411	LDL412	LDL413	LDL414	LDL415	LDL416	LDL417	LDL418	LDL419	LDL420	LDL421	LDL422	LDL423	LDL424	LDL425	LDL426	LDL427	LDL428	LDL429	LDL430	LDL431	LDL432	LDL433	LDL434	LDL435	LDL436	LDL437	LDL438	LDL439	LDL440	LDL441	LDL442	LDL443	LDL444	LDL445	LDL446	LDL447	LDL448	LDL449	LDL450	LDL451	LDL452	LDL453	LDL454	LDL455	LDL456	LDL457	LDL458	LDL459	LDL460	LDL461	LDL462	LDL463	LDL464	LDL465	LDL466	LDL467	LDL468	LDL469	LDL470	LDL471	LDL472	LDL473	LDL474	LDL475	LDL476	LDL477	LDL478	LDL479	LDL480	LDL481	LDL482	LDL483	LDL484	LDL485	LDL486	LDL487	LDL488	LDL489	LDL490	LDL491	LDL492	LDL493	LDL494	LDL495	LDL496	LDL497	LDL498	LDL499	LDL500	LDL501	LDL502	LDL503	LDL504	LDL505	LDL506	LDL507	LDL508	LDL509	LDL510	LDL511	LDL512	LDL513	LDL514	LDL515	LDL516	LDL517	LDL518	LDL519	LDL520	LDL521	LDL522	LDL523	LDL524	LDL525	LDL526	LDL527	LDL528	LDL529	LDL530	LDL531	LDL532	LDL533	LDL534	LDL535	LDL536	LDL537	LDL538	LDL539	LDL540	LDL541	LDL542	LDL543	LDL544	LDL545	LDL546	LDL547	LDL548	LDL549	LDL550	LDL551	LDL552	LDL553	LDL554	LDL555	LDL556	LDL557	LDL558	LDL559	LDL560	LDL561	LDL562	LDL563	LDL564	LDL565	LDL566	LDL567	LDL568	LDL569	LDL570	LDL571	LDL572	LDL573	LDL574	LDL575	LDL576	LDL577	LDL578	LDL579	LDL580	LDL581	LDL582	LDL583	LDL584	LDL585	LDL586	LDL587	LDL588	LDL589	LDL590	LDL591	LDL592	LDL593	LDL594	LDL595	LDL596	LDL597	LDL598	LDL599	LDL600	LDL601	LDL602	LDL603	LDL604	LDL605	LDL606	LDL607	LDL608	LDL609	LDL610	LDL611	LDL612	LDL613	LDL614	LDL615	LDL616	LDL617	LDL618	LDL619	LDL620	LDL621	LDL622	LDL623	LDL624	LDL625	LDL626	LDL627	LDL628	LDL629	LDL630	LDL631	LDL632	LDL633	LDL634	LDL635	LDL636	LDL637	LDL638	LDL639	LDL640	LDL641	LDL642	LDL643	LDL644	LDL645	LDL646	LDL647	LDL648	LDL649	LDL650	LDL651	LDL652	LDL653	LDL654	LDL655	LDL656	LDL657	LDL658	LDL659	LDL660	LDL661	LDL662	LDL663	LDL664	LDL665	LDL666	LDL667	LDL668	LDL669	LDL670	LDL671	LDL672	LDL673	LDL674	LDL675	LDL676	LDL677	LDL678	LDL679	LDL680	LDL681	LDL682	LDL683	LDL684	LDL685	LDL686	LDL687	LDL688	LDL689	LDL690	LDL691	LDL692	LDL693	LDL694	LDL695	LDL696	LDL697	LDL698	LDL699	LDL700	LDL701	LDL702	LDL703	LDL704	LDL705	LDL706	LDL707	LDL708	LDL709	LDL710	LDL711	LDL712	LDL713	LDL714	LDL715	LDL716	LDL717	LDL718	LDL719	LDL720	LDL721	LDL722	LDL723	LDL724	LDL725	LDL726	LDL727	LDL728	LDL729	LDL730	LDL731	LDL732	LDL733	LDL734	LDL735	LDL736	LDL737	LDL738	LDL739	LDL740	LDL741	LDL742	LDL743	LDL744	LDL745	LDL746	LDL747	LDL748	LDL749	LDL750	LDL751	LDL752	LDL753	LDL754	LDL755	LDL756	LDL757	LDL758	LDL759	LDL760	LDL761	LDL762	LDL763	LDL764	LDL765	LDL766	LDL767	LDL768	LDL769	LDL770	LDL771	LDL772	LDL773	LDL774	LDL775	LDL776	LDL777	LDL778	LDL779	LDL780	LDL781	LDL782	LDL783	LDL784	LDL785	LDL786	LDL787	LDL788	LDL789	LDL790	LDL791	LDL792	LDL793	LDL794	LDL795	LDL796	LDL797	LDL798	LDL799	LDL800	LDL801	LDL802	LDL803	LDL804	LDL805	LDL806	LDL807	LDL808	LDL809	LDL810	LDL811	LDL812	LDL813	LDL814	LDL815	LDL816	LDL817	LDL818	LDL819	LDL820	LDL821	LDL822	LDL823	LDL824	LDL825	LDL826	LDL827	LDL828	LDL829	LDL830	LDL831	LDL832	LDL833	LDL834	LDL835	LDL836	LDL837	LDL838	LDL839	LDL840	LDL841	LDL842	LDL843	LDL844	LDL845	LDL846	LDL847	LDL848	LDL849	LDL850	LDL851	LDL852	LDL853	LDL854	LDL855	LDL856	LDL857	LDL858	LDL859	LDL860	LDL861	LDL862	LDL863	LDL864	LDL865	LDL866	LDL867	LDL868	LDL869	LDL870	LDL871	LDL872	LDL873	LDL874	LDL875	LDL876	LDL877	LDL878	LDL879	LDL880	LDL881	LDL882	LDL883	LDL884	LDL885	LDL886	LDL887	LDL888	LDL889	LDL890	LDL891	LDL892	LDL893	LDL894	LDL895	LDL896	LDL897	LDL898	LDL899	LDL900	LDL901	LDL902	LDL903	LDL904	LDL905	LDL906	LDL907	LDL908	LDL909	LDL910	LDL911	LDL912	LDL913	LDL914	LDL915	LDL916	LDL917	LDL918	LDL919	LDL920	LDL921	LDL922	LDL923	LDL924	LDL925	LDL926	LDL927	LDL928	LDL929	LDL930	LDL931	LDL932	LDL933	LDL934	LDL935	LDL936	LDL937	LDL938	LDL939	LDL940	LDL941	LDL942	LDL943	LDL944	LDL945	LDL946	LDL947	LDL948	LDL949	LDL950	LDL951	LDL952	LDL953	LDL954	LDL955	LDL956	LDL957	LDL958	LDL959	LDL960	LDL961	LDL962	LDL963	LDL964	LDL965	LDL966	LDL967	LDL968	LDL969	LDL970	LDL971	LDL972	LDL973	LDL974	LDL975	LDL976	LDL977	LDL978	LDL979	LDL980	LDL981	LDL982	LDL983	LDL984	LDL985	LDL986	LDL987	LDL988	LDL989	LDL990	LDL991	LDL992	LDL993	LDL994	LDL995	LDL996	LDL997	LDL998	LDL999	LDL1000
WSE	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																								

Table 4. Literature data of water column total dissolved lipid concentrations (TLd, $\mu\text{g L}^{-1}$) and total dissolved lipids not including hydrocarbons (TLd-HC, $\mu\text{g L}^{-1}$). 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 $\mu\text{g L}^{-1}$	TL-HCLD $\mu\text{g L}^{-1}$
Parrish, 1987	Bedford basin, May–June 1982	44°41' N	63°39' W	bottom of surface mixed layer	75–498	71–468
Parrish et al., 1988	Scotian lough, April 1982	44°39'–44°41' N	63°34' W–63°39' W	under the pycnocline	25–54	13–48
Parrish et al., 1992	Nova Scotia inlet (Urban and Rural), August 1989	44°39' N	63°34' W–63°39' W	euphotic layer	96–156	86–144
Liu et al., 1998	Conception Bay, time series 1991–1993	47°32' N	53°06' W	euphotic layer (10–28 m)	18–56	nd
Striby and Goutx, 1997	Gibraltar straight West, June 1997	35°55'–36°06' N	5°19' W	10–230 m	nd	17–135
Striby and Goutx, 1997	Gibraltar straight East, June 1997	35°53'–36°04' N	5°51' W	10–300 m	nd	94–229
Gérin and Goutx, 1994	Almeria–Oran front, April 1991	35°43'–36°51' N	0°31'–1°55' E	0–1600 m	11–273	9–113
Striby, 2000	Almeria Oran front, December 1997	35°43'–36°51' N	1°55'–0°31' E	0–200 m	nd	2–134
Goutx et al., 1993	NW Mediterranean, Avril 1989	43°35'–43°31' N	7°29'–7°38' E	0–1000 m	45–126	33–112
Van Wambeke, 2001	NW Mediterranean, May 1995	43°25' N	7°52' E	0–50 m	nd	21–234
Bourguet et al., 2008	NW Mediterranean, March 2003	43°25' N	7°52' E	3–500 m	nd	12.4–40
Bourguet et al., 2008	NW Mediterranean, June 2003	43°25' N	7°52' E	3–500 m	nd	11.8–78
Leveau et al., 1990	Rhone plume, May 1988	43°19' N	4°5' E	plume, interface plume-sea water	50–300	35–152
Derieux et al., 1998	Gulf of Trieste, June 1995	45°39' N	13°29' E	euphotic layer	49–88	49–77
Andersson et al., 1993	Baltic sea, time series 1982	63°31' N	19°50' E	euphotic layer (0–14 m)	25–270	nd
Nichols and Espey, 1991	Malabar sewage (Sydney)	34° N	151°5' E	air-sea interface	190–580	190–580

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

Lipids are an important component of DOM produced by phytoplankton during photosynthesis and a close relationship between Chl-*a* and lipids was expected. However examinations of literature data from other systems (cf. Table 4) did not show any significant relationship between TLd-HC and Chl-*a* despite a couple of high lipid concentrations accompanying the highest Chl-*a* values in Bedford Basin (Parrish, 1987) or in the Rhone river plume (Leveau et al., 1990). Similarly, time series observations of dissolved lipid class concentrations during phytoplankton blooms have not revealed

significant correlations between Chl-*a* and TLd-HC (Morris et al., 1983; Parrish, 1987). In these studies, TLd-HC rather accumulated before and after the blooms. This suggests that either the dissolution of the detritic phytoplankton biomass into the dissolved pool need not be the major sources of dissolved lipid classes, or that only partially fractionated polar lipid classes would not be the best proxies for revealing such relationships. 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 origins and different susceptibility

to bacterial attack. Degradation rates have been reported by several authors (Harvey et al., 1995, 1997; Goutx et al., 2003, 2007; Caradec et al., 2004; Moriceau et al., 2008). Goutx et al. (2003) and Moriceau et al. (2008) 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 differences in residence times, lipid classes resulting from diagenetic processes may have masked the origin of dissolved lipids.

In our study, the AMPL peak was fractionated into its various components (Striby et al., 1999), which may be the cause of the significant relation observed between a dissolved lipid class, the glycolipids (i.e. MGDG), and specific picoplankton pigments. This relation points out the picoeucaryotes as a major source of dissolved lipids during the period investigated.

One other reason for the lack of significant relationships between Chl-*a* and dissolved lipids in our study and in previous works, may be that Chl-*a* and AMPL that are enriched in large microphytoplankton cells, in particular diatoms, are preferentially exported to depth by aggregate formation through coagulation, and/or meso- and macrozooplankton grazing. Hence, large cells are less susceptible to breakdown through lysis and grazing in surface layers, having less potential for fueling the surface dissolved pool with intracellular Chl-*a* and chloroplast lipids than small picoplankton cells do. The small picoplankton which is rich in xanthopigments, is most likely to enter the microbial loop, which would favour the export of its intracellular compounds to the dissolved pool through sloppy feeding.

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 (cf. Results Sect. 3.3 and Table 3). This pattern suggested differences in sources and formation processes of bulk DOC and CDOM during the summer to autumn transitional period. The dynamics of DOC concentrations would mostly be controlled by release of matter from picoplankton that dominated the phytoplankton biomass (Marty et al., 2008) at this time of the year, probably through lysis, grazing and sloppy feeding. CDOM would rather be formed through intramolecular reactions of a larger range of organic biomolecules from the decaying pico- and microphytoplankton, under a combination of biotic and abiotic factors including light radiation (Yentsch and Reichert, 1961; Sieburth and Jensen, 1969).

Below 60 m, the decrease of lipid concentrations suggested that stratification limited the transfer of phytoplankton lipids (and by extrapolation, of other phytoplankton material) from the productive layer to the mesopelagic layer. These conditions may result in a carbon limitation for the microbial population below this depth, which is consistent with

observations made by Van Wambeke et al. (2009) during the Dynaproc2 cruise.

4.3 Degradation status of the dissolved lipid pool

An other important component of the dissolved lipid pool was the lipid metabolites (FFA, ALC, MG and DG). Release of metabolites occurs through the enzymatic cleavage of esters bounds of source glyceride lipids (Goutx et al., 2003). When the readily available molecules derived from phytoplankton start to be depleted, bacteria enzymatic activities cleave biopolymers into monomers (Hoppe, 1993). During the Dynaproc2 experiment, bacterial production was significantly correlated with the various organic matter descriptors (particulate carbon, DOC, MGDG and CDOM) (Mével et al., 2008; Ghiglione et al., 2008), which suggests that bacteria most probably were taking benefit from a wide range of biopolymers during this transitional period, because of varying growth limiting factors (Van Wambeke et al., 2009). 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., 2009). Small lipid metabolites may be less reactive to bacteria than more complex and fresh biopolymers (Loh et al., 2004). In addition, lipid metabolite accumulation may reflect 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 $37.6 \pm 11.1\%$, $n=166$), compared to spring and summer 2003 period ($23.9 \pm 16.9\%$ ($n=12$) and $28.1 \pm 6.0\%$ ($n=16$), respectively) (Bourguet et al. 2009). At the end of the stratified period, monoacylglycerols constituted the largest pool of metabolites, which may be related to the low reactivity of these compounds to bacterial lipase attack (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; Mével et al., 2008; Raybaud et al., 2008, 2009) that were studied during the Dynaproc cruise, probably due to the exceptional hydrological calm encountered during this late summer to autumn transitional period.

In such hydrological conditions with limited physical and hydrological forcings, the impact of biology on dissolved lipid distribution likely 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 the high phytoplankton production and bacterial activity that characterized the euphotic layer during the sampling period, as reported by Marty et al. (2008) and Mevel et al. (2008), respectively, and that presumably released and consumed lipids at various rates. Below 150 m depth during leg 2, peaks of dissolved lipid and individual biomarker concentrations (cf. Figs. 2 and 8) reflected an input 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 the mechanism responsible for lipid transport to the mesopelagic layer was different from that 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), and production of fecal pellets, either in the productive layer or in the mesopelagic layer, followed by sedimentation and/or dissolution. Indeed, there were a clear day/night periodicity in the mesopelagic distributions of dissolved TG and WSE throughout the period investigated. The double signature of TG and WSE in sinking particles has already been related to fecal pellets of carnivorous euphausiids during Dynaproc 1 experiment (Goutx et al., 2000). Moreover, carnivorous zooplankton were identified as a major trophic element during the leg 2 (Mousseau et al., 2009).

The export of hydrophobic contaminants like petroleum hydrocarbons has been previously related to the vertical transport of lipid material in sedimenting particles (Andersson et al., 1993). As inferred during periods of increasing productivity, the nature of sinking particles may also impact the flux of these hydrocarbons. Bouloubassi et al. (2006) showed that the flux of fecal pellets was able to carry a significant fraction of petroleum hydrocarbons to depth. During the Dynaproc 2 cruise, the high proportion observed at 700 m during leg 2 may be related to egestion of fecal pellets from zooplankton, followed by disaggregation/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 petroleum hydrocarbons, as revealed by very high proportion ($24.7\% \pm 3.2$) in the dissolved lipids (Goutx, 1988).

Phospholipid signatures were noticeable later on during leg 2 (12 October) in the mesopelagic zone (Fig. 8). This change in phospholipid concentrations at 700 m depth between 6–8 October and 12 October amounted $1.5\text{--}2\text{ }\mu\text{g L}^{-1}$. Marine bacteria contain a range of $\sim 2\text{--}7\%$ lipids in total carbon, free or bound to proteins and polysaccharides, with most lipids in the form of membrane phospholipids ($88 \pm 5\%$ TL)

(Goutx et al., 1990; Goutx, unpublished). Because most bacteria may pass through the $0.7\text{ }\mu\text{m}$ 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 ($\times 5$) and abundance (above $9\text{ }10^5\text{ cells L}^{-1}$) (Mevel et al., 2008) and ecto-enzyme activities (F. Van Wambeke, personal communication, 2008). Using the conversion factor of Findlay et al. (1989) for naturally occurring mixed populations ($3.4\text{ }10^9\text{ cells}$ or 192 mg of C per 100 nmol of phospholipid), we evaluated the phospholipid increase as equivalent to $10^7\text{--}10^8\text{ cells L}^{-1}$ bacteria, which is far above estimated bacterial concentrations, and does not support the idea that these phospholipids would represent only a bacterial biomass increase. Phospholipids may rather indicate the presence of cell remains either derived from the flux of sinking particles described above and/or from egestion of fecal pellets by migrator zooplankton in the mesopelagic layer. It is most probable that this input of fresh biopolymers at these depth occurred through particle dissolution and bacterial enzyme attack, stimulating the production of free living bacteria and promoting a mesopelagic microbial food web, which limited the bacterial abundance according to Tanaka and Rassoulzadegan (2004). We sampled sea water along 6 profiles for POC measurement in the 0–1000 m water column during the cruise. Among the four Leg 2 profiles, three profiles (11–13 October) clearly exhibited deep POC accumulation at 700 m depth ($\times 1.5$ to 2.5 folds the concentration in the 500 m depth above) (data not shown).

Finally, the above observations combine to show that an egestion of fecal pellets at the surface or in the mesopelagic layers by zooplankton and/or migrators, and their subsequent disintegration/dissolution through bacterial activity, sloppy feeding and grazing in the mesopelagic layer is a reasonable assumption that would explain the presence of lipid signatures in the deep water layers. This scenario is consistent with previous observations that slowly sinking particles would rather dissolve within the mesopelagic layer at Dyfamed (Goutx et al., 2007). During Dynaproc 2, fecal pellets coming from the upper layers probably were emitted during the low wind period (25 September to 8 October), when high POC fluxes were recorded at 200 m depth (Marty et al., 2009), which is consistent with a slow sinking velocity for these aggregates. These observations also support 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 lead to formation of colloids known to preferentially shelter phospholipids (Liu et al., 1998).

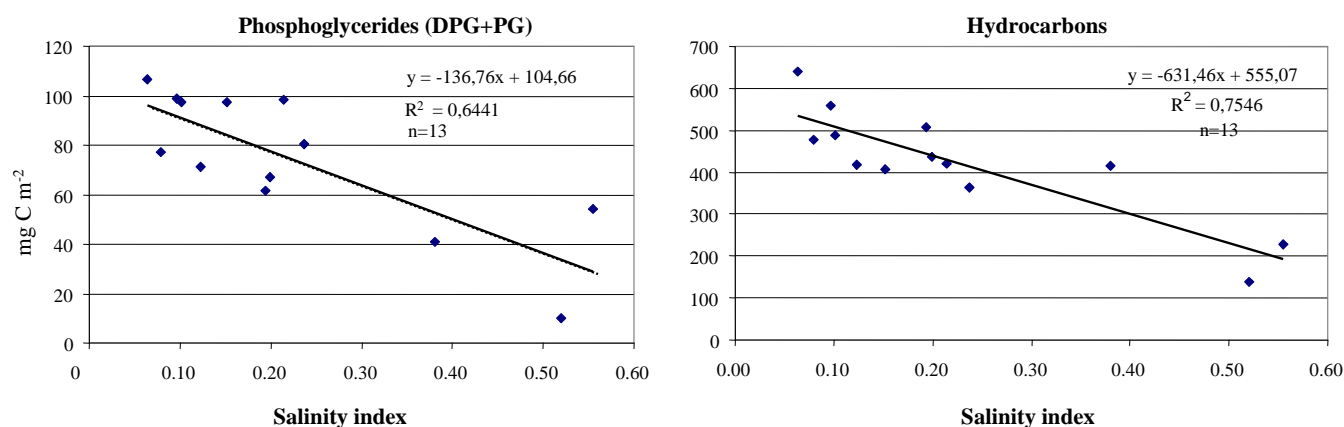


Fig. 11. Relationships between lipid biomarkers and salinity index. Lipid concentrations and Salinity index are integrated value between surface and 70 m depth.

4.5 Relationship between lipid classes and low salinity index

In order to compare chemical and biological parameters with low salinity events, an index in the range 0–1 of the presence of lowered salinity 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: $\text{Index}(\text{sta}) = (S_{\text{max}} - S(\text{sta})) / (S_{\text{max}} - S_{\text{min}})$; $S(\text{sta})$ is the average salinity in the 40–70 m layer, S_{min} is that of the water taken as reference for low salinity water (coastal waters in our case), S_{max} 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 low salinity index and lipid classes was significant (Fig. 11) showing that the low salinity water (LSW) had lower concentrations of 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 hydrocarbons (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 polycyclic aromatic hydrocarbon (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 solu-

bility at 25°C in seawater was about 68%, relative to fresh water. In our study, solubility was certainly not involved in the distribution of hydrocarbons (HC) since there was an opposite relationship between HC dissolution and salinity. Interactions between aromatic hydrocarbons 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 hydrocarbons in the high salinity water 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. This finding suggests that chronic petroleum hydrocarbon discharge are important in NW Mediterranean and/or that other sources like atmospheric inputs may be significant. 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 use in environmental studies.

5 Conclusions

This study contributes to advances in DOM characterization by documenting the concentration and composition of dissolved lipids along the 0–1000 m surface and mesopelagic water layers in the central ligurian sea, NW Mediterranean. We conclude that different processes were involved in variability of dissolved lipids at short temporal and spatial scale 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 to phytoplankton biomass where picoeucaryotes appeared to be the major source of dissolved lipids. In parallel, the variations of the system over time during the seasonal transition marked by nutrient limitations, corresponded

to lipid degradation and metabolite accumulation that were higher than previously observed earlier in the year. During the transitional period, the stratification of the system was a factor limiting the distribution of fresh dissolved matter to depth. Under these conditions, the lipid biomarker pattern in the mesopelagic layer suggested strongly that the mesopelagic community was benefitting from DOM release from sinking POM due to zooplankton trophic behaviour, before the winter convection.

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