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journal homepage: www.elsevier.com/locate/dsriThe role of phytoplankton composition and microbial community metabolism in sea–air $\Delta p\text{CO}_2$ variation in the Weddell SeaSébastien Moreau^{a,b,*}, Eugenia di Fiori^{c,d,1}, Irene R. Schloss^{b,c,e},
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ABSTRACT

The Weddell Sea is known to be a CO₂ sink due to active biological and physical pumps. Here we study the relationships of phytoplankton biomass and composition and microbial community metabolism, estimated from simulated *in situ* incubations and from nutrient's difference between surface and subsurface waters, with $\Delta p\text{CO}_2$ in the Weddell Sea, during four austral summers (2002–2005). The $\Delta p\text{CO}_2$ was significantly negative throughout the Weddell Sea in 2002 ($-17.2 \pm 28.1 \mu\text{atm}$), 2003 ($-64.1 \pm 31.3 \mu\text{atm}$), 2004 ($-54.9 \pm 61.8 \mu\text{atm}$) and 2005 ($-63.8 \pm 60 \mu\text{atm}$), indicating that the Weddell Sea acted as an atmospheric CO₂ sink during those summers. The $\Delta p\text{CO}_2$ was significantly lower in the south than in the center or north of the Weddell Sea. This was consistent with the significantly higher Chlorophyll-*a* concentrations (Chl-*a*) observed in the south ($2.3 \pm 1.9 \mu\text{g l}^{-1}$) than in the center ($1.3 \pm 1.2 \mu\text{g l}^{-1}$) or north ($1.4 \pm 1.7 \mu\text{g l}^{-1}$). In contrast, waters were mainly undersaturated in O₂, due to the upwelling of oxygen poor Warm Deep Water (WDW). The negative relationship between the $\Delta p\text{CO}_2$ and the %O₂ saturation suggested that planktonic metabolic activities played a role in these gases dynamics, along with the upwelling of WDW. However, these relationships could not be observed from the results of the incubation experiments, probably because of different temporal scales between gas exchanges in incubation experiments and *in situ* CO₂ and O₂ dynamics. The dynamics of CO₂ and O₂ were solely related to the net community production (NCP) and to the gross primary production (GPP) when only stations with Chl-*a* > 1 $\mu\text{g l}^{-1}$ were considered. A significant relationship was, however, found between $\Delta p\text{CO}_2$ and the primary production until the time of sampling for all stations when estimated from nutrients depletion between surface and subsurface waters. Finally, the distribution of CO₂ and O₂ were related to the biomass of diatoms and, contrarily to other seas, to the biomass of phytoflagellates.

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1. Introduction

Oceans play a major role in CO₂ dynamics. Indeed, 25% of the anthropogenic CO₂ released to the atmosphere every year is fixed by the global Ocean (Le Quéré et al., 2010), although its capacity to

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absorb CO₂ is decreasing in some regions (e.g. the Indian and Pacific sectors of the Southern Ocean, Lenton et al., 2012). In itself, the Southern Ocean is responsible for 4% of this global CO₂ uptake (Takahashi et al., 2009). Within the Southern Ocean, which is responsible for ~15% of the global ocean primary production (Huntley et al., 1991), coastal waters and oceanic fronts are among the most productive regions (Ducklow et al., 2006; Ferreyra et al., 2004) and may represent important CO₂ sinks. The mechanism by which CO₂ is exported from the atmosphere into deep seas by biological processes is known as the “Biological Pump” (Eppley and Peterson, 1979). In addition, within the Southern Ocean, deep water formation occurs in the south-western Weddell Sea and the Ross and Dumont d’Urville Seas (Hoppema et al., 1998; Jacobs

et al., 1970) and may also contribute to the sinking of atmospheric CO₂ to deep waters, a mechanism called the “Physical Pump” (Caldeira and Duffy, 2000). As a result, CO₂ dynamics within the Southern Ocean are closely related to primary production and the formation of deep waters (Takahashi et al., 1993).

According to Takahashi et al. (2002), the flux of CO₂ between the atmosphere and the ocean is governed by the difference between seawater and atmospheric CO₂ partial pressure ($\Delta p\text{CO}_2 = p\text{CO}_2 \text{ surface water} - p\text{CO}_2 \text{ atmosphere}$). Since atmospheric pCO₂ does not vary much with location (Takahashi et al., 2002), $\Delta p\text{CO}_2$ is mainly a function of variations in the seawater pCO₂. In turn, the seawater pCO₂ is influenced by several physical (i.e. temperature, winds, surface water mixing and CaCO₃ dissolution) and biological processes (i.e. calcification, primary production and respiration). Of these parameters, we will mainly be interested in the primary production and respiration of the planktonic community, and on how species composition may influence these processes. On one hand, phytoplankton absorbs the dissolved inorganic carbon and transforms it into organic carbon that becomes part of the pelagic food web or sinks to the deep ocean (Legendre and Le Fèvre, 1995), lowering the pCO₂ in surface waters, and thus favoring oceans to act as carbon sinks. On the other hand, respiration by autotrophs and heterotrophs increases the pCO₂ in surface waters, favoring the oceans to act as CO₂ sources. The relationship between the primary production and the respiration of the community is often represented as the balance between the gross primary production (GPP) and respiration (R) of the planktonic community, the GPP:R ratio. In other seas, this ratio represents the potential contribution of the planktonic community to the sequestration of CO₂ from surface waters and depends on the type and composition of this community (Schloss et al., 2007).

Low productive systems generally correspond to areas where the microbial loop and/or the microbial food-web (two systems

dominated by heterotrophs and small cells such as phytoflagellates) dominate (Azam et al., 1983; Legendre and Rassoulzadegan, 1995). On the contrary, highly productive systems generally correspond to areas where the multivorous or herbivorous food-webs (where microphytoplankton, e.g. micro-sized diatoms > 20 µm, is grazed on by mesozooplankton, e.g. copepods and krill) dominate (Cushing, 1989). The type of microbial community may greatly influence the potential role of the ocean as a CO₂ source or sink. Within this context, the goal of this research was to study the relationships of phytoplankton biomass, phytoplankton composition and planktonic metabolic activities with respect to $\Delta p\text{CO}_2$ in the Weddell Sea, during four austral summers (2002 to 2005).

2. Materials and methods

This work was part of the ARGAL (“Programme de coopération entre la France et l’ARGentine pour l’étude de l’océan Atlantique AUstral”) missions that took place on board the Argentinean ice-breaker “A.R.A. Almirante Irizar” between the south-western Atlantic and Southern Oceans from 2002 to 2005. Sampling was performed in the Weddell Sea along four transects during the austral summers of 2002–2005 (see Table 1 and Fig. 1 for dates and itineraries). The Weddell Sea is bounded on its western side by the Antarctic Peninsula and on its eastern side by the Princess Martha Coast with its easternmost point located at Cape Norvegia and it constitutes the western part of the Weddell Gyre (Bakker et al., 2008; Stoll et al., 1999).

The sampling methods used during this study correspond to the methods already described in Schloss et al. (2007) and Moreau et al. (2012). Atmospheric, meteorological and seawater data were recorded continuously by means of an integrated sampling system (Poisson et al., 1993). Atmospheric pCO₂ was determined in air obtained from an intake placed on the bow of the ship by means of a flow-through equalizer and an infrared analyzer (Siemens, Type Ultramat 5F). The analyzer was calibrated every 6 h with 3 standard gases containing 270.0, 361.0 and 489.9 ppm of CO₂ molar fraction (Schloss et al., 2007). In addition, surface seawater was obtained from an intake located on the ship’s exterior, at a depth of 9 m. The variables measured in surface water were: temperature (Sea-Bird SBE 38 sensor), salinity (Sea-Bird SBE 37), *in vivo* fluorescence (Turner Designs Model 10 fluorometer) and CO₂ partial pressure (pCO₂), measured through the infrared analyzer described previously and corrected for atmospheric pressure variations, drift and moisture effects as in Bianchi et al. (2005).

Table 1
Sampling dates and number of sampling stations for each of the North–South and South–North transects performed during the four austral summer cruises.

Year	North–South		South–North	
	N	Sampling dates	N	Sampling dates
2002	37	16 Feb–24 Feb	37	2 March–7 March
2003	39	18 Feb–22 Feb	37	27 Feb–3 March
2004	37	30 Jan–6 Feb	42	6 Feb–11 Feb
2005	36	6 Feb–10 Feb	33	17 Feb–21 Feb

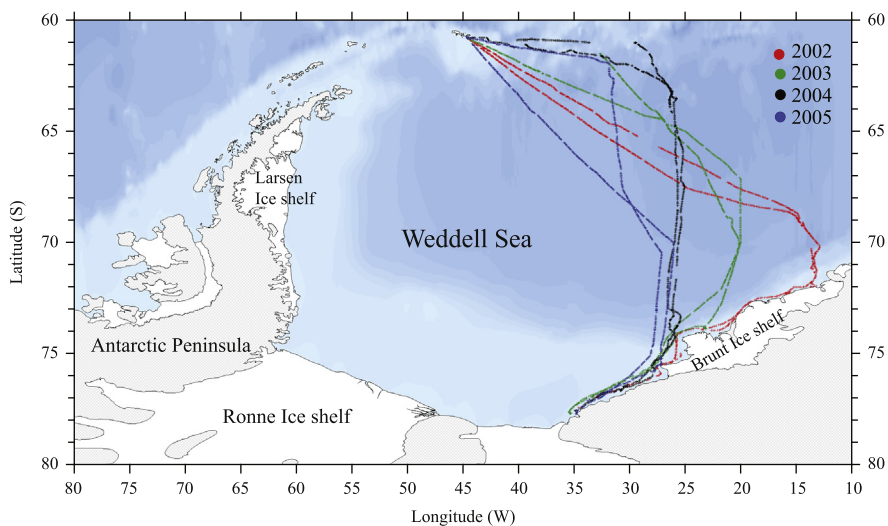


Fig. 1. Map of the Weddell Sea and itineraries of the 2002–5 transects.

The surface seawater $p\text{CO}_2$ was determined with a precision of $1 \mu\text{atm}$ (Bianchi et al., 2005). The $p\text{CO}_2$ difference ($\Delta p\text{CO}_2$) between the atmosphere and the surface ocean layer was calculated as an indicator of the potential of surface waters to act as CO_2 sinks (if $\Delta p\text{CO}_2 < 0$) or CO_2 sources (if $\Delta p\text{CO}_2 > 0$).

Discrete samples were obtained from the seawater intake every 3 h to determine the dissolved oxygen concentration ($N=71, 70, 65$ and 66 for the 2002–2005 cruises, respectively), nutrients concentration (nitrite, nitrate, phosphate and silicate; $N=74, 76$ and 78 for the 2002–2004 cruises, respectively), and chlorophyll a concentration (Chl- a ; $N=70, 62, 76$ and 69 for the 2002–2005 cruises, respectively). Moreover, discrete samples were also collected for identification and counts of phytoplankton cells ($N=40$ and 39 for the 2003 and 2004 cruises, respectively) and to perform incubation experiments of surface seawater plankton community ($N=10, 34, 9$ and 9 for the 2002–2005 cruises, respectively).

The dissolved oxygen concentration was analyzed onboard with the Winkler method and using an automatic potentiometer Mettler DL21 titrator. The coefficient of variation between replicates was 0.4. Oxygen saturation in terms of percentage was calculated as in García and Gordon (1992) using the solubility coefficients of Benson and Krause (1984) and the temperature and salinity data obtained from the seawater intake system. Nitrate + nitrite and silicate concentrations were determined with an automatic analyzer Technicon II[®]. Phosphate concentration was determined manually following the method of Strickland and Parsons (1972). The nitrite concentration was extremely low, so that, unless otherwise stated, the concentration of nitrate + nitrite is expressed as nitrate along this paper. The precisions for reactive nitrate was $\pm 0.07 \mu\text{M}$; for reactive nitrite, $\pm 0.016 \mu\text{M}$; for reactive phosphate, $\pm 0.014 \mu\text{M}$ and for reactive silicate, $\pm 0.18 \mu\text{M}$ using 5 cm cells.

Discrete samples were filtered onto Whatman GF/F filters and frozen at -20°C for further analysis of Chl- a , while the filtered fraction was used for inorganic nutrients concentration analyses. In addition, water samples were filtered using acetate of cellulose filters of 5 and $10 \mu\text{m}$ in order to quantify fractioned Chl- a concentration, excepted in 2005. All Chl- a samples were analyzed within one month after each mission. Chl- a was extracted with 90% acetone and absorbance was measured in a Beckman DU 650 spectrophotometer 24 h after extraction. Corrections for phaeopigments were only performed for Chl- a filtered through GF/F filters because the acetate of cellulose filters do not permit the acidification of the sample. Final Chl- a concentration was calculated according to Strickland and Parsons (1972) with an error of $\pm 0.05 \mu\text{g l}^{-1}$.

The samples for phytoplankton analysis were fixed with an acid Lugol solution and kept in cool and dark conditions until analysis. Cell counting and identification were performed under an inverted light microscope (Iroscope SI-PH) following the Utermöhl method (Lund et al., 1958). Part of these results (i.e. a description of *Pseudonitzschia* distribution in the Weddell Sea) can be found in Almandoz et al. (2008). The biovolume of cells was calculated as in Hillebrand et al. (1999) and corrected to account for the shrinkage of phytoplankton cells caused by the fixation of samples (Montagnes et al., 1994). The carbon content of phytoplankton cells was estimated with two different carbon-to-volume ratios for diatoms and for phytoflagellates according to Menden-Deuer and Lessard (2000). In order to simplify data analysis, phytoplankton was divided into two groups: diatoms and phytoflagellates. Phytoflagellates included diverse groups such as cryptophytes, prasino-phytes, dinoflagellates (only autotrophic species), silicoflagellates, and small ($< 5 \mu\text{m}$) and large (5 to $15 \mu\text{m}$) unidentified phytoflagellates.

Samples were incubated using dark and clear BOD bottles to estimate NCP, GPP and R. Seawater from the continuous sampling

system circulated through the incubator to keep the system at *in situ* temperatures. Incubations were run from 6 to 24 h, depending on initial *in vivo* fluorescence in order to avoid nutrient exhaustion. Nutrient analyses performed after the cruises revealed no nutrient limitation within the incubation bottles. In 2002, 2003 and 2005, samples were incubated in the ship's wet laboratory while, in 2004, incubations were done on deck. Irradiance inside the incubator simulated PAR at the sampling depth ($\sim 9 \text{ m}$), measured with a PUV-500 profiler spectroradiometer (Biospherical instruments Inc., USA). In 2004 (on-deck incubations), bottles were wrapped with neutral filters to reach $\sim 50\%$ of the sea surface irradiance, corresponding to the irradiance measured at the sampling depth (9 m).

The initial and final O_2 concentrations were determined within the incubation bottles following the Winkler method. Respiration (R) was calculated as the difference between the initial and final oxygen concentration inside the dark incubation bottles. The net community production (NCP) was calculated as the difference between the initial and final oxygen concentration inside the clear incubation bottles. The gross primary production (GPP) was computed as $R + \text{NCP}$. Following the method of Agustí et al. (2004), daily estimates of R and NCP were calculated by multiplying NCP and R by 24. Daily GPP was calculated as $\text{GPP} (\text{d}^{-1}) = \text{GPP} (\text{h}^{-1}) * \text{DL}$, where DL is day length (h) for the date and latitude where the incubation experiment was performed. The metabolic balance (or GPP:R ratio) was used to discriminate between autotrophic and heterotrophic communities with $\text{GPP:R} > 1$ and < 1 , respectively. The incubation method had a good analytical precision with average coefficients of variation between replicates of 0.19, 0.18, 0.3 and 0.1% for the years 2002–2005, respectively.

We also estimated primary production from nutrient change between winter subsurface (i.e. 50 m) and surface waters following the method of Hoppema et al. (1999). This method relies on the idea that Weddell Sea surface waters all originate from the WDW. Subsurface nutrient concentrations were not available for the present study and therefore we used the winter subsurface nutrients concentrations of Hoppema et al. (1999) considering that nutrient concentrations are stable within the WDW. In addition, for this method, one needs to assume that nutrients in surface waters are affected by biology only, which is true for phosphate, or interact only negligibly with the atmosphere, which concerns nitrate and N_2 fixation and denitrification. Then one may consider that changes in nutrient concentrations from winter subsurface values to the ones observed in the surface in the summer reflect the primary production until the time of sampling. Since the age of the Weddell Sea surface water is 2.9 years in average (Hoppema et al., 1999), the difference between the surface nutrient concentration and the subsurface winter nutrient concentrations is divided by 2.9. In addition, as freshwater inputs have an impact on nutrient concentrations and $p\text{CO}_2$, these values were normalized to a salinity of 35 (i.e. multiplying by $S/35$). Finally, the consumption of carbon was estimated from Redfield et al. (1963) ratios for nitrate (molar C:N ratio = 6.6 mol/mol) and phosphate (molar C/P ratio = 106 mol/mol), which is adequate for Weddell Sea's surface waters (Hoppema and Goeyens, 1999). These production estimates correspond to the nutrients change integrated from the winter until the moment of sampling (Hoppema et al., 2007).

Areal averages were used to describe data averages over the sampling area as in Schloss et al. (2007) and Moreau et al. (2012). Data were log-transformed to meet the assumptions of normality and variance homogeneity. Relationships between variables were described with model II linear regression analyses. One sample t -tests were used to determine if $\Delta p\text{CO}_2$ and $\% \text{O}_2$ saturation values significantly deviated from 0 and 100% respectively. ANOVAs were run to determine differences between years and between the northern ($60\text{--}66^\circ\text{S}$), the central ($66\text{--}72^\circ\text{S}$) and the southern

Table 2

Mean \pm standard deviation (std. dev.), maximum and minimum values for temperature (T , °C), salinity (S), nitrate concentrations (NO_3^- , μM), phosphate concentrations (PO_4^{3-} , μM) and silicate concentrations (SiO_4^{2-} , μM).

Variables	2002	2003	2004	2005
T max.	1.80	0.3	1.21	1.86
T min.	-1.75	-1.66	-1.60	-1.46
T mean \pm std. dev.	-0.44 \pm 1.23	-0.70 \pm 0.52	-0.61 \pm 0.53	0.00 \pm 0.63
S max.	34.36	34.39	34.3	34.28
S min.	33.34	32.46	31.79	32.76
S mean \pm std. dev.	34.07 \pm 0.23	33.75 \pm 0.37	33.67 \pm 0.34	33.80 \pm 0.31
NO_3^- max.	30.76	27.67	27.86	NA
NO_3^- min.	18.26	6.66	8.60	NA
NO_3^- mean \pm std. dev.	26.12 \pm 2.65	20.93 \pm 4.52	21.47 \pm 4.54	NA
PO_4^{3-} max.	2.08	4.65	1.89	NA
PO_4^{3-} min.	0.96	0.43	0.35	NA
PO_4^{3-} mean \pm std. dev.	1.61 \pm 0.23	1.87 \pm 1.06	1.34 \pm 0.36	NA
SiO_4^{2-} max.	80.24	84.94	75.88	NA
SiO_4^{2-} min.	34.94	19.13	12.54	NA
SiO_4^{2-} mean \pm std. dev.	65.73 \pm 8.08	51.09 \pm 14.65	53.63 \pm 15.60	NA

(72–78°S) Weddell Sea. In order to determine the respective roles of main phytoplankton groups (diatoms and phytoflagellates) and other key environmental variables (wind speed, sea surface temperature and salinity and nitrate concentration) on CO_2 dynamics in Weddell Sea, principal component analyses (PCA) were performed. The XLSTAT Version 2013.2.01 program was used for this analysis, considering the sampling stations as observations and the above factors as the variables. Pearson correlation coefficient was used as the basis for the ordination process. Wind speed (m s^{-1}) was recorded from the meteorological station of the A.R.A. Almirante Irizar icebreaker, and sea surface temperature (SST, °C) and sea surface salinity (SSS) were obtained by the underway sampling system of the ship.

3. Results

3.1. Study area

During our study through the Weddell Sea, and as previously described in Almandoz et al. (2008) for the 2004 transect, two main frontal areas could be identified: the Weddell Front (WF) located approximately at 60–62°S, formed by the meeting of northern waters from the Weddell-Scotia Confluence, with the colder and more stratified waters of the Weddell Sea (Heywood et al., 2004), and the Antarctic Slope Front (ASF) between 73–74°S, formed by the Weddell Sea waters that meet colder and fresher waters of the Antarctic Continental Shelf. As a result, three main water masses can be identified in the study area: the Weddell-Scotia Confluence waters, the oceanic Weddell Sea waters, and the neritic Weddell Sea zone (see Bakker et al., 2008 for a description of the Weddell Sea main physical structures and fronts).

3.2. Surface water temperature, salinity and nutrient concentrations

Surface water temperature varied between 1.86 and -1.75 °C (Table 2). The average surface water salinity ranged from 33.67 to 34.07 presenting extreme salinity minima near coastal waters (e.g. 31.79 in 2004; Table 2). The temperature and salinity values for the year 2004 are presented in Fig. 2a to illustrate where the WF and the ASF were encountered. In these transects, another “frontal zone” was observed close to 68°S, which corresponded to the edge of the sea ice zone. Both the WF and the ASF were encountered every year (with the exception of the ASF in 2002) between 61 and 64°S and between 72 and 74°S, respectively.

Inorganic nutrient concentration for the 2002–2004 transects are presented in Table 2. During all transects, high concentrations

of nitrate ($22.8 \pm 4.6 \mu\text{M}$), phosphate ($1.6 \pm 0.7 \mu\text{M}$) and silicate ($56.7 \pm 14.7 \mu\text{M}$) were observed. However, nutrient concentrations were lower near the frontal areas than in the surrounding waters. In 2004, low nitrate and silicate concentrations were observed close to the WF and the ASF and a clear drop in nitrate concentrations was observed at the ice-edge (Fig. 2c).

3.3. $\%O_2$ saturation and $\Delta p\text{CO}_2$

The $\%O_2$ saturation ranged from 81.2 to 110.7% with an average of $95.8 \pm 4.7\%$ (average $\%O_2$ saturation values for the years 2002–2005 at the northern, central and southern Weddell Sea are presented in Table 3). The Weddell Sea surface waters were significantly undersaturated with respect to O_2 (i.e. $\%O_2 < 100\%$, $p < 0.01$) during all years excepted locally in the northern Weddell Sea in 2002 and the southern Weddell Sea in 2004. However, O_2 supersaturation (i.e. $\%O_2$ saturation $> 100\%$) was occasionally observed in the southern Weddell Sea as shown in Fig. 3a and near the frontal areas (the WF, the ASF and the ice-edge front) as shown in Fig. 2b for the 2004 transects.

$\Delta p\text{CO}_2$ was significantly negative throughout the whole studied area in the Weddell Sea in 2002–2005 ($p < 0.01$), indicating its potential role as an atmospheric CO_2 sink during late summer (Fig. 3c). More precisely, $\Delta p\text{CO}_2$ was significantly negative throughout the Weddell Sea when separating between the northern, the central and the southern Weddell Sea ($p < 0.01$) except in the central and southern Weddell Sea in 2004 and 2002, respectively (Table 3). As shown by the box plots in Fig. 3d, $\Delta p\text{CO}_2$ was significantly lower towards the southern part of the Weddell Sea, with values of -31.8 ± 39.4 , -44.7 ± 48.9 and $-85.3 \pm 55.2 \mu\text{atm}$ for the northern, central and southern Weddell Sea, respectively. In addition, strongly negative $\Delta p\text{CO}_2$ values were generally observed near the frontal areas as shown in Fig. 2b for the 2004 transects. Finally, and as we will describe below, $\Delta p\text{CO}_2$ and $\%O_2$ were inversely related ($r = -0.49$, $p < 0.001$) and this was true for all studied years ($r = -0.43$, -0.54 , -0.94 and -0.72 , $p < 0.01$ for 2002–2005, respectively).

3.4. Chl-*a* and phytoplankton groups

Surface chlorophyll-*a* concentration (Chl-*a*) was significantly lower in 2002 than during 2003–2005 (Tables 3, $p < 0.001$). Phytoplankton exhibited an inter-annually variable and patchy distribution (Fig. 3b). However, and this was consistent every year, high Chl-*a* concentrations were observed near frontal zones and the coastal area, as shown by the 2004 transects presented in Fig. 2d. In addition, significantly higher Chl-*a* concentrations were

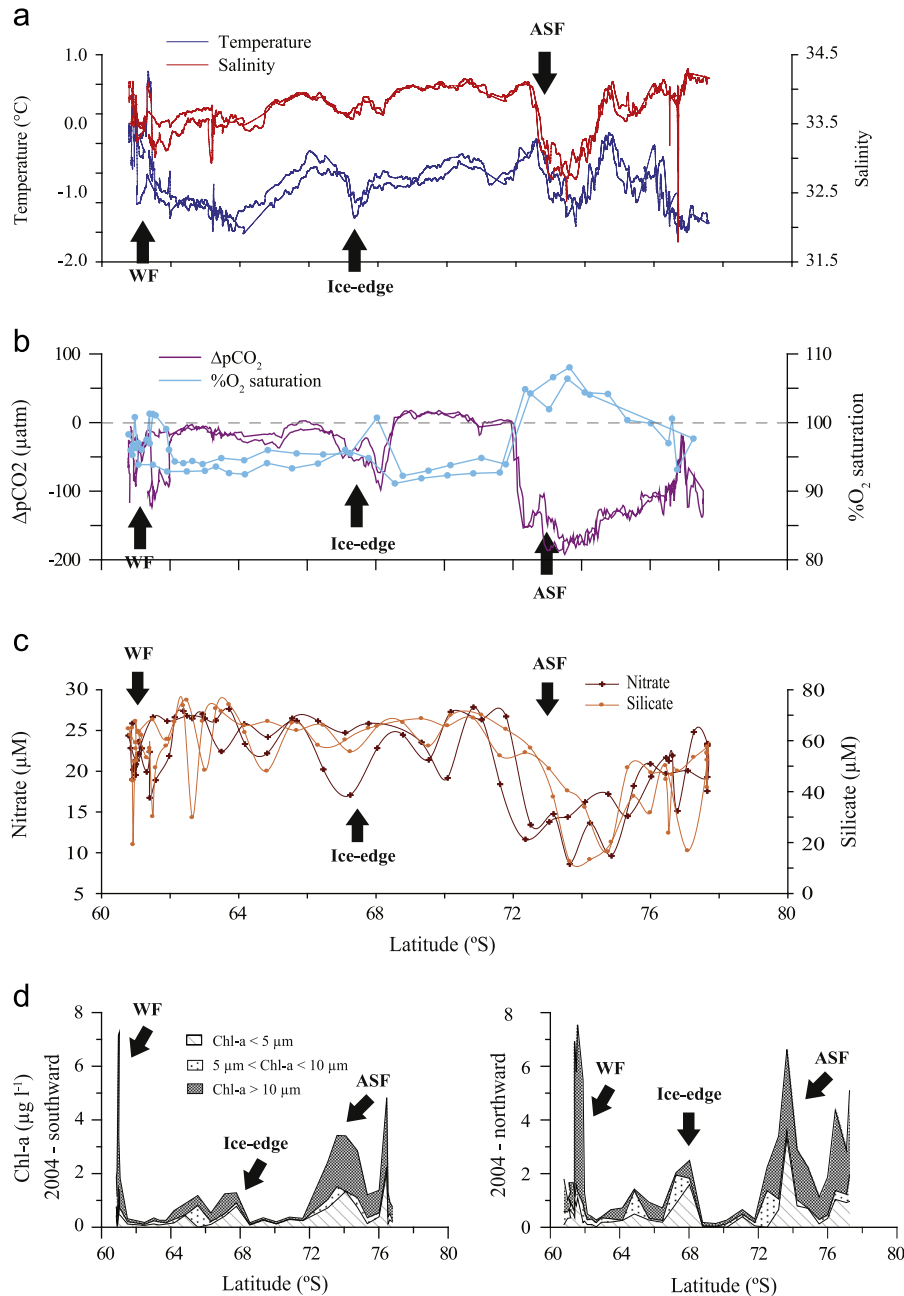


Fig. 2. (a) Sea surface temperature ($^{\circ}\text{C}$) and salinity, (b) % O_2 saturation and $\Delta p\text{CO}_2$ (μatm), (c) nitrate and silicate concentrations (μM) and (d) fractionated Chl-a concentration ($\mu\text{g l}^{-1}$) for the 2004 southward and northward transects. Fractionated Chl-a concentration corresponds to phytoplankton $< 5 \mu\text{m}$, between 5 and $10 \mu\text{m}$ and $> 10 \mu\text{m}$. The presence of the Weddell Front (WF), the sea-ice edge and the Antarctic Slope Front (ASF) is indicated on each plot.

observed in the southern Weddell Sea (with an average of $2.3 \pm 1.8 \mu\text{g l}^{-1}$) than in the northern and central Weddell Sea (with respective averages of 1.4 ± 1.6 and $1.3 \pm 1.2 \mu\text{g l}^{-1}$, $p < 0.01$).

Maximum values in total Chl-a coincided with maximum Chl-a values of both the smallest and largest phytoplankton fractions ($< 5 \mu\text{m}$ and $> 10 \mu\text{m}$, respectively), suggesting that mainly these two groups were responsible for the total biomass variability (Fig. 2d). In fact, large phytoplankton ($> 10 \mu\text{m}$) represented 50 to 54% of the total phytoplankton biomass whilst small phytoplankton ($< 5 \mu\text{m}$) represented 25–33% of it during the 2002–2004 transects (i.e. when fractionated Chl-a concentrations were available, see Fig. 2d for the 2004 data).

A total of 65 and 70 taxa were identified in the 2003 and 2004 samples, respectively. Phytoplankton was composed of diatoms, cryptophytes, prasinophytes, dinoflagellates, silicoflagellates and

of small ($< 5 \mu\text{m}$) and large (5–15 μm) unidentified phytoflagellates. In terms of carbon biomass, diatoms dominated phytoplankton (with more than 50% of the phytoplankton biomass being represented by diatoms, as defined by Schloss et al., 2007) for 35 over 40 sampled communities in 2003 and 30 over 39 sampled communities in 2004. The few places where phytoflagellates dominated phytoplankton were located near the coastal region, the center of the Weddell Gyre and south of the Polar Front (see Fig. 4 for the geographical distribution of the biomass ratio between diatoms and phytoflagellates). In terms of carbon biomass, phytoplankton was dominated by two diatom species in 2003: *Corethron pennatum* and *Fragilariopsis curta* (representing, respectively, 21.9 and 24.1% of the total phytoplankton biomass). In 2004, phytoplankton biomass was dominated by small ($< 5 \mu\text{m}$) phytoflagellates and by three diatom species: *C. pennatum*, *Dactyliosolen tenuijunctus* and *Fragilariopsis cylindrus* (representing,

Table 3

Mean values \pm standard deviation for %O₂ saturation, Δ pCO₂ (μ atm) and Chl-*a* (μ g l⁻¹) for the northern, central, southern and whole Weddell Sea and for the 2002–2005 transects. One sample *t*-tests were used to determine if Δ pCO₂ and %O₂ saturation values significantly deviated from 0 and 100% respectively. The results of the *t*-tests are indicated below (**, $p < 0.01$).

	Whole Weddell Sea			Northern Weddell Sea (60–66°S)		
	%O ₂	pCO ₂	Ch- <i>a</i>	%O ₂	pCO ₂	Ch- <i>a</i>
2002	97.66 \pm 3.46**	-17.17 \pm 28.09**	0.49 \pm 0.41	100.03 \pm 1.02	-9.22 \pm 29.69**	0.19 \pm 0.19
2003	95.69 \pm 2.41**	-64.14 \pm 31.26**	2.24 \pm 1.72	94.77 \pm 2.00**	-38.66 \pm 18.12**	1.27 \pm 0.87
2004	96.84 \pm 4.20**	-54.92 \pm 61.84**	2.24 \pm 2.18	95.77 \pm 2.57**	-28.47 \pm 44.63**	2.23 \pm 2.44
2005	92.75 \pm 6.34**	-63.84 \pm 59.97**	1.61 \pm 1.31	90.27 \pm 4.22**	-49.79 \pm 44.41**	1.45 \pm 1.06
	Central Weddell Sea (66–72°S)			Southern Weddell Sea (72–78°S)		
	%O ₂	pCO ₂	Ch- <i>a</i>	%O ₂	pCO ₂	Ch- <i>a</i>
2002	98.50 \pm 1.88**	-35.07 \pm 14.59**	0.80 \pm 0.33	93.07 \pm 3.23**	-4.45 \pm 27.14	0.43 \pm 0.41
2003	98.2 \pm 1.98**	-94.23 \pm 29.03**	2.03 \pm 1.39	94.59 \pm 1.61**	-69.82 \pm 16.02**	3.62 \pm 1.91
2004	94.05 \pm 2.28**	-11.22 \pm 27.18	0.70 \pm 0.71	102.23 \pm 4.10	-126.22 \pm 35.87**	3.09 \pm 1.64
2005	92.81 \pm 6.57**	-34.85 \pm 61.50**	1.67 \pm 1.68	95.76 \pm 7.22**	-114.2 \pm 45.13**	1.76 \pm 1.24

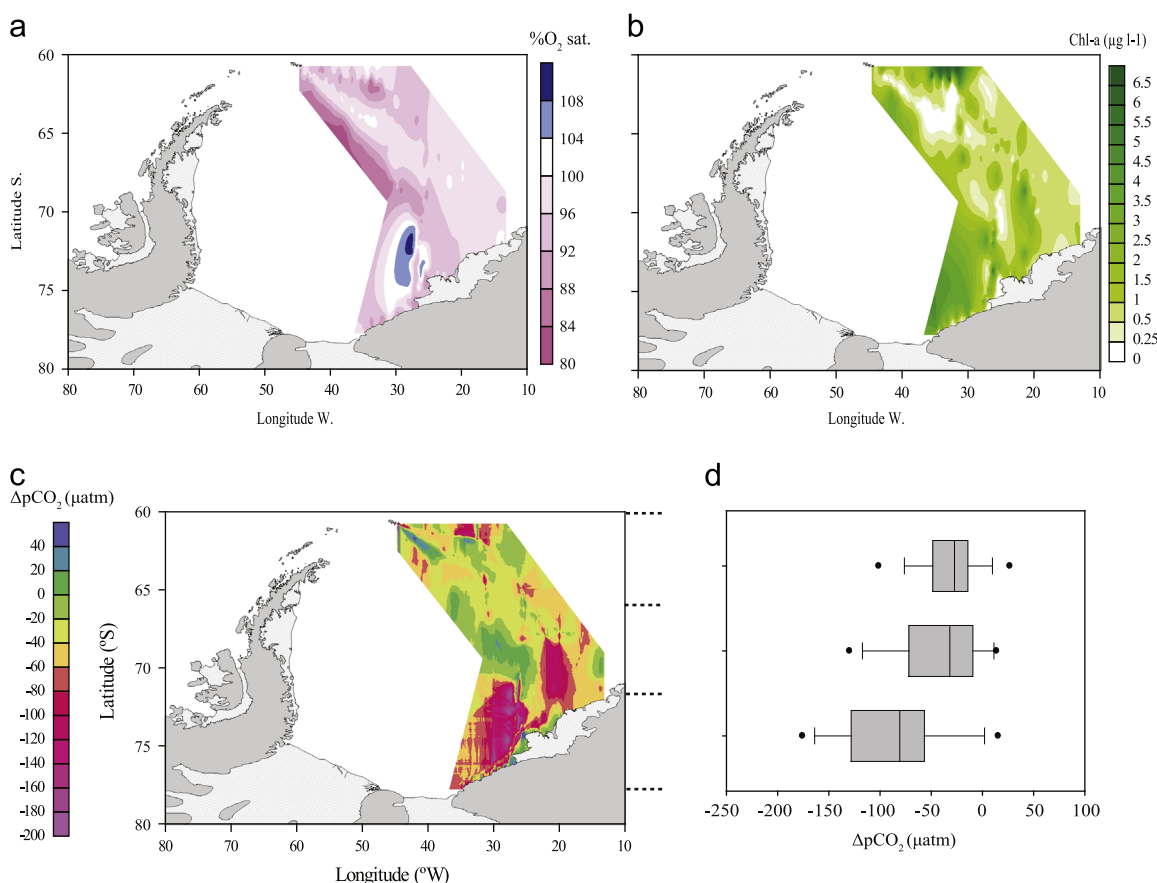


Fig. 3. (a) %O₂ saturation, (b) Chl-*a* (μ g l⁻¹) and (c) Δ pCO₂ (μ atm) data in the Weddell Sea for the 2002–2005 transects. (d) box plots representing the Δ pCO₂ (μ atm) data in the northern, central and southern Weddell Sea. The box plots indicate the 5th and 95th percentile (dots), the lower and upper quartiles and the median.

respectively, 8.4, 18.3, 14.8 and 9.3% of the total phytoplankton biomass). Finally, Chl-*a* was significantly correlated with the carbon biomass of both diatoms ($r=0.68$, $p < 0.01$) and phytoflagellates ($r=0.48$, $p < 0.01$), suggesting that biomass accumulation was positively influenced by both phytoplankton groups.

3.5. Phytoplankton and CO₂ and O₂ dynamics

A significant negative correlation existed between the Chl-*a* concentration and Δ pCO₂ for the whole data set ($r=-0.62$, $p < 0.01$, Fig. 5a and Table 4). This correlation was also significant considering every year separately ($r=-0.45$, -0.36 , -0.65 , and

-0.65 in 2002–2005, respectively, $p < 0.01$). Significant negative correlations also existed between the concentration of the small, medium and large Chl-*a* fractions and Δ pCO₂ ($r=-0.41$, -0.25 and -0.55 , $p < 0.01$, respectively, Table 4), although the small and large Chl-*a* fractions showed the greatest correlation coefficients. Finally, significant negative correlations existed between the carbon biomass of both diatoms and phytoflagellates and Δ pCO₂ ($r=-0.53$ and -0.57 , $p < 0.01$, respectively, Fig. 5b and c, Table 4).

PCA was performed including the biomass of diatoms and flagellates, Δ pCO₂, sea surface temperature (SST), sea surface salinity (SSS), nitrate and wind speed as variables and the stations as observations. The first two principal components (PC1 and PC2)

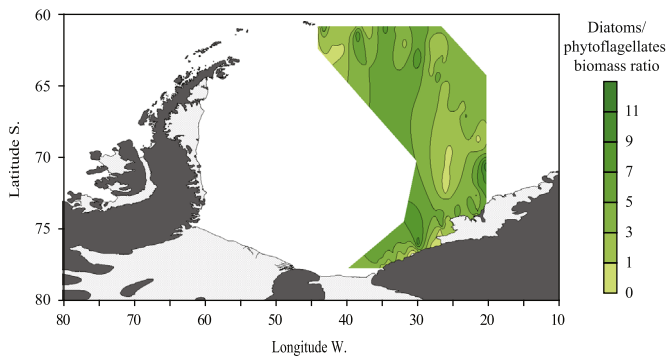


Fig. 4. Biomass ratio between diatoms and phytoflagellates in the Weddell Sea for the 2003–2004 transects.

explained 62% of the variance for 2003. When plotting the sampled stations against PC1 and PC2, a clear distribution appears (Fig. 6b), consistent with their geographical distribution along the transect (Fig. 6a). The first group of stations corresponded to the northern and central part of the Weddell Sea (stations 1 to 22, green dots). The dominant phytoplankton species in terms of carbon in this series was the diatom *C. pennatum*. The second group was constituted by stations 23 to 28, and by station 31 (red dots), and was located in the ASF area. As in the previous group, diatoms dominated carbon biomass, but in this case such dominance was shared by *C. pennatum* and *F. curta*. The lowest $\Delta p\text{CO}_2$ values were observed in this part of the transect ($\sim -120 \mu\text{atm}$). Finally, a third group in coastal waters (stations 29–39, black dots) was dominated by *F. curta* carbon biomass (Fig. 6a). Diatoms and phytoflagellates biomasses have high loadings (-0.73 and -0.61 , respectively) and are negatively and significantly correlated to PC1 while $\Delta p\text{CO}_2$ and nitrate have high loadings (-0.91 and -0.63 , respectively) on PC1 and are significantly and positively correlated to it (Fig. 6c). On the contrary, wind speed and SST correlated significantly with PC2 (with a factor loading of 0.87 and -0.73 , respectively, Fig. 6c) and SSS correlated with PC3 (factor loading -0.59). Diatoms and flagellates biomasses are inversely and significantly correlated with $\Delta p\text{CO}_2$.

As in 2003, PCA was run considering the biomass of diatoms and flagellates together with $\Delta p\text{CO}_2$ and sea surface temperature, sea surface salinity, nitrate and wind speed. The first two PC explain $\sim 58\%$ of the variance for 2004. When plotting the sampled stations against the first two principal components (PC1 and PC2) a clear distribution appears (Fig. 7b) which is consistent with their geographical distribution along the transect (Fig. 7a). A first group of stations (1–4, green dots) corresponded to the north of the Weddell Sea and presented relatively high $\Delta p\text{CO}_2$ values. A second group of stations (5–9, red dots) corresponded to the Polar Front and presented lower $\Delta p\text{CO}_2$ values. In this group, the phytoplankton biomass was dominated by diatoms and more particularly by *D. tenuijunctus*. A third group of stations (10–26, blue dots) corresponded to the central part of the Weddell Sea. In this region, phytoplankton biomass was dominated by diatoms and more particularly by *C. pennatum* and *F. cylindrus*. A fourth group of stations (27–30, purple dots) was associated with the ASF. In this group phytoplankton biomass was also dominated by *C. pennatum* and *F. cylindrus* and the lowest $\Delta p\text{CO}_2$ values were observed in this part of the transect ($\sim -170 \mu\text{atm}$). Finally, the last group of stations (31–39, black dots) corresponded to the coastal region and presented low $\Delta p\text{CO}_2$ values. In this group, the phytoplankton biomass was also dominated by diatoms. As for 2003, diatoms and phytoflagellates biomasses have high loadings (-0.78 and -0.77 , respectively) and are negatively and significantly correlated to PC1 while $\Delta p\text{CO}_2$ and nitrate have high loadings (-0.79 and -0.82 , respectively) on PC1 and are significantly and positively correlated

to it (Fig. 7c). Contrarily to 2003, wind speed correlated only significantly with PC3 (factor loading of 0.69) and SST and SSS significantly correlated with PC2 (factor loadings of 0.49 and 0.51 , respectively). In addition, as previously described for 2003, diatoms and flagellates biomasses are inversely and significantly correlated with $\Delta p\text{CO}_2$.

Finally, a significant positive correlation existed between the Chl-*a* concentration and the % O_2 saturation ($r=0.27$, $p < 0.01$, Fig. 5d and Table 4). This correlation was only significant in 2004 and 2005 ($r=0.7$ and 0.42 , $p < 0.01$, respectively). Significant positive correlations also existed between the Chl-*a* concentrations of the small, medium and large phytoplankton fractions with the % O_2 saturation ($r=0.11$, $p < 0.05$, $r=0.21$, $p < 0.01$ and 0.28 , $p < 0.01$, respectively, Table 4) and between the % O_2 saturation and the carbon biomass of both diatoms and phytoflagellates ($r=0.39$ and 0.57 , $p < 0.01$, respectively, Fig. 5e and f and Table 4).

3.6. Community metabolism and CO_2 and O_2 dynamics

The net community production (NCP) averaged $2.8 \pm 4.8 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ in the Weddell Sea over the four studied summers. NCP was higher in 2003 than during the other campaigns (Table 5), although the difference was only significant between 2002 and 2003 ($p < 0.01$). The average NCP was negative in 2002, and positive in 2003–2005. Maximum NCP values (from 5 to $15 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) were observed in coastal areas, near the ice-edge area (with a NCP of $13.2 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ observed at 67.3°S in 2003) and the ASF (with a NCP of $12.4 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ observed at 72.5°S in 2005; Fig. 8a). Finally, NCP was positively correlated to GPP ($r=0.48$, $p < 0.01$, Fig. 9a) and Chl-*a* ($r=0.41$, $p < 0.01$, Fig. 9b). NCP was also correlated significantly to the biomass of phytoflagellates and diatoms ($r=0.59$, $p < 0.01$ for phytoflagellates and $r=0.47$, $p < 0.05$ for diatoms, respectively, Fig. 9c and d).

The gross community production (GPP) averaged $5.6 \pm 4.2 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ in the Weddell Sea over the four studied summers. There were no statistical differences in GPP between years (Table 5). Maximum GPP values were observed near the sea-ice edge (with a GPP of $16.2 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ observed at 69.8°S in 2003) and the ASF (with a GPP of $16.3 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ observed at 72.5°S in 2005; Fig. 8b). In addition, GPP was positively correlated to the carbon biomass of phytoflagellates and diatoms although it was only significant for phytoflagellates ($r=0.72$, $p < 0.01$ for phytoflagellates and $r=0.49$, $p=0.15$ for diatoms, respectively, Fig. 9e and f).

Respiration averaged $4.1 \pm 4.4 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ in the Weddell Sea over the four studied summers. On the contrary to NCP, respiration reached its highest values south of the WF (with a R of $13.7 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ observed at 63.2°S in 2003) and south of the ASF (i.e. near the coast; with a R of $16.3 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ observed at 75.5°S in 2002; Fig. 8c). In addition, and consistent with NCP measurements, respiration was higher in 2002 (with an average of $8.1 \pm 1.3 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) than during 2003–2005 (although the difference was only significant between 2002 and 2004, $p < 0.01$; Table 5).

The GPP:R ratio (with an average of 3.02 ± 3.32 over the four studied summers) was > 1 every year (Table 5). However, and consistent with NCP measurements, the GPP:R ratio was lower in 2002 than in 2003–2005 (although this was not significant). Contrasting with the NCP measurements, the GPP:R ratio was highest near the WF (with a GPP:R ratio of 12.6 observed at 60.9°S in 2005) and south of the ASF (with a GPP:R ratio of 10.2 , 13.7 and 8 observed at 75.6 , 77.7 and 77.1°S in 2003–2005 respectively; Fig. 8d).

Finally, $\Delta p\text{CO}_2$ was significantly correlated to NCP ($r = -0.31$, $p < 0.05$, Fig. 10a) while the % O_2 saturation did not show any correlation with NCP (Fig. 10c). On the contrary, neither $\Delta p\text{CO}_2$ nor the % O_2 saturation were correlated to GPP or R. Only stations with

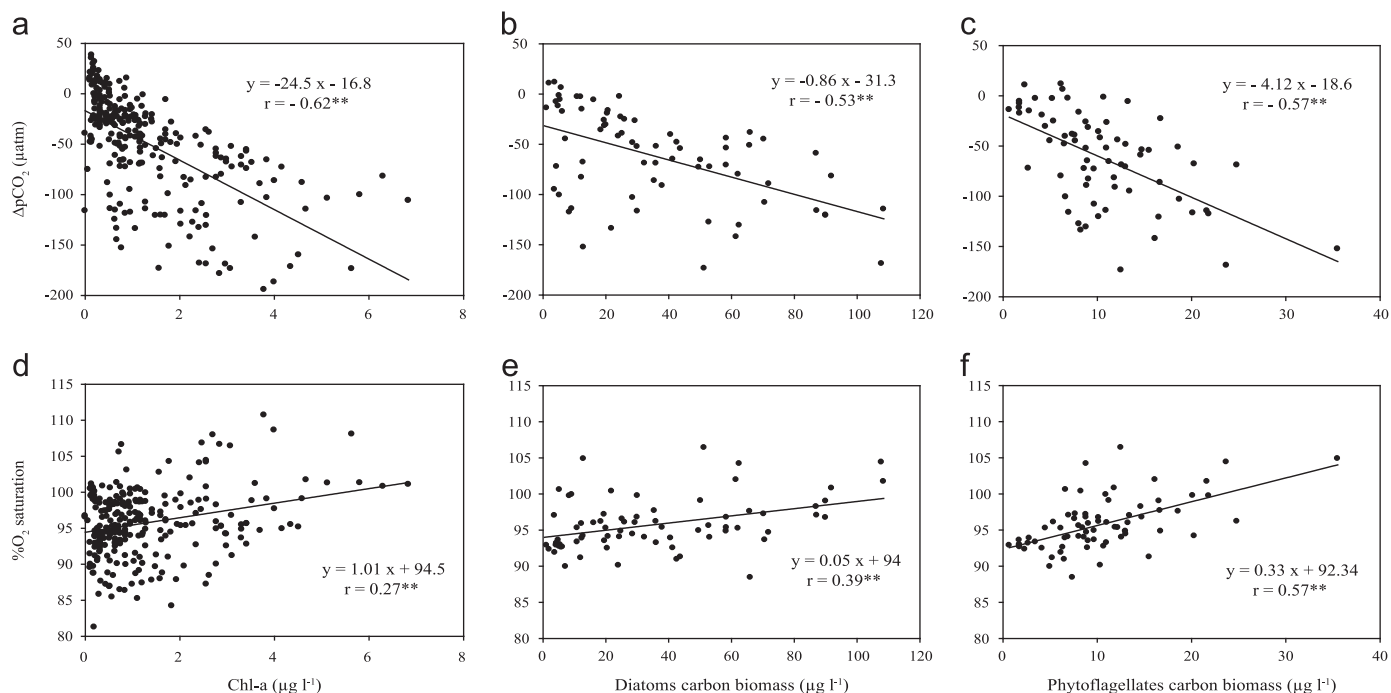


Fig. 5. Scatter plots between $\Delta p\text{CO}_2$ (μatm) and (a) Chl-*a* concentration ($\mu\text{g l}^{-1}$), (b) the carbon biomass of diatoms ($\mu\text{g C l}^{-1}$) and (c) the carbon biomass of phytoflagellates ($\mu\text{g C l}^{-1}$). Scatter plots between the $\%O_2$ saturation and d) Chl-*a* concentration ($\mu\text{g l}^{-1}$), (e) the carbon biomass of diatoms ($\mu\text{g C l}^{-1}$) and (f) the carbon biomass of phytoflagellates ($\mu\text{g C l}^{-1}$). Significant linear regressions are plotted and the equations and correlation coefficients of the regressions are indicated.

Table 4

Correlation coefficient (r) between $\Delta p\text{CO}_2$ or the $\%O_2$ saturation and the Chl-*a*, the small, medium and large Chl-*a* fractions (< 5 m, 5–10 m and > 10 m) and with the biomass of diatoms and phytoflagellates. Significance is indicated (* $p < 0.05$, ** $p < 0.01$).

r coefficient	$\Delta p\text{CO}_2$	O_2
Chl- <i>a</i>	-0.62**	0.27**
Chl- <i>a</i> ($< 5 \mu\text{m}$)	-0.41**	0.11*
Chl- <i>a</i> (5–10 μm)	-0.25**	0.21**
Chl- <i>a</i> ($> 10 \mu\text{m}$)	-0.55**	0.28**
Phytoflagellates biomass	-0.57**	0.57**
Phytoflagellates abundance	-0.44**	0.51***

a high Chl-*a* concentration (i.e. $> 1 \mu\text{g l}^{-1}$), showed significant correlations between both $\Delta p\text{CO}_2$ and $\%O_2$ saturation and GPP ($r = -0.6$, $p < 0.01$ and $r = 0.37$, $p < 0.05$ for $\Delta p\text{CO}_2$ and $\%O_2$, respectively; Fig. 10b and d).

The mean consumption of nitrate and phosphate in the Weddell Sea surface waters, estimated from nutrient change between winter subsurface and surface waters, were, respectively, 3.74 ± 1.7 and $0.32 \pm 0.1 \mu\text{mol l}^{-1}$. Based on this calculation, the mean primary production until the time of sampling was $24.67 \pm 10.9 \mu\text{mol C l}^{-1}$ using nitrate and $34.11 \pm 13.3 \mu\text{mol C l}^{-1}$ using phosphate (Fig. 11a). Primary production was higher near the fronts and the coastal zone. In addition, the estimated primary production until the time of sampling was significantly correlated to $\Delta p\text{CO}_2$ across the Weddell Sea ($r = -0.75$, $p < 0.01$, Fig. 11b).

4. Discussion

4.1. CO_2 and O_2 dynamics and spatial variability within the Weddell Sea

With several natural processes such as the “Biological Pump” and the “Physical Pump” facilitating CO_2 export from the surface to deeper waters, the Weddell Sea plays a key role in oceanic carbon

dynamics (Hoppema, 2004; Hoppema et al., 1995; Mann and Lazier, 1991). The center of the Weddell Sea is a site of upwelling of Warm Deep Water (WDW) which brings CO_2 rich waters to the surface during autumn and winter (Gordon and Huber, 1990; Hoppema et al., 1999). The role of the Weddell Sea as a sink or a source for atmospheric CO_2 will, therefore, depend on the balance between biological activity and the upwelling of CO_2 rich WDW, as hypothesized by Hoppema et al. (1995, 1999).

With significant negative $\Delta p\text{CO}_2$ values observed during the summers 2002–2005, the Weddell Sea behaved as a substantial CO_2 sink. In addition, $\Delta p\text{CO}_2$ was noteworthy lower in the southern Weddell Sea than in the central or northern Weddell Sea (Fig. 3d). Hoppema et al. (1999, 2007) suggested that an active biological uptake occurs in the Weddell Sea in summer and is responsible for a significant absorption of atmospheric CO_2 on an annual basis. For example, surface waters are usually supersaturated (Hoppema et al., 1999) or slightly undersaturated (Bakker et al., 1997) with respect to CO_2 after sea ice melts in spring, and largely undersaturated with respect to CO_2 during autumn (Hoppema et al., 2000b) suggesting that the Weddell Sea acts as a significant CO_2 sink. During the present study, high Chl-*a* concentrations were observed in the southern Weddell Sea (i.e. in relation with the ASF, the ice-edge area and the coastal waters, Figs. 2d, 3b and 5a) and may, therefore, explain the lower $\Delta p\text{CO}_2$ values observed in this area.

Fig. 12a presents the correlation between $\Delta p\text{CO}_2$ and the $\%O_2$ saturation. In this figure, the graph was divided into four quadrants. Quadrant I represents simultaneous positive $\Delta p\text{CO}_2$ and O_2 undersaturation and Quadrant III corresponds to simultaneous negative $\Delta p\text{CO}_2$ and O_2 supersaturation. If primary production and respiration are the dominant processes controlling seawater $p\text{CO}_2$ and $\%O_2$ saturation, one would expect $\Delta p\text{CO}_2$ and O_2 values to be distributed linearly between quadrant I and III. Quadrant II corresponds to simultaneous positive $\Delta p\text{CO}_2$ and O_2 supersaturation and quadrant IV corresponds to simultaneous negative $\Delta p\text{CO}_2$ and O_2 undersaturation. If physical processes (e.g. water temperature, water origin) are the dominant process controlling seawater

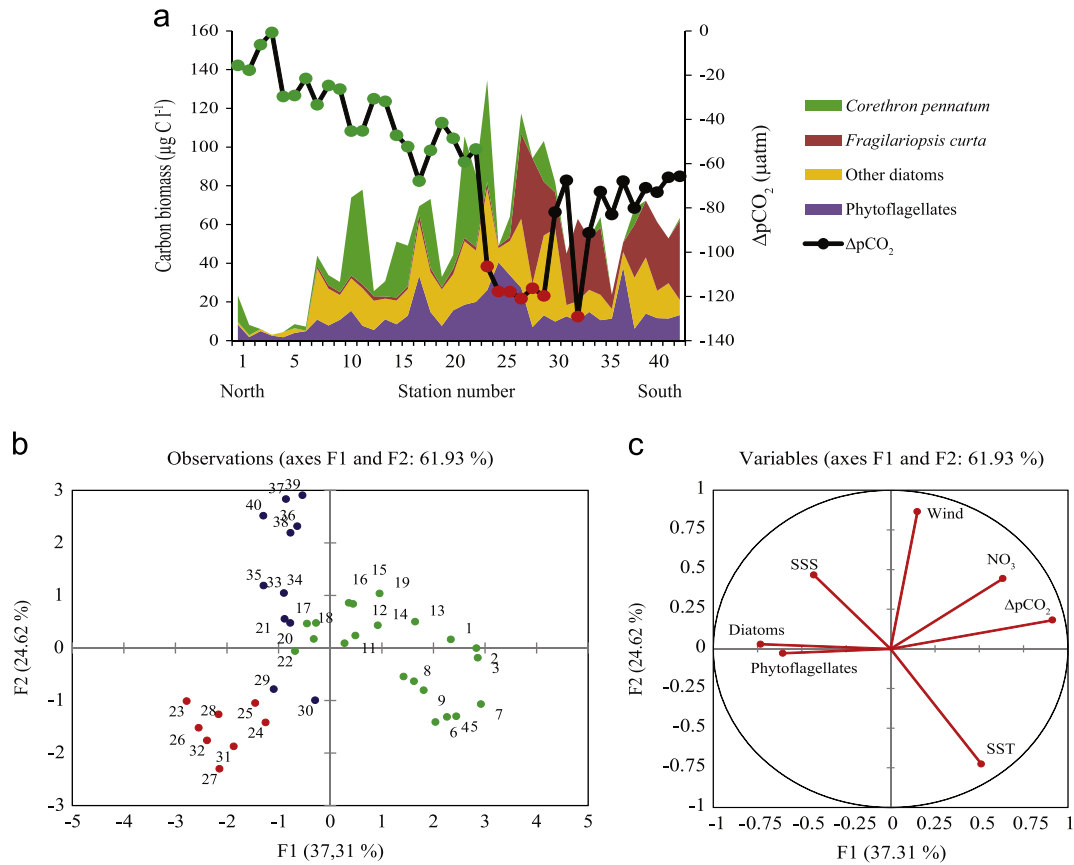


Fig. 6. (a) Carbon biomass ($\mu\text{g C l}^{-1}$) of *Fragilariopsis curta*, *Corethron pennatum*, other diatoms and phytoflagellates with the corresponding ΔpCO_2 (μatm). (b) PCA analysis showing the ordination of the observations (stations) in the space represented by the first two principal components. (c) PCA plot showing the correlations between the variables (diatoms and phytoflagellates biomasses, ΔpCO_2 , wind speed (m s^{-1}), sea surface salinity (SSS), sea surface temperature (SST) and nitrate+nitrite (NO_3)) with the two first principal components (PC1 and PC2).

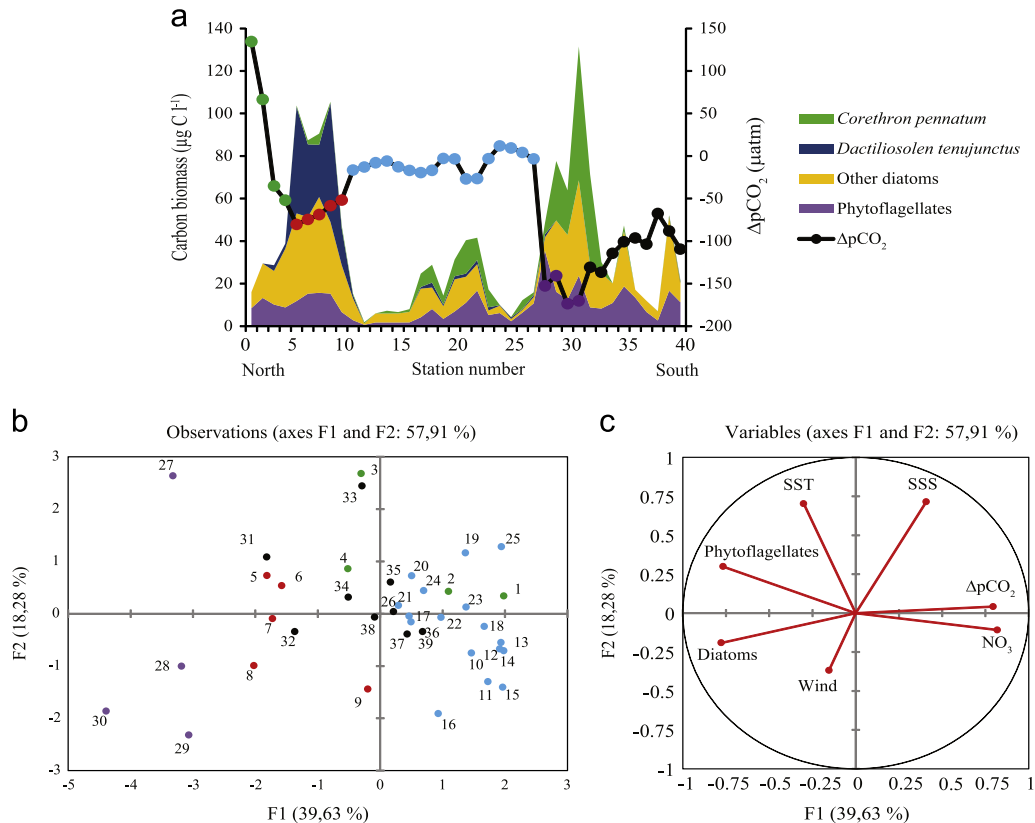


Fig. 7. (a) Carbon biomass ($\mu\text{g C l}^{-1}$) of *C. pennatum*, *Dactyliosolen tenuijunctus*, other diatoms and phytoflagellates with the corresponding ΔpCO_2 (μatm). (b) PCA analysis showing the ordination of the observations (stations) in the space represented by the first two principal components. (c) PCA plot showing the correlations between the variables (diatoms and phytoflagellates biomasses, ΔpCO_2 , wind speed (m s^{-1}), sea surface salinity (SSS), sea surface temperature (SST) and nitrate+nitrite (NO_3)) with the two first principal components (PC1 and PC2).

$p\text{CO}_2$ and $\%O_2$ saturation, one would expect $\Delta p\text{CO}_2$ and O_2 values to be distributed between quadrant II and IV. For example, in high latitude areas, cooling favors gas invasion into the surface waters (Bellerby et al., 2004; Hoppema et al., 1995, 2000b) while warming of seawater decreases gas solubility (Zeebe and Wolf-Gladrow, 2001).

In Fig. 12a, $\Delta p\text{CO}_2$ and $\%O_2$ saturation showed a significant negative correlation ($r = -0.49$, $p < 0.01$), suggesting that the net community metabolism is the main driver for CO_2 and O_2 variability in the Weddell Sea as described for the western Antarctic Peninsula by Carrillo et al. (2004) and by Moreau et al. (2012). However, the distribution of $\Delta p\text{CO}_2$ and $\%O_2$ saturation with respect to these four quadrants shows that the majority of samples (i.e. 73.2%) corresponded to case IV waters, while case waters I, II and III represented only 10.2, 3.4 and 13.2% of the samples, respectively. The distribution of $\Delta p\text{CO}_2$ and $\%O_2$ saturation over the Weddell Sea and with respect to these four quadrants is shown in Fig. 12b and no clear geographical distribution pattern could be observed.

The dominance of case IV waters and, more particularly, the O_2 undersaturation observed in the Weddell Sea may be explained by either the low surface water temperatures observed in the Weddell Sea ($\sim -0.5^\circ\text{C}$, Table 2) or the upwelling of poorly

oxygenated sub-surface waters, altering the partial pressure of this gas in the upper part of the water column (Chierici et al., 2004). However, the $\%O_2$ saturation was not correlated to the Weddell Sea surface temperature during the present study ($p > 0.05$). Therefore, it seems that the observed O_2 undersaturation was caused by the upwelling of poorly oxygenated sub-surface waters (Chierici et al., 2004). This is in agreement with Hoppema et al. (1995) who observed O_2 undersaturation in the central Weddell Sea because of the entrainment of WDW to the surface. The upwelling of WDW in the central Weddell Gyre is a permanent feature and many other authors observed the doming structure of this upwelling (e.g. Hoppema et al., 1999, 2000a). Unfortunately, the presence of upwelled WDW onto the central Weddell Sea surface waters was not determined during the present study although the presence of its doming structure was evident in 2004 as witnessed by Almandoz et al. (2008).

In addition, we observed negative $\Delta p\text{CO}_2$ in 86.4% of the stations that were sampled. Upwelled WDW is CO_2 rich (Gordon and Huber, 1990; Hoppema et al., 1999). Hence, we believe that biological production must have balanced the effect of WDW upwelling on the Weddell Sea surface water and produced these negative $\Delta p\text{CO}_2$ values, as hypothesized by Hoppema et al. (1995, 1999). This is supported by the results of the PCA analyses which showed that phytoplankton biomass mainly explained CO_2 dynamics in the Weddell Sea while wind induced gas exchanges played a secondary role. Therefore, it appears that CO_2 and O_2 dynamics in the Weddell Sea are driven both by the WDW upwelling and biological activity. For example, some O_2 supersaturation was witnessed during the study near the WF (in 2004), the ASF (in 2002, 2004 and 2005) and the sea ice edge (in 2004; Fig. 12b). These observed O_2 supersaturation indicate that, although $\%O_2$ saturation was probably altered by the upwelling of poorly oxygenated WDW, it may still have been under the influence of primary production in very productive areas such as fronts. Fronts often have high biological activity associated to one of their sides, due to the combination of turbulent and stratified

Table 5

Average \pm standard deviation of the microbial community respiration (R , $\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$), gross primary production (GPP , $\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$), net community production (NCP , $\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) and the $GPP:R$ ratio.

Year	R	GPP	NCP	$GPP:R$
2002	8.07 ± 6.2	5.19 ± 3.6	-1.75 ± 5.8	1.33 ± 1.41
2003	4.68 ± 3.9	7.07 ± 4.1	4.09 ± 4.5	2.54 ± 2.69
2004	1.06 ± 0.54	3.48 ± 3.4	2.27 ± 3.09	4.43 ± 4.82
2005	1.50 ± 1.33	4.27 ± 4.8	2.60 ± 3.84	4.53 ± 4.03

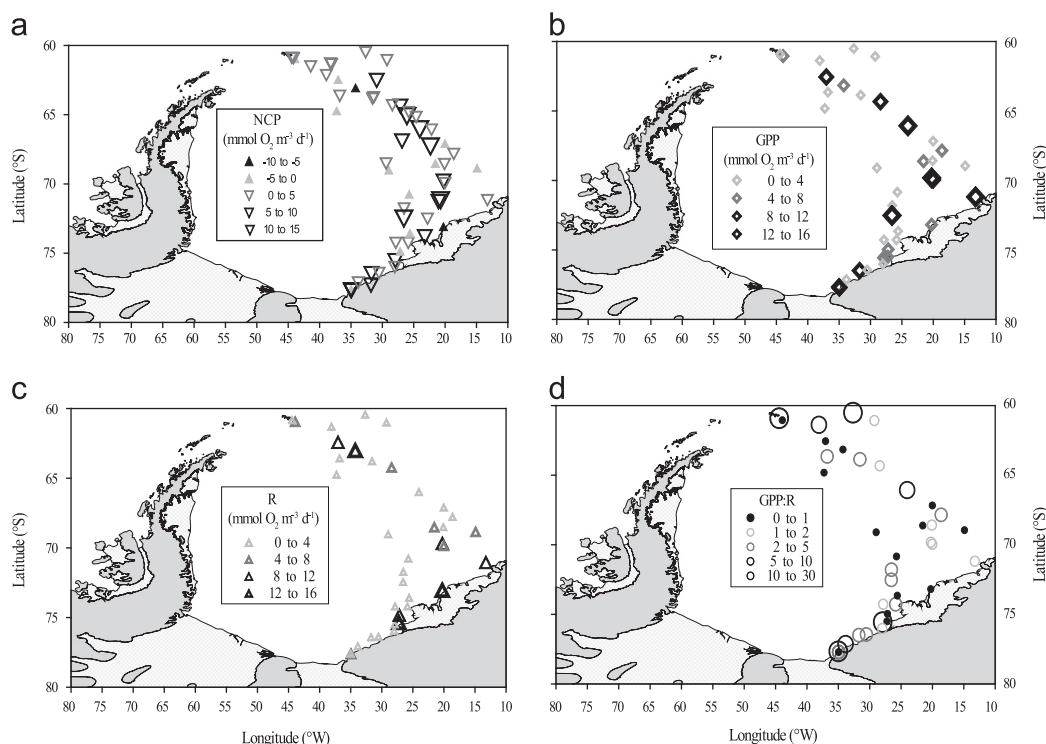


Fig. 8. (a) Net community production (NCP , $\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$), (b) gross primary production (GPP , $\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$), (c) community respiration (R , $\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) and (d) production: respiration ratio ($GPP:R$) measured through incubation experiments in 2002–2005.

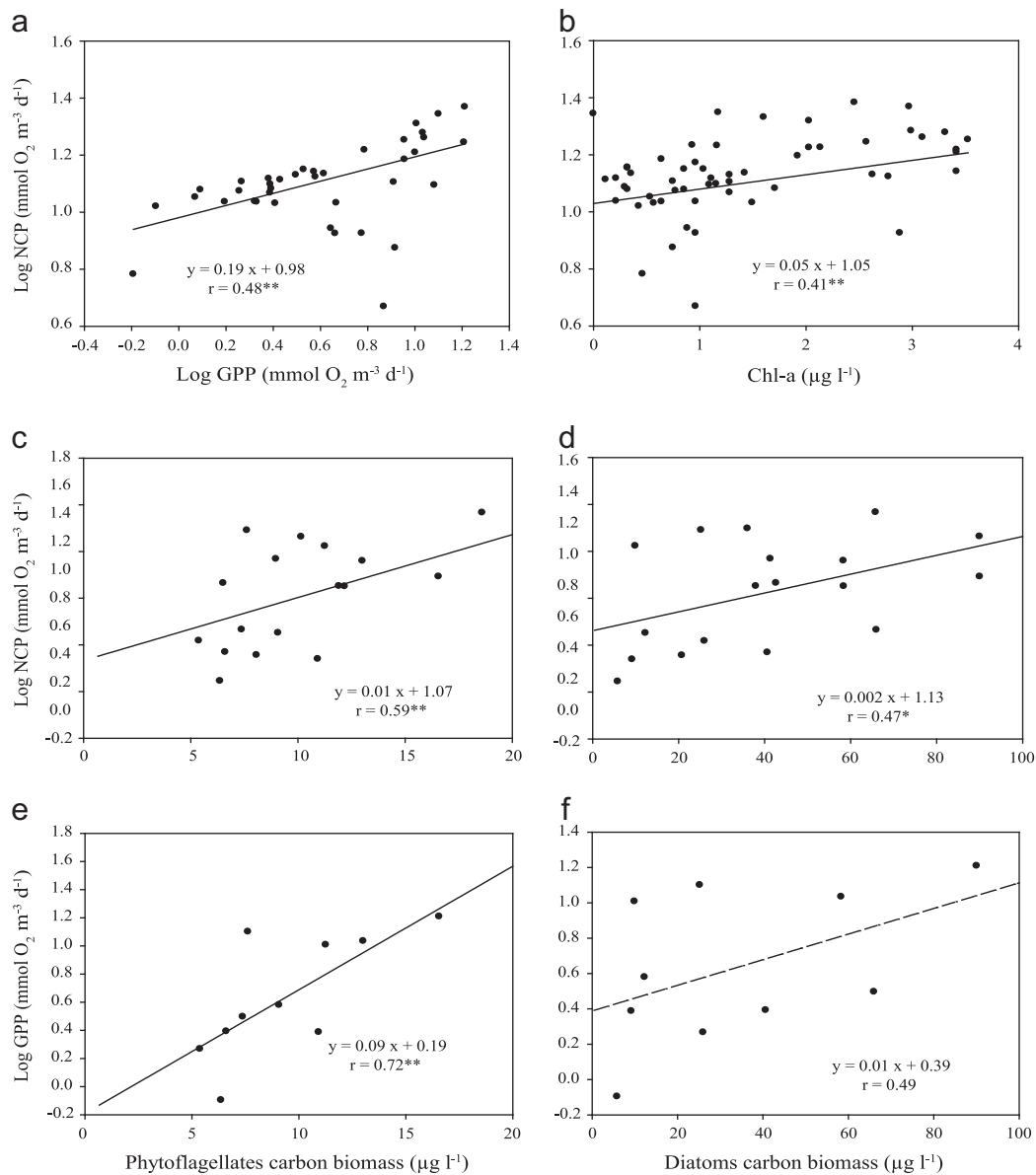


Fig. 9. Scatter plots between log(NCP) (mmol O₂ m⁻³ d⁻¹) and (a) log(GPP) (mmol O₂ m⁻³ d⁻¹), and (b) Chl-a concentration (μg l⁻¹). Scatter plots between log(NCP) (mmol O₂ m⁻³ d⁻¹) and (c) the carbon biomass of phytoplankton (μg C l⁻¹) and (d) the carbon biomass of diatoms (μg C l⁻¹). Scatter plots between log(GPP) (mmol O₂ m⁻³ d⁻¹) and (e) the carbon biomass of phytoplankton (μg C l⁻¹) and (f) the carbon biomass of diatoms (μg C l⁻¹). Significant linear regressions are plotted and the equations and correlation coefficients of the regressions are indicated.

waters that favor phytoplankton growth (Mann and Lazier, 1991). Finally, ocean-atmosphere gas fluxes may also have influenced the dynamics of O₂ and CO₂ in the Weddell Sea.

4.2. Influence of community metabolism on the Weddell Sea CO₂ and O₂ dynamics

We observed very similar primary production rates (with an average GPP of 2.8 mmol O₂ m⁻³ d⁻¹) in the Weddell Sea in summer compared to the average GPP rates of 2.83 mmol O₂ m⁻³ d⁻¹ reported by Bouquegneau et al. (1992) for spring in this area, using similar light and dark incubation experiments and with Chl-a concentrations ranging from 0.06 to 2 μg l⁻¹. However, contrarily to these authors' observations in the northwestern part of the Weddell Sea, no correlations were observed between ΔpCO₂ and GPP and between the %O₂ saturation and GPP excepted when only stations with high Chl-a concentrations (i.e. > 1 μg l⁻¹)

were considered (Fig. 10b and d). Therefore, our incubations experiments results only partly agree with the results of Bouquegneau et al. (1992) and the results of Hoppema et al. (1999, 2000a) who suggested that the center of the Weddell Sea Gyre, albeit an upwelling area, was a CO₂ sink due to primary production. These authors' hypothesis seem to only hold true in areas of high Chl-a.

In addition, Bouquegneau et al. (1992) found that O₂ and CO₂ variations in the ice-covered part of the Weddell Sea were also influenced by both respiration and upwelled water. Although the presence of upwelled waters was not determined in the present study, and although the respiration rates observed in the summer (with an average of 4.1 mmol O₂ m⁻³ d⁻¹) were similar to the respiration rates reported by Bouquegneau et al. (1992) in spring (up to 4.08 mmol O₂ m⁻³ d⁻¹), we found no correlation between the respiration of the planktonic community and the distribution of either O₂ or CO₂. The study of Bouquegneau et al. (1992) took place during spring (i.e. in October and November) and, therefore,

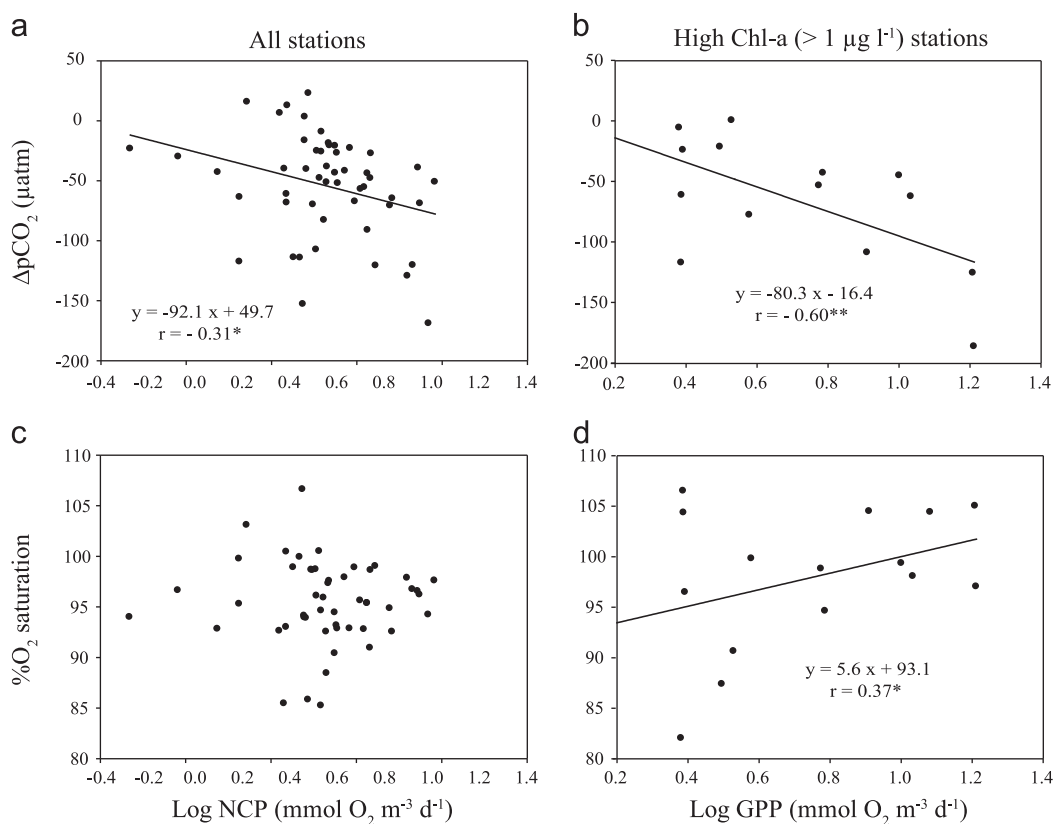


Fig. 10. (a) Scatter plot between $\Delta p\text{CO}_2$ (μatm) and $\log(\text{NCP})$ ($\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) for all stations. (b) Scatter plot between $\Delta p\text{CO}_2$ (μatm) and $\log(\text{GPP})$ ($\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) for high Chl-a ($> 1 \mu\text{g l}^{-1}$) stations. (c) Scatter plot between the $\% \text{O}_2$ saturation and $\log(\text{NCP})$ ($\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) for all stations. (d) Scatter plot between the $\% \text{O}_2$ saturation and $\log(\text{GPP})$ ($\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) for high Chl-a ($> 1 \mu\text{g l}^{-1}$) stations. Significant linear regressions are plotted and the equations and correlation coefficients of the regressions are indicated.

after the austral winter, a period when planktonic respiration is expected to be high (Garrison et al., 1986). On the contrary, the present study took place during the austral summer, which could explain the lack of correlation between gases and respiration.

The GPP:R ratio, which is an indicator of the planktonic community metabolism, was > 1 over almost all the sampled area (Fig. 8d) throughout the study (i.e. averaging 3.02 from 2002 to 2005, Table 5). In addition, the GPP:R ratio was highest near the frontal and coastal areas. However, no correlation existed between the $\% \text{O}_2$ saturation or $\Delta p\text{CO}_2$ and the GPP:R ratio. Fig. 12c represents the relationship between the $\Delta p\text{CO}_2$ and the $\% \text{O}_2$ saturation with respect to the GPP:R ratio. From this figure, there was no clear distribution pattern of the GPP:R ratio with regards to the $\Delta p\text{CO}_2$ and the $\% \text{O}_2$ saturation. Indeed, autotrophic (with GPP:R ratios > 1) and heterotrophic (with GPP:R ratios < 1) communities were found in quadrants I to IV with no clear distribution pattern. Therefore, the distribution of the GPP:R ratio would indicate that CO_2 and O_2 dynamics in the Weddell Sea are not driven by planktonic metabolic activities and are in contradiction with the negative relationship that was observed between $\% \text{O}_2$ saturation and $\Delta p\text{CO}_2$ in the Weddell Sea (Fig. 12a) and with the correlation that existed between $\Delta p\text{CO}_2$ and NCP (Fig. 10a).

As discussed by Moreau et al. (2012), who obtained a similar pattern in the western Antarctic Peninsula waters, these results may be explained by water column mixing, which may limit primary production in the surface Weddell waters by limiting light availability to phytoplankton. On the contrary, during incubation experiments, phytoplankton cells are not limited by light. In addition, as discussed by Schloss et al. (2007), CO_2 and O_2 exchanges between the sea and the atmosphere are processes that rely on longer time scales (i.e. weeks to months) than metabolic activities such as respiration and primary production (i.e. hours). Therefore, bottle incubations show

the potential of the community for CO_2 drawdown, without the limiting effects of physical factors. In this sense, the experimental determination of the relationship between microbial communities' metabolic activities and CO_2 and O_2 dynamics needs to be revisited. To do so, primary production and respiration could be estimated simultaneously by non-incubation and incubation methods, as proposed by Quay et al. (2010), and in regards to CO_2 and O_2 dynamics within the water column. In conclusion, CO_2 and O_2 dynamics in the Weddell Sea seem to be driven by both biological metabolic activities and the upwelling of WDW, but this result is not obvious from incubation experiments.

To overcome this issue, we used the method of Hoppema et al. (1999) who estimated primary production from nutrient change between winter subsurface (i.e. 50 m) and surface waters. Using this method, Bakker et al. (2008) were able to show that primary production performed by sea-ice algae and by water column phytoplankton after sea-ice melt can decrease $f\text{CO}_2$ in the Weddell Sea surface waters by up to $100 \mu\text{atm}$. In the Weddell Sea, the distribution of phytoplankton is driven by the dynamics of sea-ice (Krell et al., 2005), iron (Holm-Hansen et al., 2004), water masses (Kang et al., 2001; Mura et al., 1995) and fronts (Estrada and Delgado, 1990; Krell et al., 2005). During the present study, phytoplankton growth in the Weddell Sea was not limited by silicate, phosphate or nitrate. Indeed, observed nutrient concentrations were high when compared to the literature for the Weddell Sea (Hoppema et al., 2002, 2007). Lower nutrient concentrations were only observed near frontal areas, probably due to an enhanced nutrient uptake in these productive areas. Therefore, nutrient concentrations may be used as indicators of primary production.

The mean primary production at the time of sampling and estimated from nutrient consumption in the Weddell Sea surface

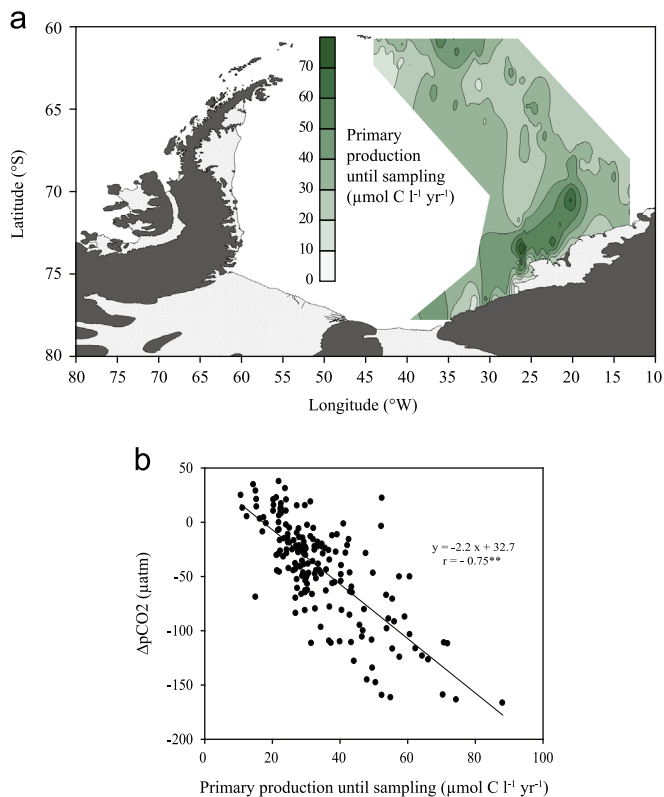


Fig. 11. (a) estimated annual primary production ($\mu\text{mol l}^{-1} \text{yr}^{-1}$) based on phosphate depletion between surface and deep Weddell Sea waters and following the method of Hoppema et al. (1999). Scatter plots between the annual primary production ($\mu\text{mol l}^{-1} \text{yr}^{-1}$) estimated with phosphate depletion between surface and deep Weddell Sea waters and ΔpCO_2 (μatm).

waters ($24.67 \pm 10.9 \mu\text{mol l}^{-1}$ using nitrate and $34.11 \pm 13.3 \mu\text{mol l}^{-1}$ using phosphate, Fig. 11a) were close to the estimations of Hoppema et al. (1999) who observed an annual primary production of 18.5 ± 2.1 and $19.2 \pm 2.3 \mu\text{mol l}^{-1} \text{yr}^{-1}$ using nitrate and phosphate depletions, respectively. It can be observed that primary production is higher near the fronts and the coastal zone (Fig. 11a), which is consistent with the incubation experiments results and the distribution of the Chl-*a* in the Weddell Sea. Moreover, contrarily to incubation experiments results, the estimated primary production was well correlated to ΔpCO_2 across the Weddell Sea (Fig. 11b), suggesting that the discrepancies observed between incubations results and CO_2 dynamics in the Weddell Sea surface waters are indeed due to differences in temporal scales. These results also agree with the hypothesis of Bakker et al. (2008) that CO_2 dynamics are driven by both biology and WDW upwelling in the Weddell Sea. On the contrary, no correlation existed between the estimated primary production until the time of sampling and the $\%O_2$ saturation. We believe this was caused by the strong air-sea O_2 exchanges that occur in the Weddell Sea. The difference between CO_2 and O_2 can be explained by the stronger solubility of CO_2 than O_2 in seawater (Sarmiento and Gruber, 2006).

4.3. Influence of phytoplankton composition on the Weddell Sea CO_2 and O_2 dynamics

In the present study, Chl-*a* concentration was significantly correlated with both the biomass of diatoms and phytoflagellates as a whole ($p < 0.01$). This is in contrast with results obtained in the southwestern Atlantic by Schloss et al. (2007) and in the western Antarctic Peninsula by Moreau et al. (2012) where these authors observed that Chl-*a* was significantly correlated with the biomass of diatoms but not with the biomass of phytoflagellates. In addition, clear relationships existed between the ΔpCO_2 and

the $\%O_2$ saturation and Chl-*a* (Fig. 5a and d) and between the ΔpCO_2 and the $\%O_2$ saturation and the biomass of both diatoms and phytoflagellates (Fig. 5b, c, e and f), indicating that these two phytoplankton groups affect CO_2 and O_2 dynamics as a whole in the Weddell Sea.

Contrarily to diatoms, phytoflagellates are usually found in areas of lower productivity in the Weddell Sea (Fryxell, 1989; Kang and Fryxell, 1993) as is the case for other Antarctic regions (Figueiras et al., 1998; Gall et al., 2001; Kang and Lee, 1995; Varela et al., 2002) and are usually believed to contribute to less carbon fixation. The correlations between the biomass of phytoflagellates and ΔpCO_2 and $\%O_2$ saturation over the whole Weddell Sea (Fig. 5c and f) are also in contrast with the results of Schloss et al. (2007) and Moreau et al. (2012) who reported no correlations between the ΔpCO_2 and the $\%O_2$ saturation and the biomass of phytoflagellates in the southwestern Atlantic and the western Antarctic Peninsula, respectively. In the present study, ΔpCO_2 averaged $-62.2 \pm 60 \mu\text{atm}$ and was negative in 70% of the stations where phytoflagellates dominated in terms of biomass. In contrast, ΔpCO_2 averaged $-62.1 \pm 43.2 \mu\text{atm}$ and was negative in 100% of the stations where diatoms dominated in terms of biomass. Likewise, ΔpCO_2 and the $\%O_2$ saturation were also significantly correlated to the small, medium and large Chl-*a* fractions (Table 4), suggesting that all phytoplankton size classes played a significant role on gas dynamics in the Weddell Sea. Finally, according to the PCA analyses described above, diatoms and phytoflagellates biomasses played the most important role in CO_2 dynamics in the Weddell Sea, both in 2003 and 2004. Wind speed, and hence ocean-atmosphere CO_2 exchanges played a secondary role in CO_2 dynamics. Other variables such as sea surface temperature and salinity seem to be of minor importance in terms of CO_2 dynamics.

In terms of carbon export, except for the genus *Fragilariopsis*, which was dominant every year in the Weddell Sea, the inter-annual variability observed during this study may have an effect on carbon sedimentation. Previous studies point towards a strong influence of small phytoflagellates (e.g. *Phaeocystis* sp.) on organic carbon sequestration in the Southern Ocean (Arrigo et al., 1999). However, Bathmann et al. (1991) showed that diatom frustules accounted for a major proportion of the organic carbon found in sediment traps deployed in the Weddell Sea. Of the dominant species observed in our study, *F. curta* and *F. cylindrus* are small pennate diatoms which are dominant sea ice algae in the Southern Ocean (Cefarelli et al., 2010; Lizotte, 2001). Some authors pointed out that these species showed an abrupt decrease during the last glacial maximum and increase during moderate climate warming (Leventer, 1998) and are, therefore, sensitive to climate change. These two diatoms species are heavily silicified and are efficiently exported to deeper waters (Annett et al., 2010). *C. pennatum* is also a silicified but larger diatom that has been shown to be a major contributor to phytoplankton biomass in the Scotia Sea (Korb et al., 2012) and carbon export in the Weddell Sea (Smith et al., 2011). Finally, our results for the Weddell Sea suggest that both diatoms and phytoflagellates play a key role in CO_2 fixation in the water column during the studied period. However, it should be noted that a significant fraction of carbon export is related to the vertical flux of diatoms contributing to the biological pump, together with the sinking of feces from zooplankton grazing (Granéli et al., 2004).

A shift in phytoplankton species from large to small cells (e.g. from diatoms to phytoflagellates) is expected in a global change context (Falkowski and Oliver, 2008; Li et al., 2009). The recent warming of the Weddell Sea deep waters observed by Robertson et al. (2002) and the expected change in the Weddell Sea regional climate (Conil and Menéndez, 2006) may trigger such a switch in phytoplankton composition. As pointed out by Moreau et al. (2012),

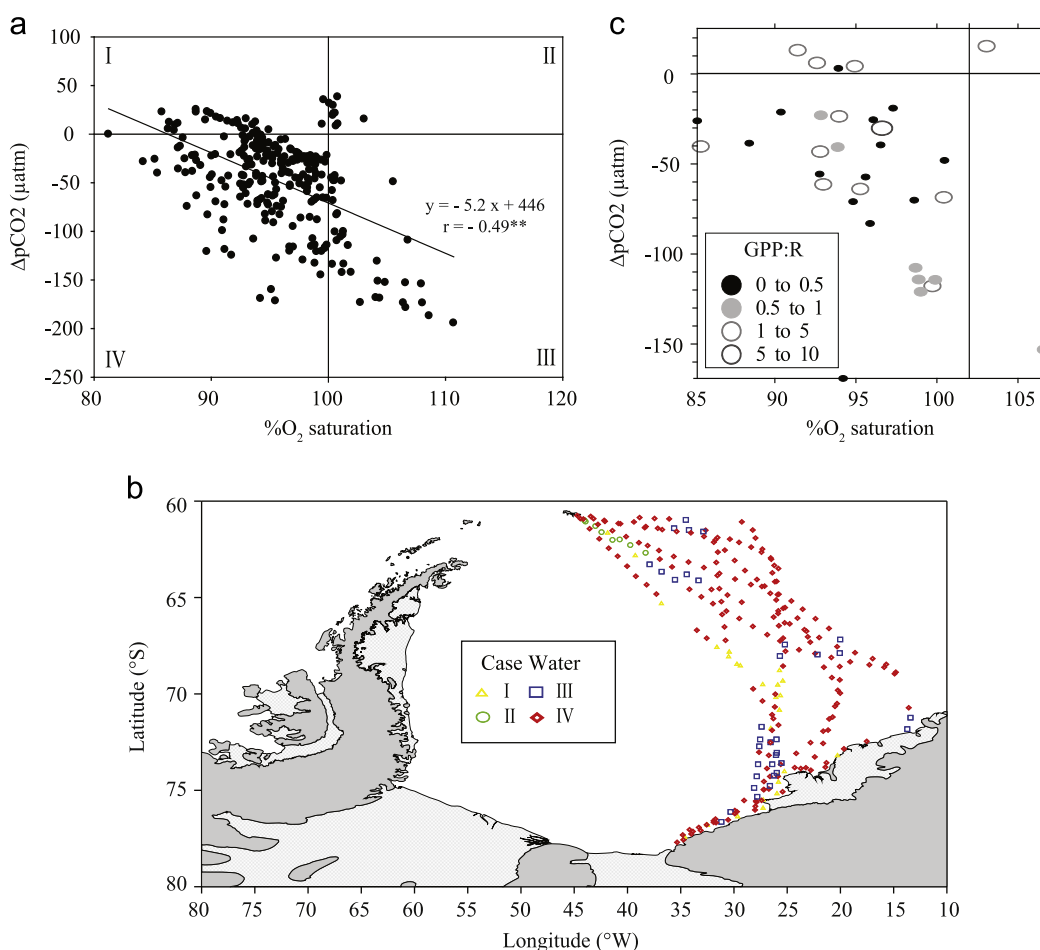


Fig. 12. (a) Scatter plot between $\Delta p\text{CO}_2$ (μatm) and the $\% \text{O}_2$ saturation for the 2002–2005 transects. The plot is divided into four quadrants whose significance is discussed in the discussion section. A significant linear regression is plotted and the equation and correlation coefficient of the regression is indicated. (b) Geographical distribution of case I, II, III and IV waters in the Weddell Sea. (c) Distribution of the GPP:R ratio with respect to $\Delta p\text{CO}_2$ (μatm) and the $\% \text{O}_2$ saturation.

such a shift in phytoplankton species might impair the role of the Antarctic Peninsula in terms of CO_2 drawdown from the atmosphere. In the Weddell Sea, the export of organic matter to deeper waters may be affected by such a switch in phytoplankton composition, although it is unclear in which way it will influence Weddell Sea surface waters CO_2 dynamics.

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