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Maria-Lorena Gonzalez, Stéphane Blain, Ingrid Obernosterer. Seasonal freshening of NW Mediterranean surface water impacts microbial heterotrophic activity and dissolved organic matter. *Estuarine, Coastal and Shelf Science*, 2019, 230, pp.106448. 10.1016/j.ecss.2019.106448 . hal-02383822

**HAL Id: hal-02383822**

**<https://hal.science/hal-02383822>**

Submitted on 28 Nov 2019

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**Seasonal freshening of NW Mediterranean surface water impacts microbial  
heterotrophic activity and dissolved organic matter**

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**Key words:** Low salinity waters, microbial heterotrophic activity, dissolved organic matter, NW  
Mediterranean Sea.

Declarations of interest: none.

## **Abstract**

The Rhone river represents the most important source of freshwater, nutrients and organic matter to the northwestern (NW) Mediterranean Sea and riverine input markedly affects biogeochemistry and ecosystem functioning in the estuarine and coastal zone. Structures of low salinity waters (LSW) originating near the river plume can also be transported along the continental shelf and offshore. The objective of the present study was to investigate the influence of LSW distant from their source, focusing on dissolved organic matter (DOM) and related microbial processes during two annual cycles (2007 and 2008) at a time series site characterized by the regular occurrence of LSW in spring (Microbial Observatory Laboratoire Arago). We observed enhanced bacterial heterotrophic production and community respiration and specific DOM features within these LSW, concurrently with low net community production. Our results suggest that LSW represent a mechanism of labile DOM supply, thereby sustaining enhanced heterotrophic microbial metabolism.

## **1 Introduction**

Riverine input represent approximately 40% of fresh water entering the ocean (Dagg et al., 2004), and thereby plays a key role in linking terrestrial and marine environments. Rivers deliver a large amount of inorganic nutrients to the adjacent coastal area, stimulating rates of primary production and associated food web processes (Frame and Lessard, 2009, Iriarte et al., 2012, Liu et al., 2004). Riverine discharge also transports terrigenous particulate (POM) and dissolved organic matter (DOM), mainly from terrestrial vegetation, to the coastal ocean (Bianchi et al., 2004, Medeiros et al., 2017, Opsahl and Benner, 1997). DOM from freshwater input of the 30 major rivers, accounts for 90,2 Tg dissolved organic carbon (DOC) per year (Raymond and

Spencer, 2015) which represents ~36% of the global DOC flux to the ocean (250 Tg DOC-C yr<sup>-1</sup>; Hedges et al., 1997). The fraction of terrigenous organic matter that is removed in the coastal ocean is not well quantified due to multiple biotic and abiotic processes involved, and the spatio-temporal heterogeneity of river-influenced ocean margins (Bianchi et al. 2011.). In large river systems, such as for example the Mississippi-Atchafalaya river, biological mineralization results in the removal of about 40% of terrestrial DOM in shelf waters (Fichot and Benner 2014). Export of terrigenous DOC from the Amazon river varies on a seasonal scale and accounts for 50% to 76% (Medeiros et al. 2015). How riverine input of nutrients and organic matter affect marine ecosystems has been investigated in a range of estuarine and coastal environments (Cole et al., 2007, Dagg et al., 2004 and reference therein). The influence of terrestrial input at varying distances from shore is, however, far less understood.

The Mediterranean Sea is a mid-latitude semi-enclosed sea, divided in an eastern extreme oligotrophic basin (<0.1 µg Chlorophyll *a* L<sup>-1</sup>) and a moderately-oligotrophic western basin (0.1 to 3 µg Chlorophyll *a* L<sup>-1</sup>) (Bosc et al., 2004), mainly due to P-limitation (Krom et al., 1991, McGill, 1965). The Rhone River discharge represents the most important freshwater source to the Mediterranean Sea (Naudin and Cauwet, 1997). The average runoff of 1750 m<sup>3</sup> s<sup>-1</sup> varies strongly with season and is highest during the frequent precipitation events in spring and autumn (Ludwig et al., 2009, Naudin and Cauwet, 1997). The Rhone River represents an important source of inorganic and organic matter of continental origin to the Mediterranean Sea (de Madron et al., 2011). Increased inorganic and organic nutrient concentrations are reported near the Rhone river freshwater plume in shelf waters (100m depth, up to about 20 nautical miles offshore) in the Gulf of Lion (Diaz et al. 2008, Sempéré et al., 2000) and the associated enhanced biological activity in the estuary and adjacent waters has been documented during

several previous field studies (Christaki et al., 2009, Joux et al., 2009, Lefevre et al., 1997, Pujo-Pay et al., 2006).

The hydrodynamics of the Rhone river plume are governed by atmospheric conditions, discharge volume and larger scale water mass circulation. When south-easterly winds predominate, the plume remains close to the coast, while north-westerly winds result in the extension of the Rhone river plume in a south-western direction (Demarcq and Wald, 1984). Intrusions of Rhone river water were detected in 5-20% of a 4-year bi-monthly survey in the Bay of Marseille (Frayse et al., 2014), indicating that these events are frequent phenomena in the coastal Mediterranean Sea. Diluted structures with low salinity waters (LSW) detached from the Rhone river plume can be transferred to open waters (Barrier et al., 2016, Diaz et al., 2008, Nencioli et al., 2011, Petrenko et al., 2017). Under conditions of north-westerly winds and in combination with a persistent slope current along the shelf break of the Gulf of Lion (Northern Current; (Raimbault and de Madron, 2003)), these LSW can be directed south-west (Fig. 1). The transit of these buoyant water masses can last up to 3 weeks, and they can be transported over relatively long distances (Diaz et al., 2008), rendering the Gulf of Lion an appropriate site for the investigation of cross-shelf exchange (Petrenko et al., 2017).

The objective of the present study was to investigate whether these structures, referred to as lower salinity waters (LSW), represent a supply of biologically labile DOM to the offshore NW Mediterranean Sea. We addressed this question by observations at the time-series site MOLA (Microbial Observatory of the Laboratoire Arago) that is characterized by the recurrence of LSW at surface in spring (Fig. 1). The combined investigation of the temporal changes in environmental characteristics and microbial processes at Station MOLA provided insight on how

90 freshwater input through these physical features could affect biogeochemistry in the offshore  
 91 Mediterranean Sea.

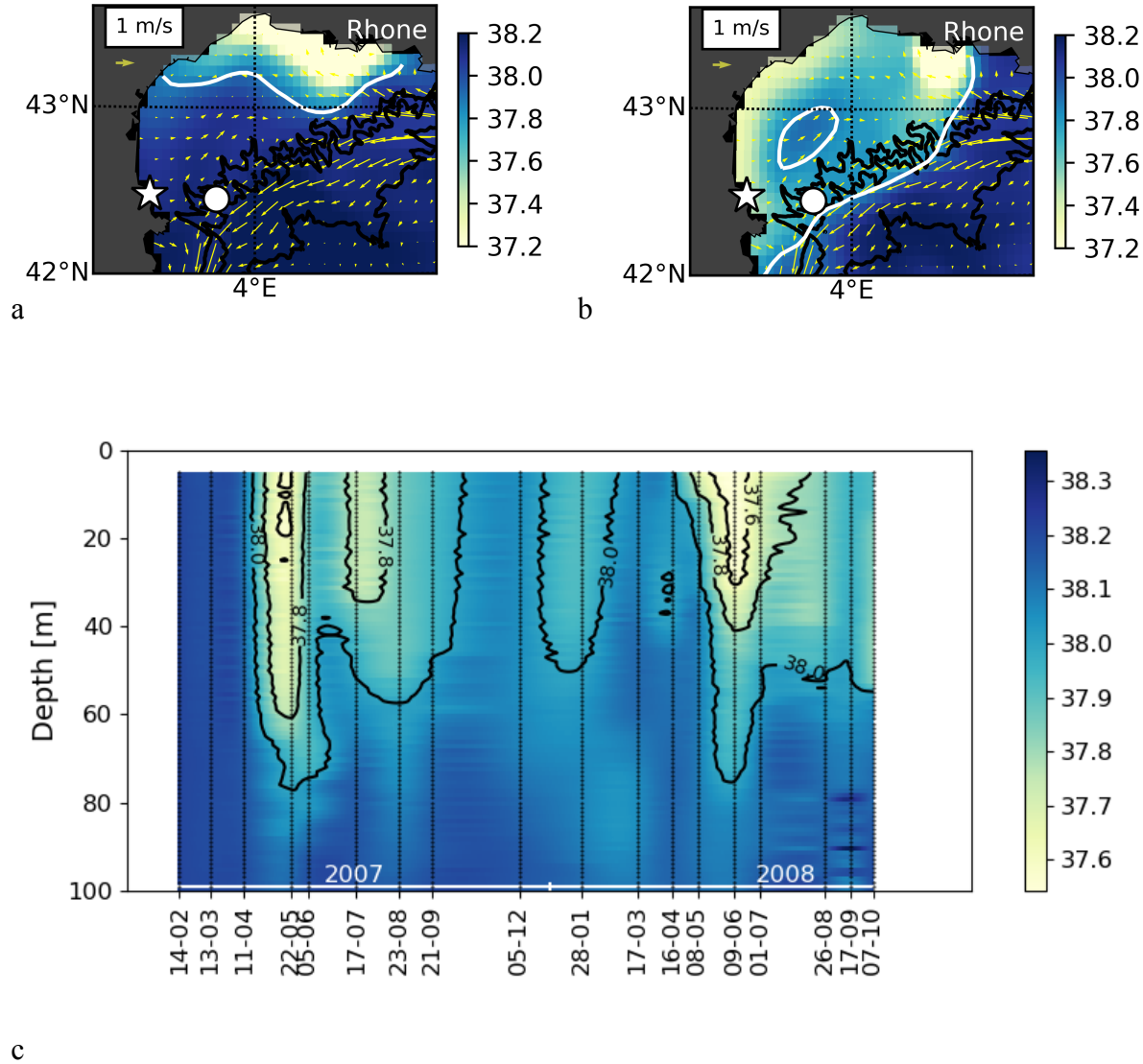


Fig. 1. Spatial and temporal distribution of salinity in the Gulf of Lion (NW Mediterranean Sea). Upper panels: Mean monthly surface salinity (4 km x 4 km) for February 2008 (left panel/a) and June 2008 (right panel/b) (February and May 2007 are shown in S1). Surface salinity distributions are provided by a circulation model overlaid with current speed and directions (yellow arrows), derived from altimetry for the date of sampling at Station MOLA (indicated by a white dot). Black lines represent isobaths (500 m, 1000 m and 2000 m). The white line denotes salinity of 37.85. Lower panel (c). Temporal changes of in situ salinity at Station MOLA

measured during the years 2007 and 2008. Star indicates Banyuls sur mer.

## 2 Material and Methods

### 2.1. Regional hydrology and seasonality

Station MOLA is located on the edge of the continental shelf at the south-western boundary of the Gulf of Lion (42.454°N and 3.688°E) (bottom depth 600m) in the NW Mediterranean Sea (Fig.1). Surface waters of this site are influenced by a northern liguro-provençal current (Raimbault and de Madron, 2003) related to water masses from the Gulf of Lion and the Rhone river. The climatological mean over the past 15 years reveals that the presence of low salinity water (LSW) is a recurrent feature during spring periods at station MOLA (Fig. S2). On a seasonal cycle, Station MOLA is characterized by vertical mixing during winter leading to the input of inorganic nutrients to surface waters ( $\sim 1 \mu\text{M NO}_3^- + \text{NO}_2^-$ ,  $\sim 0.05 \mu\text{M PO}_4^{3-}$ ) (Table S1) that sustain the spring phytoplankton bloom. During the two years considered here, maximum concentrations of Chlorophyll *a* (Chl *a*; 0.75 and 0.85  $\mu\text{g L}^{-1}$ ) (Fig. S3; Table S1) were observed in the upper 40m in March 2007 and February 2008, respectively (Laghdass et al., 2010). During summer, the water column is thermally stratified (Fig. S4) and concentrations of inorganic nutrients are low ( $< 0.35 \mu\text{M NO}_3^- + \text{NO}_2^-$ ,  $\sim < 0.03 \mu\text{M PO}_4^{3-}$ ) in the surface mixed layer (10 to 30m) and Chl *a* concentrations in surface waters remain  $< 0.2 \mu\text{g L}^{-1}$  (Laghdass et al., 2010) (Table S1).

### 2.2. Sample collection

Seawater was sampled between February 2007 and October 2008 on a monthly time scale except for the autumn-winter period when the sampling frequency was reduced due to

bad weather conditions. Samples were collected in the upper 150m water column with 12 liter Niskin bottles mounted on a rosette equipped with a SeaBird SBE 19 CTD. For bacterial heterotrophic production, and the characterization of dissolved organic matter 8 depths in the upper 150m were sampled. For the determination of microbial community respiration and net community production 6 depths in the euphotic layer were sampled (upper 80m).

### 2.3. Bacterial heterotrophic production, microbial community respiration and net community production

We used ( $^3\text{H}$ ) leucine incorporation and the centrifugation method to determine bacterial heterotrophic production (BP) ( Smith & Azam, 1992). The detailed protocol and data are reported in (Obernosterer et al., 2008; Laghdass et al., 2010). Bacterial growth rates (BGR) were determined by dividing BP by cell biomass derived from bacterial abundance. To convert abundance to biomass, we applied a conversion factor of  $12.4 \text{ fg C cell}^{-1}$  (Fukuda et al. 1998). We measured microbial community respiration (CR) and net community production (NCP) from changes in the concentration of dissolved oxygen ( $\text{O}_2$ ) in 24h light and dark incubations as described in (Lefèvre et al. 2008). Incubations were performed at Photosynthetically Active Radiation (PAR) levels of 1%, 4%, 8%, 25%, 50% and 100% of surface values, using optical density filters (Nickel screens). The outdoor incubators were connected with a running seawater system to maintain the incubation bottles at the temperature of the mixed layer. The 1% light depth was below the mixed layer depth during spring and summer with differences in temperature ranging between  $2^\circ\text{C}$  in May-June and up to  $5^\circ$  in August (Table S1). The measurements at time zero and all incubations were done in 8 replicate 125 mL borosilicate glass bottles. Dissolved  $\text{O}_2$  concentration was determined by



spectrophotometric detection of iodine following the Winkler reaction, using a Hitachi U-3010 Spectrophotometer equipped with a sipper system (Labasque et al., 2004).

#### 2.4. Dissolved organic carbon and total hydrolysable amino acids

Samples for dissolved organic carbon (DOC) and dissolved total hydrolysable amino acids (THAA) were filtered through two pre-combusted glass fiber filters (Whatman GF/F 25mm, 0.7  $\mu$ m nominal pore size). Samples for DOC were acidified ( $H_3PO_4$ , pH 2) and stored in pre-combusted glass tubes at room temperature in the dark until analysis. DOC was analyzed by high temperature catalytic oxidation (HTCO) technique (Benner and Strom, 1993) using a Shimadzu TOC-5000 analyzer.

THAA were analyzed by high performance liquid chromatography (HPLC) after liquid-phase acid hydrolysis according to a recent protocol described by (Escoubeyrou and Tremblay, 2014). This protocol uses a high volume (100  $\mu$ L) of undiluted samples injected on a robust hybrid C18 column. HPLC analyses were performed on an Ultimate 3000 Dionex system equipped with an autosampler and a fluorescence detector (excitation at 335 nm, emission at 450 nm). The separation was done with a Phenomenex Gemini C18 column (250x4.6 mm, 5  $\mu$ m, 110  $\text{\AA}$ ) and a Security Guard column (4 x 3 mm). We used the Dauwe Degradation Index (DI, (Dauwe and Middelburg, 1998)) calculated based on the relative distribution of individual AA and adapted for DOM (as reported in Peter et al., 2012, Davis et al 2009; Kaiser and Benner 2009) as an indicator for the degradation state of DOM. The original DI was calculated from Principal Component Analysis (PCA) applied to diagenetic altered sediments were  $DI = \sum ((\text{mol\% amino acid} - \text{average mol \% amino acid})/\text{standard}$

159 deviation mol%)\* PCA amino acid score) .

160

### 161 **3 Results and Discussion**

162

163 To investigate whether LSW revealed a specific biogeochemical signature at Station  
164 MOLA, we compared the depth profiles of microbial heterotrophic activity and of the DOM  
165 characteristics at the dates of the most pronounced salinity anomalies during the observation  
166 period (May 22 2007 and June 9 2008) with those of the annual medians (Fig. 2).

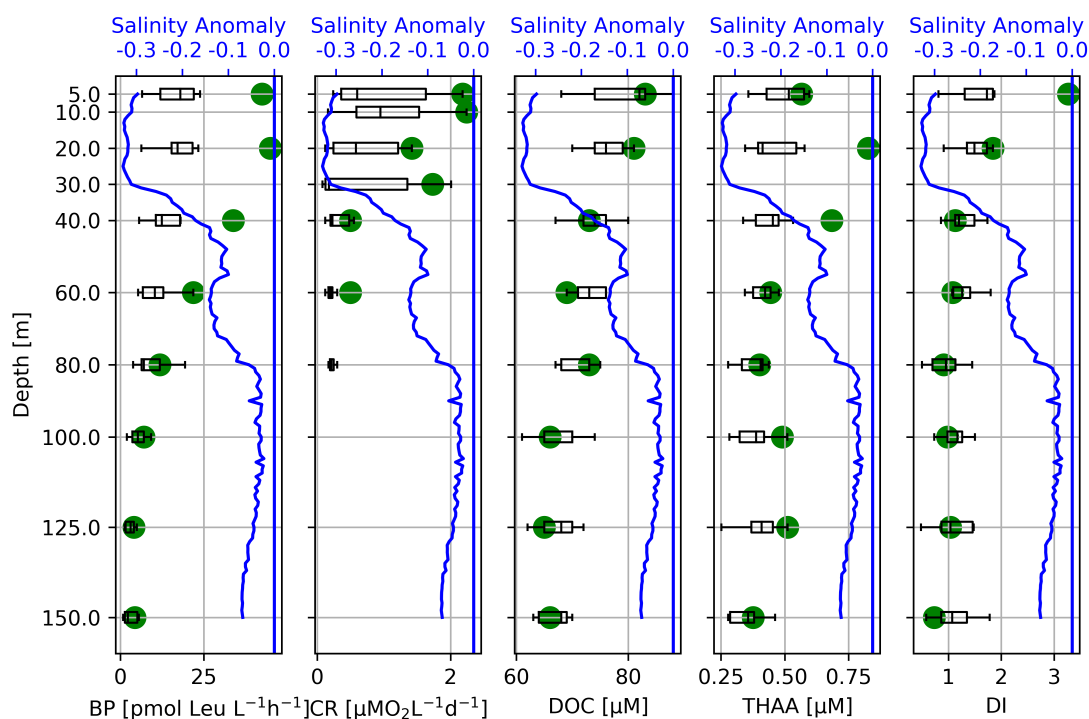


Fig. 2. Depth profiles of salinity anomaly (blue line), microbial activity and DOM characteristics (box plots) at Station MOLA for the year 2008. The black lines across the boxes represent the median annual values. The ends of the boxes define the 25<sup>th</sup> and 75<sup>th</sup> percentile and the error bars represent the 10<sup>th</sup> and 90<sup>th</sup> percentiles. Dots represent the individual value for the date for which the salinity anomaly is shown (June 9 2008). Results for 2007 are shown in Fig. S5. BP: Bacterial heterotrophic production ( $\text{pmol Leu L}^{-1} \text{h}^{-1}$ ), CR: Community Respiration ( $\mu\text{M O}_2 \text{L}^{-1} \text{d}^{-1}$ ), DOC: Dissolved Organic Carbon ( $\mu\text{M}$ ), THAA: Total Hydrolyzable Amino Acids ( $\mu\text{M}$ ), DI: Dauwe Degradation Index.

167

168       The extent of the salinity anomalies of about -0.3 was similar in both years, but lower  
169 salinity waters were present to 60m in 2007 and constrained to the upper 30m in 2008. The  
170 annual median values of BP varied between 10-20  $\text{pmol Leu L}^{-1} \text{h}^{-1}$  in the upper 60 m water  
171 column and they were below 5  $\text{pmol Leu L}^{-1} \text{h}^{-1} \geq 100 \text{ m}$  for both years. During LSW, rates of  
172 BP were 2-4 times higher than the annual medians in the upper 40 m water column, a pattern

that was particularly pronounced in 2008. Annual medians of CR varied between 0.5 and 1  $\mu\text{mol O}_2 \text{ L}^{-1} \text{ d}^{-1}$  in the upper 40 m water column and they were  $< 0.5 \mu\text{mol O}_2 \text{ L}^{-1} \text{ d}^{-1}$  below this depth. During LSW in 2008, rates of CR were up to 3-fold higher than the annual median, while differences were minor in 2007. In addition, bacterial growth rates revealed highest values (0.17 to 0.26  $\text{d}^{-1}$ ) during the LSW of both years (Table S1). These observations indicate a signature of enhanced microbial heterotrophic activity within LSW that was more pronounced in 2008 than in 2007, possibly due to a stronger dilution with surrounding water masses during our first year of observation.

To link these observations to the characteristics of DOM, we considered bulk DOC, the concentration of dissolved THAA and the DI (Fig.2). Annual medians of bulk DOC concentrations varied between 60  $\mu\text{M}$  and 80  $\mu\text{M}$  in the upper 150 m water column. In surface waters, we did not observed any pronounced differences between the annual medians and LSW. This is most likely due to the high DOC concentrations in surface waters during summer observed at our study site (Laghdass et al., 2010). The accumulation of DOC in stratified surface waters during summer is a recurrent phenomenon reported for Mediterranean waters (Avril, 2002, Romera-Castillo et al., 2010, Sánchez-Pérez et al., 2016) and other oligotrophic oceans (for BATS- (Carlson et al., 2002); for HOTS- (Mopper and Schultz, 1993)). Inorganic nutrient limitation of heterotrophic microbes has been suggested as the underlying mechanism for the observed build-up of DOC in stratified surface waters (Thingstad and Rassoulzadegan, 1999). This idea is supported by short-term (24h) incubation experiments performed at our study site revealing that labile organic carbon and phosphorus were the main limiting factors of BP during summer (Laghdass et al. 2012).

Amino acids represent a quantitatively significant and biologically labile fraction of DOM, and temporal or spatial changes of this pool can therefore provide insights to modifications of DOM characteristics (Davis et al., 2009, Kaiser and Benner, 2012). The concentrations of dissolved THAA varied between 262 and 1027 nM, with higher concentrations in the upper 40m. Within LSW in 2008, THAA concentrations were up to 2-fold higher than the annual median, a pattern that was absent in 2007 (Fig. 2 and Fig S5). The contribution of dissolved THAA to DOC, referred to as the amino acid yield, varied between 1.4-5.6% in the upper 150 m water column. The depth profiles of the amino acid yields during the LSW events were similar to those observed for dissolved THAA (data not shown). The DI is a chemical based indicator of the degradation state of organic matter, based on the relative distribution of individual amino acids (Dauwe and Middelburg 1998). Over the course of organic matter degradation, certain amino acids are selectively utilized resulting in a decrease of the DI (Dauwe et al. 1999). Based on the amino acid composition of marine plankton and sediment organic matter from varying depth layers, the DI was initially proposed to characterize the degradation stage of particulate organic matter. Its application has been extended to DOM in a range of marine (Amon et al., 2001, Davis et al., 2009, Tremblay et al., 2015; Kaiser and Benner 2009) and freshwater environments (Ylla et al. 2011, Peter et al. 2012), with values ranging from -3 to +5. The observed decreases in the DI over the course of biodegradation experiments further suggest this index to reflect changes in DOM bioavailability (Amon et al. 2001; Rochelle-Newall et al. 2004). At Station MOLA, the annual median DI varied between 1 and 1.5 and no pronounced depth profile was detectable over the 150 m water column. These positive values are indicative of overall diagenetically fresh DOM (Davis et al., 2009, Kaiser and Benner, 2009, Peter et al., 2012). In LSW, the DI was noticeably higher in the upper 20m as compared to the

respective average median values in both years (Fig. 2 and Fig S5). Thus, DOM in the uppermost water layer of LSW had a different chemical signature that is indicative of more bioavailable DOM. Complementary to the analyses illustrated in Fig. 2, we carried out a Principal Component Analysis (PCA) with the combined biogeochemical and microbial parameters of the two years from surface waters (5m) (Fig. S6). The PCA analysis revealed one group consisting of samples from May and June from both years being explained by variables of microbial activity (BP,  $r = 0.85$ ; CR,  $r = 0.77$ ; BGR,  $r = 0.88$ ) and features of DOM (dissolved THAA concentration,  $r = 0.48$ ; amino acid yields,  $r = 0.21$ ; DI,  $r = 0.52$ ) that were positively correlated with PC1. By contrast, this group was also explained by salinity, which was negatively correlated with PC1 ( $r = -0.81$ ). Taken together, these results suggest that LSW contains bioavailable DOM that sustains enhanced microbial heterotrophic activity in the offshore NW Mediterranean Sea.

This observation raises the question of the origin of the DOM within LSW. The LSW that we observe at Station MOLA most likely originates from the Rhone River and its plume (Fig. 1). The pronounced pattern observed within LSW could be due to an enrichment in compounds from recent primary production occurring in the vicinity of the estuary (Diaz et al., 2008) and in small amounts of riverine, terrigenous DOM. Besides these sources that can be considered allochthonous to our study site, *in situ* primary production within the LSW could fuel the observed enhanced microbial activity. To address this question we followed the pattern in euphotic depth integrated fluxes of net community production (NCP) and CR. Highest fluxes of NCP were observed in March and April in both years, corresponding to the spring bloom period (Fig. 3). During the LSW in May and June 2007, NCP was negative and associated with highest depth-integrated fluxes of CR, illustrating a switch from net autotrophy in March and April to

net heterotrophy in May and June 2007. During the LSW event in 2008, euphotic layer integrated fluxes of CR were again enhanced and associated with low positive (June 2008) and negative (July 2008) fluxes of NCP (Fig. 3). These NCP fluxes indicate low *in situ* primary production in LSW. The depletion in nitrate and phosphate in LSW (Table S1) could be the limiting factor of autotrophic activity, while heterotrophs can utilize these elements in organic form. These results support the idea that heterotrophic microbial processes are favored as compared to autotrophic processes within these buoyant water masses, suggesting that external rather than *in situ* produced DOM sustains heterotrophic activity.

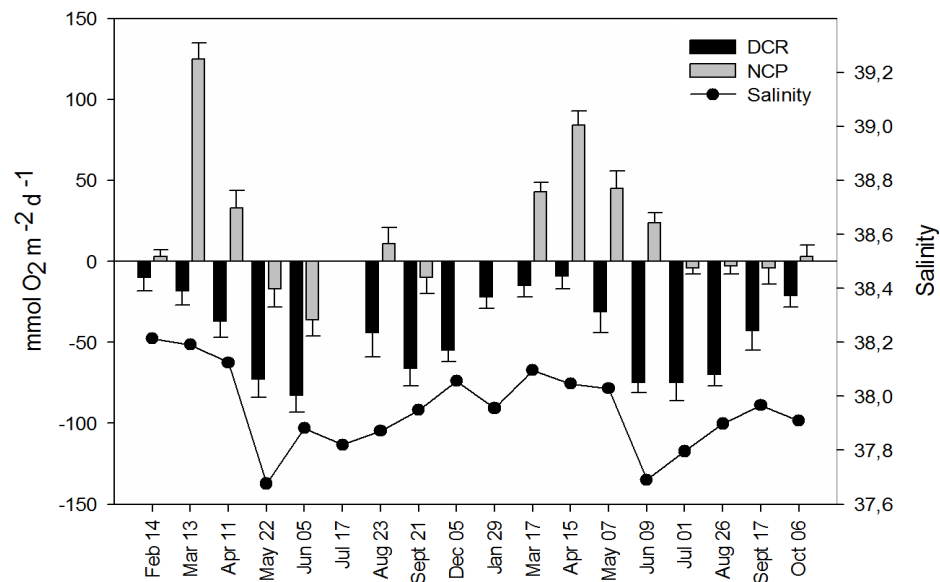


Fig. 3. Euphotic depth integrated fluxes of Net Community Production (NCP) and Community Respiration (CR) and salinity at 5m depth. Results are shown for 2007 (February 14 to December 5) and 2008 (January 29 to October 6).

Our observations from a time-series site in the NW Mediterranean Sea extend previous studies within LSW lenses in close vicinity to the Rhone river estuary and they provide insights on how biological activity in these water masses could change with time and distance from its origin. Direct measurements and satellite observations report increased autotrophic productivity in coastal LSW lenses as compared to surrounding marine waters (Auger et al., 2011, Diaz et al., 2008), and the high NCP determined *in situ* (Joux et al., 2009) suggests net autotrophy of the system in the vicinity of the estuary. With increasing distance from the plume and time since formation, inorganic nutrients are depleted and primary production is based on regenerated nutrients (Diaz et al., 2008). This suggests a scenario where autotrophic processes dominate in early stages of LSW and heterotrophic processes become more important with distance and time.

Primary production in coastal marine environments and export of terrigenous DOC are potential sources of organic carbon for the open oligotrophic ocean (Smith and MacKenzie 1987, Bauer and Druffel 1998; Medeiros et al. 2015) and proposed transport mechanisms are physical features such as for example mesoscale eddies, internal waves or currents. The resulting spatio-temporal decoupling between the origin of organic matter in the coastal zone and its respiration in open waters was suggested to explain in part the imbalance between primary production and respiration in the oligotrophic ocean (Duarte et al. 2013; Williams et al. 2013). The LSW could represent this linkage in the NW Mediterranean Sea. In addition to recent and *in situ* primary production, photochemical transformations of DOM could be an important mechanism in providing bioavailable substrates in these buoyant surface water masses in particular when compounds of terrigenous origin are present (Abboudi et al., 2008, Amon and Benner, 1996, Obernosterer and Herndl, 2000). The combination of a suite of tools including



satellite-based and autonomous instrumentation offers the possibility for a more detailed characterization and adapted sampling strategy of these mesoscale features at different locations in the open ocean. Taken together, our study illustrates the potential of water masses of estuarine origin to affect biological activity in the offshore oligotrophic ocean. The extension, lifetime and occurrence of these types of buoyant water masses will govern their impact on marine biogeochemistry and ecosystem functioning at different scales and distances from shore.

## Acknowledgements.

We thank the captain and the crew of the *R/V Nereis* for their support aboard and the members of the Service d'Observation of the Observatoire Océanologique in Banyuls for their help in sample collection. We are grateful to Louise Oriol and Jocelyne Caparros for their enthusiastic participation to the cruises to Station MOLA. We thank Karine Escoubeyrou from the platform Bio2Mar for the amino acid analyses. L. Zudaire provided the CTD profiles for all cruises. We thank 3 anonymous reviewers for their insightful comments on a previous version of the manuscript. This work was conducted as part of the national project MEDEA (INSU-LEFECYBER). This work is part of the PhD thesis of M.L. Gonzalez. M.L. González was funded by the National Doctorate Scholarship (CONICYT-Chile), INCAR (FONDAP 15110027), and LIA-MORFUN (LIA 1035). We also thank to Patricio Torres and Angel Rain for their help in the construction of some supplementary figures. Salinity data are from Copernicus and in situ data are available online (<http://www.obs-vlfr.fr/proof/index2.php>).

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