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1 **Atmospheric fluxes of soluble organic C, N, and P to the**  
2 **Mediterranean Sea: potential biogeochemical implications in the**  
3 **surface layer**

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## 29 **Abstract**

30 Linking atmospheric deposition to marine carbon and nutrient cycle is hampered by the  
31 lack of data on atmospheric fluxes of organic matter. To fill this gap, this study reports the  
32 first quantification of atmospheric fluxes of soluble organic carbon (SOC), nitrogen (SON)  
33 and phosphate (SOP) to the NW Mediterranean Sea. Simultaneous measurements of dissolved  
34 organic carbon (DOC), dissolved organic nitrogen (DON) and dissolved organic phosphate  
35 (DOP) in the surface mixed layer (SML) allowed estimating the potential contribution of  
36 atmospheric fluxes to marine DOC, DON and DOP inventories. We found an annual  
37 atmospheric flux of  $59 \text{ mmol C m}^{-2} \text{ year}^{-1}$  for SOC,  $16.4 \text{ mmol N m}^{-2} \text{ year}^{-1}$  for SON and  $23.6$   
38  $\mu\text{mol P m}^{-2} \text{ year}^{-1}$  for SOP, with proportions of SON and SOP to total soluble nitrogen and  
39 phosphate of 40% and 25%, respectively. Assuming these annual fluxes valid for the entire  
40 western Mediterranean basin, atmospheric fluxes would be higher than DOC, DON and DOP  
41 fluxes from the Rhône River by a factor of 6, 17 and 2, for C, N and P, respectively, which  
42 highlights the importance of atmospheric deposition as a source of DOC, DON and DOP to  
43 surface waters of the western Mediterranean Sea. Inventories of DOC, DON and DOP in the  
44 surface mixed layer displayed similar trends over the study period with maximum values at  
45 the end of the stratification period. DOP inventories contributed by  $85 \pm 11\%$  to total  
46 dissolved phosphate (TDP) pool and exhibited a labile fraction (LDOP) of  $27 \pm 19\%$ . The  
47 contribution of atmospheric SOC, SON and SOP to the DOC, DON and DOP pools in the  
48 SML were estimated for the stratification period, and suggested a low contribution of SOC to  
49 DOC pool (3%) and moderate contributions of both SON and SOP to DON (12%) and DOP  
50 (4.5%) pools for this period of time, respectively. The labile fraction of SOP (LSOP) was  
51 quantified throughout the sampling period and showed a high variability ranging from 0 to  
52 97%. Atmospheric fluxes of LSOP contributed by 7% to LDOP pool and could sustain up to  
53 8% of the heterotrophic prokaryotic phosphate demand in the SML of the NW Mediterranean  
54 Sea during the stratification period. The results obtained in this study stress the need to  
55 include atmospheric fluxes of organic matter in marine biogeochemical models to achieve a  
56 more complete picture of carbon and nutrient cycle in the Mediterranean Sea.

57 **Keywords:** atmospheric deposition, organic carbon, organic nitrogen, organic  
58 phosphate, C:N:P ratios, dissolved organic matter, Mediterranean Sea.

## 59 **1. Introduction**

60 The oligotrophic regions cover a significant portion of the global ocean (60%) [Eppley  
61 and Peterson, 1979]. These areas are characterized by low concentrations of surface nutrients  
62 because of strong stratification and low upward supply of nutrients. In the surface layer, the  
63 pool of dissolved organic matter (DOM) plays an important role in maintaining the biological  
64 activity as it's an important source of energy and nutrient [Sandberg et al., 2004]. The  
65 concentration of dissolved organic nitrogen (DON) and phosphate (DOP) exceed those of  
66 inorganic nutrients by an order of magnitude [Bronk, 2002; Lomas et al., 2010] and can serve  
67 as nitrogen and phosphate source for microbial growth [Sipler and Bronk, 2015 and  
68 references therein; Karl and Björkman, 2015 and references therein]. The seasonal variability  
69 of dissolved organic carbon (DOC) in the euphotic zone has been recorded in the subtropical

70 and temperate areas of the ocean [Carlson et al., 1994; Santinelli et al., 2013]. The lag time  
71 between DOC production and consumption, causes DOC accumulation in the upper layers  
72 [Carlson et al., 1994; Thingstad et al., 1997; Santinelli et al., 2013]. Part of the DOC which is  
73 accumulated in the surface layer is exported to the deep by diffusion and/or due to both deep  
74 water formation and winter vertical mixing constituting an important pathway for the export  
75 of carbon from the surface to the deep ocean [Letcher and Moore, 2015]. At the global ocean,  
76 DOM provides of about 20% of global export production [Hansell et al., 2009]. In addition,  
77 the elemental ratios of the DOM pool deviate widely from the Redfield ratio being enriched  
78 on C in comparison to N and P which suggests a higher carbon export efficiency compared to  
79 particulate organic matter [Church and Ducklow, 2002; Hopkinson and Vallino, 2005].

80 Accurate quantification of DOM sources is needed to achieve a complete picture of C  
81 and nutrient cycle in the oligotrophic ocean. In the open ocean, DOM pool is produced mainly  
82 by the biological activity in the euphotic layer [Carlson and Hansell, 2015 and references  
83 therein]. The microbial activity has been identified to be involved in recalcitrant DOM  
84 (RDOM) generation [Taylor et al., 1985; Brophy and Carlson, 1989; Jiao et al., 2010] which  
85 can persist in the ocean for millennia and is therefore a reservoir for carbon storage in the  
86 ocean [Jiao et al., 2010, 2014]. Besides local production, external sources may contribute  
87 significantly to the DOM pool. River flux from land to ocean is an important source of DOM  
88 to marine environment, at the scale of the global ocean [Meybeck, 1982] and of the  
89 Mediterranean Sea [Ludwig et al., 2009; Panagiotopoulos et al., 2012; Ferreto et al., 2017]. In  
90 open waters, where there is little riverine input, groundwater discharge or sediment  
91 resuspension, atmospheric deposition becomes a significant source of elements to the surface  
92 ocean [Jickells et al., 2005]. However, to date, most measurements of atmospheric deposition  
93 to the open ocean have focused on the inorganic fraction [e.g. Duce et al., 1991; Zhang et al.,  
94 2010; Guieu et al., 2014] and data on atmospheric fluxes of organic matter to the open ocean  
95 are scarce [e.g. Kanakidou et al., 2012] biasing our knowledge on the biogeochemical role of  
96 atmospheric deposition in the surface ocean. And yet, the quantification of the atmospheric  
97 flux of organic matter could be important since the anthropic emissions of N and P have been  
98 enhanced greatly by demographic growth, industrialization, and agricultural intensification.  
99 Anthropogenic reactive nitrogen production including inorganic reduced forms of nitrogen  
100 (e.g.  $\text{NH}_3$ ,  $\text{NH}_4^+$ ), inorganic oxidized forms (e.g.  $\text{NO}_x$ ,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_3$ ) and organic  
101 compounds (e.g. urea, amines, proteins, nucleic acids) could reach 270 T g N  $\text{yr}^{-1}$  in 2050  
102 [Galloway et al., 2004]. Similarly, P mobilization rose from about 50 Mt P  $\text{yr}^{-1}$  in preindustrial  
103 time to 155 Mt P  $\text{yr}^{-1}$  in 2000 [Smil, 2000]. In that context of increasing anthropic emissions  
104 in the atmosphere, including variable components of organic matter, it seems important to  
105 assess how atmospheric organic matter fluxes could influence the biogeochemistry of DOM  
106 in ocean surface waters with consequences on carbon export.

107 The Mediterranean Sea is an oceanic basin representative of an enclosed mini-ocean. Its  
108 own conveyor belt and fast circulation times compared to open ocean make it highly reactive  
109 to external forcing particularly matter fluxes at the interfaces [Mermex group, 2011 and  
110 references therein]. The Mediterranean Sea is of oligotrophic character due, among others, to  
111 a pronounced thermal stratification occurring especially during the summer period which

112 delimits a depleted nutrients surface layer from the deeper [Moutin and Raimbault, 2002;  
113 Pulido-Villena et al., 2010]. During the stratification period, both autotrophic and  
114 heterotrophic prokaryotic activities are P-limited [Thingstad et al., 1998; Van Wambeke et al.,  
115 2002]. Nutrient limitation has been hypothesized to enhance DOC accumulation during the  
116 stratification period in the Mediterranean Sea [Thingstad et al., 1997]. In this oceanic region,  
117 DOC fluxes play a crucial role in the supply of fresh carbon to the deep water [Ramondene  
118 et al., 2016] both through vertical winter mixing and deep-water formation. In situ  
119 measurements estimate that DOC export fluxes are greater or similar than the mean export of  
120 POC [Santinelli, 2015 and references therein]. Similarly, a recent modelling study based on  
121 varying C:P quotas of planktonic cells, estimated that DOC is responsible of 64% and 90% of  
122 the carbon export in the western and eastern Mediterranean basin, respectively [Guyennon et  
123 al., 2015]. The Mediterranean Sea is subjected to continuous atmospheric fluxes of  
124 anthropogenic sources. Moreover, it receives a noticeable flux of dust from arid regions of  
125 North Africa, in the form of strong pulses [Guerzoni et al., 1999], as well as seasonal inputs  
126 from biomass burning [Mermex group, 2011 and references therein]. The supply of new  
127 nutrients to the Mediterranean Sea from atmospheric deposition and their impact on the  
128 activity of phytoplankton and heterotrophic prokaryotes have been extensively addressed  
129 [Ridame and Guieu, 2002; Pulido-Villena et al., 2008; Marin et al., 2017]. In contrast, little  
130 attention has been paid to the organic fraction of atmospheric deposition precluding the  
131 evaluation of its biogeochemical role in the Mediterranean Sea [e.g. Pulido-Villena et al.,  
132 2008; Markaki et al., 2010; Sanchez-Pérez et al., 2016].

133 The aims of this study were to quantify atmospheric fluxes of soluble organic carbon  
134 (SOC), nitrogen (SON), and phosphate (SOP) and to estimate the relative contribution of this  
135 external source to the inventory of the surface DOC, DON and DOP pools in the NW  
136 Mediterranean Sea during the stratification period. For this purpose, we coupled field  
137 observations of atmospheric deposition of SOC, SON, and SOP and of DOC, DON and DOP  
138 dynamics in the marine surface layer.

## 139 **2. Material and Methods**

### 140 **2.1. Atmospheric deposition sampling**

141 Bulk atmospheric deposition (dry plus wet deposition) was sampled twice a month at  
142 Frioul Island (43.26° N 05.29° E) in Marseille Bay in the NW Mediterranean Sea (Fig. 1)  
143 from February 2015 to July 2016. The collector was set up on a cliff at 40 m above sea level  
144 and consisted on an open funnel (314 cm<sup>2</sup>) connected to a sampling HDPE bottle (2 L) with a  
145 nylon membrane (40 µm) in the neck of the funnel preventing contamination from plants,  
146 debris and insects. The height of the collector was 2 m above the ground level. Prior to  
147 sampling, the collector was cleaned with 10% hydrochloric acid solution and ultrapure water.  
148 Every sampling day, the collector was recovered and transferred to the laboratory in a clean  
149 plastic bag. Under a laminar flow hood, the inner walls of the funnel were rinsed with 100 mL  
150 of ultrapure water after having removed debris deposited on the nylon membrane by means of  
151 a plastic clamp. The volume of the rainfall was then determined by the difference in the  
152 weight of the sampling bottle before and after sampling to which the volume of ultrapure  
153 water added to rinse the funnel was subtracted. If the sample volume collected was less than

154 600 mL (volume needed to perform all analysis), this one was made up to 600 mL with  
155 ultrapure water. Two hundred mL were filtered through a pre-weighed GF/F filter for the  
156 determination of particulate matter content as dry weight (60°C, 24h). The remaining volume  
157 (400 mL) was filtered through a pre-cleaned (10% HCl + ultrapure water) 0.2 µm  
158 polycarbonate filter for chemical analyses.

## 159 **2.2. Seawater sampling**

160 Seawater was sampled monthly between April 2015 to June 2016 on board the *R / V*  
161 *Tethys II* at the permanent time series MOOSE ANTARES offshore station (42.81° N, 6.79°  
162 E). Due to unfavorable weather conditions, samplings on November 2015 and between  
163 January and March 2016 could not be conducted. Seawater samples were collected at 4 to 7  
164 depths between the surface and 200 m from the Niskin bottles for dissolved organic carbon  
165 (DOC), dissolved organic nitrogen (DON), dissolved organic phosphate (DOP), labile  
166 dissolved organic phosphorus (LDOP), heterotrophic prokaryotic abundance (HPA),  
167 heterotrophic prokaryotic production (HPP), and community respiration (CR). Data on in situ  
168 temperature, salinity, oxygen concentrations, and fluorescence were also collected from a  
169 SeaBird CTD. For DOM measurements, seawater samples were filtered on board through pre-  
170 cleaned (10 % HCl + ultrapure water) 0.2 µm pore size polycarbonate filters and were kept  
171 frozen until analysis. Samples were collected in duplicate into acid washed HDPE 60 mL  
172 bottles.

173 For heterotrophic prokaryotic abundance (HPA), heterotrophic prokaryotic production  
174 (HPP) and community respiration (CR) unfiltered seawater was sampled. For HPA, duplicate  
175 subsamples (1.8 mL) were collected, fixed with 200 µl of paraformaldehyde (20 %), kept at  
176 ambient temperature for 15 min, placed in the freezer (-20 °C) available on board, and then  
177 stored at -80 °C in the laboratory until analysis. For CR, samples were siphoned directly from  
178 the Niskin bottle into eight oxygen bottles. Four bottles from each depth were immediately  
179 fixed with Winkler reagents, and the remaining bottles were incubated 24 h in the dark in a  
180 tap water bath to minimize temperature variation.

## 181 **2.3. Analytical methods**

182 DOC was measured using a Shimadzu (Model TOC-V total) carbon analyzer with a  
183 quartz combustion column filled with 1.2% Pt on silica pillows (Sempéré et al., 2008). Prior  
184 to analysis, samples were acidified with a few drops of orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85%).  
185 The daily calibration curve was based on 5 (0, 50, 100, 150 and 300 µM) and 4 (0, 50, 100  
186 and 150 µM) standard solutions of potassium acid phthalate (1000 ng L<sup>-1</sup>) for atmospheric  
187 SOC and marine DOC, respectively. One hundred µl of sample were injected between 3 and 5  
188 times for each sample and standard. The analytical precision of the procedure, based on 3 to 5  
189 injection and analyses of the same sample, was 1.5% on average. The accuracy of the  
190 instrument and the system blank were determined by analyzing reference materials (D.  
191 Hansell, Rosenstiel School of Marine and Atmospheric Science, Miami, USA), including the  
192 Deep Seawater reference (DSR) and low carbon water (LCW) reference materials. The  
193 average DOC concentrations in the DSR and LCW reference standards were 45 ± 2 µM C, n=  
194 24 and 1 ± 0.3 µM C, n= 24, respectively. Batch number references were Batch#15, Lot#01-  
195 15 for DSR and Lot#12-01-B2 for LCW.

196 DON and DOP concentrations were estimated from the difference between two  
197 determinations of dissolved inorganic nitrogen (DIN) and phosphate (SRP for soluble reactive  
198 phosphate). The first determination took place after hydrolysis of the sample (total dissolved  
199 nitrogen and phosphate, TDN and TDP) and the second one on non- hydrolyzed sample (DIN  
200 and SRP). DIN and TDN in both atmospheric and marine samples were analyzed by  
201 continuous flow according to Aminot and Kerouel (2007) using a Technicon autoanalyser  
202 with an estimated accuracy of 20 nM. TDN was analyzed after persulfate wet-oxidation  
203 [Pujo-Pay et al., 1997]. For atmospheric samples, SRP and TDP were analyzed  
204 spectrophotometrically on a 10-cm cell after Murphy and Riley (1962) method. TDP was  
205 obtained after UV digestion [Armstrong et al., 1966]. For marine samples, due to low  
206 concentrations expected, SRP and TDP were analyzed spectrophotometrically by using a long  
207 waveguide capillary cell (LWCC) according to Pulido-Villena et al. (2010). The LWCC was  
208 2.5 m long and the limit of detection, estimated as three times the standard deviation of 10  
209 measurements of the blank was 0.8 nM. The labile fraction of DOP in marine (LDOP) and  
210 atmospheric samples (LSOP) was obtained after an enzymatic hydrolysis with alkaline  
211 phosphatase (AP) from *Esherichia Coli* [Feuillade and Dorioz., 1992; Suzumura et al., 2012;  
212 Hashihama et al., 2013]. The AP was diluted with pure water to prepare a working AP  
213 solution of 0.2 U mL<sup>-1</sup>. Equal volumes (0.6 mL) of AP working solution and Tris buffer (0.5  
214 M) were added to 30 mL of the sample. Samples were incubated during 3 hours in the dark at  
215 a temperature between 25 and 30 °C before phosphate concentration analysis. The duration of  
216 the incubation was checked with glucose 6-phosphate in the same conditions of the sample to  
217 determine if this duration was sufficient to achieve the whole DOP hydrolysis. To assess any  
218 contamination, phosphate concentration was measured in 30 mL of milli-Q water in which 0.6  
219 mL of working AP and Tris buffer were introduced.

220 Heterotrophic prokaryotic abundance (HPA) counts were performed by cytometry with  
221 a FACSCalibur at the MIO-PRECYM flow cytometry platform. Heterotrophic prokaryotic  
222 cells were stained with SYBR Green II (Molecular Probes) 1:10 diluted for 15 minutes in the  
223 dark at ambient temperature, and were detected by their signature in a plot of side scatter  
224 (SCC) versus FLI (green fluorescence). Cells were characterized by 2 main optical signals  
225 collected from the 488 nm laser: side scatter (SSC, related to cell structure) and green  
226 fluorescence (530/488 nm), related to nucleic acids staining. Regions were established on the  
227 SSC versus green fluorescence plot in order to discriminate cells with high nucleic acid  
228 (HNA) content from cells with low nucleic acid (LNA) content. Abundance of heterotrophic  
229 prokaryotic cells were determined for each subgroup.

230 Heterotrophic prokaryotic production (HPP) was estimated using the <sup>3</sup>H-leucine  
231 incorporation method [Kirchman et al., 1993], adapted with the centrifuge method [Smith and  
232 Azam, 1992]. Triplicate aliquots of 1.5 mL were taken for each depth plus one trichloacetic  
233 acid (TCA, 5% final) control. The Leucine tracer was used at 20 nM final concentration (with  
234 a mix of 14 nM hot leucine (L-[<sup>3</sup>H] leucine, Perkin Elmer® specific activity 106 Ci mmol<sup>-1</sup>)  
235 and 6 nM cold leucine) in incubation lasting 2 hours in the dark. The incorporation of Leucine  
236 was stopped with the addition of TCA (5% final concentration), then, they were kept at - 4°C  
237 until analysis (within few days). After three runs of centrifugation/aspiration of the

238 supernatant (once with the fixed sea water sample, once with a 5 % TCA rinse, once with an  
239 80 % ethanol rinse), the pellet was resuspended in Scintillation liquid. We used the standard  
240 conversion factors of 1.5 kg C mol Leu<sup>-1</sup> [Kirchman et al., 1993], assuming no isotopic  
241 dilution as checked occasionally from concentration kinetics.

242 Community respiration (CR) was determined from the decrease in oxygen concentration  
243 before and after incubation. O<sub>2</sub> concentrations were measured following the Winkler method  
244 [Carrit and Carpenter, 1966] and a respiratory quotient of 1 [Del Giorgio and Cole, 1998] was  
245 applied to convert to C units. A minimum and maximum value of heterotrophic prokaryotic  
246 respiration (HPR) was estimated by multiplying the CR by 33% and 78% which represent the  
247 range of the contribution of HPR to CR in the NW Mediterranean Sea [Lemée et al., 2002].

#### 248 **2.4. Experimental assessment of atmospheric SOC bioavailability**

249 The bioavailability of atmospheric SOC was experimentally assessed on one sample of  
250 atmospheric deposition collected on April 2016 during a Saharan dust event. A natural  
251 inoculum of marine heterotrophic prokaryotes was added to sterile filtered rainwater. The  
252 rainwater sample was filtered through 0.2 µm and adjusted to a marine salinity of 35 using  
253 precombusted (450°C, 6 hours) NaCl crystals. A concentrated inoculum of marine  
254 heterotrophic prokaryotes was prepared using surface marine water (5 m) collected at the  
255 MOOSE ANTARES offshore site, which was subsequently filtered on board through a 40 µm  
256 mesh plankton and then by a 0.8 µm Nuclepore polycarbonate filter. Finally, the heterotrophic  
257 prokaryotes were concentrated 15 times from 1.5 L of the < 0.8 µm filtrate using a 0.2 µm  
258 Nuclepore polycarbonate filter. At the end of the filtration, a volume of 100 mL of the  
259 supernatant was recovered with the 0.2 µm filter and was sonicated during 5 mn in order to  
260 recover heterotrophic prokaryotes attached to the filter. The objective of this concentration  
261 approach was to limit the amount of DOC added with the inoculum which allowed setting the  
262 DOC contained in rainwater as the main C source in the incubations. HPA and HPP of the  
263 inoculum were 1.6 x 10<sup>6</sup> cells mL<sup>-1</sup> and 126 ng C L<sup>-1</sup> h<sup>-1</sup>, respectively, indicating that the  
264 procedure did not seem to affect the vitality of the heterotrophic prokaryote community.  
265 Controls consisted of ultrapure water adjusted to a salinity of 35 in which the same inoculum  
266 of heterotrophic prokaryotes were added. The experimental bottles were incubated in the dark  
267 at controlled temperature during 11 days. The experiment was run in triplicate. Subsamples  
268 were taken at selected times during the incubation for the determination of HPA, HPP and  
269 DOC.

270 The percentage of the labile SOC (LSOC) was calculated as:

$$271 \quad LSOC (\%) = \frac{[SOC]_{initial} - [SOC]_{final}}{[SOC]_{initial}} \times 100.$$

#### 272 **2.5. Calculations**

##### 273 **2.5.1. Air-mass back trajectories**

274 Five-day air-mass back trajectories were calculated at 500, 1000 and 3000 m asl for  
275 each sampling date using the Hybrid Single-Particle Lagrangian Integrated Trajectories  
276 (HYSPLIT) trajectory model (Draxler and G. Rolph, 2003, NOAA Air Resources Laboratory,



277 Silver Spring, Maryland, available at <http://www.arl.noaa.gov/ready/hysplit4.html>) provided  
278 by the NOAA Air Resources Laboratory (ARL).

### 279 **2.5.2. Heterotrophic prokaryotic phosphate demand (HPPD)**

280 HPPD, i.e. the phosphate channeled through the heterotrophic prokaryotes, was  
281 estimated by dividing the heterotrophic prokaryotic production (HPP) by the C:P ratio of  
282 heterotrophic prokaryotic biomass provided in the literature for natural environments. A  
283 conservative range of C:P ratios, between 29 (minimum value reported for oceanic bacteria in  
284 nature, Cotner et al. 1997 and references therein) and 106 was used for this calculation.

285 For sampling dates lacking HPP measurements (between April and August 2015), HPP  
286 was estimated from HPR (derived from CR) and heterotrophic prokaryotic growth efficiency  
287 (HPGE). HPGE (%) was calculated for each sampling date where both HPP and HPR data  
288 were available (Sep., Oct. and Dec. 2015, and from Apr. to Jun. 2016)  
289 as,  $HPP/(HPP + HPR) \times 100$ . For each sampling date, a minimum and maximum value of  
290 HPGE was estimated corresponding to the minimum and maximum HPR calculated from  
291 measured CR. Average  $HPGE_{\min}$  was  $4.7 \pm 3.3\%$  and average  $HPGE_{\max}$  was  $10.2 \pm 6.5\%$ .

### 292 **2.5.3. Inventories in the surface mixed layer**

293 The mixed layer depth for the marine sampling dates (running from April 2015 to June  
294 2016) was determined following De Boyer Montegut et al. (2004) according to the depth  
295 profiles of potential density and temperature. DOC, DON, DOP and biological inventories  
296 were calculated for depth intervals in the MLD by vertical trapezoidal integration assuming  
297 that the concentration at 0 m is the same as at 5 m:

$$\int_{z1}^{z2} f(x) = (z2 - z1) [(f(z1) + f(z2))/2]$$

## 298 **3. Results**

### 299 **3.1. Atmospheric fluxes of soluble organic matter (SOM)**

300 Between April 2015 and July 2016, atmospheric fluxes of soluble organic carbon (SOC)  
301 ranged between 32 and 588  $\mu\text{mol C m}^{-2} \text{ day}^{-1}$  (Fig. 2A). Atmospheric fluxes of soluble  
302 organic nitrogen (SON) ranged between 7 and 367  $\mu\text{mol N m}^{-2} \text{ day}^{-1}$  (Fig. 2B) and of soluble  
303 organic phosphorus (SOP) between 0.01 and 0.59  $\mu\text{mol P m}^{-2} \text{ day}^{-1}$  (Fig. 2C). The  
304 contribution of the organic fraction to the total soluble fluxes of nitrogen and phosphate  
305 ranged between 12 and 83% ( $41 \pm 14\%$ ) and between 4 and 57% ( $25 \pm 14\%$ ), respectively.  
306 The maximum atmospheric flux of soluble organic matter (SOM) was recorded during April  
307 and May 2015 when 23% of both SOC and SON and 39% of SOP was deposited. During the  
308 rest of the time-series, atmospheric fluxes of SOM were more homogeneous. Considering the  
309 entire study period ( $n = 33$ ), atmospheric fluxes of SOM were significantly related to  
310 precipitation rates ( $r = 0.43$ ,  $p < 0.01$  for SOC,  $r = 0.66$ ,  $p < 0.001$  for SON and  $r = 0.38$ ,  $p <$   
311  $0.05$  for SOP). No significant correlations were observed between atmospheric fluxes of SOM  
312 and the atmospheric flux of particulate matter.

### 313 **3.2. Bioavailability of soluble organic phosphate and carbon in atmospheric deposition**

314 The atmospheric flux of labile soluble organic phosphate (LSOP) ranged from 0 to 0.28  
315  $\mu\text{mol m}^{-2} \text{ day}^{-1}$  over the study period. The contribution of LSOP to the atmospheric flux of  
316 SOP showed an important variation during the study period, ranging from 0 to 97% ( $44 \pm$   
317 27%).

318 The labile fraction of soluble organic carbon (LSOC) in atmospheric deposition was  
319 estimated only once, through a biodegradation experiment made on a rainwater sample  
320 collected in April 2016 (see Material and Methods). In the control treatment, the  
321 concentration of DOC at the beginning of the incubations was  $7 \mu\text{M}$  and it remained constant  
322 during the 11-day incubation. The heterotrophic prokaryote abundance (HPA) decreased over  
323 the experiment and heterotrophic prokaryotic production (HPP) did not exceed  $0.35 \text{ ng C L}^{-1}$   
324  $\text{h}^{-1}$ . In the rainwater treatment, the concentration of DOC at the beginning of the incubations  
325 was  $62 \mu\text{M}$  and it decreased by  $18 \pm 3 \mu\text{M}$  in eleven days which leads to a labile fraction of  
326 29% at this time-scale. During the incubation period, HPA and HPP in the rainwater treatment  
327 increased by  $6.6 \pm 3.3 \times 10^5 \text{ cells mL}^{-1}$  and  $221 \pm 17 \text{ ng C L}^{-1} \text{ h}^{-1}$  respectively.

### 328 **3.3. Dissolved organic matter (DOM) and heterotrophic prokaryotes in the surface layer**

#### 329 **3.3.1. Depth profiles**

330 Vertical profiles of DOC, dissolved organic nutrients (DON, DOP and LDOP),  
331 dissolved inorganic nutrients (DIN and SRP) and biological activity (HPA, HPP and CR) for  
332 all sampling dates are reported in figures S1 to S6. DOC concentration ranged between  $39 \mu\text{M}$   
333 (June 2015 at 200 m) to  $86 \mu\text{M}$  (June 2015 at 5 m). Overall, the depth profiles of DOC were  
334 similar during the study period, presenting a slight decrease from the surface to 200 m (Fig.  
335 S1). The depth profiles of DON and DOP presented quasi-constant concentrations between  
336 the surface and 200 m. DON concentration ranged from  $1 \mu\text{M}$  (August 2015 at 200 m) to a  
337 maximum of  $10 \mu\text{M}$  (July 2015) (Fig. S2). DOP concentration ranged between  $24 \text{ nM}$  (April  
338 2016 at 5 m) to  $130 \text{ nM}$  (August 2015 at 200 m) (Fig. S3). LDOP ranged between 0 and  $34$   
339  $\text{nM}$  with maximum values observed above the pycnocline decreasing with depth to reach  
340 minimal values at 200 m (Fig. S3). In contrast to DON and DOP, DIN and soluble reactive  
341 phosphate (SRP) were low above the pycnocline, ranging from the detection limit to  $0.34 \mu\text{M}$   
342 for DIN and between 2 and  $47 \text{ nM}$  for SRP. Concentrations increased with depth and reached  
343 the highest values ( $8 \mu\text{M}$  for DIN and  $300 \text{ nM}$  for SRP) at 200 m (Fig. S4).

344 The abundance of heterotrophic prokaryotes (HPA) ranged between 3 and  $18 \times 10^5 \text{ cells}$   
345  $\text{mL}^{-1}$  throughout the study period (Fig. S5). The community respiration (CR) ranged from  
346 non-detectable values to  $0.5 \mu\text{mol O}_2 \text{ Kg}^{-1} \text{ day}^{-1}$  (Fig. S5). Heterotrophic prokaryotic  
347 production (HPP) data are available only from September 2015 and ranged from undetectable  
348 values to  $46 \text{ ng C L}^{-1} \text{ h}^{-1}$  (Fig. S6). Both HPA, HPP and CR showed higher values in surface  
349 waters and a general decrease with depth.

#### 350 **3.3.2. Depth-integrated inventories**

351 The integrated inventories DOC ( $\text{mol m}^{-2}$ ), DON ( $\text{mol m}^{-2}$ ), DOP and LDOP ( $\text{mmol}$   
352  $\text{m}^{-2}$ ) in the surface mixed layer (SML) displayed similar trends during the marine sampling  
353 dates with maximum inventories observed in December 2015 (Fig. 3). Over the study period,

354 SML inventories of DOC ranged between 1.0 and 2.3 mol m<sup>-2</sup> (Fig. 3A). SML inventories of  
355 DON and DOP ranged between 0 and 0.2 mol m<sup>-2</sup> (Fig. 3B) and between 0.5 and 2.1 mmol m<sup>-2</sup>  
356 (Fig. 3C), respectively. DON and DOP contributed of 98 ± 2% and of 85 ± 11% for TDN  
357 and TDP in the SML over the study period, respectively. Inventories of LDOP ranged  
358 between 0.14 and 1.02 mmol m<sup>-2</sup> in the SML (Fig. 3C) and, on average, contributed by 27 ±  
359 19% to the DOP pool.

### 360 **3.4. C:N:P molar ratios in atmospheric SOM and marine DOM**

361 C:N molar ratios in atmospheric soluble organic matter (SOM) ranged between 1.6 and  
362 10.5 (Fig. 4A) with an average value of 5.2 ± 2.3. Marine DOM showed higher C:N ratios,  
363 ranging from 2 to 43 with an average of 13.8 ± 6.5. C:P ratios in atmospheric SOM ranged  
364 between 352 and 4 200 with an average of 1 228 ± 849. Marine DOM C:P ratios were  
365 generally of the same order of magnitude ranging from 326 to 2 850 with an average of 1 227  
366 ± 538 except for August and December 2015 when the C:P ratio was higher in atmospheric  
367 deposition (Fig. 4B). N:P ratios in atmospheric SOM ranged between 55 to 2 013 with an  
368 average value of 308 ± 349 and a maximum observed during October 2015. Marine DOM  
369 N:P ratios were generally lower than in atmospheric SOM and evolved between 9 and 376  
370 with an average value of 100 ± 55 (Fig. 4C).

## 371 **4. Discussion**

### 372 **4.1. Atmospheric fluxes**

373 Very few data on atmospheric fluxes of SOC have been reported for the Mediterranean  
374 Sea, in particular using frequent deposition data collected over at least one year [Pulido-  
375 Villena et al., 2008; De Vicente et al., 2012]. The annual atmospheric flux of SOC obtained in  
376 this study (59 mmol m<sup>-2</sup> year<sup>-1</sup>) is slightly lower than reported in the Ligurian Sea (Cap Ferrat  
377 site 129 mmol m<sup>-2</sup> year<sup>-1</sup>) [Pulido-Villena et al., 2008] and in the southern Spain [De Vicente  
378 et al., 2012]. Annual atmospheric flux of SOC in our study is higher than the atmospheric flux  
379 (through dry deposition) estimated from the concentration of organic carbon in aerosols  
380 collected in the Eastern Mediterranean Sea (Finokalia site: 15 mmol m<sup>-2</sup> year<sup>-1</sup>) [Theodosi et  
381 al., this issue]. The literature on atmospheric fluxes of SON and SOP to the Mediterranean  
382 basin is also very limited. The annual atmospheric flux of SOP obtained in this study (69  
383 μmol P m<sup>-2</sup> year<sup>-1</sup>) is slightly higher than that reported by Migon and Sandroni (1999) (32  
384 μmol P m<sup>-2</sup> year<sup>-1</sup>) and lower than reported by Violaki et al. (this issue) (1160 and 940 μmol P  
385 m<sup>-2</sup> year<sup>-1</sup> for the western and eastern basin, respectively). The average contributions of SON  
386 and SOP to the total soluble nitrogen and phosphate (TSN, TSP) over the study period were  
387 40% and 25%, respectively. The contribution of SON to TSN in our study was higher than  
388 that previously observed by Markaki et al. (2010) while the contribution of SOP to TSP was  
389 lower than those reported in the Mediterranean basin [Markaki et al., 2010; Violaki et al., this  
390 issue]. Anyhow, given the few existing data, it is difficult to conclude if the observed  
391 differences reflect a spatial or inter-annual variability or if they are caused by differences in  
392 the sampling protocols and analytical methods.

393 To our knowledge, there are no reported measurements of atmospheric fluxes of SOC,  
394 SON and SOP simultaneously, a single modelling study quantified these atmospheric fluxes

395 at the global ocean scale [Kanakidou et al., 2012]. For the first time, in this study, coupled  
396 atmospheric fluxes of SOC, SON and SOP were quantified in the NW Mediterranean Sea.  
397 Over the study period, atmospheric fluxes of SOC, SON and SOP were significantly inter-  
398 correlated suggesting a common source and similar transport patterns. The atmospheric fluxes  
399 of SOC, SON and SOP were significantly correlated with precipitation rates indicating a high  
400 efficiency in atmospheric deposition of SOM via rain events in the NW Mediterranean Sea.  
401 These rain events occurred in 80% of our sampling dates and showed important amplitude of  
402 variability (between 0.4 and 47 mm). Hereafter, to get further insight on factors controlling  
403 the observed atmospheric fluxes of SOM, we have discriminated sampling dates presenting  
404 precipitation rates higher than 10 mm from the rest of sampling. Precipitation rates higher  
405 than 10 mm were recorded in 8 out of 33 sampling dates. In these samples, differences in  
406 SOM atmospheric fluxes observed may be attributable to the differences in rain amount. The  
407 maximum atmospheric flux of soluble organic matter was observed during the rain event of  
408 April 2015 (Fig. 2) and coincided with a maximum precipitation rate (47 mm during 15 days).  
409 This agrees with the observations by Pan et al. (2010) who reported high atmospheric fluxes  
410 of SOC coinciding with important rain events in Northern China. However, two other rainfall  
411 events of the same magnitude (32 and 37 mm during 15 days) were not accompanied by such  
412 a significant atmospheric flux of SOM, suggesting that other factors than rain amount  
413 controlled the magnitude of atmospheric flux of SOM in the study area. Back trajectories  
414 showed air masses coming from the North for the rain event of April 2015 whereas they came  
415 from the West and East during the rainfall of September 2015 and from the South with a  
416 Saharan influence for the rainfall of April 2016. These observations suggest that the  
417 maximum atmospheric fluxes of SOC, SON and SOP in the NW Mediterranean Sea result  
418 from a combination of an anthropogenic influence and an important precipitation rate. Indeed,  
419 anthropogenic emissions are known to enhance the presence of organic aerosols in the  
420 atmosphere [Kanakidou et al., 2000; 2005; Sempéré and Kawamura, 2003]. In the opposite,  
421 the minimum atmospheric flux of SOC, SON and SOP coincided with the rain event of April  
422 2016, suggesting that atmospheric fluxes with a desert signature are poorly enriched in  
423 soluble organic matter. This observation contrasts with Pulido-Villena et al. (2008) who  
424 reported a maximum atmospheric flux of dissolved organic carbon coinciding with a Saharan  
425 dust event. The Saharan dust event reported in Pulido-Villena et al. (2008) delivered a much  
426 higher particle flux ( $215 \text{ mg m}^{-2} \text{ day}^{-1}$ ) than that reported in our study ( $5.2 \text{ mg m}^{-2} \text{ day}^{-1}$ ). The  
427 high SOC flux observed by Pulido-Villena et al. (2008) was perhaps a result of heterogeneous  
428 reactions between organic compounds and mineral dust in the troposphere (Usher et al. 2003  
429 and references therein).

#### 430 **4.2. Marine dissolved organic matter (DOM)**

431 To date, technical limitations have dramatically constrained the data coverage on DOP  
432 concentration in surface waters of the Mediterranean Sea. Indeed, the quantitative estimation  
433 of DOP relies upon an accurate measurement of SRP concentration, which is below the  
434 detection limit given by the conventional colorimetric method (20 nM) in the surface layer  
435 during most part of the year [Moutin and Raimbault, 2002; Pulido-Villena et al., 2010]. In this  
436 study, an alternative high sensitive SRP analysis method, involving the Long Wave Guide  
437 Capillary Cell (LWCC), was applied allowing to get accurate measurements of SRP

438 concentration and, thus, of DOP in the NW Mediterranean area. Therefore, this study  
439 provides the first complete dataset on the temporal variation of DOC, DON, DOP and LDOP  
440 concentration in surface waters of the NW Mediterranean Sea.

441 DOC concentrations obtained over the study period are consistent with values reported  
442 for surface waters of the NW Mediterranean Sea [Avril, 2002; Pujo-Pay et al., 2011] as well  
443 as for the other parts of the Mediterranean Sea [Sempéré et al, 2002; 2003; Pujo-Pay et al.,  
444 2011; Santinelli et al., 2012]. Likewise, DON concentrations reported in this study are in good  
445 agreement with previously reported data in the Mediterranean Sea [Diaz et al., 2001; Pujo-  
446 Pay et al., 2011]. DOP concentrations above the pycnocline ranged between 25 and 78 nM  
447 with an average of 52 nM compared to few nanomoles of SRP. These concentrations compare  
448 well with DOP concentrations measured in the Eastern Mediterranean Sea using the same  
449 technology [Krom et al., 2005]. LDOP concentrations were in the same range as SRP  
450 concentrations in upper waters. However, the increase of SRP concentration below the  
451 pycnocline was not accompanied by an increase of the LDOP concentration in agreement  
452 with the observations by Hashihama et al. (2013) in the oligotrophic western North Pacific  
453 and East China Sea. This suggests that LDOP was still actively hydrolyzed below the  
454 pycnocline despite the high concentration of SRP. The elevated DOC concentrations in the  
455 upper waters and the slight decrease observed with increasing depth could suggest a net  
456 accumulation of carbon in the surface layer. The net accumulation of organic carbon is the  
457 difference between sources and sinks which are mainly attributed to biological processes in  
458 the marine environments. Phytoplankton activity and their grazer's or viruses activity are  
459 considered as the main primary DOM sources in the euphotic layer [Carlson and Hansell,  
460 2015 and reference therein]. The quasi-constant DON and DOP profile between the surface  
461 and 200 m observed in our study, could suggest a balance between production/consumption  
462 and import/export processes of both DON and DOP.

463 Concerning the integrated DOM inventories in the SML (Fig. 3), DOC, DON and DOP  
464 followed the same trend over the study period suggesting a control through common  
465 processes. The maximum integrated inventories were observed during December 2015 which  
466 suggests an accumulation at the end of the stratification period (Fig.3A, B and C). DON and  
467 DOP contributions to the TDN and TDP are important in the SML over the study period and  
468 are in good agreement with reported literature data in the Mediterranean Sea [Moutin and  
469 Raimbault, 2002; Santinelli et al., 2012]. The labile fraction of DOP (LDOP) also contributed  
470 significantly ( $27 \pm 19\%$ ) to the SML DOP pool over the study period. This contribution was  
471 higher than that observed in the oligotrophic Western Pacific and Eastern China ( $12 \pm 7\%$ )  
472 [Haschima et al., 2013]. Contrarily to DOP, LDOP did not accumulate at the end of the  
473 stratification period and could therefore sustain the autotrophic and heterotrophic activity in  
474 the P-depleted upper waters of the NW Mediterranean Sea.

### 475 **4.3. Elemental ratios in both atmospheric SOM and marine DOM**

476 C:N:P ratios of SOM in atmospheric deposition did not show a seasonal pattern, but  
477 seemed rather to be related to a punctual dominance of the atmospheric flux of one of the  
478 three elements. Except for a few sampling dates, C:N:P ratios displayed relatively constant  
479 values. For example, the average C:N ratio was higher between April and September (2015)

480 (Fig. 4A), linked to the high SOC fluxes. C:N ratios obtained in this study were in good  
481 agreement with C:N ratios of water soluble fraction of aerosols reported in both northern and  
482 southern Pacific (Sempéré and Kawamura, 2003). At the opposite, for C:P ratios, two  
483 sampling date deviates from the mean (Fig. 4B) but in this case linked to very low fluxes of  
484 SOP rather than deviations in SOC flux. Finally, the N:P ratio showed two maximum values  
485 linked to the lowest fluxes of SOP (Fig. 4C). The N:P ratios were, in average, higher in the  
486 organic fraction ( $308 \pm 349$ ) than in the inorganic fraction ( $175 \pm 234$ ) and were of the same  
487 order of magnitude as previously reported [Krom et al., 2004; Markaki et al., 2010].

488 The precise quantification of DOP concentration above 2 nM using the LWCC  
489 technique, allowed assessing for the first time the temporal variability in elemental C:N:P  
490 ratios of DOM above the pycnocline in the NW Mediterranean Sea. C:N, C:P and N:P  
491 showed average values over the study period of  $13 \pm 3$ ,  $1430 \pm 410$  and  $112 \pm 47$ ,  
492 respectively, without any seasonal trend. Elemental ratios of marine DOM showed different  
493 values, in average, than atmospheric deposition of SOM. Indeed, C:N ratios of marine DOM  
494 were somewhat higher than in atmospheric SOM while N:P ratios were higher in atmospheric  
495 deposition due to high atmospheric fluxes of SON. The lack of signature of atmospheric  
496 deposition in C:N:P ratios of marine DOM could suggest a quick transformation of  
497 atmospheric SOM in the upper waters. C:N:P ratios in atmospheric deposition may thus affect  
498 C:N:P ratios in DOM above the pycnocline, but it is difficult to establish a direct link on one  
499 year of data. The incorporation of the data obtained in this study into ocean biogeochemical  
500 models would certainly help to get further insight on the contribution of atmospheric  
501 deposition on elemental ratios of DOM.

#### 502 **4.4. Potential biogeochemical implications of atmospheric fluxes of SOM**

503 Assuming ranges obtained in this study for atmospheric fluxes valid for the whole  
504 western Mediterranean Sea, annual atmospheric fluxes of SOC, SON and SOP represent  
505 0.2%, 1.2% and 0.5% of modelled atmospheric flux of SOM at the global ocean scale  
506 (Kanakidou et al., 2012, Table 1). A comparison with the major input fluxes of DOM to the  
507 Western Mediterranean Sea (rivers and straits) highlights that annual atmospheric fluxes of  
508 carbon can account for 20 to 25% of the net inputs through Gibraltar and Sicily straits while  
509 annual atmospheric fluxes of nitrogen are in the same order of magnitude. Annual  
510 atmospheric flux of organic phosphate was lower than straits net inputs, accounting between 1  
511 and 3% of them (Table 1). In comparison to the Rhône river, which is the most affluent river  
512 in the Mediterranean Sea, atmospheric fluxes of SOC, SON and SOP were higher than DOC,  
513 DON and DOP fluxes delivered from that river by a factor of 6, 17 and 2 respectively (Table  
514 1). These results highlight the need of accounting for atmospheric inputs, particularly in  
515 biogeochemical models, in order to achieve an accurate budget of DOM in the Mediterranean  
516 Sea.

517 One of the key points of our study is the simultaneous survey of atmospheric SOM  
518 fluxes and marine DOM inventories which provides a direct quantification of the contribution  
519 of the atmospheric SOM deposition to surface DOM pool. In this study, we choose to  
520 quantify this contribution over the period from April 2015 to October 2015 which  
521 corresponds to the stratification period, when the surface mixed layer (SML) was isolated

522 from the deep layers making the atmospheric deposition a major source. The contribution of  
523 atmospheric SOM to the DOM pool in the SML during that period was calculated by dividing  
524 the atmospheric cumulative integrated flux (Table 3) by the surface mixed layer DOM  
525 inventories (Table 2) during that period. The contribution of atmospheric deposition of SOM  
526 to the DOM pool during that period in the surface layer of the NW Mediterranean Sea were  
527 low for SOC (3%), SOP (4.5%) and moderate for LSOP (7%) and SON (12%) (Table 3).

528 A better understanding of the role of atmospheric deposition of SOM relies on the  
529 knowledge on its bioavailability. Previous studies examining the effects of atmospheric inputs  
530 have focused on the inorganic fraction [Maranon et al., 2010; Pulido-Villena et al., 2014;  
531 Herut et al., 2016]. The few reported studies on the bioavailability of atmospheric organic  
532 matter concerned organic nitrogen [Timperley et al., 1985; Peierls and Paerl, 1997, Seitzinger  
533 and Sanders, 1999; Seitzinger et al., 2002] and none of these studies took place in the  
534 Mediterranean Sea. This study presents the first examination of the bioavailability of  
535 atmospheric SOC and SOP to marine heterotrophic prokaryotes, and suggests that a  
536 substantial fraction of atmospheric SOC (29% over 11-days period) and SOP ( $44 \pm 27\%$ )  
537 would be bioavailable. The quantification of the labile fraction of SOP (LSOP) derived from  
538 atmospheric deposition can have important consequences in the P-depleted Mediterranean  
539 surface waters since marine heterotrophic prokaryotes could hydrolyze labile DOP to alleviate  
540 P stress. Atmospheric LSOP being quantified over the study period, we have assessed its  
541 potential contribution to the heterotrophic prokaryotic phosphate demand (HPPD, Table 2), in  
542 the SML during the period between April and October 2015 (Table 3). The LSOP: HPPD  
543 ratio was calculated by dividing minimal and maximal atmospheric fluxes by minimal and  
544 maximal HPPD (Table 3) and suggested low to moderate contributions of LSOP to the  
545 heterotrophic prokaryotic phosphate demand (Table 3). The atmospheric LSOC may  
546 contribute also to the heterotrophic prokaryotic carbon demand (HPCD). However, to  
547 estimate this contribution, the bioavailability of atmospheric samples of different origins at  
548 different periods would be necessary.

## 549 **5. Concluding Remarks**

550 This work provides a unique data set of simultaneous atmospheric fluxes of soluble  
551 organic matter (SOM) and marine dissolved organic matter (DOM) inventories in the NW  
552 Mediterranean Sea and leads to the following major conclusions: (1) A substantial fraction of  
553 atmospheric deposition of nitrogen and phosphate to the Mediterranean Sea is in the form of  
554 soluble organic matter accounting of 40% and 25%, respectively. (2) In the surface mixed  
555 layer, DOP contributed by  $85 \pm 11\%$  to TDP with  $27 \pm 19\%$  of the DOP pool as LDOP. (3)  
556 Atmospheric deposition is a significant source of soluble organic matter to upper waters of the  
557 western Mediterranean Sea, greater than river input. (4) The direct contribution of  
558 atmospheric deposition of SOM to surface DOM pool is low to moderate although further  
559 research on its bioavailability is needed to understand its biogeochemical role in the NW  
560 Mediterranean Sea. Overall, the results obtained in this study highlight the need of  
561 incorporating atmospheric fluxes of SOM into biogeochemical models to better constrain the  
562 DOM cycle in upper waters in oligotrophic regions such as the Mediterranean Sea.

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573

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888 **Figure captions**

889 **Figure 1.** Location of the sampling sites: atmospheric deposition at the Frioul Island  
890 and sea water sampling at the ANTARES site. Both sampling sites are included in the  
891 MOOSE observation network (<http://www.moose-network.fr/>).

892 **Figure 2.** Temporal evolution of atmospheric fluxes ( $\mu\text{mol m}^{-2} \text{day}^{-1}$ ) of soluble organic  
893 carbon (SOC; panel A), total soluble and soluble organic nitrogen (TSN, SON; panel B), total  
894 soluble, soluble organic and labile soluble organic phosphate (TSP, SOP, LSOP; panel C), for  
895 each 2-week sample collected at the Frioul Island between March 2015 and July 2016.  
896 Arrows point to rain events higher than 30 mm. The vertical line differentiates the year 2015  
897 from the year 2016.

898 **Figure 3.** Integrated inventories of dissolved organic carbon (DOC; panel A), dissolved  
899 organic nitrogen (DON; panel B), dissolved organic phosphate and labile dissolved organic  
900 phosphate (DOP and LDOP; panel C) in the surface mixed layer over the study period. The  
901 mixed layer depth (MLD, m) is also plotted in each panel. The vertical line differentiates the  
902 year 2015 from the year 2016.

903 **Figure 4.** C:N (panel A), C:P (panel B) and N:P (panel C) molar ratios of soluble  
904 organic matter in atmospheric deposition (line with squares) and of marine dissolved organic  
905 matter between the surface and 200 m depth (box plots: the central mark represents the mean  
906 value for all depths, the edges of the box are the 25th and 75th percentiles, the whiskers  
907 extend data points to the minimum and the maximum, and the outliers are plotted  
908 individually).

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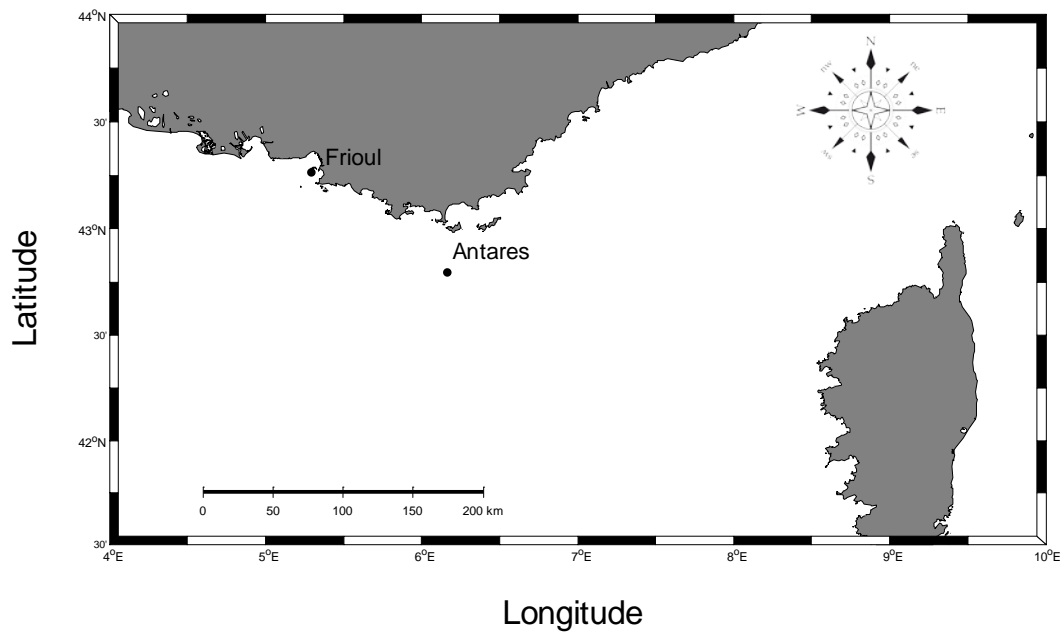


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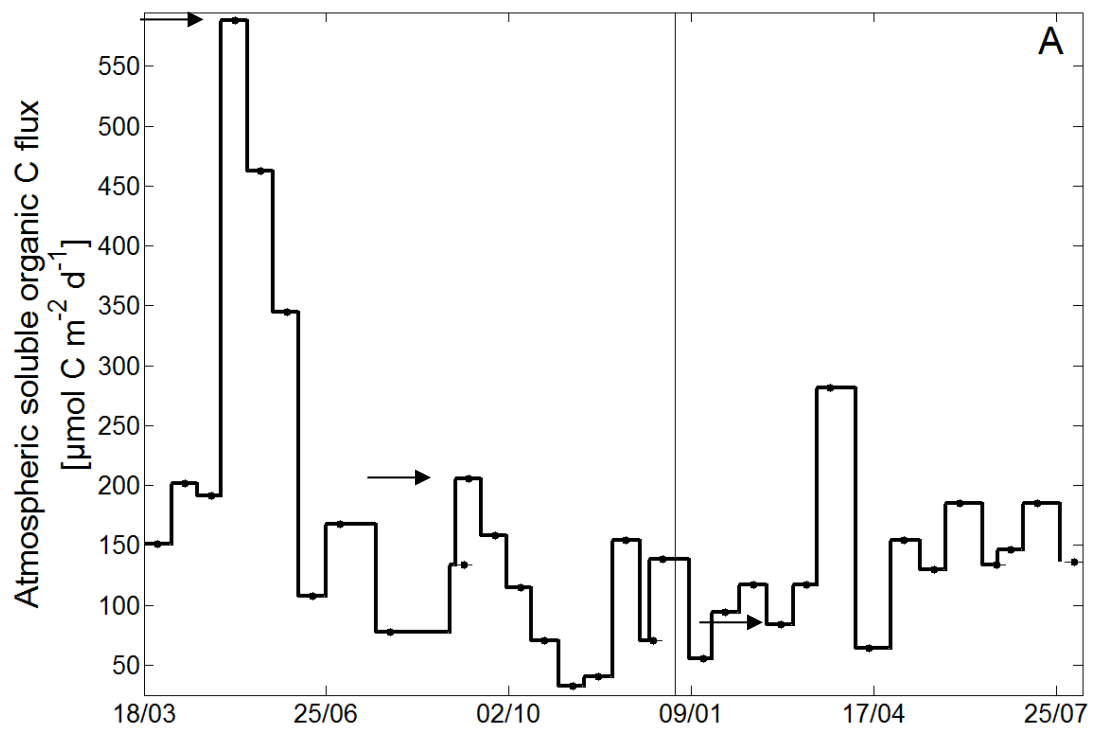
**Figure 1**



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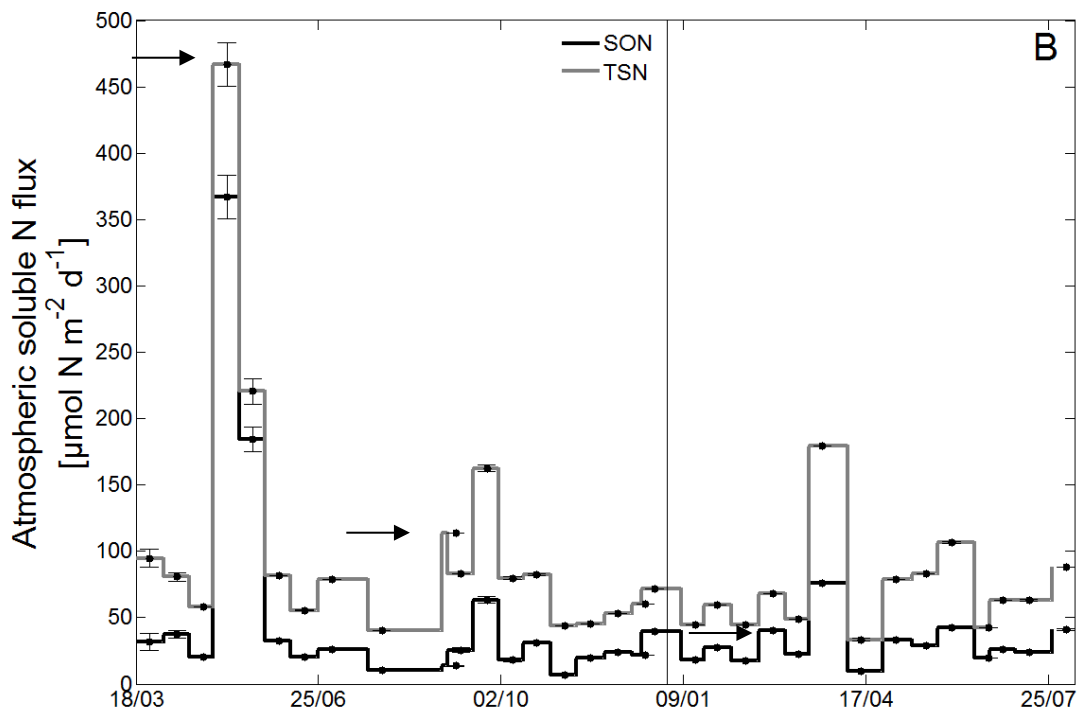
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**Figure 2**



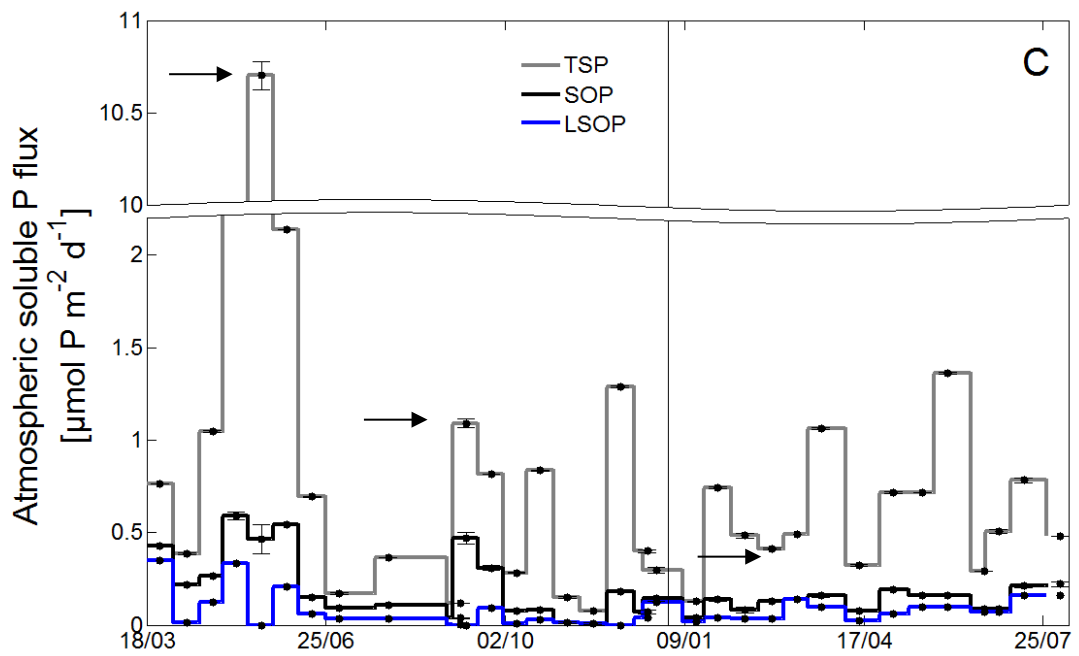
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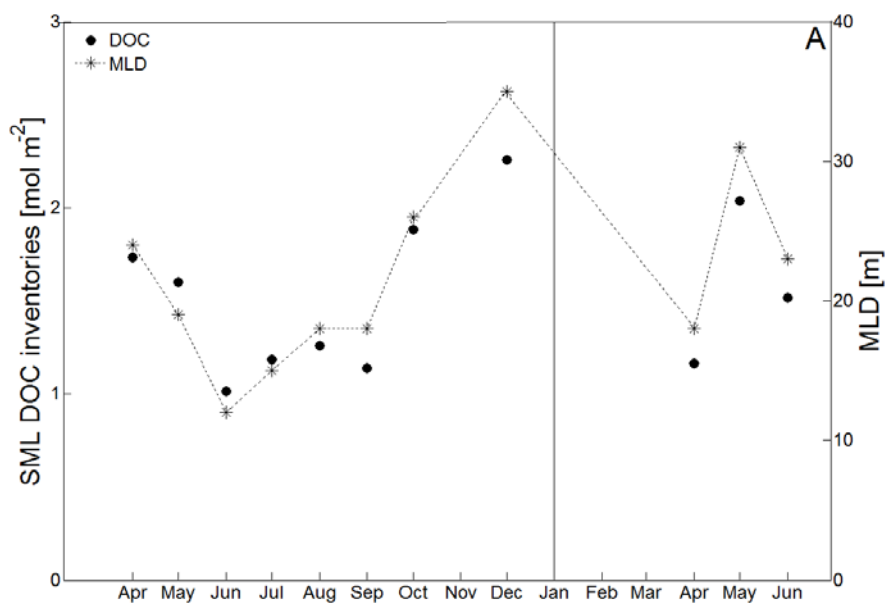


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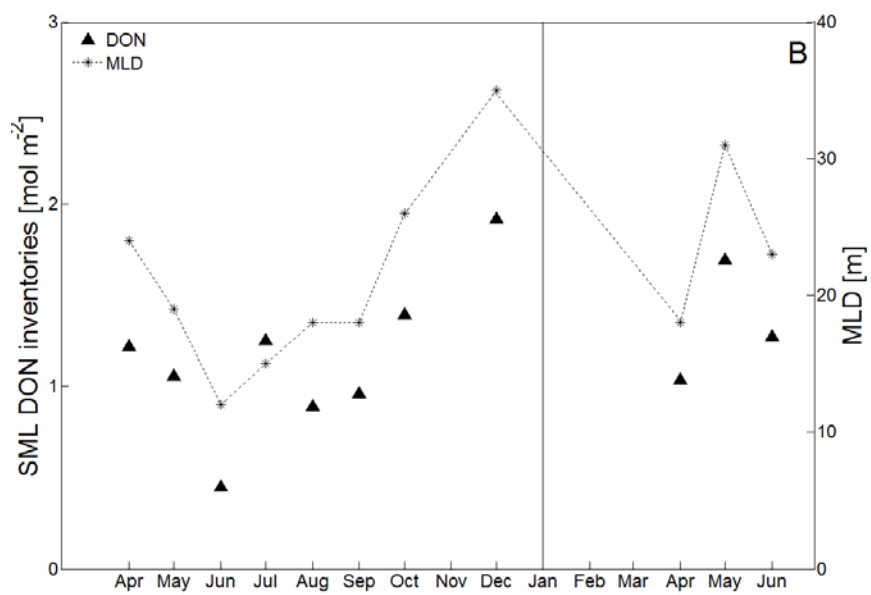
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Figure 3

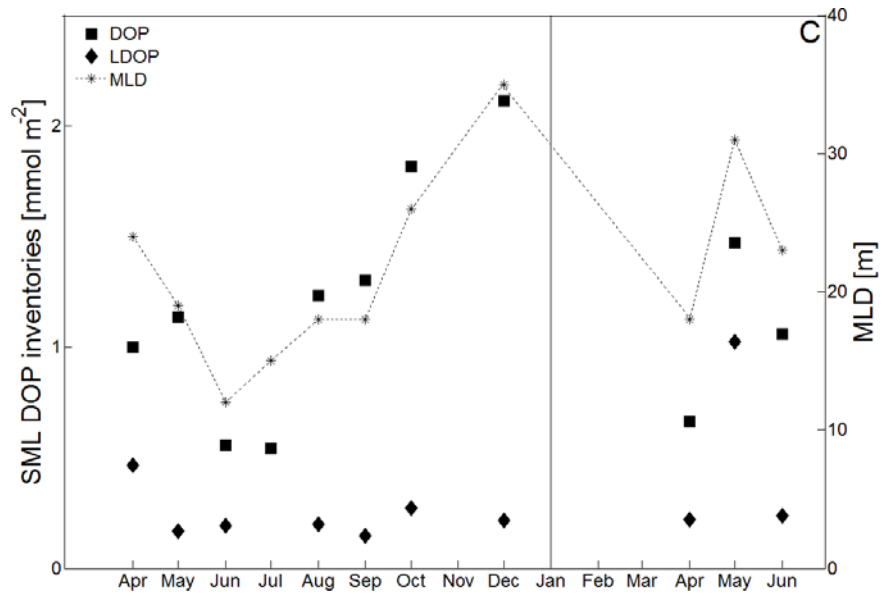


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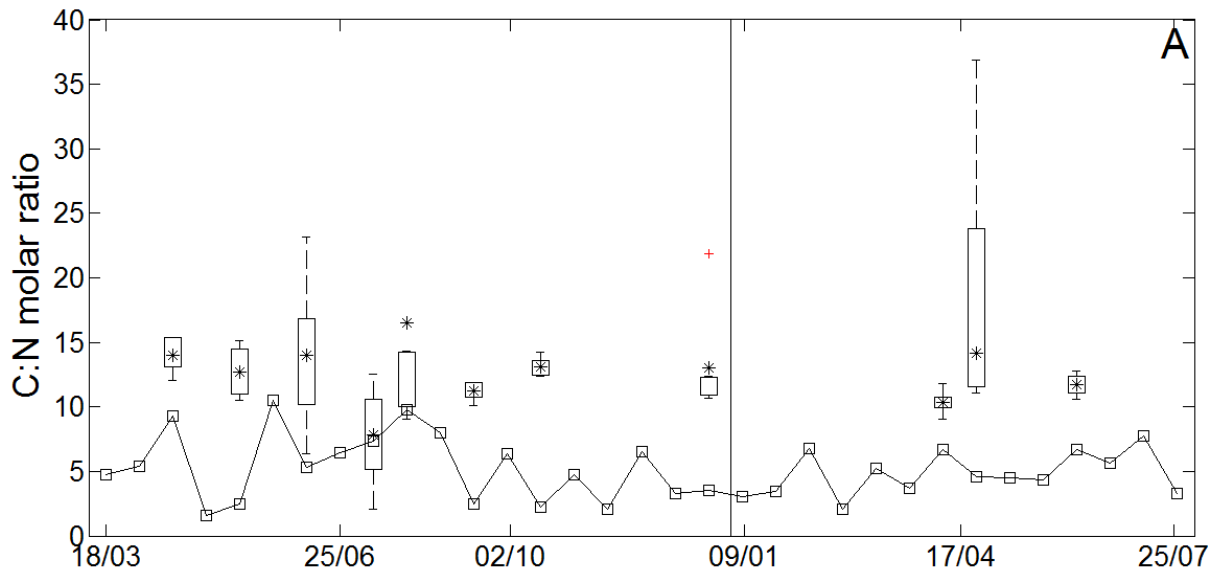


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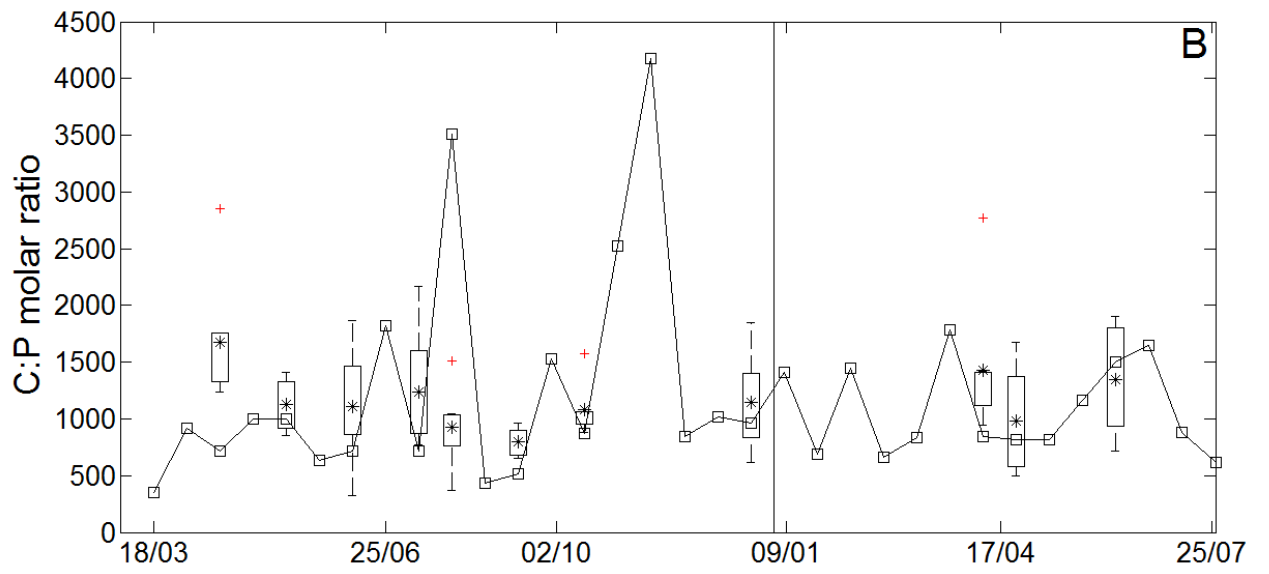


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**Figure 4**

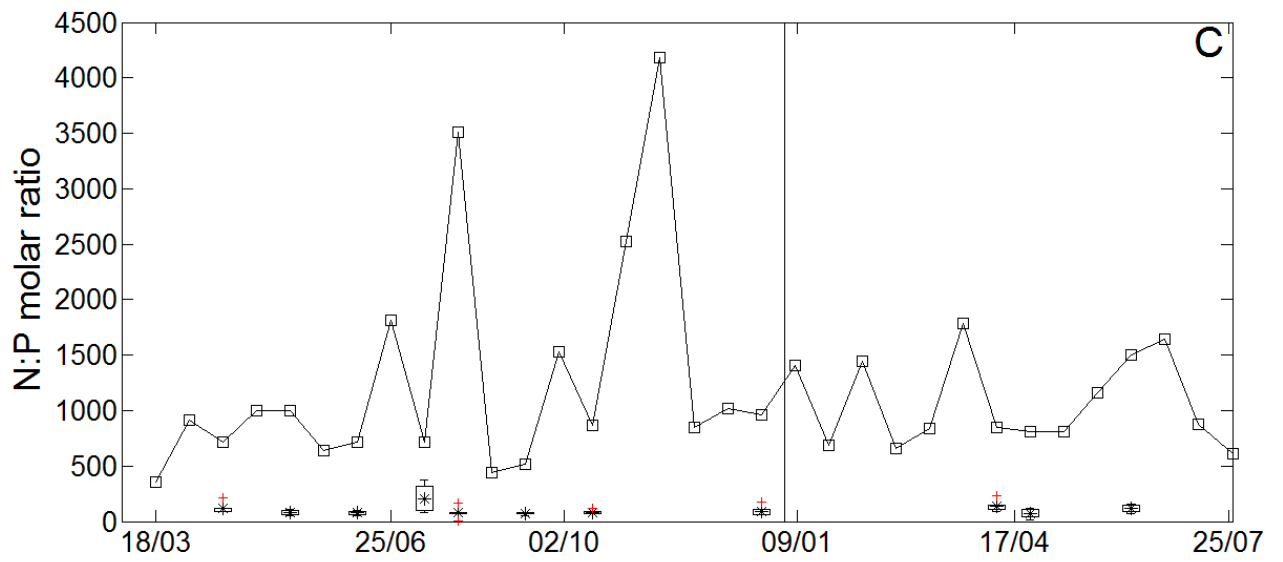


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956 **Table 1:** Annual atmospheric fluxes of soluble organic carbon (SOC), soluble organic  
 957 nitrogen (SON) and soluble organic phosphate (SOP) extrapolated to the western  
 958 Mediterranean basin compared to dissolved organic carbon (DOC), dissolved organic  
 959 nitrogen (DON) and dissolved organic phosphate (DOP) fluxes from the Rhône River and net  
 960 inputs from Sicily and Gibraltar straits.

	Atmospheric flux <sup>a</sup>	Rhône flux <sup>b</sup>	Global modeled atmospheric flux <sup>c</sup>	Straits net inputs
DOC (x 10 <sup>12</sup> g C yr <sup>-1</sup> )	0.595	0.104	230	2.4 - 3.1 <sup>d</sup>
DON (x 10 <sup>12</sup> g N yr <sup>-1</sup> )	0.193	0.011	16	0.01 - 0.56 <sup>e,f</sup>
DOP (x 10 <sup>12</sup> g P y <sup>-1</sup> )	0.002	0.001	0.35	0.07 - 0.16 <sup>e,f</sup>

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962 <sup>a</sup>This study, annual atmospheric flux extrapolated to the whole western Mediterranean Sea area (0.84 x 10<sup>6</sup> km<sup>2</sup>)

963 <sup>b</sup>Annual integrated flux (between December 2014 and December 2015) (data courtesy of the MOOSE  
 964 network:<https://doi.org/10.6096/MISTRALS-MOOSE.767> )

965 <sup>c</sup> From Kanakidou et al (2012)

966 <sup>d</sup> From Santinelli (2015)

967 <sup>e</sup> From Pujó-Pay et al (2011)

968 <sup>f</sup> From Coste et al (1987)

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986 **Table 2:** Depth-integrated inventories (means  $\pm$  standard deviation) within the surface mixed  
 987 layer calculated between April and October 2015 ( $\text{mmol m}^{-2}$ ). DOM-related inventories:  
 988 DOC: dissolved organic carbon, DON: dissolved organic nitrogen, DOP: dissolved organic  
 989 phosphate, LDOP: labile dissolved organic phosphate. Biological activity-related inventories:  
 990 HPA: heterotrophic prokaryotic abundance, HPP: heterotrophic prokaryotic production, HPR:  
 991 heterotrophic prokaryotic respiration, HPPD: Heterotrophic prokaryotic phosphate demand.  
 992 Details on the estimation of HPR and HPPD can be found on the text (sections 2.3 and 2.5,  
 993 respectively).

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	The stratification period
DOM inventories; [ $\text{mmol m}^{-2}$ ]	
DOC	$(1.4 \pm 0.3) \times 10^3$
DON	$(1 \pm 0.3) \times 10^2$
DOP	$1.1 \pm 0.4$
LDOP	$0.2 \pm 0.1$
Molar ratio	
C:N:P	1360:102:1
Biology inventories	
HPA; [ $\text{cells m}^{-2}$ ]	$(2.4 \pm 1.2) \times 10^{13}$
HPP; [ $\text{mmol C m}^{-2} \text{ day}^{-1}$ ]	$2.2 \pm 1.5 - 2.3 \pm 1.5$
HPR; [ $\text{mmol C m}^{-2} \text{ day}^{-1}$ ]	$(19.8 \pm 15.1) \times 10^3 - (46.7 \pm 35.6) \times 10^3$
HPPD; [ $\text{mmol P m}^{-2} \text{ day}^{-1}$ ]	$(11.4 \pm 8.9) \times 10^{-3} - (55.7 \pm 43.7) \times 10^{-3}$

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1010 **Table 3:** Cumulative integration of atmospheric fluxes ( $\text{mmol m}^{-2}$ ) and molar ratios of soluble  
1011 organic matter (SOM) for the period between April-02 and October-29 (2015). SOC: soluble  
1012 organic carbon, SON: soluble organic nitrogen, SOP: soluble organic phosphate, LSOP: labile  
1013 soluble organic phosphate. Contribution (%) of atmospheric fluxes of SOM to marine surface  
1014 pool of dissolved organic matter (DOM) and to heterotrophic prokaryotic C and P demand in  
1015 the mixed layer depth during that period.

1016 \*Contributions - related to DOM pool:  $C_{\text{DOC}}$ ; contribution of atmospheric SOC to DOC pool,  
1017  $C_{\text{DON}}$ ; contribution of atmospheric SON to DON pool,  $C_{\text{DOP}}$ ; contribution of atmospheric SOP  
1018 to DOP pool and  $C_{\text{LDOP}}$ ; contribution of atmospheric LSOP to LDOP pool.

1019 \*\*Contributions - related to marine heterotrophic prokaryotes:  $C_{\text{HPPD}}$ ; contribution of  
1020 atmospheric LSOP to heterotrophic prokaryotic phosphate demand. Contribution related to  
1021 marine heterotrophic prokaryotes demand were calculated by using the minimum and the  
1022 maximum flux of atmospheric labile SOC and SOP observed for each period.

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April-2 to October-29 (2015) cumulative atmospheric flux; [ $\text{mmol m}^{-2}$ ]	
SOC	41.6
SON	11.9
SOP	$49.2 \times 10^{-3}$
LSOP	$13.6 \times 10^{-3}$
Molar ratio	
C:N:P	841:241:1
Contributions to surface DOM pool; (%)*	
$C_{\text{DOC}}$	3
$C_{\text{DON}}$	12
$C_{\text{DOP}}$	4.5
$C_{\text{LDOP}}$	6.8
Contribution to heterotrophic phosphate demand; (%)**	
$C_{\text{HPPD}}$	0 - 8.6

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1031 **Supplementary figures**

1032 **Figure S1** : Dissolved organic carbon (DOC) vertical depth profiles between the surface  
1033 and 200 m at the ANTARES station during the study period.

1034 **Figure S2** : Dissolved organic nitrogen (DON) vertical depth profiles between the  
1035 surface and 200 m at the ANTARES station during the study period.

1036 **Figure S3** : Dissolved organic phosphate (DOP) and labil dissolved organic phosphate  
1037 (LDOP) vertical depth profiles between the surface and 200 m at the ANTARES station  
1038 during the study period.

1039 **Figure S4** : Soluble reactive phosphate (SRP) and dissolved inorganic nitrogen (DIN)  
1040 vertical depth profiles between the surface and 200 m at the ANTARES station during the  
1041 study period.

1042 **Figure S5**: Heterotrophic prokaryotic abundance (HPA) and community respiration  
1043 (CR) between the surface and 200 m at the ANTARES station during the study period.

1044 **Figure S6**: Heterotrophic prokaryotic production (HPP) between the surface and 200 m  
1045 at the ANTARES station during the study period.

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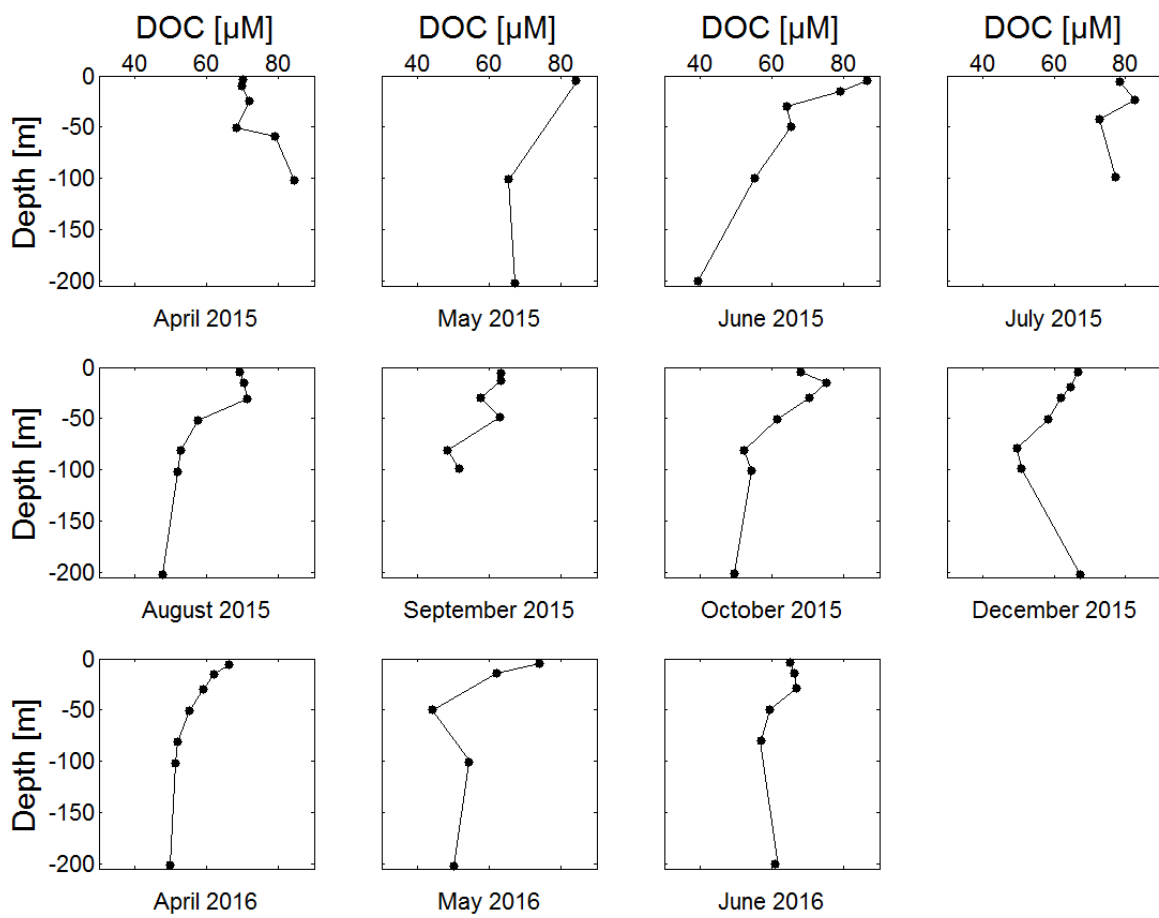
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1062 **Figure S1**



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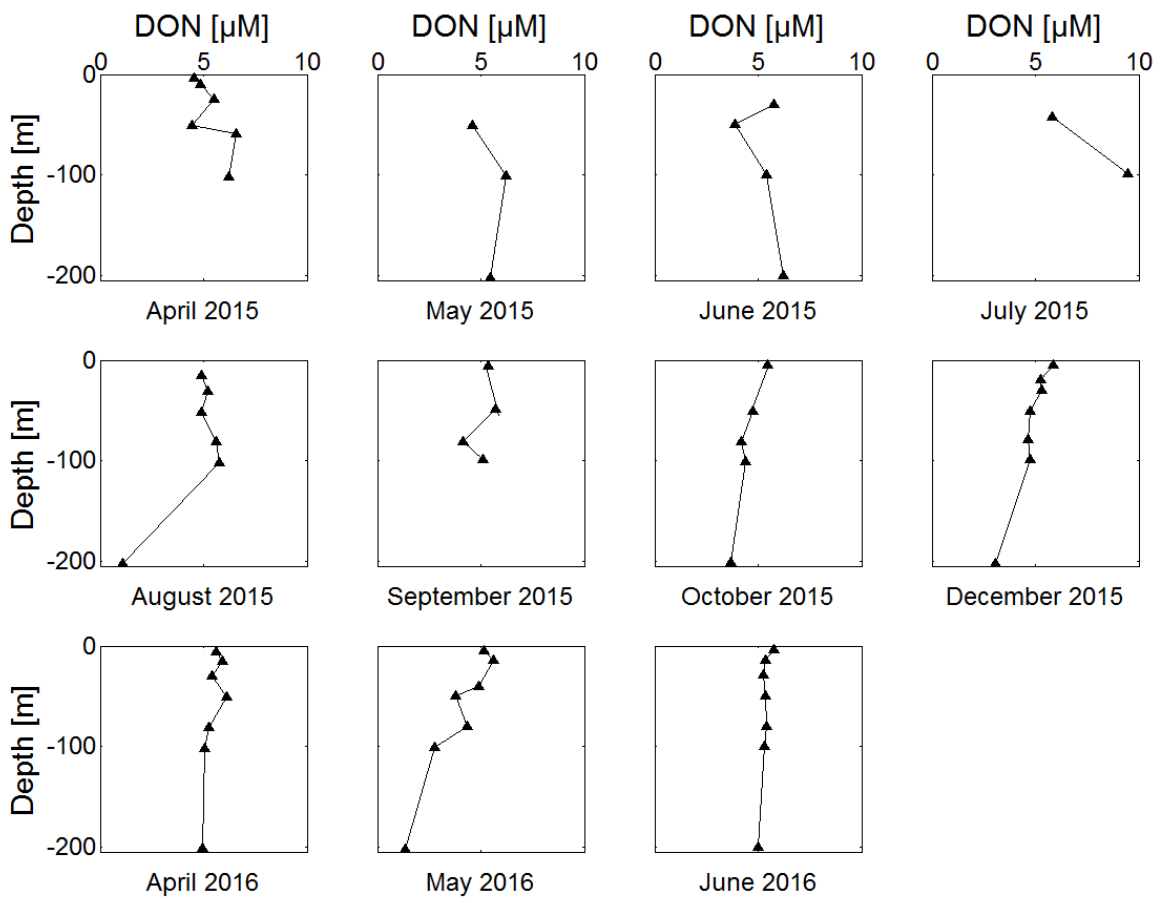
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1075 **Figure S2**



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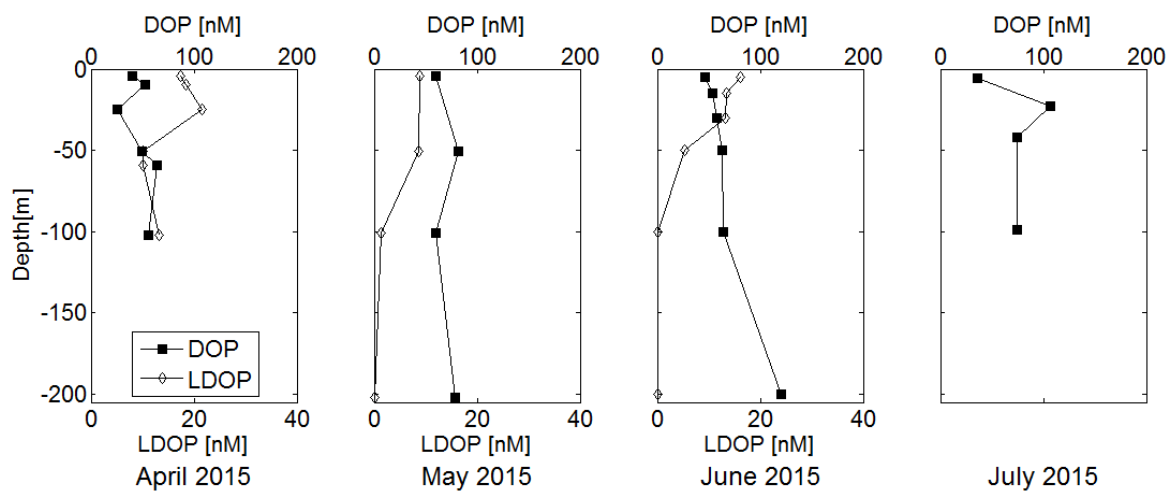
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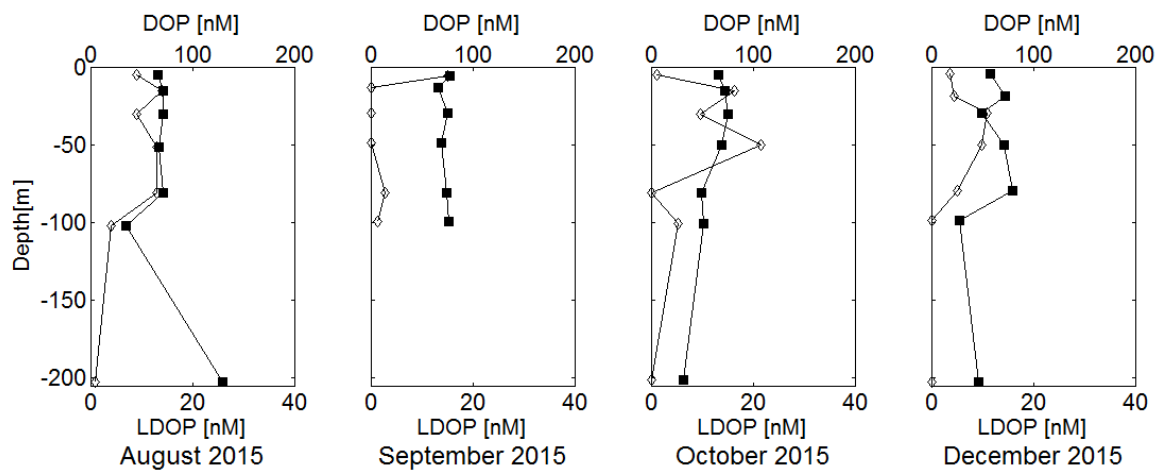
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1089 **Figure S3**

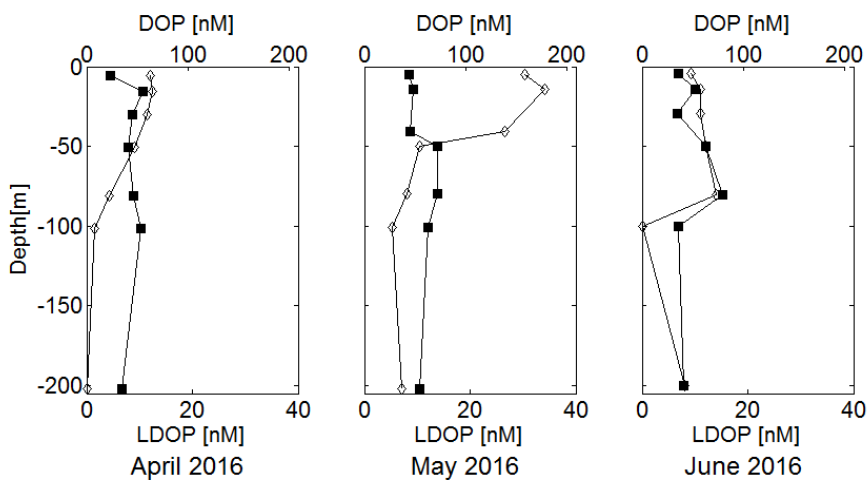


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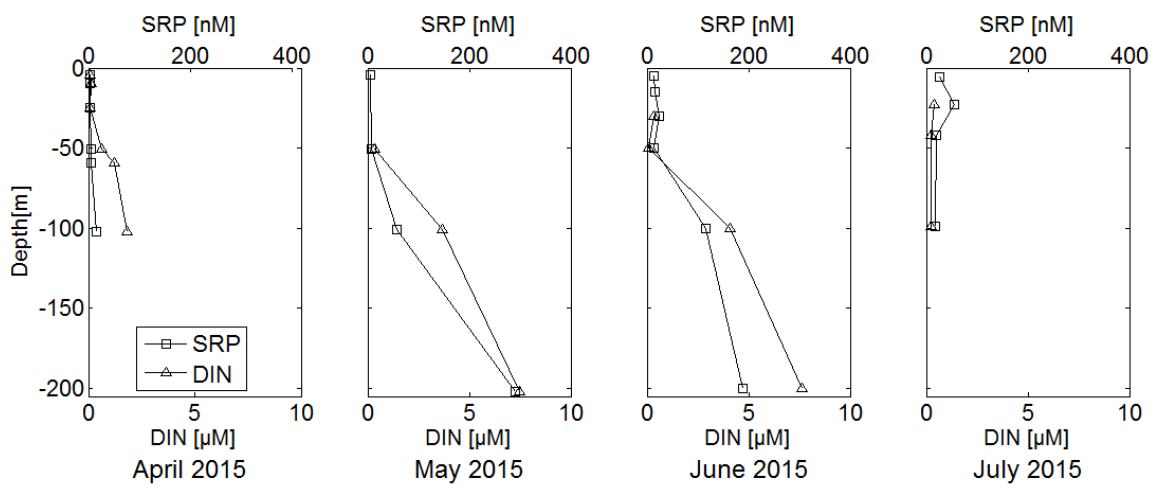


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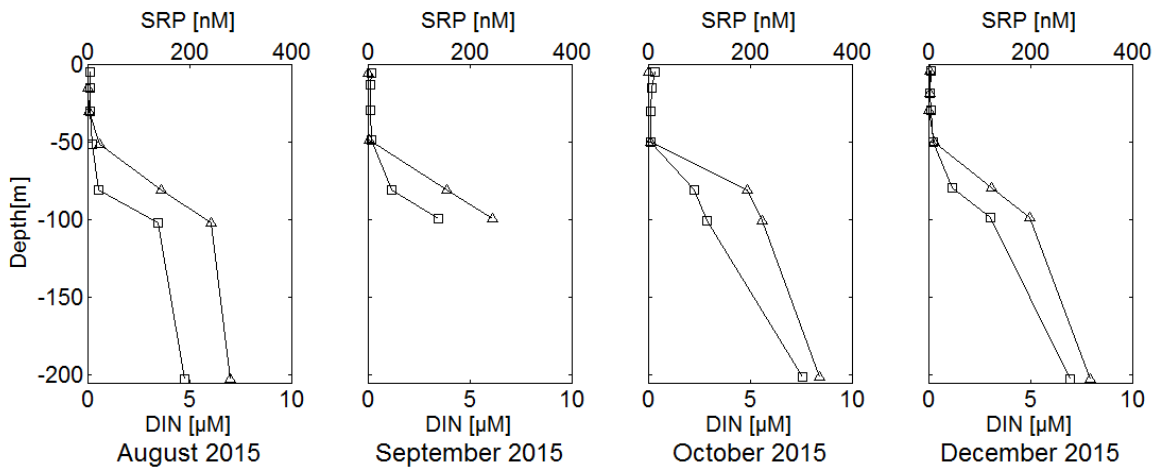
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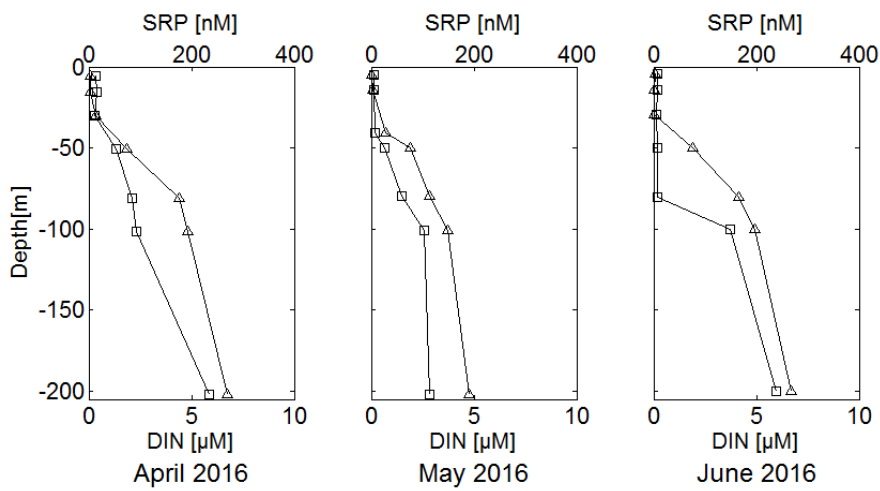


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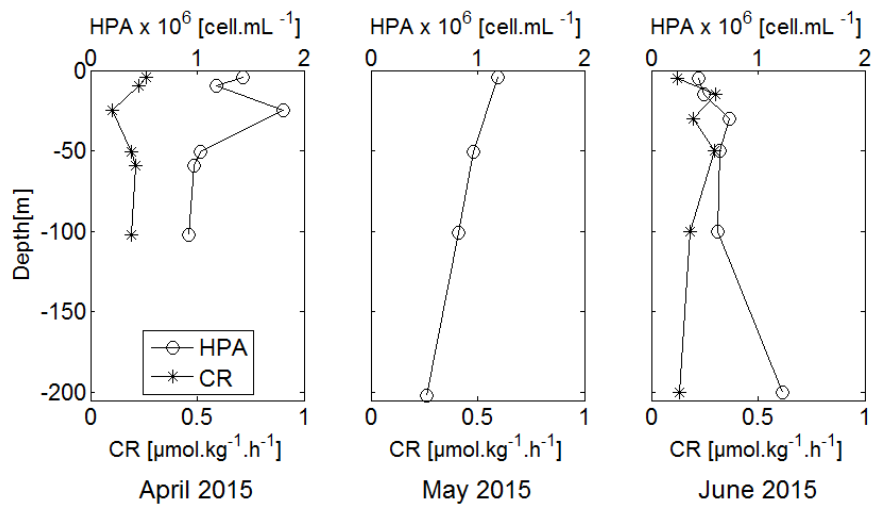


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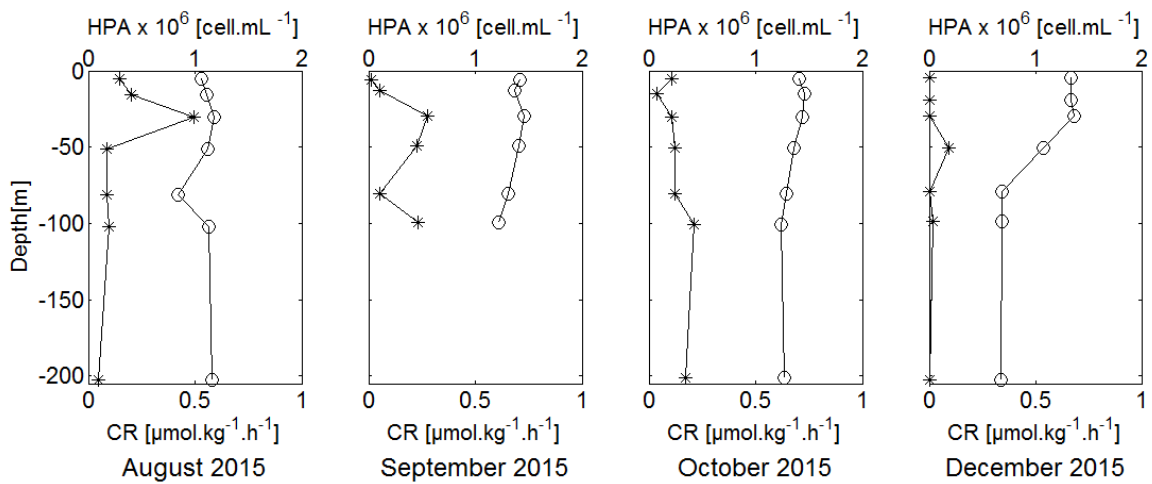
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1103 **Figure S5**



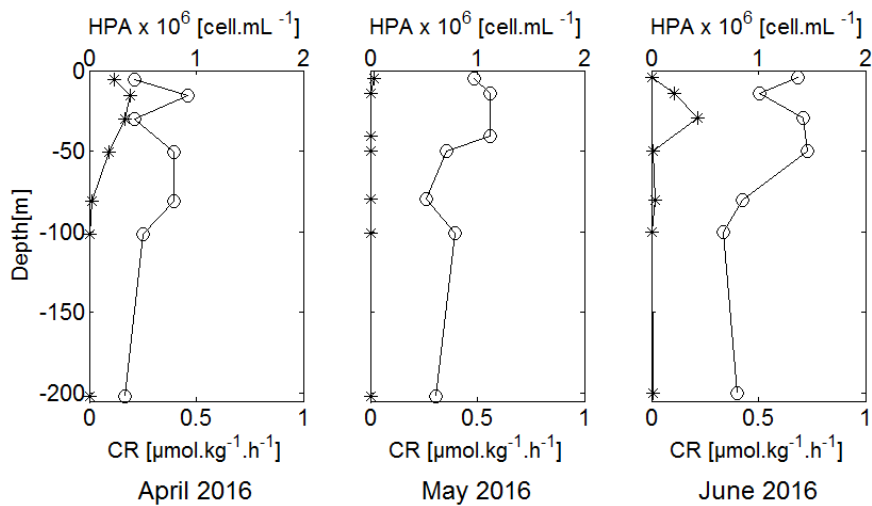
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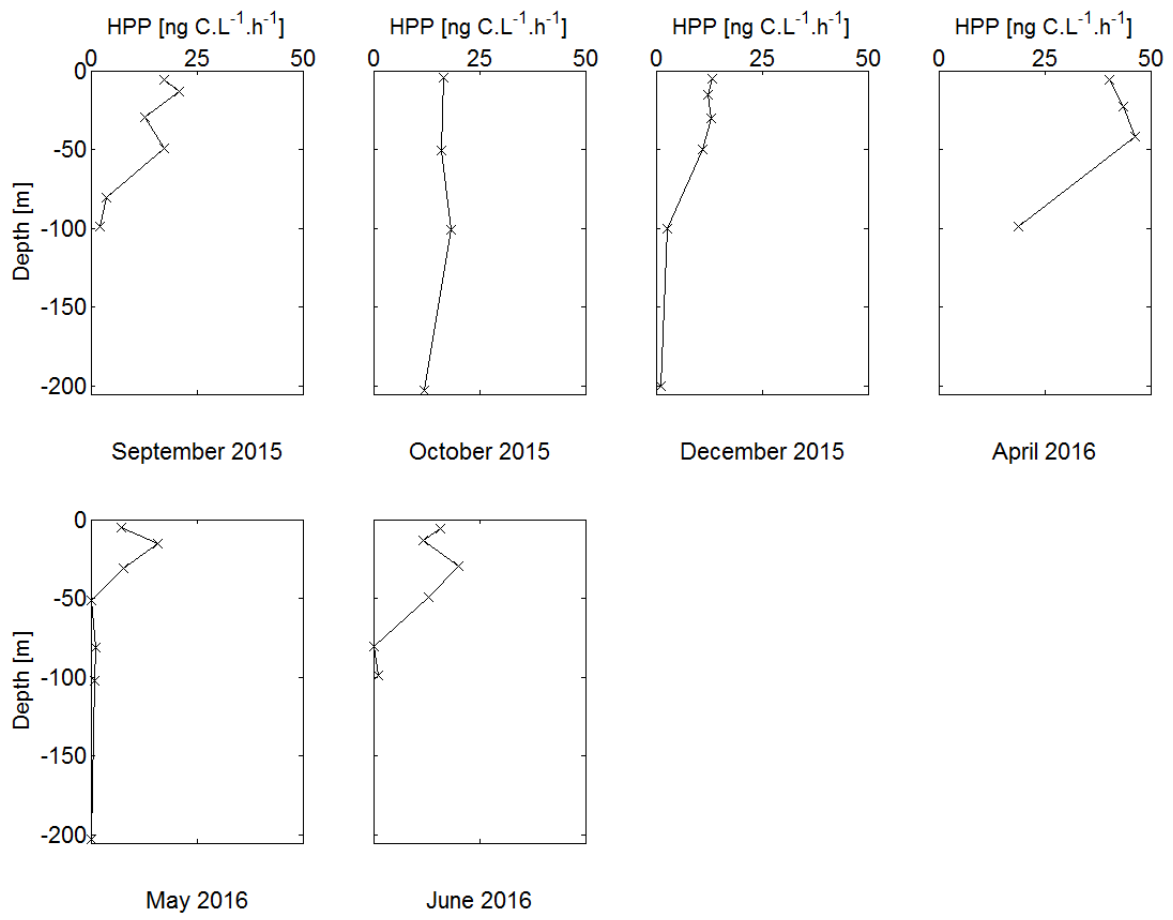
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1110 **Figure S6**



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