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Abstract: Water samples (0-200 m) were collected in a coastal area of the Ross Sea in January 2014, with the aim of evaluating the physical and biological forcing on the carbonate system variability at a mesoscale level (distance between consecutive stations of about 5-10 km). Remote sensing supported the determination of the sampling strategy and helped positioning each sampling station. Total alkalinity, pH, dissolved oxygen, phytoplankton pigments and taxonomic composition were investigated in combination with measurements of temperature, salinity and current speed. The total inorganic carbon, the sea water CO2 partial pressure, the saturation grade for calcite and aragonite were calculated from the measured total alkalinity and pH. In addition, continuous measurements of atmospheric CO2 concentration was carried out during all duration of the sampling. LADCP measurements revealed the presence of a significant change in current speed and direction in correspondence of a well demarked frontal line. The frontal zone was characterized by intense gradients in both temperature and salinity. The total phytoplankton biomass was relatively high in all stations and the highest values of Chlorophyll-a were found in the layer between 20 to 50 m, with the dominant taxonomic group being haptophyceae.

The carbonate system properties in surface water exhibit the presence of mesoscale variability with a horizontal length scale of about 10 km. Sea-ice melting, through the expected input of low salinity water, results in a dilution of the total alkalinity and inorganic carbon, even if our observations suggest that phytoplankton activity was the major forcing of the distribution of the carbonate system variables. In fact, higher CO3- and consequently higher Ω and pH in the surface layer were found in correspondence with stations where the highest values of Chlorophyll-a were recorded. The surface calculated Δ pCO2 pattern follows both MODIS data and in situ Chlorophyll-a measurements, confirming that the investigated area acted as a sink of CO2, with fluxes ranging from -0.5 ± 0.4 to -31.0 ± 6.4 mmol m-2 d-1. The large range observed in the flux values is due to both the spatial variability of sea water pCO2 and to the wind speed irregularity experienced during the survey.



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W. Fennel, E. Hofmann Editors in Chief Journal of Marine System

Genova, 04th June 2015

Dear Dr. Fennel and Dr. Hofmann,

I submit you the manuscript "Physical and biological forcing on the mesoscale variability of the carbonate system in the Ross Sea (Antarctica) during the summer season 2014." by Paola Rivaro and co-workers for publication in "Mesoscale and high-frequency variability in the Ross Sea (Antarctica)," Special Issue of Journal of Marine Systems (McGillicuddy, Budillon and Kustka, Guest Editors).

Sincerely,

Paola Rivaro

1	Physical and biological forcing on the mesoscale variability of the carbonate system in the
2	Ross Sea (Antarctica) during the summer season 2014.
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23 pigments

24 Abstract

Water samples (0-200 m) were collected in a coastal area of the Ross Sea in January 2014, with the aim of evaluating the physical and biological forcing on the carbonate system variability at a mesoscale level (distance between consecutive stations of about 5-10 km). Remote sensing supported the determination of the sampling strategy and helped positioning each sampling station.

Total alkalinity, pH, dissolved oxygen, phytoplankton pigments and taxonomic composition were investigated in combination with measurements of temperature, salinity and current speed. The total inorganic carbon, the sea water CO_2 partial pressure, the saturation grade for calcite and aragonite were calculated from the measured total alkalinity and pH. In addition, continuous measurements of atmospheric CO_2 concentration was carried out during all duration of the sampling.

LADCP measurements revealed the presence of a significant change in current speed and direction in correspondence of a well demarked frontal line. The frontal zone was characterized by intense gradients in both temperature and salinity. The total phytoplankton biomass was relatively high in all stations and the highest values of Chlorophyll-a were found in the layer between 20 to 50 m, with the dominant taxonomic group being haptophyceae.

40 The carbonate system properties in surface water exhibit the presence of mesoscale variability 41 with a horizontal length scale of about 10 km. Sea-ice melting, through the expected input of low 42 salinity water, results in a dilution of the total alkalinity and inorganic carbon even if our 43 observations suggest that phytoplankton activity was the major forcing of the distribution of the 44 carbonate system variables. In fact, higher CO_3^- and consequently higher Ω and pH in the surface 45 layer were found in correspondence with stations where the highest values of Chlorophyll-a were 46 recorded. The surface calculated ΔpCO_2 pattern follows both MODIS data and in situ Chlorophyll-a measurements, confirming that the investigated area acted as a sink of CO₂, with fluxes ranging 47

from -0.5 ± 0.4 to -31.0 ± 6.4 mmol m⁻² d⁻¹. The large range observed in the flux values is due to both the spatial variability of sea water pCO₂ and to the wind speed irregularity experienced during the survey.

51 **1. Introduction**

52 The Ross Sea is one of the most productive regions of the Southern Ocean, thanks to both the 53 high levels of biomass and primary production, and high flows of biogenic material accumulated on 54 the continental shelf (Smith and Gordon, 1997; Saggiomo et al., 1998; De Master 2002; Saggiomo et al., 2002; Armand et al., 2005; Arrigo et al., 2008; Smith and Comiso, 2008; Catalano et al., 55 56 2010). Ocean colour satellite imagery shows that the extent of the phytoplankton bloom is 57 extremely variable in the shelf areas of the Ross Sea, even when the surface waters are ice free 58 (Reddy and Arrigo, 2006). In fact, the Ross Sea is characterized by a complex array of ecosystems, 59 each contributing differently to the primary production processes at the basin scale (Peloquinand 60 Smith, 2007). Many differences are known to exist between coastal/offshore waters and 61 position/thickness of the Upper Mixed Layer (UML) in the specific composition of phytoplankton 62 communities, as well as in the origin and development of the blooms and transfer of C along the 63 trophic chains (Saggiomo et al., 2002; Mangoni et al., 2004; Smith et al., 2010).

64 The phytoplankton blooms occur during the austral spring and summer, especially in the 65 waters next to the marginal ice, polynya and continental shelves (Sullivan et al, 1993; Moore and Abbott, 2000; Saggiomo et al., 2002; Garrity et al 2005; Reddy and Arrigo, 2006; Mangoni et al., 66 67 2009a). Furthermore, a restricted number of functional groups contribute to this productivity, and 68 dominance varies at different temporal and spatial scales (Mangoni et al., 2004; Smith et al. 2010). 69 The phytoplankton blooms are dominated by diatoms such as Fragilariopsis and Pseudonitzschia 70 species (Leventer and Dunbar, 1996; Henry et al, 1999; Armand et al, 2005; Saggiomo et al., 2000) 71 and by haptophyte like *Phaeocystis antarctica* (Arrigo et al., 1999; Goffart et al., 2000; Smith et al. 72 2001; Di Tullio et al., 2003). Diatoms account for about 75% of the primary production in the

73 Southern Ocean, regulate the cycle of silicon and support most food webs in the Antarctic (Knox, 1994; Treguer et al., 1995; Henry et al, 1999; Smith and Asper, 2001; Mangoni et al., 2004). 74 Phaeocystis antarctica often occurs in colonial form, but also as solitary cells, and the two forms 75 76 have distinct ecological roles. The colonies of *Phaeocystis antarctica* are not preferred by most of 77 herbivorous micro- and meso-zooplankton and are removed through sinking and aggregation 78 (Verity and Smetacek, 1996; Caron et al., 2000; DiTullio et al. 2000; Haberman et al. 2003). 79 Therefore, the relative abundance of diatoms or *Phaeocystis antarctica* in the phytoplankton 80 communities in this area can play an important role in shaping its food web, and can impair the 81 absorption of carbon and exports to the bottom (Di Tullio et al., 2000; Sweeney et al. 2000; Rind et 82 al., 2005; Schoemanna et al., 2005; Shields and Smith, 2009).

83 The Ross Sea is a key region for the impact of global carbon cycle and air-sea carbon dioxide 84 fluxes (CO₂) (Arrigo et al., 1999; Arrigo et al., 2008; Catalano et al 2010; Mangoni et al., 2009b; 85 Iudicone et al., 2011). A modelling study has shown that the Ross See shelf waters are a strong trap for CO₂, due to high biological productivity, intense winds, high ventilation rates and extensive 86 87 winter sea ice cover (Arrigo et al., 2008). The same study also confirmed that the Ross Sea has an 88 important role in the anthropogenic CO₂ (CO_{2antr}) sequestration, as several studies have reported 89 (Caldeira and Duffy, 2000; Sabine et al., 2004; Sandrini et al., 2007), taking into account the 90 Antarctic Bottom Water (AABW) production processes taking palece in the area (Orsi and 91 Wiederwohl, 2009).

Throughout the ocean, mesoscale processes on spatial scales of 10–100 km and temporal ranges from hours to days, have first-order impacts on phytoplankton physiochemical controls, and are critical in determining growth patterns and distribution, but the mechanisms responsible for this variability are not yet well understood (Kaufman et al., 2014). The circulation of the Antarctic Surface Waters (AASW) in the Ross Sea is largely affected by the presence of small-scale structures such as eddies, fronts or filaments. These mesoscale structures can penetrate deep below 98 the ocean surface layer and hence can influence the intensity of the bloom by supplying nutrients 99 and trace elements, such as iron, to the surface waters (Sweeney et al. 2003; McGillicuddy et al., 100 2007).

101 Little is known about the effect of the mesoscale structures on the carbonate system and 102 specially on the air-sea CO₂ fluxes and carbon export (Chen et al., 2008: González-Dávila et al., 103 2003 and 2006). The main features of the carbonate system in the Ross Sea have been already 104 described, showing both a large spatial and seasonal variability, highlighting the importance of a 105 deeper understanding (Manno et al., 2007; Sandrini, et al., 2007; Rivaro et al., 2014). In this 106 context, the investigation of the mesoscale physical and biological forcing that determine the 107 carbonate system variability is of particular importance in order to predict future modifications 108 associated with climate change in the Ross Sea.

109 To this purpose, the RoME (Ross sea Mesoscale Experiment) project used a combination of 110 remote sensing and high resolution in situ ship measurements during its cruise in the austral 111 summer 2013-14, as part of the Italian National Program of Research in Antarctica (PNRA -112 Programma Nazionale di Ricerca in Antartide). Remote sensing supported both the sampling 113 strategy determination and the placement of in situ station within a wider context. Three mesoscale 114 experiments were carried out in three different areas in the Ross Sea. In this paper we report the 115 observations pertaining to water samples collected in a coastal area (Fig. 1 A) with a distance 116 between consecutive sampling stations of about 5-7 km (herein called RoME 2 experiment). The 117 objectives are to evaluate a mesoscale variability of the carbonate system and to investigate the role 118 played by physical and biological forcing on it and on the local air-sea CO₂ flux.

119 **2. Materials and Methods**

120 **2.1** Sampling strategy and water sampling.

In situ data were collected aboard the R/V Italica, as part of the PNRA – Ross Sea Mesoscale
 Experiment (RoME) project. The biogeochemical parameters were investigated at 12 stations

123 consisting of 5-7 depths (2-200 m) synoptically sampled from 26 to 28 January 2014 within the so 124 called RoME 2 mesoscale survey (Fig. 1 A). Surface and intermediate layers were sampled in all stations, while Sampling down to the bottom layer was performed at stations 33, 36, 39, 43 and 45. 125 126 The position of the stations was chosen accordingly to the MODIS (Moderate Resolution Imaging 127 Spectroradiometer) Aqua and Terra satellites level-2 products relative to the previous 12/24 hours. 128 Sea surface temperature (SST) and surface chlorophyll-a concentration (Chl-a) maps at 1 km 129 resolution (Fig.1 B-C) were generated, analyzed and transmitted on board in order to place and to 130 realize the casts in correspondence of both high and low chlorophyll signals allowing investigation 131 of high spatial variability. The sampling depths were chosen mainly according to the fluorescence 132 profile. Station 35 was revisited after 2 days (station 45).

Hydrological casts and water sampling were carried out using a SBE 9/11 Plus CTD, with
double temperature and conductivity sensors, coupled with a SBE 32 plastic coated carousel
sampler, on which 24 12-L Niskin bottles were mounted. A couple of Lowered Acoustic Doppler
Current Profiler (LADCP) was deployed together with the CTD to obtain current fields every 10 m
from surface to maximum reached depth.

138 2.2 Analytical procedures

140

139 2.2.1 Dissolved oxygen, phytoplankton pigments and taxonomic composition.

141 automated micro-titrations (Grasshoff, 1983) with a potentiometric detection of the end point using

Dissolved oxygen (O_2) was measured on board according to the Winkler method by

- 142 a Methohm 719 titroprocessor. The measurement precision was $\pm 0.5 \text{ mg L}^{-1}$.
- Samples for the determination of phytoplankton communities were collected at five or six
 depths in the layer 0-100 m. Four litres of seawater were drawn from the Niskin bottle.
- 145 Successively, after mixing ,sub samples were distributed for total biomass and size-fractionated
- 146 Chl-a and phytoplankton functional groups determination by spectrofluorometric and HPLC
- 147 analyses, respectively and for a taxonomical analysis.

Fractionation of phytoplankton biomass was performed by serial filtration. One subsample was collected on a Whatman GF/F filter (GF/F tot); two subsamples were passed through a Nitex net (20 μ m mesh size) and a Nuclepore membrane (2 μ m pore size) and thus collected on Whatman GF/F filters. For more details, see Mangoni et al. (2004). The filters for spectrofluorometric analyses of Chl-a and phaeopigments were stored at -80°C, analyzed with a Varian Eclipse spectrofluorometer according to Holm Hansen et al. (1965). The instrument was checked daily with a Chl-a standard solution (from Anacystis nidulans by Sigma).

155 For HPLC pigment analysis, two-three liters of seawater were filtered under low-light 156 conditions onto Whatman GFF filters (47 mm diameter), quickly frozen in liquid nitrogen, and then 157 stored at -80 °C until pigment analysis. Pigment separation was performed by Hewlett Packard 158 HPLC (mod. 1100) according to Vidussi el al. (1996). Calibration of the instruments was carried 159 out using 20 different pigments provided by the International Agency for 14C Determination, VKI 160 Water Quality Insitute. Two marker pigments were used to define the contribution of the major taxa: fucoxanthin (FUCO) for diatoms and 19'- hexanoyloxyfucoxanthin (HEX) and Chlorophyll-c₃ 161 162 (Chl-c₃) for *Phaeocystis antarctica* (DiTullio et al., 2007). Calculation of the relative abundance of 163 various phytoplankton groups from the pigment concentrations was carried out using the 164 CHEMTAX program (Mackey et al., 1996). 165 Samples for phytoplankton identification were collected at four different depths according to 166 florescence profile and preserved with formaldehyde (4% final concentration).

167 Cell counts were performed with an inverted light microscope (Zeiss Axiophot) according to168 the Utermöhl method (Utermöhl 1958).

169 $2.2.2 A_T$ and pH measurements.

170 Water samples for A_T and pH analyses were collected in a 500-mL borosilicate glass bottle, 171 using standard operating procedures described in the DOE 2007 handbook (DOE, 2007). The 172 samples were poisoned in the container with saturated HgCl₂ solution to stop biological activity 173 from altering the carbon distributions in the sample before analysis. Samples were then stored in 174 dark, cold $(+4^{\circ}C)$ conditions.

A_T and pH were measured using the methods described in Rivaro et al. (2010). The pH was 175 176 expressed in the pH total scale, (i.e. $[H^+]$ as moles per kilogram of seawater, pH_T) and it was 177 determined using a potentiometric method that employed a combination glass/reference electrode 178 with an NTC temperature sensor. The Tris(hydroxymethyl)aminomethane (TRIS) buffer used to 179 standardize the pH electrode was prepared according to the DOE handbook (DOE 2007). The 180 salinity of the TRIS buffer was 35. Both the TRIS buffer and the seawater samples were brought to 181 the same temperature (25 ± 0.1 °C) using a thermostatic water bath, before the measurements were conducted. The pH_T measures at 25°C were then recalculated at in situ temperature and pressure 182 183 conditions (pH in situ).

The accuracy and precision of A_T measurements were evaluated using the CRM batch 123 provided by A. G. Dickson (Scripps Institution of Oceanography). The precision for A_T measures was $\pm 4.0 \ \mu mol \ kg^{-1}$, and the recovery was 99.8%. The precision of the pH measurement was \pm 0.007 units and was evaluated by repeated analysis of the A_T certified material. The accuracy of the pH measurement is strongly dependent by the composition of the TRIS buffer solution, but no certified material is available at present. Therefore, this figure of merit was not determined.

190

2.3 Auxiliary carbonate system parameters calculation.

191 The CO₂SYS program (CO₂-Sys, Pierrot et al. 2006) was used to calculate the total inorganic 192 carbon (C_T), the sea water CO₂ partial pressure (pCO_{2SW}), the saturation grade for calcite (Ω_{Ca}) and 193 aragonite (Ω_{Ar}), from the measured A_T and pH. Equilibrium constants of CO₂ (K1 and K2) of 194 Millero (2006) and total hydrogen ion scale (mol kg_{SW}⁻¹) for pH were used for the calculation. The 195 estimated probable errors for the calculated parameters of the carbon system, using pH and AT as 196 input measurements are ± 3.8 µmol kg⁻¹ and ± 2.1 µatm, for C_T and pCO₂, respectively.

197 **2.4** Atmospheric CO_2 measurements and sea-air CO_2 fluxes calculation.

198	Continuous measurements of atmospheric CO_2 concentrations (p CO_{2atm}) were carried out
199	during all the duration of RoME 2 experiment by means of a Siemens Ultramat 5E analyzer
200	assembled for shipboard use (Ori et al., 1996). The measurement system is based on the comparison
201	between signals from two infrared absorbing cells, one filled with a flux of synthetic air with a
202	constant CO ₂ concentration (~ 380 μ atm) and the other filled with the air sample. The air sample
203	were carefully dried by means of a cold trap (t <-40°C). The instrument was calibrated using the
204	WMO-X85 scale by means of working standards with concentrations of 385 and 447 µatm carefully
205	determined at the Monte Cimone Observatory (Sestola, Italy), a baseline site of the Italian
206	Meteorological Service. CO2 concentrations were acquired at 0.5 Hz frequency and offline
207	processed to remove spikes due to the possible contamination from the ship chimney during the
208	CTD stations. The data were then filtered in order to consider only those with winds blowing from -
209	$90^{\circ}/+90^{\circ}$ with respect to the air inlet toward the ship bow. For the CO ₂ flux calculation, pCO _{2atm}
210	concentration for each station was obtained averaging at least 1200 values, collected at the
211	meantime of the sea water sampling, and the data were corrected to 100% humidity at in situ sea
212	surface temperature (SST) and salinity (SSS).
213	The sea-air CO ₂ flux (F, in mmol $m^{-2} d^{-1}$) was computed as
214	$F = ks(\Delta p CO_2) (1)$
215	where k is the CO ₂ gas transfer velocity (cm h^{-1}), s is the solubility of CO ₂ (mol kg ⁻¹ atm ⁻¹)
216	and ΔpCO_2 is the difference between the pCO _{2SW} and the pCO _{2atm} . Ship-based wind speed data at
217	10 m height (u) were used for the calculation of the gas transfer velocity (k) according to
218	Wanninkhof formulation (1992):

219 $kCO_2 = 0.31u^2(660/ScCO_2)^{0.5}$ (2)

220 where $ScCO_2$ is the Schmidt number for CO_2 .

221 **2.5** *Ancillary data*.

222 Melt water percentage in the upper surface layer (MW%) was calculated considering the

difference between the salinity measured at the surface (S_{meas}) and the salinity measured in the same station at greater depth (S_{deep} , i.e. 200 m), surely not influenced by sea-ice melting, assuming an average sea-ice salinity of 6 (Rivaro et al., 2012, Rivaro et al., 2014):

226 MW%=
$$(1 - \frac{S_{meas} - 6}{S_{deep} - 6})*100.$$
 (3)

Mixed Layer Depth (MLD) was determined for each cast considering an increase of in situ
 density (σt) >0.05 over 5 m depth interval.

3. Results

230 **3.1** *Physical properties.*

231 The 9/S diagram of the RoME 2 experiment (Fig.2) shows the presence of peculiar Ross Sea 232 water masses. The surface layer from -30 m to -50 m is occupied by a local expression of Antarctic 233 Surface Water (AASW). This water mass seems to be characterized by core parameters that are different from typical AASW definition. In fact, during RoME 2 experiment AASW core is found 234 235 at a depth of about -50 m with salinity values close to 34.6 and potential density values lower than 236 27.9 kg m-3. These values are slightly saltier, colder and denser than expected for typical AASW and more similar to typical Modified Circumpolar Deep Water (MCDW) core parameters. Anyway 237 O₂ content data (see Fig.2) show high oxygen concentration that help us in excluding MCDW 238 239 presence. Differences from AASW typical values are probably due to the very local and seasonal 240 conditions experienced during RoME 2. Summer insulation and the connected ice melting are also 241 responsible for the increased temperatures and lower salinities of the very surface layer (depth 242 shallower than -30 m).

243 The variability observed in surface layers is not found in the intermediate and deep layers 244 (depth from 100 m to about 1000 m) that are occupied by High Salinity Shelf Water (HSSW) and 245 Ice Shelf Water (ISW) with typical 9 and S values. HSSW is characterized by a salinity maximum 246 greater than 34.7, potential temperature near the freezing point and potential density greater than 247 27.9 kg m-3 (Budillon et al., 2002; Rivaro et al., 2014). The coldest water mass identified during
248 the experiment is the local ISW (Budillon and Spezie, 2000) with potential temperature below the
249 freezing point and salinity of about 34.7.

In terms of spatial variability, a frontal zone seems to be present long the convergence (black dotted line in Fig. 3) between two circulation systems and is characterized by intense gradients in terms of temperature and salinity (see also section 4.3). This pattern is consistent with information showed in the 9/S diagram of the RoME 2 experiment (Fig.2). Fresh and cold water masses, possibly influenced by melting and then driven offshore by eastwards currents measured at stations 36, 41, 43, 44, are only observed at stations 41, 43, 44 on the western side of the front. Stations 34 and 35/45 show mixed T and S characteristics between coastal and eastern water masses.

The existence of this front is also evident in terms of U and V components of the observed currents (see Fig. 3, Fig. 9 C and D). LADCP measurements reveal the presence of a significant gradient across the frontal line as well as an inversion of resulting current directions just east of station 35/45, as confirmed by the analysis of geostrophic currents derived from CTD data (not shown). Finally the absence of any upwelling signal (see section 4.3) associated to the presence of any cyclonic circulation centred in the middle of the studied area seems to offer a further confirmation of the existence of a meridionally oriented front at about 165.6°E .

264

3.2 Chemical and biological properties.

The measured A_T and pH together with the calculated C_T , pCO₂, Ω_{Ca} , Ω_{Ar} , and O₂ are compiled in Table 1. The A_T and the C_T range between 2313.4 and 2364.9 µmol kg⁻¹ and 2016.9 and 2265.6 µmol kg⁻¹, respectively with the lowest values at the surface, in good agreement with previous data collected in the Ross Sea (Sandrini et al., 2007; Rivaro et al., 2014). The pH ranges between 8.42 and 7.96, with the highest values at the surface and decreasing values with depth. As expected, C_T and A_T correlated significantly and positively with the S distribution (r = 0.79 and 0.92, respectively). A strong positive correlation was observed between the A_T and the C_T (r =0.61, n = 61) and a negative correlation was found between pH and C_T (r =-0.98, n = 61). The

pCO₂values calculated for surface sea water are well below the atmospheric measured values (cf. Table 3), ranging from 146 to 236 μ atm and a general increase is observed with depth up to 450 μ atm about calculated at 200 m. All of the samples result oversaturated with respect both to the calcite and aragonite, but near corrosive level of aragonite saturation state (Ω_{Ar}) (~1.0) is found only in correspondence to the deepest samples collected at stations 39 and 43 (1080 and 775 m, respectively).

The O_2 concentration has a decreasing trend from the surface to 200 m water depth in each station. In some stations (34, 36, 41, 43 and 45), higher values (from 10.4 to 12.6 mg L⁻¹), above the saturation level (104-113%) were found in the upper 20 m of the water column.

The total phytoplankton biomass was relatively high in all stations. In situ Chl-a values at 282 surface varied from 0.904 to 2.556 mg m^{-3} (average 1.525) with integrated values ranging from 283 115.3 to 371.3 mg Chl-a m⁻² (average 231,9) (Table 2). Chl-a concentrations along the water 284 column varied between 0.582 and 3.785 mg m⁻³, with the highest values found in the sub-surface 285 layer of station 41 at 30 m depth. The surface Chl-a concentrations were well correlated ($r^2=0.98$) 286 287 with those throughout the 0–100-m layer only for the stations 34, 35, 36, 43 and 45. The micro-288 phytoplankton was the most abundant size fraction in all stations and highly correlated with the 289 total biomass (Fig. 4).

The highest values of Chl-a were found in the layer between 20 to 50 m, with the dominant taxonomic group being haptophyceae. The maximum diatom biomass occurred only in the surface layers (0-20 m) while in deep-water (below 35 m), haptophyceae dominated the phytoplankton community (Fig. 5).

The taxonomic analyses confirm the dominance of haptophyceae and bacilarriophyceae that make up 90 % of the phytoplankton community. The haptophyceae are constituted by *Phaeocystis antarctica* in the colony. The *Fraglariopsis* spp., *Pseudo-nitzschia* spp. and *Cylindroteca* *closterium* are the more abundant species of diatoms. All stations were characterized by quite a
 similar vertical structure of phytoplankton communities. In the upper layer, the phytoplankton
 community is characterized by diatoms and the deeper layer was dominated by *Phaeocystis antarctica*.

The community structure along the water column for some stations (34, 35, 39 and 45) is shown in Fig. 6. In Stations 34 and 35, at surface layer, a 42% of *Phaeocystis antarctica* and 56% of diatoms is fond, while along depth there is a 99% increase of *P. antarctica* to 60 m. In stations 49 and 55, the diatoms dominate the surface with 67% and 97%, respectively; while along depth, the percentage of the *P. antarctica* increases by 97% to 60 m.

4. Discussion

307

4.1 Mesoscale drivers affecting the carbonate system chemistry in surface water.

308 The carbonate system properties in surface water exhibit the presence of mesoscale variability 309 with a horizontal length scale of about 10 km, which could be connected to both physical and 310 biological forcings.

311 The melting of the sea ice plays an important role in controlling the summer AASW physical 312 and chemical features in the Ross Sea. The RoME cruise was characterized by largely ice-free 313 conditions over most of the southern Ross Sea and wide open sea areas were present. Solar heating 314 encourages sea ice melting with the formation of the UML occupying the surface layer of the 315 AASW. To evaluate any effect of the sea ice melting on the physical and chemical properties at the 316 surface, we calculated the percentage of melted water (MW%), which varies from 0.9 % (in station 317 40, where the salinity reached the highest surface value of 34.43) to 3.1% (at station 44, where the 318 lowest salinity of 34.43 was measured) with a mean value of 2.1%. The UML depth and the 319 irradiance are two of the main factors affecting the communities and structure of phytoplankton and 320 its dynamics, as the presence of a shallow pycnocline allows the phytoplankton to remain in the 321 euphotic layer (Mitchell and Holm-Hansen, 1991; Arrigo et al., 1999).

322 A very shallow UML depth was calculated for the sampled stations $(16 \pm 5 \text{ m})$, comparable to 323 other data reported for coastal areas of the Ross Sea (Massolo et al., 2009). The lowest depth was 324 calculated at station 44 (7 m), whereas the deepest was at stations 35 and 39 (23 and 24 m, 325 respectively). The significant negative correlation (Pearson's r = -0.76, p = 0.05) found with the 326 MW% outlines the role of the melting sea ice in the UML depth settling, very shallow UML are 327 found in correspondence of high MW percentages. The MW% also co-varied significantly and negatively with surface A_T (Pearson's r -0.96, p = 0.05) and C_T (Pearson's r - 0.72, p = 0.05), 328 329 consistently with the fact that the distribution of surface A_T and C_T is controlled by the factors 330 linked to observed salinity values. Therefore, the addition of the melting sea-ice, which has low 331 salinity, results in a dilution of the A_T and C_T . 332 The A_T-C_T relationship can be used to determine whether the cause of their variability is due to processes such as photosynthesis-respiration or CaCO₃ production-dissolution (Bates et al., 333 334 1998). Thus, surface and subsurface (10-30 m) A_T and C_T were normalized (A_{T34.5} and C_{T34.5}) to a 335 constant salinity of S=34.50 (roughly the long-term average salinity of the Ross Sea upper water 336 column) to remove the effects of dilution from the melting sea ice (Dumbar et al., 2003). 337 Photosynthesis and respiration can influence C_T but not A_T, whereas CaCO₃ production-dissolution 338 acts on both C_T and A_T at a ratio ranging between 1:1 and 1:2 depending on the ratio of organic 339 carbon production to CaCO₃ production (Robertson et al., 1994). A_{T34,5} and C_{T34,5} range from 2344.4 to 2373.3 μ mol kg⁻¹ and from 2062.9 to 2225.0 μ mol kg⁻¹, respectively. A_{T34.5} variability is smaller 340 $(29 \ \mu mol \ kg^{-1})$ than $C_{T34.5}$ variability (162 $\mu mol \ kg^{-1})$ and is linearly related to $C_{T34.5}$ as follows: 341 $A_{T34.5} = -0.118 + 2612.3 C_{T34.5} (r^2 = 0.57)$ 342 (4). 343 This relationship indicates that photosynthesis-respiration, rather than CaCO₃ production-344 dissolution equally controls C_T variability in surface and subsurface water. The phytoplankton role 345 in determining the C_T concentration is confirmed by the high pH in correspondence of the low

 $C_{T34.5}$ values, as a result of the displacement of the carbonate equilibrium related to CO_2

347 consumption (Fig. 7 A), by the observed O₂ super saturation (Fig. 7 B) and by the negative 348 correlation between Chl-a and $C_{T34.5}$. Chl-a was used to investigate the role of biological CO₂ 349 drawdown on the variability of the carbonate system and Ω . CO₂ is consumed through 350 photosynthesis, thus the CO_2 concentrations in the surface water decrease. This leads to higher CO_3^{-1} 351 and consequently higher Ω and pH in the surface layer in those stations where the highest values of 352 Chl-a were recorded. Basing on these results, during the RoME 2 mesoscale experiment, the distribution of the carbonate system in surface waters was largely controlled throughout the 353 354 phytoplankton activity, more than throughout the physical forcing. In support of this finding, we can take in to account also that the A_{T34.5}:C_{T34.5} ratio is close to the value found by Bakker et al. 355 356 (2008) for the Weddell Sea and consistent with data reported by Anderson and Sarmiento (1994) for 357 organic matter production.

358

4.2 Mesoscale physical and biological forcing on the local air-sea CO_2 flux.

359 The production of organic matter in the surface waters consumes C_T and make pCO_{2SW} 360 decrease, potentially enhancing the uptake of CO₂ from the atmosphere. Surface pCO_{2SW} data were 361 below the atmospheric mean value and had a large spatial variability (146-236 µatm), whereas the 362 measured pCO_{2atm} varied in a very narrow range (from 391.7 to 392.2 µatm). The pCO_{2SW} values 363 show a small-scale heterogeneity and are comparable to those reported for the Ross Sea surface 364 waters during the summer season (Bates et al, 1998; Tortell et al., 2011). Therefore, the computed 365 air-sea CO_2 (ΔpCO_2) gradient was negative, corresponding to a net transfer of CO_2 from the atmosphere to the ocean. The solubility is one pivotal mechanism in controlling the oceanic uptake 366 367 of CO₂ across much of the Southern Ocean. However, in geographically limited areas where intense 368 biological production occurs, such as the Ross Sea, Terra Nova Bay, polynyas and other ice 369 marginal areas or coastal areas of the Ross Sea, biological processes become important for 370 transferring CO₂ from the atmosphere to the ocean (Bates et al., 1998; Arrigo et al., 2008; Laika et 371 al., 2009; Rivaro et al., 2014). The greatest air-sea CO₂ disequilibrium occurred at stations 34 and

372 44 (-241.6 µatm and -243.4 µatm) in correspondence of enhanced O₂ super saturation (112-113%) 373 and high pH_T values (8.42 at both stations). SST and Chl-a maps derived from MODIS level 2 374 datasets indicated the occurrence of productive processes during our survey. Satellite images 375 captured a few hours before the RoME 2 sampling, showed a relatively inhomogeneous chlorophyll 376 distribution in the study area, with filaments characterized by chlorophyll concentrations higher (~1.4 mg m⁻³) than the surrounding water (~0.4 - 0.5 mg m⁻³, Cf. Fig.1C). In particular, starting 377 from 25th January, higher Chl-a concentrations were observed in the correspondence of stations 378 from 34 to 36. During the following days (see 28th January map) this increase in Chl-a 379 380 concentration assumes a horseshoe shape, including a larger number of stations. In situ fluorometer 381 measurements have some good correspondence with satellite maps, even if time and depth selection 382 must be taken into account (see Fig.1C and 9E for satellite and in situ data respectively). The 383 ΔpCO_2 pattern (Fig. 8A) follows both MODIS data and in situ Chl-a measurements (Fig.8B). Chl-a 384 concentration measured either in situ or estimated from satellite radiance, is the most commonly 385 used proxy of phytoplankton biomass (Uitz et al., 2006; Boyce et al, 2010; Siegel et al., 2013). 386 However, this property is strongly influenced by phytoplankton community composition. 387 Our data showed that in the first layer of the water column, the phytoplankton community is 388 characterized by a mixed population, heavily dominated by diatoms respect to the haptophyceae. 389 The phytoplankton assemblage results from a differential photosynthetic response of the two 390 groups, with *P. antarctica* being able to photosynthesize more effectively (and presumably grow) at 391 lower irradiances than diatoms (Arrigo et al., 1999). Also, the physiological state and light history 392 of the phytoplankton communities have to be considered. In the upper layer of some stations (33, 393 34, 41, 43, 44, 45) through taxonomic analysis, a senescent diatoms were shown with empty cells, 394 so what we see is the result of different processes occurred in the area. It has been recognized that, 395 diatoms are less effective in consuming C_T or producing dissolved organic carbon (DOC) that Phaeocistis antarctica (Arrigo et al., 2000). The investigated region overall acted as a sink of CO₂, 396

with fluxes ranging from -0.5 ± 0.4 to -31.0 ± 6.4 mmol m⁻² d⁻¹ (Table 3). In particular, the CO₂ air– sea flux at stations 38, 39, 40 and 41 was several times lower than at the other stations. The large range observed in the flux is due to the significant spatial variability of pCO_{2sw} and wind speed encountered during the RoME 2 survey. In fact, wind speed is the main driver of the air–sea flux, together with the Δ pCO₂ and the lowest flux were calculated in those stations characterized by the weaker hourly averaged wind. On the contrary, the strongest CO₂ sink was observed at station 34 where low pCO_{2sw}, high pH_T and high wind speed were observed.

404 The revisited station (45), shows a slightly higher flux value with respect to its first sampling 405 (station 35). Enhanced flux is mostly due to a higher wind speed than to an eventual higher CO_2 406 removal. In fact no increase of photosynthetic activity, as represented by Chl-a values is found at 407 48 hours distance.

408

4.3 Influence of the mesoscale physical forcing on the vertical distribution.

409 Cruise plan and station location allowed to analize the main oceanographic parameters along 410 several NW-SE transects and one longer NE-SW section. Temperature and salinity data of the main 411 longitudinal transect (stations 39, 40, 45, 41, 43) from surface to 200 m depth are showed in Fig. 9 412 A and B. T/S pattern highlights the presence of fresher and colder water masses in the western part 413 of the transect (stations 43, 41, 45) as well as saltier and warmer ones in the eastern stations (39, 414 40). The deepening of colder water in correspondence of station 45 and the maximum eastward 415 extension of fresher water masses suggest that station 45 is next to a front, where a convergence 416 between different water masses could be located. Sections of the current zonal and meridional 417 components, measured each 10 m depth by LADCP along the same transect, confirm this 418 hypothesis. An abrupt change in current direction is observed from station 41 to 40 both in terms of 419 U (Fig. 9 C) and V components (Fig. 9D) suggesting the presence of a convergence, possibly 420 associated to the frontal position of station 45. Moreover, the calculation of geostrophic flow along 421 the analyzed transect confirms this pattern, showing a change in current directions in

422 correspondence of the front. Similar results from all analyzed transects lead us to reconstruct the 423 general circulation of the studied area as well as the front position, sketched in Fig. 3. 424 The frontal zone centred on station 45 is reflected in the distribution of the carbonate system properties in the upper part of the water column. Higher pH and Ω_{Ar} and lower C_T and pCO_{2sw} were 425 426 observed in correspondence of the less saline waters of the western part of the section, also 427 occupying a thicker layer (30-40 m) than in the eastern part (Fig. 10). Here we also observed higher Chl- a concentrations (Table 2) and O₂ super saturation. A general homogeneous distribution of C_T 428 429 and of the other carbonate system properties was observed in the waters below 50 m with an 430 increasing trend with depth. This trend is reasonably due to an increasing pCO_{2sw}, which decreases 431 the pH and the Ω_{Ar} as well. Thus, while the effect of the frontal zone on the carbonate properties 432 was visible in the surface and sub surface layer it is no more evident in the deeper layer. 433 Generally, the presence of water masses connected to sea-ice melting results in low Ω due to dilution of $[CO_3^{2-}]$ as it has been reported in several studies both in Arctic and Antarctic seas 434 435 (Mattsdotter Björk et al., 2014), nevertheless our data sustain the hypothesis that the biological 436 activity was the main cause for the observed carbonate system properties distribution. The effect of 437 biological processes on the Ω_{Ar} have been already reported in the Ross Sea on a large spatial and temporal scale (Mattsdotter Björk et al., 2014), but no paper reports such effect on a small scale like 438 those we focused on in this study. 439 440 Therefore, the dilution due to the melting sea ice had a small direct effect on Ω_{Ar} , but it has an 441 indirect effect too, taking into account that UML and the stability of the water column depend on it.

The stations characterized by lower salinity values (45, 43 and 41) also showed a shallower
UML (~15 m) than station 39 and 40 (~23 m), suggesting a positive feedback with the
phytoplankton activity.

Phytoplankton distribution described in our results is in agreement with Arrigo et al. (1999)
and Annett et al. (2010) asserting that deep mixing promotes growth of *P. antarctica* as a result of

447 the positive buoyancy of its mucilaginous form (Leventer and Dunbar, 1996), and an ability to 448 adapt to a large range of irradiance levels (Arrigo et al., 1999). Conversely, a stratified water 449 column favours diatoms, which are better adapted to higher light levels and would otherwise sink 450 quickly due to their silica frustules, such that they accumulate preferentially in stratified and in 451 shallow-mixed layer regions, conditions typically found in ice edges water column (Arrigo et al., 452 1999; Arrigo et al., 2000, Goffart et al., 2000, Smith et al., 2010). In the first layer, the phytoplankton community is characterized by a mixed population, heavily dominated by diatoms 453 454 respect to the haptophyceae. *Phaeocystis antarctica* was numerically dominant immediately following deepening of the mixed layer and determined the maximum values of Chl-a. 455

456 **5. Conclusion**

457 The importance of mesoscale structures in the distribution and spatial variability of the 458 carbonate system properties of the upper 200-m layers and in local air-sea CO_2 flux was 459 investigated in the coastal area of the Ross Sea.

460 The satellite images revealed a number of small structures in the study area, confirmed by 461 strong correspondence with in-situ data. Our results document a high resolution spatial 462 heterogeneity in surface waters carbonate system properties and, to our knowledge, our study is the 463 first to quantify the magnitude and distribution of the CO_2 flux at a mesoscale level in a shelf area 464 of the Ross Sea. The distribution of the carbonate system in surface waters was controlled largely 465 throughout the phytoplankton activity more than the physical forcing.

The dominance of diatoms versus haptophyceae is found to have particular implications for the ratios of nutrient drawdown and carbon export. Should phytoplankton communities shift from P. antarctica to diatom dominance in response to enhanced upper ocean stratification (Sarmiento et al., 1998), then our data indicate that the CO₂ drawdown estimated from the C/P ratio, would be reduced in these areas by about 50%.

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629 **Caption of figures.**

Fig. 1. A) Map of the sampling stations from 26th to 28th January 2014. Station 35 was revisited
after 24 hours about (station 45). The insets show the region of study inside the Ross Sea.
B) The position of the sampled stations (blue circles) with respect to the MODIS SST . C) The
position of the sampled stations (blue circles) with respect to the MODIS surface Chl - a . Satellite
data retrieved from Aqua and Terra satellites level-2 data at 1 km resolution, relative to 25th (left)
and 28th (right) January 2014 .

- 638 **Fig. 2.** Potential temperature/salinity (θ /S) diagram of the sampled stations. The colour scale refers 639 to dissolved oxygen concentration (mg L⁻¹).
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Fig 3. A simplified scheme of the main currents acting in the study area during the RoME 2
experiment. Current speed and directions are derived by LADCP observations collected every 10 m
from surface to maximum reached depth..

Fig. 4. Correlation between the total biomass and size fraction for all stations.

Fig. 5. Vertical profiles of mean and standard deviation of the total biomass (Chl-a concentration)
 and of the relative contribution of diatoms and haptophyceae to the phytoplankton community
 (percentage) in all stations.

Fig.6. Percentage contribution of diatom species, Pheocystis antarctica, Dinophiceae and
Phytoflagellates in the water column for stations 34, 35, 39 and 45 (A, B, C and D, respectively).

 $\begin{array}{ll} 653\\ 654\\ \text{ Fig. 7. Scatter plot of surface and subsurface (10-30 m) normalized total alkalinity (A_{T34.5}) and \\ 655\\ \text{ normalized total inorganic carbon (C}_{T34.5}). The colour scale refers to pH values (A), O_2 saturation \\ 656\\ \text{ percentage (B).} \end{array}$

658 **Fig. 8.** Surface calculated ΔpCO_2 (pCO_{2SW} - pCO_{2air}) (µatm) (A) and Chl-a (mg L⁻¹) distribution 659 (B).

Fig. 9. Sections of temperature (A), salinity (B), zonal (C) and meridional (D) current components
and in situ fluorimeter (E) from surface to 200 m depth along the transect across stations 39, 40, 45,
41, 43.

- **Fig.10.** Sections of $C_T(A)$, pH (B), pCO₂ (C), $\Omega_{Ar}(D)$ and O₂ (E) from surface to 200 m depth along the transect across stations 39, 40, 45, 41, 43.
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Table 1. Carbonate system and O_2 (mg L⁻¹ and saturation percentage) data from RoME 2 water column sampling stations. 671

Station	Depth	A _T	pН	pCO ₂	CT	Ω	Ω	02	02
	(m)	(µmol kg ⁻¹)		(µatm)	(µmol kg ⁻¹)	Calcite	Aragonite	mg L ⁻¹	% sat
33	2	2350.8	8 25	236	2135 1	37	23	12.6	114
	18	2350.0	8.06	379	2233.8	23	14	9.4	79
	40	2351.8	8.09	348	2223.0	2.5	1.1	9.9	83
	80	2354.1	8.05	384	2238.1	2.2	1.5	99	83
	120	2356.4	8.06	378	2239.4	2.2	14	99	82
	135	2357.6	8.01	426	2257.1	2.0	1.2	9.2	77
	400	2354.6	7.98	445	2259.3	1.8	1.1	9.4	79
34	2	2336.9	8.42	148	2037.2	5.0	3.1	12.5	112
	10	2341.7	8.37	172	2069.7	4.5	2.8	12.3	111
	30	2364.7	8.24	243	2163.6	3.4	2.2	11.4	99
	60	2359.4	8.14	309	2203.6	2.8	1.7	10.7	91
	220	2352.5	8.15	292	2198.3	2.6	1.7	9.2	76
35	2	2350.5	8.40	156	2057.8	4.9	3.0	12.0	108
	35	2371.5	8.24	242	2168.2	3.5	2.2	11.5	101
	70	2357.2	8.10	338	2219.2	2.5	1.6	10.3	87
	110	2352.9	8.05	390	2238.4	2.2	1.4	10.0	84
	200	2349.0	8.00	428	2250.1	1.9	1.2	9.2	77
36	2	2332.9	8.32	194	2086.4	4.1	2.6	11.6	104
	10	2345.1	8.35	179	2081.4	4.4	2.8	12.0	108
	20	2343.0	8.32	196	2109.5	3.9	2.5	12.1	105
	40	2358.1	8.21	263	2172.8	3.2	2.0	11.5	100
	160	2349.9	8.00	431	2251.9	1.9	1.2	9.3	78
37	2	2332.0	8.38	165	2060.3	4.5	2.8	9.1	75
	25	2357.0	8.23	249	2163.9	3.3	2.1	11.8	105
	60	2350.0	7.96	479	2265.6	1.8	1.1	11.3	98
	80	2348.6	8.00	439	2252.9	1.9	1.2	9.2	77
	200	2344.0	8.00	430	2246.9	1.9	1.2	9.2	76
38	2	2314.8	8.34	185	2063.8	4.2	2.6	11.6	104
	37	2362.4	8.19	277	2184.3	3.1	1.9	11.1	97
	50	2351.1	8.06	377	2230.7	2.3	1.4	10.0	84
	100	2353.3	8.00	436	2255.9	2.0	1.2	9.0	75
	200	2338.9	8.00	431	2241.7	1.9	1.2	8.5	71
39	2	2349.0	8.30	206	2108.9	4.0	2.5	11.3	102
	20	2351.4	8.26	230	2136.1	3.6	2.3	11.0	98
	50	2350.6	8.14	306	2192.7	2.8	1.8	10.8	94
	200	2332.8	7.98	454	2243.0	1.8	1.1	8.9	74
	1080	2347.3	7.97	420	2248.0	1.6	1.0	9.2	77

40	2	2362.6	8.35	181	2097.0	4.4	2.8	12.1	109
	30	2364.9	8.20	268	2179.9	3.2	2.0	11.2	98
	60	2346.6	8.11	337	2207.3	2.5	1.6	10.5	89
	100	2341.7	7.99	443	2247.4	1.9	1.2	9.2	76
	200	2342.0	7.99	435	2245.7	1.9	1.2	9.1	75
41	2	2342.0	8.37	172	2072.3	4.5	2.8	12.2	109
	20	2348.9	8.35	181	2086.9	4.4	2.7	12.4	111
	30	2349.4	8.27	221	2130.0	3.7	2.3	11.7	103
	80	2344.1	8.04	396	2232.0	2.2	1.4	9.6	81
	200	2358.0	7.98	451	2265.6	1.9	1.2	9.3	77
43	2	2315.9	8.38	165	2044.3	4.5	2.8	11.8	106
	20	2338.2	8.33	188	2090.7	4.1	2.6	12.0	107
	40	2364.4	8.21	261	2175.3	3.2	2.0	11.6	101
	200	2352.4	8.01	423	2251.4	2.0	1.2	9.2	76
	775	2362.1	7.97	430	2264.0	1.7	1.1	9.4	78
44	2	2313.4	8.42	146	2016.9	4.9	3.1	12.6	113
	30	2360.4	8.10	342	2222.8	2.5	1.6	10.4	88
	100	2357.9	8.02	420	2254.5	2.0	1.3	9.7	81
	188	2350.8	8.02	415	2247.5	2.0	1.3	9.4	78
45	2	2341.3	8.34	186	2083.0	4.3	2.7	11.9	102
	10	2349.1	8.35	178	2082.9	4.4	2.8	12.1	109
	25	2360.4	8.33	188	2106.1	4.2	2.7	10.5	94
	100	2364.4	8.06	376	2244.0	2.3	1.4	10.0	83
	200	2351.7	8.01	419	2249.8	2.0	1.2	9.3	77
	701	2358.3	8.01	398	2249.8	1.8	1.2	9.5	79

Station	mg Chl a m ⁻³	mg Chl a m ⁻²		
33	1.130	115.3		
34	2.556	371.3		
35	1.953	320.5		
36	1.220	246.5		
37	1.612	133.3		
38	0.904	225.9		
39	1.002	166.4		
40	1.171	202.5		
41	1.621	212.3		
43	1.521	277.4		
44	2.308	234.9		
45	1.301	276.2		

Table 2. Mean values of surface and integrated Chl-a in the 0-100 m layer.

Table 3. Atmospheric dry-pCO2 (pCO2 dry, μatm), atmospheric pCO2 corrected to 100% humidity697(pCO2 wet, μatm) air-sea CO2 gradient (ΔpCO2, μatm) and calculated CO2 flux (mmol m⁻² d⁻¹).

Station	Wind speed (m s ⁻¹)	pCO ₂ dry (µatm)	pCO ₂ wet (µatm)	ΔpCO ₂ (µatm)	F (mmol m ⁻² d ⁻¹)
33	21.7 ± 1.2	392.0	389.3	-153.2	-23.7 ± 2.8
34	19.6 ± 1.9	392.2	389.6	-241.6	-31.0 ± 6.4
35	11.4 ± 1.4	392.1	389.5	-233.6	-10.0 ± 2.6
36	13.3 ± 1.3	392.1	389.5	-195.9	-11.6 ± 2.4
37	10.5 ± 1.2	391.7	389.2	-224.3	-8.3 ± 2.1
38	8.7 ± 1.2	391.9	389.3	-204.6	-5.2 ± 1.5
39	8.3 ± 1.2	391.9	389.3	-183.1	-4.1 ± 1.3
40	4.7 ± 1.1	391.8	389.3	-208.1	-1.5 ± 0.8
41	2.8 ± 0.9	391.9	389.3	-217.6	-0.5 ± 0.4
43	12.8 ± 1.3	391.7	389.1	-224.4	-12.4 ± 2.6
44	11.2 ± 2.1	391.7	389.1	-243.0	-10.1 ± 4.2
45	14.5 ± 2.9	391.7	389.0	-203.5	-14.1 ± 6.2

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A)



-1.9 -1.68 -1.46 -1.24 -1.02 -0.8 -0.58 -0.36 -0.14 0.08 0.3 0.52 0.74 0.96 1.18 1.4 1.62 1.84 2.06 2.28 2.5



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C)

Fig.1



Fig.2

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Fig.3

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Fig.4

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Fig.5



Fig. 6

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B)

Fig.7



A)

Chl-a (mg m⁻³)



B)

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Fig.9

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